INORGANIC COLLOID CHEMISTRY

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BY

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VOLUME I

THE COLLOIDAL ELEMENTS

NEW YORK
JOHN WILEY & SONS, INC.
LONDON: CHAPMAN & HALL, LIMITED
1933

PRINTED IN U. S. A

PRESS OF
BRAUNWORTH & CO., INC
BOOK MANUFACTURERS
BROOKLYN, NEW YORK

DEDICATED TO

WILDER D. BANCROFT

WITH GRATITUDE AND ESTEEM

PREFACE

Under the general title Inorganic Colloid Chemistry will be given a critical survey of the colloidal behavior of the elements and their inorganic compounds with particular reference to the rôle they have played in the development of the theories and applications of colloid science. Because of the growing importance of this field of knowledge, the time is past when the student of inorganic chemistry can afford to disregard entirely or to pass over lightly the colloidal characteristics of inorganic substances. For this reason it is hoped that the present work will be useful not only for reference purposes but also as a text which will serve alike to emphasize the importance of the colloid chemistry of the elements and their inorganic compounds and to introduce the principles of colloid chemistry from the point of view of their specific applications to inorganic substances. To this end, special attention has been given to a systematic arrangement of the subject matter and to outlining the same by a generous use of section and paragraph headings.

As the title, The Colloidal Elements, indicates, the first volume is concerned primarily with the methods of formation, properties, and applications of the elements in the colloidal state. After a chapter dealing with general methods of preparation, separate divisions of the volume are devoted in turn to the metals and the non-metals. In so far as practicable, the several elements are taken up in the order in which they appear in the periodic table. In the descriptive portions of the text are included the methods of procedure for preparing the several sols and for investigating their characteristic colloidal properties. In the theoretical sections, critical discussions are given of the mechanism of sol formation, the composition and constitution of sols, the physical and chemical properties of sols, and the nature of adsorption processes. In the sections dealing with applications, consideration is given to the principles which underlie the more important uses of the colloidal elements in the industrial arts and in biology. Throughout the book, attention is directed to obvious gaps in our knowledge which can be filled only by carefully planned and executed experimentation.

I am indebted to Dr. Elroy J. Miller for his helpful criticism of the chapters on Colloidal Carbon and Colloidal Iodine.

November 15, 1932
Houston, Texas

HARRY B. WEISER

CONTENTS

PART I

THE METALLIC ELEMENTS

PART II

THE NON-METALLIC ELEMENTS

THE COLLOIDAL ELEMENTS

CHAPTER I

THE FORMATION OF COLLOIDAL ELEMENTS

Substances are obtained in the colloidal state either by gathering smaller particles, molecules, or atoms into particles of colloidal dimensions or by subdividing material in mass into particles of colloidal dimensions. The first process is called condensation or precipitation, and the second process, dispersion. Condensation methods are by far the most important in the preparation of colloidal elements, and they will be considered first.

CONDENSATION METHODS

The elements are most commonly obtained in the colloidal state in the form of what are known as colloidal solutions or sols, in which the element in a high state of subdivision is dispersed in a liquid or solid medium. Two general methods of preparing sols of the elements are widely used: the first involves precipitation as a result of chemical reaction in solution or of replacement of solvent; and the second consists in the condensation of vapors, especially of metallic vapors formed in the electric arc.

Precipitation from Solution

The first systematic study of the form in which substances precipitate as a result of reactions in solution was made by von Weimarn,[1] who emphasized that substances pass through the colloidal state during the precipitation process.

Von Weimarn's Theory.—Von Weimarn points out that precipitation from solution takes place in two stages: the first, in which the molecules in solution condense to crystalline nuclei; and the second, which is concerned with the growth on the nuclei as a result of diffusion.

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[1] "Zur Lehre von den Zuständen der Materie" (1914).

The initial rate of precipitation, W, is expressed in von Weimarn's equation

$$W = K\frac{Q - L}{L} = K\frac{P}{L}$$

where K is a constant; Q, the total concentration of the substance that is to precipitate; and L, its solubility. $Q - L = P$ is the absolute supersaturation, and P/L is the percentage supersaturation.

The velocity of growth, V, on nuclei is given by the Nernst-Noyes equation

$$V = \frac{D}{S}\cdot O\cdot (Q - L)$$

where D is the diffusion coefficient; S, the thickness of the adherent film; O, the extent of surface; and Q and L have the same significance as above.

In actual practice, W cannot be measured, and V either cannot be measured at all or only with greatest difficulty. Accordingly, von Weimarn introduced what he termed the "precipitate form coefficient," N, which is related to the mean magnitude of the single crystals in gram molecules Gm, by the expression

$$Gm \times N = \text{constant}$$

N may be represented qualitatively and in some cases approximately quantitatively by the expression

$$N = \frac{P}{L}$$

which means that, in the simplest case, the form of a precipitate is determined exclusively by the prevailing percentage supersaturation at the moment the precipitation starts. If this is approximately true, then for the substances x, y, and z

$$N_x = \frac{P_x}{L_x}; \quad N_y = \frac{P_y}{L_y}; \text{ and } \quad N_z = \frac{P_z}{L_z}$$

Now if the mean size in gram molecules of the particles in the several precipitates is to be the same, that is, if

$$N_x = N_y = N_z$$

then

$$\frac{P_x}{L_x} = \frac{P_y}{L_y} = \frac{P_z}{L_z}$$

This is the simplest form of von Weimarn's law of corresponding states for the precipitation process.

As would be expected, the simple formulation is seldom applicable quantitatively, since in most cases a number of factors other than percentage supersaturation influence the value of N and hence the mean particle size; and the magnitude of these factors is, in general, different with different substances. To take care of these several factors, von Weimarn introduces a multiplier, J, into the equation for N, which now becomes

$$N = J\frac{P}{L}$$

But as a rule the value of J is not the same for different substances; hence the expression for von Weimarn's law of corresponding states becomes

$$J_x\frac{P_x}{L_x} = J_y\frac{P_y}{L_y} = J_z\frac{P_z}{L_z}$$

in which J_x, J_y, and J_z are specific variable multipliers, "the product of all other factors in addition to P/L which influence the crystallization process. These factors must be expressed in abstract numbers equivalent to that for P/L."[2] This means simply that von Weimarn's law becomes quantitative and generally applicable by using variable multipliers which may include an indefinite number of unevaluated variables. Among the several factors which are lumped together in the variable multipliers are: the effect of the viscosity of the reaction medium, the variation in solubility with the size of the primary particles, polymerization of the reactant molecules, molecular complexity of the reactants, adsorption, the presence of dust particles, the extent of agitation on mixing, the specific tendency to form nuclei, the specific tendency to grow on nuclei, etc.

Fortunately, in a number of cases the von Weimarn formulation may be used to advantage in its simplest form. This is true under the following conditions: (1) if the factors influencing the precipitation process which are lumped together in von Weimarn's J are relatively unimportant as compared with the prevailing P/L value at the moment of precipitation; (2) if the factors included in J are significant but are approximately equal for the precipitation of the two or more substances under consideration.

In cases where the J factors may be disregarded, von Weimarn's

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[2] Von Weimarn: Kolloid-Beihefte, **18**, 48 (1923).

equation $N = J \cdot P/L$ means that the nature of the precipitate is determined by the percentage supersaturation and the solubility prevailing at the moment precipitation begins. Thus, with a given value of P, a very soluble substance will form slowly and deposit relatively large crystals, whereas, for the same value of P, a quite insoluble substance will precipitate rapidly in a finely divided flocculent or gelatinous state. Since the metals are so insoluble it follows that in general they can be caused to precipitate from solution in a finely divided form. The problem in their colloid synthesis is to prevent the growth or agglomeration of the primary particles into secondary aggregates which are so large that they settle out under the influence of gravity. In general, sol formation is accomplished the more readily, the lower the solubility of the precipitating substance and the higher the dilution. In actual practice, the methods employed involve precipitation as finely divided particles which are prevented from growing beyond a certain size or from agglomerating into large aggregates by means of suitable strong adsorption, including protecting colloids, or by keeping the concentration of agglomerating agents low by choice of reaction or by dilution.[3] The types of chemical reactions which have been found to yield sols of the elements are reduction, oxidation, and dissociation.

Reduction without Protecting Colloids.—Reduction with or without the use of protecting colloids is by far the most important chemical reaction for preparing the elements in the sol state. Noteworthy examples are the preparation of gold sol by reduction with hydrogen peroxide[4] and the reduction of silver oxide by hydrogen.[5] The respective reactions may be represented as follows:

$$2HAuCl_4 + 3H_2O_2 \rightarrow 2Au + 8HCl + 3O_2$$

$$Ag_2O + H_2 \rightarrow 2Ag + H_2O$$

Both these reactions have received extended study and throw much light on the following factors as they influence sol formation: concentration of reactants, presence of nuclei, purity of solutions, and the nature of the containing vessel. All these several factors will be considered in detail in the chapters dealing specifically with colloidal gold and colloidal silver.

Elements that have been obtained in the sol state by reduction

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[3] *Cf.* Bancroft: J. Phys. Chem., **18**, 556 (1914).

[4] Dörinckel: Z. anorg. Chem., **63**, 344 (1909).

[5] Kohlschütter: Z. Elektrochem., **14**, 49 (1908); Kolloid-Z., **12**, 285 (1913).

processes include gold, silver, platinum, palladium, iridium, rhodium, ruthenium, osmium, mercury, bismuth, copper, selenium, and tellurium.

Reduction with Protecting Colloids.—The stability of colloidal dispersions may be greatly increased by precipitating the finely divided particles in the presence of hydrophilic or water-soluble colloids such as gelatin, tannin, gum arabic, casein, glue, starch, albumin, and the sodium salts of protalbinic and lysalbinic acids formed by the saponification of albumin. The stabilizing action is due to adsorption of the hydrophilic colloid by the colloidal particles. In many cases the protecting colloid plays the combined rôle of reducing and stabilizing agent. For example, highly stable gold and silver sols are obtained by reduction of solutions of salts of the respective metals with tannin or sodium protalbinate.

Oxidation.—The oxidation process which is most important in sol formation is the oxidation of hydrogen sulfide by sulfur dioxide. Since most of the sulfur is precipitated in the colloidal state, the reaction which takes place is usually represented by the equation:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The actual reaction, however, is much more complicated, leading to the formation of a number of the thionic acids as well as colloidal sulfur.[6] It is now known that the presence of small amounts of one or more of the thionic acids is essential to the formation of a stable sulfur hydrosol.[7]

Dissociation.—Dissociation processes are seldom encountered in the preparation of sols in liquid media. A noteworthy example is the thermal dissociation of nickel carbonyl in benzol with the formation of a brown to black benzosol of nickel. The dissociation may be represented as follows:

$$Ni(CO)_4 \rightarrow Ni + 4CO$$ [8]

A number of salts can be caused to dissociate under such conditions that dispersions of the corresponding metals in a solid medium are formed. Thus Lorenz[9] showed that crystals of lead chloride, silver

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[6] Wackenroder: Arch. Pharm., **48**, 272 (1840).

[7] Freundlich and Scholz: Kolloid-Beihefte, **16**, 234 (1922); Bassett and Durrant: J. Chem. Soc., 2919 (1931).

[8] Ostwald: Kolloid-Z., **15**, 204 (1914); Hatschek and Thorne: **33**, 1 (1923).

[9] Lorenz and Eitel: Z. anorg. Chem., **91**, 46, 57, 61 (1915); Kolloid-Z., **18**, 177. (1916)

chloride, silver bromide, and thallous chloride, as ordinarily prepared, contain ultramicroscopic particles, probably of the respective metals, since optically empty crystals are obtained if the molten salts are treated with a mixture of chlorine and hydrogen chloride gases. Another example of such a colloidal system is blue rock salt, which consists of colloidal sodium dispersed in crystals of sodium chloride. This dispersion may be prepared synthetically by exposing the crystals of rock salt to cathode rays.[10] The most important dissociation process of this type is the darkening of the silver halides by light. This darkening results from the presence in the salt crystals of colloidally dispersed metallic silver formed as a result of dissociation of a minute amount of the crystal.

Replacement of Solvent.—If a solution of an element in a good solvent is poured into a liquid in which the element is highly insoluble, precipitation results and in certain cases a sol is formed. Thus, sulfur and phosphorus hydrosols are obtained by pouring alcoholic solutions of the elements into water.[11] This preparation is free from the stabilizing thionates formed by the oxidation process above referred to and so is relatively instable, coagulating spontaneously and settling out in a few days.

Condensation in Vacuum

If the vapors of a metal are allowed to come in contact with the same metal in mass, the colliding molecules always adhere to it. On the other hand, if the surface with which the metal molecules collide is different, there is a critical temperature above which little or no condensation takes place. Thus, mercury vapor adheres to or is adsorbed by a glass surface without reflection if the glass surface is colder than $-135°$. The critical temperature for mercury vapor on a silver surface is $+575°$.[12]

On account of the complete reflection of metallic vapors by a glass wall above the critical point, it is possible to obtain a high degree of supersaturation of the metal vapors. Thus, Wood[13] and Hamburger[14] heated a cadmium wire electrically in vacuum and obtained vapors of the metal which did not condense on a glass wall at ordinary tem-

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[10] Siedentopf: Physik. Z., **6**, 855 (1905).

[11] Von Weimarn and Malyschew: Kolloid-Z., **8**, 216 (1911).

[12] Knudsen: Ann. Physik, (4) **50**, 472 (1916); *cf.* Semenoff and Schalnikoff: Z. Physik, **38**, 738 (1926); Khanton, Semenoff, and Schalnikoff: Trans. Faraday Soc., **28**, 169 (1932).

[13] Phil. Mag., (6) **32**, 364 (1916).

[14] Kolloid-Z., **23**, 177 (1918).

perature. The wall was then touched with a plug of cotton, previously dipped in liquid air, with the result that rapid condensation took place at the point of cooling and continued on the surface film of metal after the cooling was stopped. A similar phenomenon was observed with magnesium and zinc, but not with silver, gold, platinum, tungsten, molybdenum, nickel, iron, or copper.

It is of particular importance that the metallic condensates formed on a wall cooled below the critical temperature are much more finely divided than those formed above the critical point. Moreover, the lower the temperature above the critical point, the finer is the state of subdivision of the condensed metal. Hamburger showed that there was a definite connection between the temperature of the metal gas and the degree of subdivision of the condensate on the walls of a glass vessel at room temperature. Thus elements of a very high melting point, such as carbon, tungsten, and platinum, which could be heated to a high temperature, deposited in an extremely minute state of subdivision; whereas elements like gold, silver, and copper, which could not be heated so high, deposited in somewhat coarser particles; and the easily fusible metals like zinc and cadmium gave the coarsest deposits. In general, the greater the difference in temperature between the metal vapors and the wall of the containing vessel, in other words the greater the supersaturation, the finer will be the degree of dispersion of the condensed molecules.

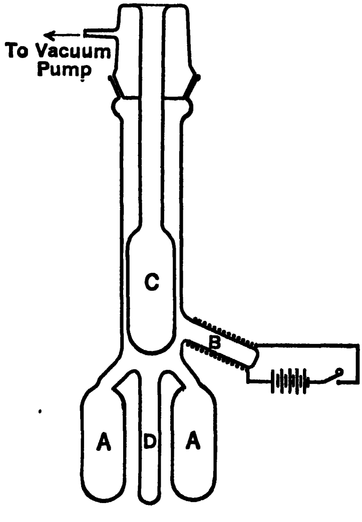

FIG. 1.—Apparatus for preparing sols according to Roginsky and Schalnikoff.

Sols by the Method of Roginsky.—The condensation of vapors on a cold surface in vacuum has been applied by Roginsky and Schalnikoff[15] to the preparation of a number of sols. The method consists essentially in condensing the vapors of the elements at the temperature of liquid air together with a medium which is liquid at ordinary temperatures. A diagram of the apparatus is shown in Fig. 1. The liquid is placed in the vessels A_1 and A_2, and the element in the side arm *B* which is heated electrically. The ground-glass

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[15] Kolloid-Z., 43, 67 (1927).

stopper contains a vessel *C* for liquid air and an outlet tube for connecting with the vacuum pump. The vessel *D* is for catching the sol after it is formed.

The method of procedure is as follows: The liquid containers are immersed in liquid air for some time, and then the vessel is evacuated to a pressure of around 10^{-5} mm by a series of Langmuir pumps. The vessel *C* is filled with liquid air, and the liquid containers are allowed to warm up enough to permit the vaporization and subsequent condensation of liquid on the liquid-air tube. The metal is then vaporized and condenses with the liquid on the cold tube, giving a frozen, highly dispersed sol. The relative amounts of metal vapor and liquid vapor which are allowed to condense are regulated by the temperature of the vessels A_1, A_2, and *B*. After a sufficient amount of solid sol is obtained, the liquid air is removed from *C*, and as the tube warms up the sol melts and collects in the container *D*. In some cases, as soon as the liquid air is removed, the solid film on the liquid-air tube is mixed with the excess of liquid to which a small amount of a protecting colloid or other dispersing agent is added.

By suitable regulation of conditions, hydrosols were prepared of mercury, cadmium, sulfur, selenium, and phosphorus; and organosols of mercury, cadmium, sodium, potassium, rubidium, and cesium. The organic liquids employed were benzol, hexane, xylol, and toluol, and, in a few cases, ether and alcohol. The method appears to be especially useful in the preparation of organosols in liquids which are decomposed by the electric arc when the latter is used to vaporize the metals.

Condensation in Gases

Vaporization without an Electric Arc.—If the vapors of a boiling element are conducted into a liquid, condensation takes place sometimes with the formation of a stable sol. Thus, Nordlund[16] boiled mercury violently and conducted the stream of mercury vapors into cold water containing suitable stabilizing electrolytes such as ammonia, ammonium salts, and citrates. Hydrosols were obtained which were richer in the more highly dispersed particles the colder the water. The particles were positively charged if the vapors were condensed in the presence of ammonium salts, and negatively charged in the presence of citrates. Sulfur and selenium sols may be prepared by a

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[16] Kolloid-Z., 26, 121 (1920).

similar procedure.[17] Svedberg[18] is of the opinion that the condensation takes place in the gas phase, that is, in the mixture of water and mercury vapor.

Sols may be prepared by passing an electric current of high intensity through a foil or wire of metals such as platinum and lead submerged in a liquid.[19] The metals are vaporized partly by the Joule heat and partly by an arcing between portions of the wire as it melts and breaks apart. The condensation of the vaporized metal takes place in part in the gas phase formed by volatilization of liquid in contact with the hot wire and in part in the gas-liquid boundary.

Mukhopadhyaya[20] modified the above method in an ingenious way to prepare sols of elements such as sulfur, selenium, and arsenic which vaporize relatively easily. A thin, uniform coating of the element in question was obtained on a platinum wire by dipping the electrically heated wire into the finely powdered element. The coated wire was then immersed in water, and sufficient current was passed to cause it to glow, vaporizing the element enveloping it. The vapors condensed probably in the gas phase, giving sols.

Fürth[21] dusted metals in air by means of an arc arranged in a covered porcelain crucible which collected the dust. Hydrosols of silver, gold, lead, and copper were obtained by shaking up the metallic dust with water. The silver sol was the most satisfactory obtained by this method, but it contained large amounts of oxide and nitrate.[22] Fairly stable sols of this element in benzol and alcohol were also prepared.

Vaporization in the Direct-current Arc. Bredig's Method.—The formation of colloids by passing an arc between electrodes under water is usually classified as a dispersion rather than a condensation process of sol formation. Svedberg[23] points out, however, that the action of the arc consists essentially in the formation of metal gas which subsequently condenses into particles of colloidal dimensions. From this point of view the electrical disintegration method is essentially a condensation process. It should be emphasized, however, that the phenomenon is probably not always just a simple vaporizarion and condensation. Thus with a strong oscillatory discharge

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[17] Gutbier: Z. anorg. Chem., **152**, 163; **155**, 199; **158**, 99 (1926).

[18] "Colloid Chemistry," 2nd ed., 38 (1928).

[19] Svedberg: Kolloid-Z., **24**, 1 (1919).

[20] J. Am. Chem. Soc., **37**, 292 (1915).

[21] Kolloid-Z., **34**, 224 (1924).

[22] MacMahon and Varma: Chem. Abstracts, **25**, 2896 (1931).

[23] "The Formation of Colloids," 19 (1921).

Benedicks[24] observed small craters in the electrodes which he attributed to the action of the liquid on molten metal, the vaporization of the former hurling the latter out of the crater in the form of minute granules.[25] The arcing process in certain cases is admittedly complex, yet it seems probable, as Svedberg contends, that the most important function of the arc, in the actual procedures employed, is to vaporize the metal which subsequently condenses to a sol.[26]

Bredig[27] was the first to use the direct-current arc under water for the preparation of metal hydrosols, and the process is frequently referred to as the Bredig method. Two thick wires of the metal under consideration are placed in cold water or preferably in very dilute alkali or acid, and an electric arc is struck between them. A current of 5–10 amperes at 30–110 volts is satisfactory. The arrangement for preparing sols by this method is shown diagrammatically in Fig. 2. Bredig obtained hydrosols of silver, gold, platinum, palladium, and iridium. Mercury hydrosols can be obtained in this way also, by using as one electrode a jet of mercury and as the other a pool of the element into which the jet falls through the water.[28]

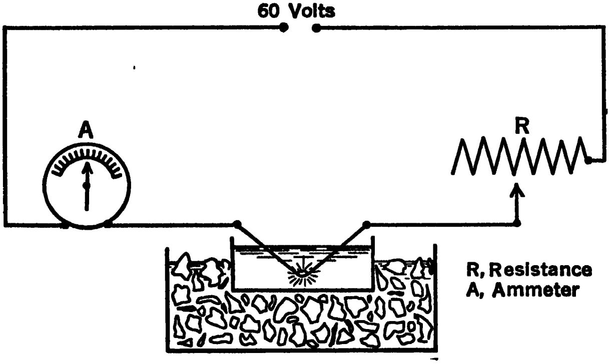

FIG. 2.—Bredig's arrangement for preparing sols by electrical pulverization.

The Bredig method is unsatisfactory for the preparation of sols in organic media[29] because of the decomposition of the liquid by the arc.

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[24] Arkiv Mat. Astron. Fysik, 8, No. 7, 1 (1912); Kolloid-Z., 11, 263 (1912); Kolloid-Beihefte, 4, 234 (1913).

[25] *Cf.*, however, Svedberg: "The Formation of Colloids," 34 (1921).

[26] *Cf.* Kutscherow: Kolloid-Z., 11, 165 (1912).

[27] Z. angew. Chem., 11, 951 (1898).

[28] Nordlund: Kolloid-Z., 26, 121 (1920).

[29] Burton: Phil. Mag., (6) 11, 475 (1906).

Svedberg minimized this effect by not allowing the arc to pass directly between the electrodes but by placing the metal to be dispersed in the form of small pieces of foil between fixed electrodes of an element such as aluminum which is difficult to vaporize. By passing a current of 20–50 milliamperes at 110–120 volts there is a play of fine sparks between the fragments of metal, and sol formation results without a great deal of decomposition of the organic dispersion medium.

Decomposition of the organic liquid can be decreased, also, by enclosing the arc so that it does not come in direct contact with the liquid. Moreover, the temperature of the arc and hence the extent of vaporization of the metal can be increased by enclosing the arc. Svedberg[30] enclosed silver electrodes in a quartz tube provided with a small hole in front of the arc. By forcing nitrogen into both ends of the tube the silver vapor formed in the arc is forced out of the small aperture. If the hot vapor is brought in contact with a solid or liquid surface, the metal condenses in much finer particles than are obtained with the free arc in the gas. Sols are readily obtained by placing the enclosed arc under the liquid dispersion medium.

Although the decomposition of the organic dispersion medium is less when the arc is enclosed than when it is in contact with the liquid, the sols formed with Svedberg's apparatus are greatly contaminated by colloidal silica resulting from volatilization of the quartz tube. To get around this difficulty in preparing silver sol, Giles and Salmon[31] substituted silver for quartz so that neither the arc nor the dispersion medium came in contact with anything but silver. The apparatus, a diagram of which is shown in Fig. 3, is prepared as follows: Two silver tubes are soldered together one in front of the other in the form of a cross, their interiors communicating through a small hole. The cross is soldered to a cylindrical cooling jacket as shown. In the ends of the horizontal table are fitted two brass T-tubes in the inside of which glass tubes carrying silver wires are fixed by rubber bungs. The vertical silver tube is fitted at the bottom with a brass tap silvered inside and at the top with an ordinary cork and outlet tube. Nitrogen led into the horizontal tube, as shown, picks up the silver vapor in the arc, carries it through the small hole connecting the two tubes, and bubbles up through the dispersion medium in the vertical tube. The arc using 6 amperes and 60 volts is operated by hand.

With the aid of the above apparatus, fairly stable silver sols were

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[30] "The Formation of Colloids," 25 (1921).

[31] J. Chem. Soc., 123, 1597 (1923).

obtained in aqueous alcohol but not in absolute alcohol. By substituting other metals for silver the apparatus may be adapted for preparing other metallic sols.

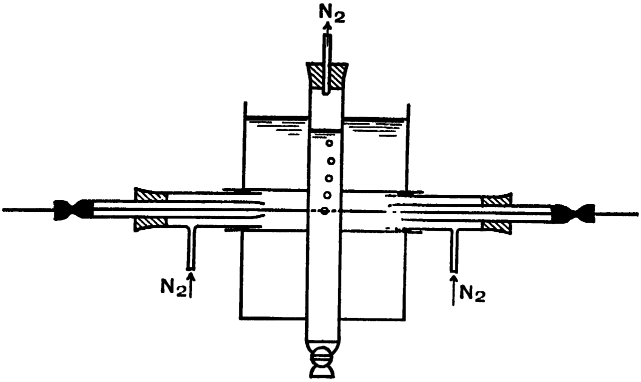

FIG. 3.—Giles and Salmon's arrangement for electrical pulverization with an enclosed arc.

Vaporization in the Oscillating Arc. Svedberg's Method.—The most satisfactory method for vaporization of metals in the preparation of sols was worked out by Svedberg. He employed an alternating arc of high frequency, a so-called oscillatory current with a period of 10^{-7} to 10^{-4} second. Two forms of such an arc were employed: the

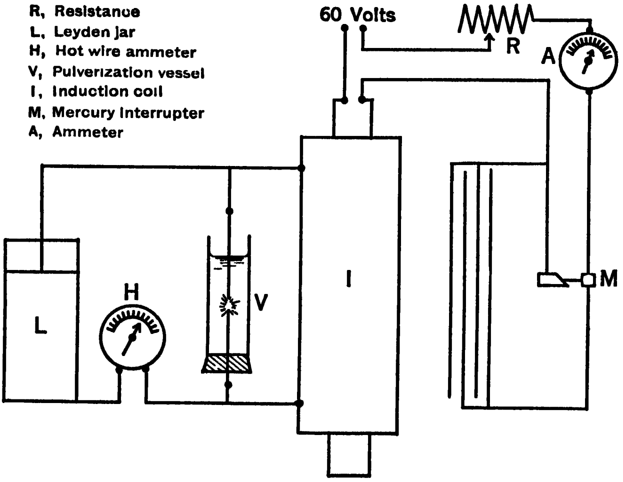

FIG. 4.—Svedberg's arrangement for the electrical pulverization of metals with a damped oscillating arc.

damped oscillatory are[32] produced by a Leyden jar circuit, and an undamped oscillatory arc[33] (wave current) obtained by connecting the oscillatory arc to a direct-current potential of 400–500 volts.

The arrangement for obtaining a damped oscillatory arc is shown diagrammatically in Fig. 4. Using this arrangement under the proper conditions, sols of almost all the metals were obtained in a wide variety of dispersion media such as water; methyl, ethyl, propyl, butyl, and amyl alcohols; ethyl ether; acetone; chloroform; etc. In marked contrast to the action of the direct-current arc, sol formation in the oscillatory arc was accompanied by little or no decomposition of the medium. It was found that the conditions for sol formation were most favorable and the decomposition of the organic medium least when the capacity was chosen as high as possible and the length of spark, the self-induction, and the resistance as small as possible.

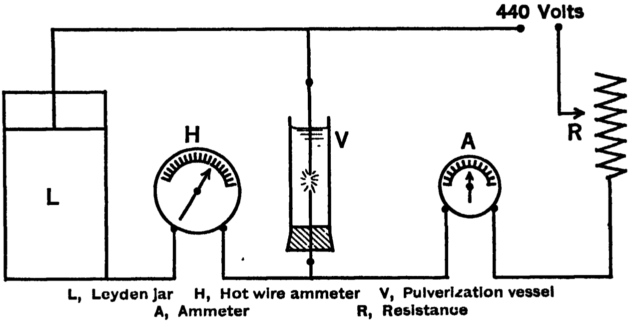

FIG. 5.—Svedberg's arrangement for the electrical pulverization of metals with an undamped oscillating arc.

As already indicated, apparently two different processes are going on in the oscillating arc: vaporization and subsequent condensation of metal; and a real dispersion of molten metal. The particles formed by dispersion of molten metal are much larger than those formed by condensation of vapor. Thus Börjeson in Svedberg's[34] laboratory showed that the radius of cadmium particles formed by real dispersion in ethyl alcohol ranged from 0.5 to 25μ while the mean value of the radius of the condensation product was about 5 mμ. The particles of the former settled out on standing.

To obtain an undamped oscillating arc the arrangement shown

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[32] Svedberg: Ber., **39**, 1705 (1906).

[33] Börjeson and Svedberg: Kolloid-Z., **25**, 154 (1919); Svedberg: Physik. Z., **15**, 361 (1914).

[34] "The Formation of Colloids," 33 (1921).

diagrammatically in Fig. 5 was employed by Svedberg.[35] With a 500-volt direct current the resistance should be about 300 ohms. This gives a current of about 0.1 ampere in the direct-current line when the arc is oscillating and about 2 amperes effective current in the oscillating circuit with a capacity of 4×10^{-3} microfarad. Such an arc has the advantage over the undamped arc in giving more colloidal metal per unit current and less decomposition of the dispersion medium per unit of dispersed metal (see page 156).

Fraser and Gibbard[36] prepared gold and silver sols by the use of a continuous high-frequency electrical discharge of sufficient intensity to produce a sinusoidal spark.

DISPERSION METHODS

Dispersion methods are frequently considered to be the most important for the preparation of colloidal metals, since the formation of metal sols by arcing under liquids is generally listed as a dispersion process. As already pointed out, such a classification is unsatisfactory since it is now known that the primary action of the arc in the arcing process is to volatilize the metal, the sol resulting from the subsequent condensation of the metallic vapors. True dispersion methods that yield colloidal elements are mechanical disintegration, electrochemical disintegration, addition of a peptizing agent, removal of agglomerating agents, and partial solution.

Mechanical Disintegration

The formation of disperse systems by mechanical grinding can be accomplished in certain cases. Thus Wegelin[37] obtained hydrosols of silicon and antimony and of the oxides of tungsten, titanium, molybdenum, and vanadium by grinding in an agate mortar; but he had no success with copper, bismuth, tellurium, selenium, sulfur, and graphite.

When sols cannot be made simply by grinding, it is usually assumed that this process alone will not yield sufficiently small particles. This is not necessarily true, since very minute primary particles may coalesce at certain points, giving aggregates that have the outward appearance of single coarse particles. As an aid to the mechanical dispersion and to prevent coalescence, von Weimarn[38] suggested

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[35] Börjeson and Svedberg: Kolloid-Z., **25**, 154 (1919).

[36] Can. J. Research, **7**, 133 (1932).

[37] Kolloid-Z., **14**, 65 (1914).

[38] "Grundzüge der Dispersoidchemie," 82 (1911).

grinding the dry solid to be dispersed with an indifferent solid which will dissolve on mixing with the dispersion medium. He suggested, further, that successive dilution with the solid and grinding might yield sols of successively increasing degree of dispersion. This principle was first applied by Pihlblad,[39] who obtained aniline blue and sulfur hydrosols of varying degree of dispersity by grinding varying ratios of the solids to be dispersed with urea and shaking the resulting mixture with water. The urea dissolved, leaving the finely divided insoluble solids in the sol state. Von Weimarn and Utzino[40] have prepared hydrosols of a number of substances, including the elements sulfur, selenium, tellurium, silver, mercury, and gold, by the above method, using glucose as the neutral diluting agent.

Electrochemical Disintegration

If a caustic soda solution is electrolyzed with a lead cathode, the metal disintegrates when the current density exceeds a critical value, and the solution is colored black by minute particles of metallic lead. Similar results can be obtained with cathodes of arsenic, antimony, bismuth, thallium, and tin.[41] The disintegration of the cathode is due to the formation of an alloy of the metal and sodium which is promptly destroyed in contact with water. It is probable that the disintegration of electrodes with an alternating current of high current density results from the formation of a hydrogen or metallic alloy which subsequently breaks down, leaving the electrode material in a highly dispersed state.[42]

Addition of Peptizing Agent

The addition of suitable peptizing agents to gelatinous precipitates of the hydrous oxides and salts disintegrates the aggregates of primary particles into units of colloidal dimensions as a result of strong adsorption, usually preferential adsorption of an ion. This constitutes a general method for preparing salt and oxide sols, but it is of limited applicability in preparing sols of the elements. A few cases, however, seem to belong under this heading. Thus Wedekind[43] reduced

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[39] Z. physik. Chem., **81**, 420 (1912); Svedberg's "The Formation of Colloids," 110 (1921).

[40] Kolloid-Z., **32**, 149 (1923); Alexander's "Colloid Chemistry," **1**, 659 (1926).

[41] Reed: J. Franklin Inst., **139**, 283 (1895); Bredig and Haber: Ber., **31**, 2741 (1898); Sack: Z. anorg. Chem., **34**, 286 (1903).

[42] Haber: Trans. Am. Electrochem. Soc., **2**, 192 (1902); van Name and Gräfenberg: Z. Elektrochem., **10**, 303 (1904).

[43] Z. Elektrochem., **9**, 630 (1903).

zirconia with magnesium, or zirconium potassium fluoride with potassium, and obtained finely divided zicronium which was in part converted to a hydrosol by treating with hydrochloric acid and washing. Similarly Kužel[44] obtained hydrosols by thoroughly pulverizing tungsten, molybdenum, silicon, zirconium, and titanium, treating the respective powders alternately with acid and alkali, and washing with water between treatments. The sol formation may be the result of the partial solution process to be described in the next paragraph, but it is undoubtedly due in part to a peptization of aggregates into their finely divided primary constituents. In this connection it is of interest that Kužel's colloids prepared as above described were at one time used in the manufacture of filaments for incandescent lights. Thus, the tungsten sol was coagulated and the plastic coagulum was pressed through fine holes, giving a fragile wire which was heated to sinter the particles together into a solid wire. The process is obsolete now since it has been found that filaments can be drawn from pure tungsten.

Removal of Agglomerating Agent

If a precipitate is thrown down in a finely divided form, it is sometimes possible to repeptize it into the sol state by washing out the excess of electrolytes which are responsible for its agglomeration. No sol is obtained if the electrolytes are adsorbed so strongly that they cannot be washed out or if the primary particles have coalesced into units too large to remain dispersed. This method is frequently employed in the preparation of salt and hydrous oxide sols but is of limited application in preparing sols of the elements. Noteworthy examples of elementary sols formed by washing out the agglomerating agent are Carey Lea's silver sol, sulfur sols of uniform particle size, and Gutbier's selenium sol.

Partial Solution

About a century ago, Berzelius[45] obtained tellurium in what is now recognized as a hydrosol by passing oxygen through a solution of potassium telluride. The first stage in the process consists in the precipitation of relatively coarse particles of tellurium in accord with the reaction:

$$K_2Te + O_2 + H_2O \rightarrow Te + 2KOH$$

[44] Austrian Pat., Cl. 12b, A 2573 (1906); Brit. Pat., 25,864 (1906).
[45] Pogg. Ann., **32**, 1 (1834).

In the second stage, the tellurium particles are partly dissolved with the formation of K_2TeO_3, thus:

$$Te + 2KOH + O_2 \rightarrow K_2TeO_3 + H_2O$$

and the particles are thereby reduced to colloidal dimensions and a hydrosol results.[46]

A similar behavior was observed by von Weimarn[47] with the element sulfur. An alcoholic solution of the element was cooled in liquid air with the formation of a clear, very highly dispersed alcosol. On warming slowly, the dispersity decreased, owing partly to agglomeration of the primary particles and partly to solution of smaller particles and reprecipitation on larger ones. This manifested itself in a slight blue opalescence which gradually became stronger and more whitish. As the temperature rose still more, the dispersity increased, owing to resolution of the particles, and the blue opalescence characteristic of the highly dispersed sol appeared once more. Ultimately the opalescence vanished as the particles dissolved completely.

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[46] *Cf.* Svedberg: "The Formation of Colloids," 107 (1921).

[47] "Grundzüge der Dispersoidchemie," 69, 77 (1911).

PART I

THE METALLIC ELEMENTS

CHAPTER II

COLLOIDAL GOLD: FORMATION AND COMPOSITION

Colloidal gold was known several centuries before the concept colloid originated. Thus, around 1600, Parcelsus described the preparation of "aurum potable, oleum auri, quinta essentia auri" by the reduction of auric chloride with the alcoholic extract of plants,[1] followed by the addition of sugar or syrup. The mixture, which was red in color, could be concentrated to an oily consistency without coagulating, probably because of the presence of protecting colloids in the alcoholic plant extracts used in its preparation. This aurum potable or potable gold of the alchemists was supposed to have fabulous medicinal virtues, curing all manner of diseases. It was claimed that "gold receives its influence from the sun which is, as it were, the heart of the world and by communicating these influences to the heart it serves to fortify and cleanse it from all impurities." The nature of aurum potable was pretty clearly recognized by Juncher,[2] Macquer,[3] and others in the eighteenth century. Thus Macquer writes: "However, all these gold tinctures are nothing but gold which is made extremely finely divided, floating in an oily fluid." In this connection, it is interesting to note that Fulhame[4] described the production of red and purple colors on silk by dipping the fabric in gold solution and subsequently precipitating the metal in a finely divided state by reduction with hydrogen or a solution of phosphorus in ether. Almost a century later this process was patented in Germany.[5]

Four years before Graham[6] began the publication of his fundamental researches, Faraday[7] described the preparation of stable highly dispersed hydrosols of gold by treating chlorauric acid with a variety of reducing agents, notably solutions of yellow phosphorus.

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[1] *See* Zsigmondy-Thiessen: "Das kolloide Gold," Leipzig, 4 (1925).

[2] Conspectus chemiae theoreticopracticae, Magdeburg, **1**, 882 (1730).

[3] "Dictionnaire de chymie," Paris, **3** (1774).

[4] Abstract in Ann. chim., **26**, 58 (1798).

[5] Odernheimer: German Pat., 63,842 (1890).

[6] Phil. Trans., **151**, 183 (1861); J. Chem. Soc., **15**, 216 (1862); **17**, 318 (1864).

[7] Phil. Trans., **147**, 145 (1857).

He recognized clearly the heterogeneity of the preparations and the influence of concentration and purity of the solutions on their color, turbidity, and stability. He examined the Tyndall cone in the varicolored suspensions and noted that the color change from red to blue on adding electrolytes was due to agglomeration of minute particles, invisible in the microscope, into larger aggregates which ultimately settled out. The report of Faraday's work has a distinctly modern flavor although it was written three-quarters of a century ago.

No survey of the earlier observations on colloidal gold would be complete without some reference to purple of Cassius first prepared by Andreas Cassius in 1663 by reduction of gold chloride with stannous chloride, and to gold ruby glass first made by Kunkel in 1679 by adding purple of Cassius to molten glass. As a result of the observations of Zsigmondy[8] in the latter part of the nineteenth century, it was definitely established that the color of purple of Cassius is due to colloidal gold dispersed in stannic oxide, and the color of ruby glass results from the presence in the glass of extremely finely divided metallic gold. Essentially the same point of view was expressed but not proved by J. B. Richter[9] almost a century before.

FORMATION OF GOLD HYDROSOLS

The method of preparing gold hydrosol most frequently employed consists in the reduction of chlorauric acid with a suitable reducing agent. The number of reducing agents that can be used is quite large,[10] the resulting sols showing wide variation in stability and color. The conditions of formation and the mechanism of the sol formation process with the most commonly used reducing agents will be considered in some detail.

Reduction with Formaldehyde—Zsigmondy's Sol

The gold hydrosol prepared by reduction of chlorauric acid with formaldehyde[11] according to the method of Zsigmondy will be considered first since this preparation has been so widely used in the study of colloids in general and of colloidal gold in particular.

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[8] Ann., **301**, 361 (1898).

[9] "Uber die neueren Gegenstände der Chemie," Breslau (1802); Ostwald: Kolloid-Z., **4**, 5 (1909); *cf.*, *also*, Faraday: Phil. Trans., **147**, 145 (1857).

[10] Svedberg lists 64 in "Herstellung kolloider Lösungen," 208 (1909).

[11] Other aldehydes may be used, Garbowski: Ber., **36**, 1215 (1903); Knaffl-Lenz: Kolloid-Z., **28**, 149 (1921).

Procedure without the Addition of Gold Nuclei.—The specific directions worked out by Zsigmondy[12] are as follows: A 120 cc portion of specially purified water is heated rapidly to boiling in a 300–500 cc beaker of resistance glass. During the heating are added 2.5 cc of a solution containing 6 g of $HAuCl_4 \cdot 4H_2O$ per liter and 3 cc of an 0.18 *N* potassium carbonate solution of highest purity. After the solution starts to boil vigorously, the flame is removed, and 3–4 cc of a dilute solution of formaldehyde (0.3 cc of commercial formol in 100 cc of water) is added quite rapidly in two portions, stirring vigorously with a rod of resistance glass until a bright red gold sol is formed. Finally, the sol is boiled for a short time to complete the reduction and to remove the excess formaldehyde.

The reactions which take place may be represented by the following equations:

$$HAuCl_4 + 2K_2CO_3 + H_2O \rightarrow Au(OH)_3 + 2CO_2 + 4KCl$$

$$2Au(OH)_3 + K_2CO_3 \rightarrow 2KAuO_2 + CO_2 + 3H_2O$$

$$2KAuO_2 + 3HCHO + K_2CO_3 \rightarrow 2Au + 3HCOOK + KHCO_3 + H_2O$$

This agrees with the finding of Vanino and Hartl[13] that 11 mols of potassium hydroxide are required to give 2 mols of gold; and with Naumoff's observation that gold sol results from adding formaldehyde directly to a solution of potassium aurate.

As ordinarily prepared, Zsigmondy's gold sols contain less than 0.1 g of gold per liter. Wintgen and Hacker[14] showed that sols containing as much as 2.7 g per liter can be obtained by throwing down the particles in the original sol with the supercentrifuge and repeptizing them in a small amount of water.

To reproduce the formation of stable, clear red sols, Zsigmondy[15] emphasizes at length the necessity for following precisely his method of procedure, using specially purified water and reagents and very carefully cleaned resistance glassware. In spite of his detailed directions, the method does not yield uniformly reproducible results in the hands of other investigators, and the procedure has been modified from time to time.[16]

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[12] Ann., **301**, 29 (1898); Z. anal. Chem., **40**, 712 (1901).

[13] Kolloid-Z., **1**, 272 (1907).

[14] Kolloid-Z., **61**, 335 (1932).

[15] "Das kolloide Gold," 33 (1925).

[16] *Cf.* Steubing: Ann. Physik, (4) **26**, 331 (1908); Morawitz: Kolloid-Beihefte, **1**, 323 (1910); Elissafoff: Z. physik. Chem., **79**, 418 (1912); Naumoff: Z. anorg. Chem., **88**, 38 (1914).

Observations carried out in the author's laboratory indicate that altogether too much emphasis has been placed on the necessity for using water of a very low conductivity in preparing Zsigmondy sol. In view of the fact that a solution of electrolytes is reduced and electrolytes are formed as reduction products, it is apparent that slight traces of ordinary electrolyte impurities will have little or no effect.[17] In the following section it will be shown that the nature of the containing vessel and the presence of organic material, dust particles, etc., may be much more important variables than the presence of a trace of electrolyte impurity.

Effect of the Containing Vessel.—In a series of attempts to prepare reproducible gold sols by Zsigmondy's method, 5 cc of 0.001 *M* potassium chloraurate and 5 cc of 0.004 *M* potassium carbonate were heated to boiling in a 250 cc Pyrex flask connected with a reflux condenser and treated with 5 cc of 0.002 *M* formaldehyde. The boiling was continued at a constant rate, and observations were made of the time for attaining the maximum color and of the appearance of the sol. In the first part of Table I are given a few typical results with flasks that yield unsatisfactory sols; and in the second part, some data with a flask that gives a fairly good sol. Before each experiment the flasks

TABLE I

EFFECT OF THE NATURE OF THE CONTAINING VESSEL ON THE FORMATION OF ZSIGMONDY'S SOL

Flask No.	Time for max. color, minutes	Appearance of sol
1	19.0	Reddish purple; cloudy
2	13.0	Reddish purple; less cloudy than 1
3	37.0	Reddish purple; fairly clear
3*a*	3.0	Light purple; cloudy; gold on flask
4	1.5	Red; slightly opalescent
1*a*	36.0	Purple; fairly clear
1*b*	40.0	No sol; gold deposited on flask
1*c*	3.5	Purple; cloudy; gold on flask
1*d*	5 0	Purple; very cloudy; gold on flask
4*a*	1.5	Clear red; some gold on flask
4*b*	1.0	Red; slightly cloudy; some gold on flask
4*c*	1.5	Red; slightly cloudy; some gold on flask

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[17] *Cf.* Weiser and Milligan: J. Phys. Chem., **36**, 1950 (1932).

were boiled with aqua regia, thoroughly rinsed, and steamed. From these and scores of similar observations, it is apparent that the nature of the surface of the flask is an important factor in initiating the reduction process and in determining the reproducibility of the resulting sol. In the absence of gold nuclei, the precipitation of gold is apparently initiated at some crack or point on the surface of the container. A flask in which a sol has once formed may contain minute gold particles in a roughened portion of the surface. Other things being constant, such a flask will tend to yield reproducible sols repeatedly. Indeed Thiessen[18] recognized that sols formed better in some flasks than in others and that the more often the flasks were used the better they became.

In attempting to determine the effect of dust particles on the sol formation process, the water and reagents other than the gold solution were first ultrafiltered through a cellophane membrane using a gold-plated ultrafilter. The absence of sol formation under these conditions was attributed at first to the removal of nuclei. Later it was found that a trace of some inhibitor was extracted from a rubber gasket in the ultrafilter during the ultrafiltration process.

The importance of preventing the vessels and reagents from coming in contact with rubber is well illustrated by the following observations. A small sheet of thoroughly washed vulcanized rubber was digested for one hour with one liter of water. Small amounts of this water were added to separate portions of the reaction mixture used in preparing the sols described in Table I. A flask was employed which always gave a good sol in the absence of water that had been in contact with rubber. Some typical observations are given in Table II.

TABLE II

EFFECT OF WATER CONTAMINATED BY RUBBER ON THE FORMATION OF ZSIGMONDY'S SOL

Contaminated water added, cc	Appearance of sol
0	Clear red; some gold on flask
0.2	Clear bright red; no gold on flask
0.4	Clear bright red; no gold on flask
0.6	Very cloudy; instable; some gold on flask
0.8	No sol; some gold on flask

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[18] Kolloid-Beihefte, **29**, 124, 132 (1929).

It appears that a little of the contaminated water favors the formation of a bright red sol but as much as 0.8 cc in a total volume of 100 cc completely inhibits the formation of a sol.

Effect of Concentration of Gold Solution on Particle Size.—The particles of colloidal gold formed by reduction processes are in general larger the higher the concentration of the gold salt reduced.[19] This would not be predicted from the von Weimarn theory, which states that, provided the process of direct crystallization is complete, the mean size of the individual crystals is greater the higher the concentration of reactants (the higher the percentage supersaturation at the moment precipitation begins, *cf.* page 1). Von Weimarn[20] explains the anomalous behavior by postulating that hydrolysis of the gold salt with the formation of $Au(OH)_3$, which is subsequently reduced to AuOH and finally to Au, is the initial and therefore the important step in determining the degree of dispersity as it is influenced by the concentration of reactants. In such instances, "The principal reacting molecules are obviously the molecules of water, and it is by the ratio of their number to the number of hydrolyzing salt molecules that the velocity, as well as the degree of completeness of the hydrolytic process, is determined."[21] In other words, the greater active mass of the water and not the lower concentration of chlorauric acid in the more dilute solutions is assumed to account for the higher dispersity in such solutions, since the higher the dilution the greater the number of nuclei formed by hydrolysis and hence the smaller the individual particles.

The mechanism of the formation of Zsigmondy sol which von Weimarn proposes in order to show that the process is strictly in accord with his theory, is ingenious, but there are certain lines of evidence which indicate that it is not correct.

In the first place, Thiessen[22] showed that all the conditions which increase the degree of hydrolysis of a given chlorauric acid solution prior to the addition of reducing agent decrease the number and hence increase the size of the particles formed in a given time.

In the second place, it was demonstrated in the author's laboratory[23] that, even in the absence of appreciable hydrolysis of gold salt, the gold particles are smaller the more dilute the solution. In

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[19] Zsigmondy: "Zur Erkenntniss der Kolloide," 136, 173 (1905); Svedberg: Kolloid-Z., **4**, 168 (1909).

[20] Kolloid-Z., **48**, 346 (1929).

[21] Von Weimarn: Chem. Rev., **2**, 227 (1926).

[22] Kolloid-Beihefte, **29**, 122 (1929).

[23] Weiser and Milligan: J. Phys. Chem., **36**, 1950 (1932).

support of this, in Fig. 6 are reproduced the results of some observations of particle size on gold sols formed by the addition of different reducing agents to varying concentrations of neutral potassium chloraurate.

It is apparent from these considerations that the percentage supersaturation at the beginning of precipitation is not the only factor and may not be the most important one in determining the primary particle size in the formation of colloidal gold. In the absence of added nuclei, the size of the primary gold particles in a sol will be determined, for a given concentration of reactants, by the velocity with which nuclei form spontaneously and the velocity with which the particles grow on the spontaneously formed nuclei. Now it is to be expected from the Nernst-Noyes formulation (see page 2) that

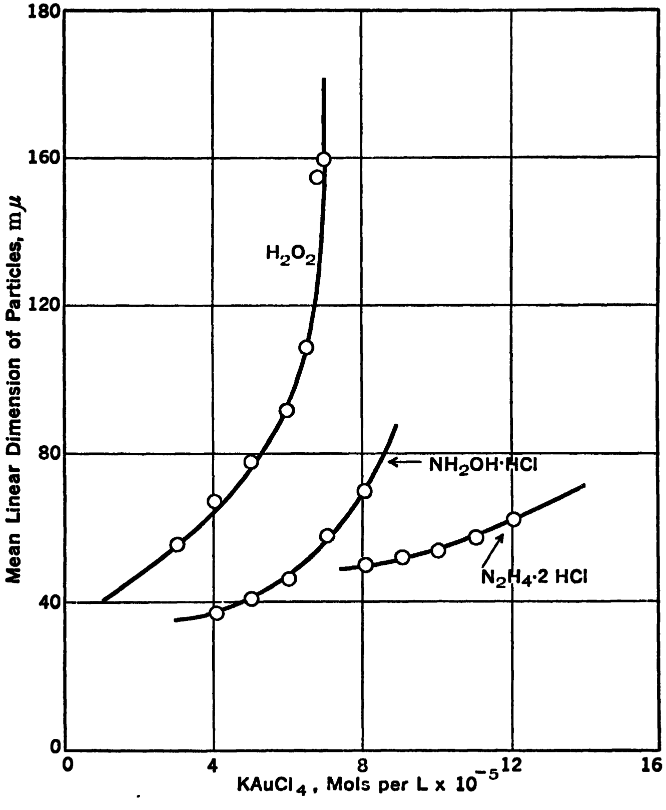

FIG. 6.—Effect of concentration of gold salt solution on the particle size of colloidal gold obtained by reduction with H_2O_2, $NH_2OH \cdot HCl$, and $N_2H_4 \cdot 2HCl$.

the velocity of growth on added nuclei will be greater the greater the absolute supersaturation of the solution with respect to gold, in other words, the greater the initial concentration of gold salt. The same thing will apply to the rate of growth on nuclei formed spontaneously. In general, to obtain very highly dispersed particles the velocity of formation of nuclei must be relatively rapid and the growth on the effective nuclei must be relatively slow. Since gold is extremely insoluble, the percentage supersaturation of the metal is relatively high at all concentrations of the gold salt under consideration, Under these circumstances the rate of formation of nuclei is not directly proportional to the percentage supersaturation, but is relatively more rapid at the higher dilutions. Moreover, at the higher dilutions, the rate of growth on nuclei is relatively slower so that relatively more nuclei can form before the supply of gold is exhausted. For both these reasons the size of the primary particles is smaller in the sols formed from the more dilute solutions of gold salt.

Von Weimarn may contend that the larger particles formed in the more concentrated solutions are aggregates rather than primary particles. There is no evidence to support this view under the experimental conditions used in obtaining the data shown graphically in Fig. 6. All the sols were perfectly clear, and the ultramicroscopic examination showed no indication of aggregate formation. Moreover, it is well known that particles grow by direct precipitation of gold on gold nuclei added to the reduction mixture, and there is no reason to believe that the process is any different in the presence of spontaneously formed nuclei. In this connection, if one insists that $Au(OH)_3$ and AuOH are precipitated as intermediate products in the reduction process, then the growth on gold nuclei must result from initial precipitation of $Au(OH)_3$ on such particles followed by reduction to AuOH and subsequently to gold. Although this could be true to a certain extent, it seems to be altogether unnecessary to assume such a mechanism since it is probably not in general accord with the facts.

Effect of the Nature of the Reducing Agent on Particle Size.—The marked effect of varying conditions of reduction on the number of particles in a gold sol is illustrated clearly by some observations of Thiessen[24] that have been reproduced graphically in Fig. 7. Dilute solutions of chlorauric acid were made slightly alkaline with potassium carbonate and were treated with different reducing agents. The number of particles in the several sols was counted by the aid of the

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[24] Thiessen: Kolloid-Beihefte, **29**, 122 (1929).

slit ultramicroscope. In the diagram the number of particles in 1 cc is given, assuming that the hydrosols were all reduced to a volume of 100 cc. In general, it was noted that those reducing agents which retard the growth of nuclei give sols with a large number of particles, and vice versa. Thus, with potassium thiocyanate the number of particles is enormously greater than with the other reducing agents, in accord with the usual observation that sulfur compounds retard the growth on nuclei.

Interdependence of Rate of Nuclei Formation and Growth on Nuclei.—That the velocity of nuclei formation and the velocity of growth on nuclei are to a certain extent interdependent, is rendered very probable by the fact that Hiege,[25] Reitstötter,[26] and others[27] have found means of influencing them separately. Thus the spontaneous formation of nuclei is reduced by ammonium salts, and especially by potassium ferro- and ferricyanide. In accord with this, it was observed that the reduction is noticeably retarded by small amounts of the salts, provided no gold nuclei are added; but if such

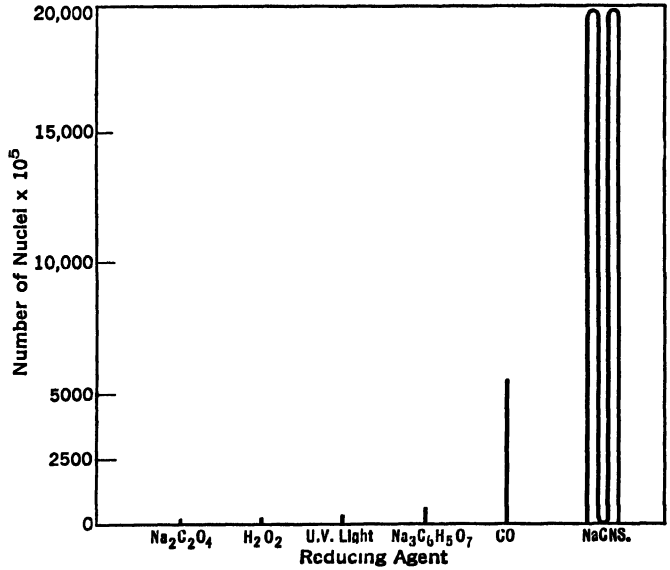

FIG. 7.—Effect of the nature of the reducing agent on the number and size of gold particles.

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[25] Hiege: Z. anorg. Chem., **91**, 145 (1915).

[26] Kolloid-Beihefte, **9**, 222 (1917).

[27] Thiessen: Z. anorg. Chem., **180**, 57 (1929); Kolloid-Beihefte, **29**, 122 (1929).

nuclei are added, the reduction takes place rapidly, indicating that the retarding effect of the salt is to cut down the spontaneous formation of nuclei rather than to inhibit their rate of growth. In the process of determining the size of particles by depositing gold on added nuclei, the spontaneous formation of new nuclei is prevented by adding a small amount of potassium ferrocyanide.[25] The spontaneous formation of nuclei is greatly retarded and the growth of particles promoted by using hydroxylamine hydrochloride and hydrazine sulfate as reducing agents in the preparation of gold sol.[24]

The velocity of growth of particles is cut down by organic colloids such as gelatin, soap, oil, and fats, and to a lesser extent by inorganic electrolytes such as potassium bromide and iodide. That these act primarily as growth inhibitors is evidenced by the fact that the rate of growth is cut down irrespective of whether gold nuclei are added or not.

To obtain gold sols with a graded number of particles without the addition of gold nuclei, Thiessen[24] devised the unique method of adding to a dilute solution of chlorauric acid one reducing agent, such as potassium thiocyanate, which is particularly effective in bringing about the formation of nuclei, and after a certain fixed interval, a second reducing agent like hydroxylamine which causes growth on nuclei already present but suppresses the further formation of nuclei.

Procedure with the Addition of Gold Nuclei.—The most satisfactory method for obtaining gold sols with a graded number of particles of definite size is the classic procedure of Zsigmondy,[28] which consists in adding a small amount of sol containing very fine particles of gold to the gold chloride solution before reduction. A very satisfactory nuclear solution is obtained by adding 2.5 cc of 0.6% chlorauric acid and 3–3.5 cc of 0.18 N potassium carbonate to 120 cc of water followed by the addition of 0.5 cc of an ether solution of phosphorus prepared by diluting the saturated solution to 5 times its volume. After standing 24 hours a red sol results which contains particles too small to be seen with the ultramicroscope. When such a nuclear solution is added to the solution of gold salt followed by adding the reducing agent, the nuclei of gold serve as centers around which the condensation takes place. The individual particles grow as long as any gold remains to be reduced. Obviously the size which the particles attain ultimately will depend on the number of nuclei and the amount of gold in the solution. If too few nuclei are added,

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[28] Z. physik. Chem., 56, 65, 77 (1906).

some may form spontaneously. As already noted, this may be prevented or greatly retarded by adding a small amount of potassium ferrocyanide to the solution before reduction.

With suitable reduction mixtures adjusted so that no nuclei arise, it is possible to prepare series of gold sols with varying degrees of dispersity simply by adding varying amounts of gold nuclei to the reduction mixtures. It is possible also to determine the size of the invisible nuclei by adding them to the reduction mixture and allowing them to grow large enough for observation with the ultramicroscope (see page 58).

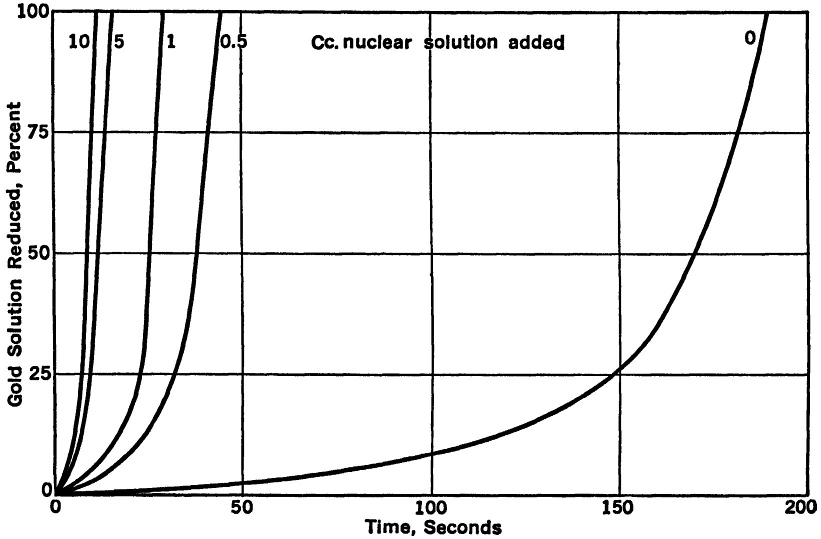

FIG. 8.—Effect of nuclei on the rate of reduction of gold solutions.

In investigations of this kind, Thiessen[29] found the smallest gold particles which would act as condensation nuclei to be 1.1×10^{-7} cm or 0.11 mμ in diameter. The minimum size of the effective nuclei is very much smaller than will act to start crystallization in supersaturated salt solutions, probably because the degree of supersaturation obtained in the reduction process is much higher than is obtained in supersaturated solutions of salts.

The effect of the addition of nuclei on the velocity of the reduction process[30] is shown diagrammatically in Fig. 8. The reduction

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[29] Z. anorg. Chem., **180**, 110 (1929).

[30] Zsigmondy-Thiessen: "Das kolloide Gold," 90 (1925).

mixture recommended by Zsigmondy was boiled to remove carbon dioxide and was cooled to 70°, after which formaldehyde was added with or without the previous addition of nuclear liquid. The rate of reduction in the presence of varying amounts of nuclei was estimated by colorimetric comparison with standardized gold sols. The percentage of the total amount of gold salt reduced is plotted as ordinate against the time in seconds as abscissa. The presence of even a small amount of added nuclei enormously increases the rate of the reduction process. The relatively long period of inhibition in the absence of nuclear solution is a measure of the time necessary for the spontaneous appearance of effective nuclei.[31]

Reduction with Formaldehyde—von Weimarn's Sol

Von Weimarn[32] discovered a method of preparing gold sols by reduction with formaldehyde which gives clear, red, stable preparations without the use of special distilled water, chemicals, and glassware.

Procedure.—Von Weimarn's original directions are as follows: To 500 cc of boiling water are added all at once 10 cc of 0.1% chlorauric acid and 10 cc of an alkaline formaldehyde solution prepared by mixing 90 cc of 0.2 *N* potassium hydroxide or carbonate with sufficient commercial 35% formaldehyde to make 100 cc. A red gold sol forms at once, and if the mixture is boiled for an hour it is very stable.

The Stabilizing Agent.—The stability of the von Weimarn sol prepared as above described is probably due in large measure to the formation of condensation products of dilute formaldehyde in dilute alkaline solution. These products are a mixture of sugar-like substances which are termed formoses.[33] Under certain conditions the formoses give a resinous substance which acts as a good protecting colloid for the gold. Von Weimarn[34] demonstrated conclusively that the resinous substance, which he called H-dispersoid, is not the reducing agent in his process. Thus he added 10 cc of the dilute alkaline formaldehyde solution referred to above, to 500 cc of water and boiled for an hour. The volume decreased in this time to between 75 and 90 cc, but there was not the slightest yellow coloration which characterizes the presence of even a trace of the resinous body. On

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[31] Zsigmondy and Hückel: Z. physik. Chem., **116**, 291 (1925); *cf. also*, Zakowski: Kolloid-Beihefte, Ambronn Festschrift, **23**, 117 (1926).

[32] Kolloid-Z., **33**, 230 (1923); **36**, 1 (1925).

[33] Loew: Ber., **21**, 270 (1888).

[34] Kolloid-Z., **53**, 352 (1930).

the other hand, if 10 cc. of 0.1% chlorauric acid was added to the water before adding the alkaline formaldehyde, the solution after boiling for an hour had a resinous smell and showed a yellow coloration when the gold particles were dissolved by adding a small amount of $N/10$ potassium cyanide. Apparently the colloidal gold reduced by the formaldehyde, catalyzes the formation of formoses just as do lead and iron.[33]

Von Weimarn found that, if too little alkali was present in the alkaline formaldehyde solution, stable red gold sols were not obtained. On the other hand, if the reduction of the gold salt was not quite complete, the resulting red preparations were quite stable even though the amount of resinous protective colloid was so small that it could not be detected after dissolving the gold particles.

It is significant that the concentrations of reagents noted above are not binding. On the contrary, von Weimarn points out that various concentrations will lead ultimately to the formation of red sols which differ with different conditions of formation but which are readily reproduced by adhering to a given set of conditions. Von Weimarn emphasizes the importance of the intermediate formation of a blue hydrous Au_2O as a step in the formaldehyde reduction to the metal sol (*cf.* page 26). From this point of view it is necessary to the sol formation process that the hydrous oxide sol which first forms should be stable or that the reduction of this intermediate product to gold should take place rapidly while the hydrous oxide is still in the nascent state. To ensure stability the conditions of preparation must yield a small amount of the resinous condensation product of formaldehyde which acts as a protecting colloid or a trace of unreduced gold salt must remain in the sol. By suitable variation in conditions, stable sols of a wide variety of colors can be formed.

Zsigmondy's Sol and von Weimarn's Sol Contrasted.—Zsigmondy[35] in his monograph on colloidal gold discusses von Weimarn's sol very briefly, but in this discussion he refers to the uncleanly method of procedure used by von Weimarn and characterizes the sol as a protected colloid that bears only a superficial resemblance to the pure gold sol obtained by the cleanly procedure of Zsigmondy. This characterization of von Weimarn's work appears to be altogether without justification.[36] Since the same reagents were used by both investigators, the only essential difference being in the order in which

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[35] "Das kolloide Gold," 44 (1925).

[36] *Cf.* von Weimarn: Kolloid-Z., **39**, 278 (1926); **48**, 346 (1929); **53**, 352 (1930).

they were added and the concentrations, it seems altogether likely that the difference between the two preparations is by no means as great as Zsigmondy would have one believe. Von Weimarn admits that the stable sols produced by his relatively simple and easily reproducible method of procedure always contain stabilizing agents—a condensation product of formaldehyde or unreduced gold salt or both—even though the presence of such stabilizing agents cannot be readily detected. Zsigmondy, on the other hand, thinks that his procedure gives pure gold without any stabilizing electrolyte or protective agent whatsoever because he cannot detect the same experimentally. The author is inclined to believe that the difference is one of degree and not of kind. Zsigmondy's preparation undoubtedly contains some protective agent, although his method of procedure gives distinctly less than von Weimarn's. It is for this very reason that Zsigmondy's sols are more difficult to reproduce satisfactorily and are less stable.

Reduction with Hydrogen Peroxide

Formation without Gold Nuclei.— A gold hydrosol is obtained by adding a few drops of a solution of hydrogen peroxide[37] to a dilute solution of chlorauric acid, for example, 2 cc of the 0.6% acid in 100 cc of pure water. The sol which results at this concentration is somewhat cloudy, and the particles are not uniform in size. If the solution is made slightly alkaline with potassium carbonate before adding the reducing agent, the resulting sol is blue and quite cloudy even when the concentration of gold salt is very low. Beaver and Muller[38] noted that at 85° pure red sols are formed if the *p*H value of the gold solution being reduced by hydrogen peroxide is between 7.5 and 9, the head of the absorption band under these conditions being at a wave length of approximately 5140Å. With either higher or lower *p*H values of the solution, the color tends toward blue. At room temperature, beautiful red sols are obtained by adding hydrogen peroxide to dilute solutions of potassium chloraurate.[39]

Instead of using hydrogen peroxide only as reducing agent, Nicol[40] recommends the use of the equimolecular compound of urea and hydrogen peroxide which is sold under the trade name of "Hyperol" or "Ortizin." The bulb of a 500 cc flat-bottomed flask of resistance

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[37] Dörinckel: Z. anorg. Chem., **63**, 344 (1909).

[38] J. Am. Chem. Soc., **50**, 304 (1928).

[39] Weiser and Milligan: J. Phys. Chem., **36**, 1950 (1932).

[40] J. Soc. Chem. Ind., **46**, 179 T (1927); **47**, 343 T (1928).

glass is filled with water collected directly from the condenser. To this are added 5 cc of a freshly made 2% solution of potassium carbonate and 5 cc of a 1% aqueous solution of sodium chloraurate. After heating rapidly over a free flame to 80° with occasional swirling, 3 cc of a solution containing 0.15 g of Hyperol in pure alcohol is added and the contents of the flask boiled to remove volatile impurities. The sol obtained in this way is bright red in color and is said to be readily reproducible. Since no protecting colloid is used or formed in the process, Zsigmondy's objection to von Weimarn's easily reproducible sol (see page 33) does not hold. Nicol recommends its use in Lange's spinal fluid test (see page 102).

Effect of Light.—Nordenson[41] in Svedberg's laboratory, found that the reduction of dilute chlorauric acid by hydrogen peroxide is greatly accelerated and the degree of dispersion of the particles is considerably increased, if the reduction mixture is exposed to light of short wave length such as that obtained from a strong mercury vapor lamp. The number and size of the particles can be regulated by the time of exposure, as indicated by the results shown in Fig. 9. For a given concentration of gold salt the number of particles in the sol is increased enormously and the size correspondingly diminished by a few seconds' exposure to the light. Nordenson showed that the rate of reduction of chlorauric acid by light is relatively slow; hence the speeding up of the reduction cannot be due to the formation of gold nuclei by the reducing action of the light. Apparently the light acts in some way by favoring the formation of condensation nuclei from the supersaturated solution of gold.

In this connection, attention should be called to the interesting observation of Holmes[42] that the diffusion of oxalic acid into silica gel containing chlorauric acid leads to the periodic formation of gold bands varying in color from red to blue to green. Davies[43] showed that the banding is not a Liesegang phenomenon, as was suspected, but results from periodic precipitation of gold under the influence of the varying light of the laboratory. If the reaction is carried out wholly in the dark, yellow gold crystals are formed but no bands.

Formation with Gold Nuclei.—The addition of a suitable amount

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[41] Z. physik. Chem., **90**, 603 (1915); *cf.* Pelletier: Schweigg. J., **31**, 317 (1800); Döbereiner: **68**, 86 (1831); Sonstadt: Eder's Jahrbuch Phot. Ind., 466 (1899); Vanino: Kolloid-Z., **2**, 51 (1907); Hartwagner: **16**, 79 (1915); Thiessen: Kolloid-Beihefte, **29**, 122 (1929).

[42] J. Am. Chem. Soc., **40**, 1187 (1918).

[43] J. Am. Chem. Soc., **44**, 2705 (1922); **45**, 2261 (1923); Cadenhead: Can. Chem. Met., **10**, 201 (1926).

of gold nuclei to the gold salt solution before reduction gives clear red sols both in the presence and in the absence of alkali carbonate. If too few nuclei are added, the sols are blue and cloudy. Apparently, hydrogen peroxide retards the spontaneous formation of a large number of nuclei and favors the rapid growth of the particles. Groll[44] adopts the following procedure to obtain a uniform red sol: 100 cc of pure water is divided equally in three beakers. To the first is added 1.4 cc of a solution containing 1 g of chlorauric acid in 150 cc, to the second 0.6 cc of the gold solution, and to the third 1 cc of 30% hydrogen peroxide. The solutions are neutralized exactly with 0.1 *N* sodium hydroxide, and the hydrogen peroxide is poured into the second beaker. In a short time a clear red nuclear solution is formed which is poured into the first beaker and stirred. This method

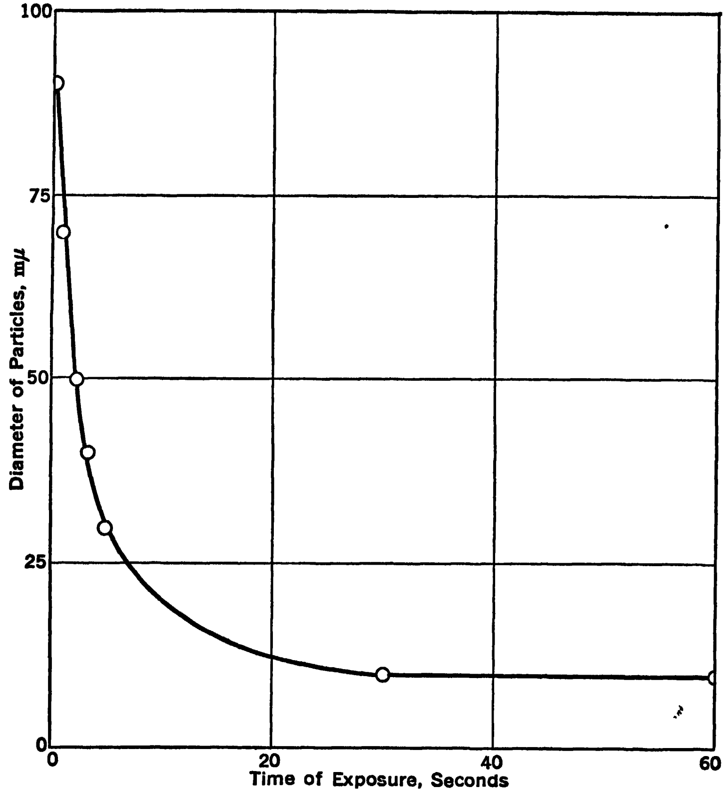

FIG. 9.—Effect of ultraviolet light on the reduction of $HAuCl_4$ by H_2O_2.

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[44] Chem. Weekblad, 13, 617 (1916).

of procedure serves to adjust the *p*H value and to regulate the number of particles in the sol.

Reduction by hydrogen peroxide in the presence of added nuclei has been found very satisfactory for preparing gold sols of a definite degree of dispersion and for determining the size of particles in very highly dispersed sols (see page 58). It is necessary for the success of both these operations that no nuclei should form spontaneously during the reduction process. To realize this condition, Westgren[45] showed that the concentration of chlorauric acid must not be less than 10^{-4} N and the number of added nuclei not less than 5×10^{-9} per cc. It is of interest to note that in the hydrogen peroxide reduction process, as in the formaldehyde process, the tendency for the spontaneous formation of nuclei is greater and the rate of growth of particles is less, the greater the dilution.

In addition to gold particles, many other kinds of small particles will act as nuclei in the hydrogen peroxide reduction process.[46] Among these are nuclei of platinum, silver, mercury, tin, copper, bismuth, cadmium, zinc, iron, alumina, arsenic trisulfide, antimony trisulfide, and sulfur.

Mechanism of the Process.—The reaction taking place in the reduction of chlorauric acid by hydrogen peroxide may be represented by the equation:

$$2HAuCl_4 + 3H_2O_2 \rightarrow 2Au + 8HCl + 3O_2$$

Since neither the reducing agent itself nor the products formed, except the hydrochloric acid, are electrolytes, the course of the reaction may be followed by measuring the change in electrical conductivity of the mixture. This has been done by Svedberg[47] with the results shown diagrammatically in Fig. 10. The addition of the reducing agent to a freshly prepared chlorauric acid solution causes a rapid increase in conductivity of about 30% represented by the line *A–B*, and at the same time the yellow color of the gold solution decreases appreciably. After the initial rise, the conductivity remains constant or rises very slowly for a considerable interval as indicated by the line *B–C* on the curve, and the color of the solution changes but little. After the induction period is over, the conductivity rises rapidly, *C–D* on the curve, accompanied by a sudden red coloration and the appearance of particles easily visible in the ultramicroscope. During

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[45] Svedberg's "The Formation of Colloids," 64 (1921).

[46] Börjeson: Kolloid-Z., **27**, 18 (1920).

[47] "The Formation of Colloids," 62 (1921).

the period of induction it is probable that extremely minute primary particles are first formed which agglomerate and coalesce, ultimately giving particles which are sufficiently large to act as condensation nuclei. When the intensity of color reaches the maximum, the conductivity attains the maximum value for 4 HCl.

The addition of condensation nuclei before adding the reducing agent causes the conductivity as well as the color intensity of the sol to increase proportionally to the time, *A–D′* in Fig. 10. If the nuclei are added during the induction period, say at the point *C′*, the reaction starts at once and goes promptly to completion, *C′–D″*.

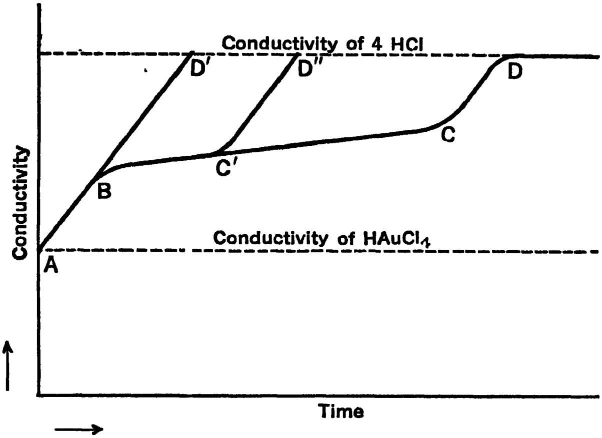

FIG. 10.—Variation of conductivity with time in the reduction of $HAuCl_4$ by H_2O_2.

Reduction with Phosphorus

The classic method of Faraday[48] for the production of colloidal gold consists in the use of a solution of phosphorus in an organic liquid, as reducing agent. A satisfactory preparation is obtained by adding 2.5 cc of 0.6% chlorauric acid and 3 cc of 0.18 *N* potassium carbonate to 120 cc of pure water followed by the addition of 1 cc of a pure ether solution of phosphorus prepared by diluting the saturated solution with 4 or 5 times its volume of ether. In the cold, the mixture changes to a brown color and gradually becomes red, the reaction being complete in about 24 hours. The particles of the sol are so fine that no light cone is visible in the ultramicroscope. The formation of the red sol can be hastened by boiling the reduction mixture after it has stood 10 to 15 minutes. This serves to drive off

[48] Phil. Trans., **147**, 145 (1857); *cf.* Vanino and Hartl: Ber., **37**, 3620 (1904).

the excess ether, and the excess phosphorus can be oxidized by a current of air. If care is taken in the preparation, uniform particles 2–3 mμ in diameter are obtained. In case an insufficient amount of phosphorus is used, the sol is blue, probably because the gold salt is reduced only to blue hydrous Au_2O and not to gold.[49]

The reducing agent in the formation of gold sol with phosphorus is probably a lower oxide of the element which is formed first.[50] The reason for the very high degree of dispersion of the particles is not obvious. The most probable assumption is that the oxidation of phosphorus gives rapidly an abundance of ion nuclei which serve as condensation centers. At the same time, the presence of ether seems to have a marked effect in cutting down the growth of particles.[51]

Because of the fineness of the particles and their fairly uniform size, gold sols formed by reduction with phosphorus are frequently employed as nuclear liquids in the preparation of gold sols with a graded number and size of particles.

Reduction with Substituted Ammonias

Hydroxylamine.—The addition of a dilute aqueous solution of hydroxylamine to the chlorauric acid-potassium carbonate mixture used in Zsigmondy's process gives a deep blue hydrosol.[52] If no alkali is added, a suspension consisting of relatively large particles of gold is formed,[53] probably because hydroxylamine retards the spontaneous formation of nuclei and favors the rapid growth of particles.[54] Accordingly, sols formed in the absence of nuclei contain relatively large particles. On the other hand, a series of sols with particles of widely varying size can be prepared by the addition of nuclei in varying amounts to the solution of gold salt before adding the reducing agent. This is well illustrated by the results summarized in Table III, which gives the conditions for forming sols of like gold content but with varying particle size. The solutions *A*, *B*, and *C*, as noted in the table were prepared as follows: (*A*) 12.5 cc of 0.6% chlorauric acid was diluted to 400 cc, 5 cc of 0.18 *N* potassium carbonate added, and the mixture diluted to 500 cc; (*B*) 120 cc of gold sol prepared by reduction with phosphorus as described above (see

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[49] Zsigmondy-Thiessen: "Das kolloide Gold," 52 (1925).

[50] Galecki: Kolloid-Z., **11**, 105 (1912).

[51] Thiessen: Z. anorg. Chem., **134**, 366 (1924).

[52] Gutbier: Z. anorg. Chem., **31**, 448; **32**, 348 (1902).

[53] Zsigmondy: Z. anorg. Chem., **99**, 105 (1917).

[54] *Cf.* Thiessen: Kolloid-Beihefte, **29**, 122 (1929).

TABLE III

GOLD SOLS WITH VARYING PARTICLE SIZE OBTAINED BY REDUCTION WITH HYDROXYLAMINE IN THE PRESENCE OF NUCLEI

Solutions mixed, cc			Ratio of linear dimension of particles Sol : nuclei	Properties of sol
A	*B*	*C*		
87.5	25.0	87.5	2 : 1	Red, clear
98.4	3.12	98.4	4 : 1	Red, clear
99.8	0.39	99.8	8 : 1	Red, somewhat cloudy
100.0	0.049	100.0	16 : 1	Reddish, cloudy
100.0	0.006	100.0	32 : 1	Blue, cloudy

page 38), was diluted to 200 cc; (*C*) the gold equivalent of hydroxylamine hydrochloride was dissolved in 1000 cc of water. In the experiments, solutions *A* and *B* were mixed in such proportion that the gold content was constant. Reducing agent *C* was then added dropwise at first and finally poured in very slowly with constant stirring. The particle size was determined ultramicroscopically.

From these observations it is obvious that, the greater the number of added nuclei, the smaller the particles and the redder and clearer the sol. The experiments merely serve to emphasize the importance of the spontaneous formation of nuclei on the size of particles in a sol formed without the addition of nuclear liquid. In this spontaneous formation of nuclei, specific factors appear to be quite as important as the prevailing percentage supersaturation of gold in the solution from which it separates.

Hydrazine.—The reduction of gold solutions with hydrazine in either acid, neutral, or alkaline solutions gives cloudy, highly colored, blue sols.[55] As in the case of hydroxylamine as reducing agent, the addition of nuclei in varying amounts before reduction gives sols that vary in color from clear bright red to blue. To prepare sols with a graded number of particles, 2.5 cc of 0.6% chlorauric acid is diluted to 120 cc, the nuclei added, and finally a small amount of 0.8% hydrazine hydrate or sulfate. In the presence of a suitable amount of nuclei, clear red sols are obtained in acid solution. If alkali carbonate is added before the reduction, the sols are always blue, irrespective of the number of added nuclei. The red sols are beautifully colored but are rather instable.

[55] Gutbier: Z. anorg. Chem., **31**, 448; **32**, 348 (1902); Zsigmondy: **99**, 105 (1917).

Reduction with Gaseous Reducing Agents

Carbon Monoxide.—A reproducible gold sol is obtained by conducting carbon monoxide into either a cold or warm solution of chlorauric acid between 0.004% and 0.10% concentration.[56] The stronger solution takes on a faint red color after 2–3 minutes, later becoming violet, and finally purple as the reduction is completed. If the monoxide is prepared by the action of sulfuric acid on oxalic acid, the dioxide formed simultaneously need not be removed. Large amounts of sol can be prepared in a single operation if the reducing agent is conducted in for a sufficient length of time.

Hydrogen.—A gold sol is obtained also by reduction of a dilute solution of gold salt with hydrogen.[57] The method gives reproducible results only when carried out in the light and in a slightly alkaline solution.[58] Visible light is all that is necessary, but from what has been said (see page 35) it is probable that ultraviolet light would be better.

By impinging a hydrogen flame on a dilute solution of chlorauric acid, Donau[59] prepared a red sol which forms at the point of contact of the flame with the solution. It is claimed that the reducing agent in this case is a lower oxide of nitrogen.[60]

Nitrogen Oxides.—If the electric sparks from a Ruhmkorff coil are passed between two metallic electrodes held near the surface of a dilute solution of chlorauric acid, a sol is obtained as a result of the action of the reducing gases formed during the discharge.[61] If the discharge is passed between one dry electrode and one liquid electrode formed by placing the metal electrode in the solution, or between two liquid electrodes, hydrogen peroxide is obtained which reduces the gold compound, giving sols. At the negative electrode coarsely dispersed particles are obtained and the sol varies in color from violet to blue; at the positive electrode the particles are very small and the sol is red. The addition of nuclear liquids always leads to the formation of bright red sols.

Acetylene.—A garnet-red gold sol results on adding an ether solution of chlorauric acid to a saturated aqueous solution of

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[56] Donau: Monatsh., **26**, 525 (1905).

[57] Vanino: Ber., **38**, 463 (1905); Fuchs and Pauli: Kolloid-Beihefte, **21**, 209 (1926).

[58] Janek and Schmidt: Kolloid-Z., **52**, 289 (1930); Schmidt: **55**, 333 (1931).

[59] Monatsh., **34**, 335 (1913).

[60] Halle and Pribram: Ber., **47**, 1398 (1914).

[61] Naumoff: Kolloid-Z., **32**, 95 (1923).

acetylene.[62] Although the sol is distinctly acid, it is highly stable probably because of the presence of an organic protecting agent.[63]

Reduction with Protecting Colloids

The use of a reducing agent which has also the property of a protecting colloid usually leads to the formation of red gold sols with a high degree of stability. Such sol mixtures possess more of the properties of the protecting agent than of gold. The reason is that the metallic particles are covered by a film of the protecting colloid or the smaller primary particles are adsorbed at points on the surface of the large micelles of the protecting colloid. The water-peptizable colloids most commonly used as reducing agents in the synthesis of colloidal gold are tannin and the so-called sodium protalbinate and lysalbinate formed by the saponification of albumin.

Tannin.—Tannin in its double rôle of reducing agent and protecting colloid makes possible the preparation of a stable, deep-red gold sol without taking any special precautions.[64] To 100 cc of distilled water preferably, although tap water will do, is added 5 to 10 cc of a 0.01% solution of chlorauric acid. After making neutral to litmus and heating, a freshly prepared 1% aqueous solution of tannin is added drop by drop until an intense red coloration is obtained. In the presence of a slight excess of tannin the sol is very stable, but it may be made quite sensitive to the action of electrolytes by avoiding an excess of the protecting colloid. Beaver and Muller[65] showed that the hydrogen ion concentration of the solution to be reduced has a marked effect on the time of reduction and on the color and stability of the resulting sol. Solutions of gold of varying *p*H value were made by adding varying amounts of potassium carbonate to chlorauric acid solution. After the concentrations were adjusted to 0.025 g of gold per liter, the solutions were heated to 65° and a constant amount of tannin was added at a uniform rate with uniform stirring. The time for the first appearance of color was noted, and the nature of the preparation was observed. The results are given in Table IV. As in the case of sols formed with hydrogen peroxide, there is an optimum *p*H range in which clear bright red sols are formed.

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[62] Blake: Am. J. Sci., (4) **16**, 381 (1903); *cf.* Domanitzkii: Chem. Abstracts, **23**, 5383 (1929).

[63] Lottermoser: Abegg's "Handbuch anorgan. Chem.," 834 (1908).

[64] Garbowski: Ber., **36**, 1215 (1903); Ostwald: "Kleines Praktikum der Kolloidchemie," 2 (1920).

[65] J. Am. Chem. Soc., **50**, 304 (1928).

TABLE IV

EFFECT OF *p*H ON GOLD SOLS FORMED BY REDUCTION WITH TANNIN

*p*H	Time of reduction, seconds ± 10%	Nature of preparation
3.16	312	Grayish suspension
3.43	217	Bluish suspension
3.76	17	Purple suspension
4.16	16 5	Violet sol
4.53	9.3	Red sol
4 72	5	Red sol
7.66	14	Red sol
8 95	17	Red sol, trace of blue
9 36	30	Bluish red sol
9.63	58	Violet sol

Sodium Protalbinate and Lysalbinate.—To prepare a gold sol by the aid of sodium protalbinate and lysalbinate, Paal[66] adds a dilute solution of chlorauric acid to a weak solution of the reducing agent. A precipitate results which is peptized by the careful addition of an excess of dilute alkali. The mixture is then warmed on the water bath, giving an intense red sol which is purified by dialysis. The sol may be precipitated by excess alcohol or may be evaporated to dryness. The dried powder is readily peptized by shaking with water to form relatively concentrated sols.

Biological Fluids, etc.—Protective action also plays a rôle in the formation of gold sols by reduction with biological fluids such as saliva,[67] serum, cerebrospinal fluid, and urine,[68] and with plant extracts from leaves,[69] flowers,[70] and moss.[71] Also certain aromatic phenols,[72] ethereal oils,[73] carbohydrates,[74] alkaloids,[75] and other organic compounds which possess a high molecular weight or

[66] Ber., **35**, 2236 (1902).

[67] Von Weimarn: Japan J. Chem., **3**, 123 (1926).

[68] Utzino: Kolloid-Z., **41**, 28 (1927).

[69] Janek: Kolloid-Z., **41**, 242 (1927); Iwase: **44**, 42 (1928).

[70] Von Weimarn: Kolloid-Z., **44**, 41 (1928).

[71] Gutbier, Huber, and Kuhn: Kolloid-Z., **18**, 57 (1916).

[72] Stoeckl and Vanino: Z. physik. Chem., **30**, 98 (1899); Henrich: Ber., **36**, 609 (1903): Garbowski: Ber., **36**, 1215 (1903).

[73] Vanino and Hartl: Ber., **39**, 1696 (1906).

[74] Vanino: Kolloid-Z., **2**, 51 (1907); Lerdler: Suppl. I, 23 (1907).

[75] Charmandaijan: Kolloid-Z., **49**, 133 (1929).

which undergo condensation, give sols with an abnormally high stability, indicating that colloid protection or strong adsorption plays an important part in the sol-forming process.

Reduction in the Presence of Protecting Colloids

Cases of colloidal gold synthesis in which the reducing agent plays the simultaneous rôle of protecting colloid are rare compared to those in which the protecting colloid and reducing agent are added separately. Thus if a small amount of gelatin[76] or tannin is added to the solution of gold salt before reduction, the stability of the resulting sol is greatly increased. Wuth[77] strongly recommends the addition of a mere trace of tannin to the gold salt solution before reduction with formaldehyde, in preparing a reproducible sol for Lange's cerebrospinal fluid test (see page 102).

Among other substances which may be used, more or less successfully, as protecting colloids for gold are gum arabic,[78] starch,[79] soaps,[80] saponin,[81] quince extract,[82] and linseed oil.[83] The addition of silica sol[84] to chlorauric acid before reduction prevents the formation of large particles of gold even when the salt concentration is relatively high. Apparently the gold salt or the element at the moment of liberation is adsorbed by the hydrous oxide particles, and the growth of the gold particles is thereby retarded or prevented.[85] In all these cases the properties of the gold are modified or masked more or less completely by the adsorbed protecting agent.

Reduction in the Presence of Colloidal Electrolytes

Berkman[86] patented a process for the preparation of stable, relatively highly concentrated sols of gold and other metals which are described as free from electrolyte and protecting colloid. The method consists essentially in reduction of the gold solution in the

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[76] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900).

[77] Münch. med. Wochschr., **75**, 472 (1928).

[78] Gutbier: Kolloid-Z., **9**, 175 (1911).

[79] Gutbier and Weingärtner: Kolloid-Beihefte, **5**, 244 (1913).

[80] Rideal and Bircumshaw: Chem. Abstracts, **17**, 3121 (1923); Iredale: J. Chem. Soc., **119**, 625 (1921); Papaconstantinou: J. Phys. Chem., **29**, 319 (1925); Kolloid-Z., Zsigmondy Festschrift, **36**, 329 (1925).

[81] Gutbier, Huber, and Haug: Kolloid-Z., **29**, 25 (1921).

[82] Gutbier and Wagner: Kolloid-Z., **19**, 287 (1916).

[83] Gutbier, Huber, and Kuhn: Kolloid-Z., **18**, 263 (1916).

[84] Küspert: Ber., **35**, 2815 (1902).

[85] Hiege: Z. anorg. Chem., **91**, 145 (1915).

[86] German Pat., 529,625 (1931).

presence of lyophilic colloidal electrolytes such as the soaps, or by means of colloidal electrolyte reducing agents such as mercury sulfosalicylic acid and its salts or phenylhydrazine sulfonic acid, followed by prolonged dialysis which is said to remove both the electrolyte and the protecting colloid responsible for the fine state of subdivision of the particles. The method is ingenious, but the author is of the opinion that the sols formed in this way are not entirely free from protecting colloids. Von Weimarn prepared highly stable sols which contained too little "formose" to detect, but there is no doubt that the stability of von Weimarn's sols is due in large measure to the trace of protecting colloid which they contain.

Electrical Synthesis

The Arc Process.—Gold sols are obtained by passing an arc between gold electrodes immersed in a liquid using a direct-current arc according to Bredig's method or an oscillating arc according to Svedberg's method already described (see page 12). The latter is preferable for preparing organosols with very small particles. Thus Börjeson[87] prepared an alcosol with an oscillating arc, in which the radius of the gold particles was 2.8 mμ.

Although it is theoretically possible to obtain stable hydrosols by the aid of the arcing process in the absence of any electrolyte impurity, actually the presence of some electrolyte appears to be essential if the stability is maintained very long. Thus Bredig recommended the use of 0.001 N sodium hydroxide instead of pure water in preparing sols by his method; and Whitney and Blake[88] obtained more stable sols by sparking across gold electrodes in very dilute hydrochloric acid than in water. Beans and Eastlick[89] have confirmed and extended these observations. Thus they found that Bredig's method yields stable sols in the presence of chloride, bromide, iodide, and hydroxyl ions in concentrations ranging from 0.00005 to 0.005 N; but not with fluoride, nitrate, sulfate, or chlorate ions of the same concentration. The upper limit of concentration for a given anion is governed somewhat by the precipitating power of the cation for the negative sol. The lower limit of electrolyte concentration required to produce a red sol is, within a wide range, independent of the concentration of the sol formed. The stabilizing effect is not

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[87] Svedberg's "The Formation of Colloids" (1921).

[88] J. Am. Chem. Soc., **26**, 1376 (1904).

[89] J. Am. Chem. Soc., **37**, 2667 (1915); *cf.* Bendien: Chem. Weekblad, **23**, 168 (1926); Eirich and Pauli: Kolloid-Beihefte, **30**, 113 (1930).

produced by dispersion of the gold in pure water and subsequent addition of the electrolyte. It seems to be closely related to the ability of the ion to form stable compounds of gold which can act as stabilizing electrolytes for the sol. The significance of this will be discussed in a later section of this chapter.

A sol formed by electrical disintegration in hydrochloric acid may be purified and concentrated by what Pauli and Russer[90] term electrodecantation. In this process the sol is electrolyzed between the membranes of an electrodialyzing apparatus, the particles moving away from the cathode membrane and concentrating in the region of the anode membrane. The lighter liquid layer around the cathode membrane rises and spreads out while the heavier sol settles, giving two layers. To effect further purification, the upper layer is removed, an equal amount of water added, and the process repeated.

Organosols have been prepared by electrical dispersion in methyl, ethyl, *n*-propyl, and isobutyl alcohols, and in ethyl malonate. If there were any occasion for it, it is probable that sols could be formed in almost any organic medium by suitable electrical dispersion methods.

If an electric arc is passed between gold electrodes enclosed in a porcelain crucible, the vapors of the metal collect in a finely divided form on the cold walls of the vessel. On shaking with liquids, some of the smaller particles are dispersed but the resulting sols are instable.[91]

Electrolysis.—An interesting experiment which leads to the formation of a gold sol consists in what has been termed electrolysis without electrodes.[92] A metal anode is dipped into a dilute chlorauric acid solution while the cathode (an aluminum ring or disc) is located 4 or 5 cm above the solution, the whole system being exhausted to the vapor pressure of the solution. With a current of 10–60 milliamperes and a voltage of 500, the metal is liberated as a fine powder. At the higher current density and with sufficiently dilute solutions, typical colored sols are obtained.

COLLOIDAL GOLD IN SOLIDS

Gold has been obtained in the colloidal state in a number of solids. Two of these are of technical importance: gold purple of Cassius and gold ruby glass.

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[90] Kolloid-Z., **58**, 22 (1932).

[91] Fürth: Kolloid-Z., **34**, 224 (1924).

[92] Corbino: Atti accad. Lincei, (6) **5**, 377 (1927); *cf.* Gubkin: Wied. Ann., **32**, 114 (1887).

Purple of Cassius

Formation.—The addition of stannous chloride to a solution of auric salt first gives a red coloration followed by the settling out of a purple or brown precipitate known as gold purple of Cassius, named for Andreas Cassius of Leyden who discovered it in 1663. Because of its wide use as a pigment in the ceramic industry a number of recipes have been given for its preparation. The substance varies in color and composition with the method of formation. It is readily obtained by adding to 4 liters of water, 200 cc of 0.6% chlorauric acid and 250 cc of stannous chloride (containing 3 g tin per liter) solution in dilute hydrochloric acid. After standing 3 days, the purple precipitates as a dark violet powder, leaving a clear, supernatant liquid free from gold or tin. After washing by decantation until free from chloride, it is filtered on a suction funnel. If the hydrous precipitate is suspended in water to which is added a little ammonia, it is peptized by boiling, forming a clear purple sol.

Rhythmic bands of purple of Cassius in silica gel are obtained by allowing stannous chloride to diffuse into a gel containing chlorauric acid.[93] A suitable gel is prepared by adding 12.5 cc of water glass, density 1.16, to 12.5 cc of 3 *N* hydrochloric acid and 1 cc of 1% chlorauric acid. After standing in a test tube 3 days the gel is covered with 3 cc of a solution containing the equivalent of 10 g anhydrous stannous chloride and 1 g stannic chloride in 90 cc of water.

Constitution.—Certain earlier investigators as Richter and Gay Lussac believed purple of Cassius to be a mixture, but Berzelius thought it was a definite chemical individual, for several reasons: the purple possesses a purple color, whereas a mixture of gold and stannic oxide is brick red; gold is not separated from purple of Cassius by aqua regia, but it is from an ordinary mixture; mercury does not extract gold from the purple as it does from a mixture; and finally, as already noted, the purple is converted into a purple liquid by treating with a dilute solution of ammonia. But in spite of all this positive evidence of the chemical individuality of the purple, we now know that Berzelius' view is incorrect. From analysis of purples, Buisson[94] found the composition to be variable. Debray[95] believed that gold forms a kind of color lake with stannic oxide which is soluble in ammonia. Schneider,[96] on the other hand, recognized the colloidal character

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[93] Davies: J. Am. Chem. Soc., **45**, 2261 (1923).

[94] J. pharm., **16**, 631 (1830).

[95] Compt. rend., **75**, 1025 (1872).

[96] Z. anorg. Chem., **5**, 80 (1894).

of the purple and concluded rightly that its ammoniacal solution is a mixture of colloidal gold with colloidal hydrous stannic oxide. In support of this view, Zsigmondy[97] showed that a mere trace of ammonia will peptize a relatively large amount of the freshly precipitated purple, and that the purple color will not pass through parchment during electrolysis as electrolytes do. Finally, he settled the question definitely[98] by coagulating with nitric acid suitable mixtures of colloidal stannic oxide and pure colloidal gold, obtaining purples of different shades and intensities almost identical with the products formed in other ways. The gold is not combined chemically with stannic oxide, but the usual properties of gold are masked to a large extent by the protective action of the hydrous oxides.

Gold Ruby Glass

Formation.—Gold ruby glass is readily obtained by melting a lead or barium glass and adding a small amount of gold as gold chloride or in the form of purple of Cassius as was done by Kunkel, the discoverer of the glass. If the melt is cooled quickly the glass will be colorless; but if cooled slowly, or if the cold glass is heated rapidly to a temperature well below the melting point, it assumes a beautiful clear red color. Ultramicroscopic observations of Zsigmondy and Siedentopf[99] showed that the red color is due to myriads of colloidal gold particles of the size to transmit red light. If the temperature is too high or the time of heating too long, the red color may change to violet and then to blue, owing to growth or agglomeration of particles. Similar color changes in gold hydrosols are well known. The addition of some stannous oxide to the glass acts as a protecting agent, retarding the transformation from red to blue on prolonged warming.[100]

Colorless Gold Glass.—Although the cause of the color in gold ruby glass is understood, it is not obvious why the chilled melt is colorless at first. This cannot be due to the presence of a colorless gold salt,[101] since Zsigmondy showed that the mass is colorless even when a strong reducing agent is present. Zsigmondy is of the opinion that the original colorless gold glass consists of a supersaturated

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[97] Ann., **301**, 361 (1898).

[98] *Cf., however,* Pauli: Kolloid-Z., **28**, 50 (1921).

[99] Ann. Physik, (4) **10**, 1 (1903); Zsigmondy-Alexander: "Colloids and the Ultramicroscope," 168 (1909).

[100] Bellamy: J. Am. Ceram. Soc., **2**, 313 (1919); *cf., also,* Fuwa: J. Japan Ceram. Soc., **34**, 163, 213, 260 (1926); **35**, 214 (1927).

[101] *Cf., however,* Silverman: J. Am. Ceram. Soc., **7**, 796 (1924).

solution of metallic gold in the vitreous mass together with extremely minute gold nuclei which arise from the supersaturated solution on cooling. During the subsequent heating, the nuclei grow, at the expense of the supersaturated solution, to particles large enough to transmit red light. No reason is given by Zsigmondy for assuming that the gold in the original colorless glass is in true solution, and, from analogy with the alkali metals,[102] one might expect a solution of metallic gold to have the same color as gold vapor. This is not necessarily the case, however, since metals cathodically disintegrated and atomically dispersed in a suitable salt layer do not color it.[103] Since Zsigmondy assumes that part of the gold in the colorless glass is dispersed into particles too small to affect the beam of light, the possibility should not be overlooked that all the gold is in this state. In this connection von Weimarn[104] points out that, in natural gold-bearing quartz, the gold may appear in colorless dispersion.

The amount of gold in ruby glass is quite small, 0.01% giving a pink color and 0.1% a bright red. Since a borax bead is colored red by a mere trace of gold, the borax bead test may be used to detect the presence of small amounts of the element in solution.[105]

Colloidal Gold in Various Solids

Müller[106] prepared colloidal dispersions of gold in magnesia, lime, barium sulfate, calcium sulfate, calcium phosphate, zinc oxide, lead monoxide, and alumina by suspending the several solids in a dilute solution of chlorauric acid, reducing the gold salt with a suitable reducing agent such as an alkaline solution of dextrose or glycerin, drying, and igniting the resulting products.[107] By suitable variations in conditions, "purples" of a variety of shades and intensity of color were obtained. Blank and Urbach[108] prepared colored crystals of the alkali halides by adding gold chloride to the fused salts and allowing them to cool. The color appeared after solidification and changed on cooling, the final color depending on the rate of cooling and the nature of the salt, being red-violet with potassium chloride, blue to green with potassium bromide, and yellow with potassium iodide.

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[102] Svedberg: Ber., **39**, 1705 (1906); *see* page 151.

[103] Weber and Oosterhuis: Proc. Acad. Sci., Amsterdam, **19**, 597 (1916).

[104] Kolloid-Z., **11**, 287 (1912).

[105] Donau: Monatsh., **25**, 913 (1904).

[106] J. prakt. Chem., (2) **30**, 252 (1884).

[107] *Cf.* Antony and Lucchesi: Gazz. chim. ital., (2) **26**, 195 (1896).

[108] Naturwissenschaften, **15**, 700 (1927); Sitzber. Akad. Wiss. Wien, II*a*, **137**, 147 (1928); **138**, 701 (1929).

Ultramicroscopic observation disclosed that the color was due to the presence of colloidal gold which agglomerated into small clumps on dissolving the salt.

Moissan[109] obtained purples which owe their color to colloidal gold by distilling the element with stannic oxide, alumina, magnesia, zirconia, silica, and lime.

If freshly precipitated finely divided solids such as alumina,[110] barium sulfate,[111] and calcium carbonate are shaken with colloidal gold, the particles are adsorbed on the surface of the precipitates, giving colored bodies which resemble the color lakes. Fibers mordanted with alumina likewise adsorb colloidal gold.

COMPOSITION OF GOLD HYDROSOLS

Sols Formed by Zsigmondy's Method.—Faraday[112] in his researches three-quarters of a century ago showed that preparations which we now call gold hydrosols contain particles that are essentially pure gold. That such is the case was definitely established by Scherrer[113] as a result of x-ray analysis of the coagulum from a gold sol. The x-ray pattern was found to be identical with that obtained from macroscopic crystals of gold even when the length of the edge of the primary particle of colloidal gold, which was assumed to be cubical, was no greater than 1.86 $m\mu$.[114]

Zsigmondy[115] analyzed the coagulum from a red gold sol prepared by the formaldehyde process and found it to contain no more than a trace of unreduced gold compound. To account for the charge and stability of the sol, Pauli[116] assumed the presence of unreduced gold salt on the surface of the colloidal particles; but when he attempted to find such compounds in the coagulum from a sol prepared by reduction with tannin,[117] he was unsuccessful in his quest. Thiessen[118] repeated with particular care the analysis of the coagulum

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[109] Compt. rend., **141**, 977 (1905).

[110] Zsigmondy: "Kolloidchemie," 5th ed., **2**, 26 (1927).

[111] Vanino: Ber., **35**, 662 (1902).

[112] Phil. Trans., **147**, 145 (1857).

[113] Zsigmondy's "Kolloidchemie," 3rd ed., 399 (1920); Freundlich: Ber., **61**, 2219 (1928).

[114] *Cf.* Zsigmondy: Kolloid-Beihefte, **23**, 21 (1926).

[115] Ann., **301**, 29 (1898).

[116] Kolloid-Z., **28**, 49 (1921).

[117] Kautzky and Pauli: Kolloid-Beihefte, **17**, 294 (1923).

[118] Z. anorg. Chem., **134**, 393 (1924).

and the filtrate from a Zsigmondy gold sol and showed that neither unreduced gold salt nor oxide was present in the sol in sufficient amount to be detected.

Since there is no disagreement so far as the experiments are concerned, it would appear that the matter should be settled. The difficulty is that, in the total absence of impurities in the precipitate, the cause for the charge on the particles and the stability of the sol is not obvious. In the course of their investigations Pauli and his coworkers[119] observed that precipitated gold contains water which is not driven off at 100°. This was confirmed by Thiessen,[120] who showed that a temperature of 600° is necessary to drive off the last trace of water from a gold coagulum. Since it is a usual thing for metals, especially when finely divided, to adsorb moisture, Thiessen made the very probable assumption that the small amount of water held by colloidal gold above 100° is adsorbed by the particles. Pauli, on the other hand, assumed that this water is chemically combined on the surface of the particles as a gold hydroxy acid, $HAu(OH)_4$.

To account for the negative charge on the colloidal particles, both Zsigmondy[121] and Thiessen[122] assume the preferential adsorption of hydroxyl ions from water or alkali by the surface of the particles. In support of this view, Zsigmondy points out that sols formed in the presence of alkali are, in general, more stable than those formed in its absence. Moreover, Thiessen and Heumann[123] observed an increase in the mobility of the particles on adding a little alkali to a well-dialyzed Zsigmondy sol, indicating that the charge on the particles is increased; and Iwase[124] found that the stability of von Weimarn's gold sol toward electrolytes was increased by the presence of potassium hydroxide. Pauli, on the other hand, attributes the charge to the partial ionization of $HAu(OH)_4$ on the surface of the particles.[125] This is equivalent to preferential adsorption of the complex ion, a portion of the corresponding hydrogen ion existing in the intermicellar solution.

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[119] Kautzky and Pauli: Kolloid-Beihefte, **17**, 294 (1923); Adolf and Pauli: Kolloid-Z., **34**, 29 (1923).

[120] Z. anorg. Chem., **134**, 393 (1924).

[121] Mikrochemie, **2**, 50 (1924).

[122] Z. anorg. Chem., **134**, 400 (1924); Osterr. Chem.-Ztg., **29**, 133 (1926).

[123] Z. anorg. Chem., **148**, 382 (1925).

[124] Bull. chem. soc., Japan, **4**, 120 (1929).

[125] Pauli: Mikrochemie, **2**, 47 (1924); Kautzky and Pauli: Kolloid-Beihefte, **17**. 294 (1923); Eirich and Pauli: **30**, 113 (1930).

There is no apparent way to distinguish between the views of Pauli and Zsigmondy. Pauli[126] thought he had brought forth evidence in support of his hypothesis when he showed that a well-dialyzed sol formed by reduction has a higher conductivity than the dialysis water, and that the hydrogen ion concentration increases gradually during the dialysis, attaining a value that is definitely on the acid side when the constant conductivity is reached. According to Pauli this increased acidity is not due to carbon dioxide dissolved from the air, to silica from the glass vessels, or to colloidal organic acids from the dialyzing membranes.[127] Assuming that the facts are as stated, these observations which Pauli considers to be so important are obviously not significant since the small acidity observed in the well-dialyzed sol would follow whether one postulates that the charge on the particles results from preferential adsorption of hydroxyl ions from water or from preferential adsorption of the complex anion from the $HAu(OH)_4$ which Pauli assumes to be present. It is evident that Pauli has involked the presence of $HAu(OH)_4$ to account for the retention of water by the colloidal particles above 100° because, at the time, this was the most probable complex that he could think of for explaining the charge on the particles in the pure sol. It hardly seems likely that Pauli would go so far as to postulate the formation of definite complex compounds to account for the retention by active adsorbent charcoal of benzol and alcohol at temperatures considerably above the boiling point of the pure liquids.[128]

Zsigmondy and Thiessen throw out Pauli's suggestion that $HAu(OH)_4$ exists in a gold sol on the ground that no one has ever prepared the compound and even if anyone had, there is no direct evidence of its existence in a gold sol. This gesture would be much more impressive if it were not for the fact that the evidence for the preferential adsorption by the gold particles of hydroxyl ion from water, or even from alkali, is likewise altogether indirect. A good reason for assuming the existence in the sol of a complex ion like $[Au(OH)_4]^-$ is that such an ion, containing an atom common to the adsorbent, is likely to be strongly adsorbed. In the case at hand, however, there seems to be no necessary reason for assuming a strongly adsorbed complex ion when the hydroxyl ion itself is likely to be rather strongly adsorbed by gold. From adsorption studies with

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[126] Adolf and Pauli: Kolloid-Z., **34**, 29 (1924).

[127] Fuchs and Pauli: Kolloid-Beihefte, **21**, 195 (1925).

[128] Berl and Schwebel: Z. angew. Chem., **36**, 552 (1923).

salt and oxide adsorbents, Paneth[129] and Fajans[130] were led to conclude that those ions will be relatively strongly adsorbed by salts whose compounds with the oppositely charged ions of the ion lattice are slightly soluble or weakly ionized. This rule was found to hold very well indeed in the adsorption of various anions by barium sulfate[131] and is applicable in a general way to the adsorption of anions by silver iodide.[132] Since the hydroxides or hydrous oxides of both univalent and trivalent gold are highly insoluble, one would expect relatively strong adsorption of hydroxyl ion by gold.

The assumption that the elements of water in precipitated gold are present as the complex electrolyte, $HAu(OH)_4$, appears not to have been taken seriously even by Pauli himself, since recent observations on a gold sol formed by electrical methods led him to conclude that the stabilizing ion in gold sols, generally, is $[AuCl_2]^-$, which decomposes after coagulation to $[AuCl_4]^-$, Cl^-, and gold, the ions going into solution so that the precipitate is free from chloride (*cf.* page 54).

In this connection the author is inclined to believe that a more important factor than the charge on the particles, in determining the stability of the so-called "pure" gold sols prepared by Zsigmondy's method, is the presence of a small amount of a condensation product of formaldehyde formed during the precipitation. This, however, does not eliminate the necessity of accounting for the negative charge on the particles.

Von Weimarn[133] insists that the complete absence of unreduced gold compounds in a Zsigmondy sol has not been established and believes that there is always more or less AuOH present even though it is difficult to detect. Von Weimarn brings forth this claim in support of his contention that a gold sol prepared by reduction methods always results from reduction of colloidal particles of AuOH formed as an intermediate stage in the process. Even though this compound is a necessary intermediate stage in the formation of colloidal gold (which the author does not admit), it still does not

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[129] Physik. Z., **15**, 924 (1914); Horovitz and Paneth: Z. physik. Chem., **89**, 513 (1915).

[130] Fajans and Beer: Ber., **46**, 3486 (1913); Fajans and Richter: **48**, 700 (1915); *cf.* Hahn, Erzbacher, and Fiechtinger: Ber., **59**, 2014 (1926); Hahn: Naturwissenschaften, **14**, 1196 (1926).

[131] Weiser and Sherrick: J. Phys. Chem., **23**, 205 (1919); Weiser: "The Colloidal Salts," 187 (1928).

[132] Beekley and Taylor: J. Phys. Chem., **29**, 942 (1925).

[133] Kolloid-Z., **45**, 203 (1928); **48**, 346 (1929).

follow that some of it must remain after the reduction has been carried as far as it will go. This does not mean that AuOH is not present in many gold sols formed by reduction methods. Indeed, Thiessen[134] showed that the blue gold sols prepared by reduction with hydrazine hydrate according to Gutbier's method (see page 140) may contain as much as 50% of the blue oxide. Similarly, a gold sol formed by reduction with an ether solution of phosphorus always contains unreduced gold compounds either as salt or as hydrous aurous oxide; and Zsigmondy's gold sols may contain appreciable amounts of unreduced compounds if the reduction mixture is not boiled.

Sols Formed by Electrical Disintegration.—As already noted, stable sols are formed by the Bredig process only in the presence of small amounts of ions such as chloride, bromide, iodide, and hydroxyl, but not of sulfate and fluoride. One explanation of this is that the halogen and hydroxyl ions are preferentially adsorbed by the gold particles, imparting to them a relatively high negative charge. The difficulty with this assumption is that one would not necessarily expect strong adsorption of these simple univalent ions by the particles of elementary gold. Moreover, a stable sol is not obtained in the presence of divalent sulfate, which one would expect to be adsorbed much more strongly than the univalent halides. A more plausible explanation involving the formation of complex ions such as $[AuCl_4]^-$ and $[AuBr_4]^-$ which should be strongly adsorbed was suggested by Beans and Eastlick[135] and extended by Eirich and Pauli[136] and Pauli and Russer.[137] According to the latter, if a spark is passed between gold electrodes in dilute hydrochloric acid, for example, there is oxidation of a little of the gold to AuCl, which subsequently reacts with HCl to give $HAuCl_2$. Although this compound is instable one might expect it to be stabilized by strong adsorption of the complex anion with the gold atom in the complex oriented toward the gold atoms in the lattice, as represented diagrammatically in Fig. 11. In this diagram, which is similar to that suggested by Weiser[138] for the hydrous oxide sols, the colloidal particle consists essentially of crystalline gold on the surface of which are adsorbed $[AuCl_2]^-$ ions constituting the inner layer of an ionic double layer. The outer portion of this double layer is a diffuse layer of hydrogen ions. Part of

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[134] Z. anorg. Chem., **134**, 357 (1924); *cf.* Steubing: Ann. Physik, (4) **26**, 335 (1908).

[135] J. Am. Chem. Soc., **37**, 2667 (1915); *cf.* Shear: Dissertation, Columbia University (1925).

[136] Kolloid-Beihefte, **30**, 113 (1930).

[137] Kolloid-Z., **58**, 22 (1932).

[138] J. Phys. Chem., **35**, 1, 1368 (1931).

these are held by electrostatic attraction to the adsorbed $[AuCl_2]^-$ ions so strongly that they will not influence a hydrogen electrode; but the remainder, because of a relatively higher kinetic energy, get into the intermicellar solution, which is indicated in the figure beyond the dotted circle. Because of the diffuseness of the outer layer, the particles possess a negative charge balanced by an equivalent amount of hydrogen ions in the intermicellar solution. If the stabilizing electrolyte is an alkali salt, the alkali cations will be the so-called contra ions which constitute the diffuse outer layer.

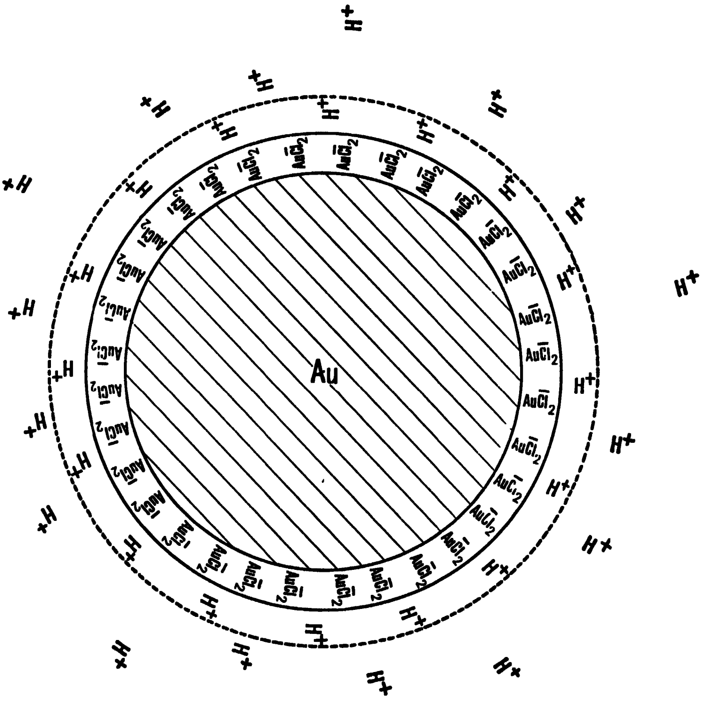

FIG. 11.—Diagrammatic representation of the constitution of a colloidal gold micelle stabilized by preferential adsorption of $[AuCl_2]^-$ ions. The H^+ ions beyond the dotted circle are in the intermicellar solution.

Pauli and Russer examined the sol formed by electrical disintegration in the presence of hydrochloric acid, followed by concentrating and purifying by electrodecantation (see page 46). The hydrogen ion concentration was measured and the chloride as ion and as the constituent of the complex anion was determined in the supernatant solution obtained on coagulating the sol by freezing. The results showed that the ratio of HCl to $HAuCl_4$ in the supernatant solution was approximately 2 to 1. To account for this, Pauli and Russer assumed that the stabilizing ion is $[AuCl_2]^-$ and that this is released during the coagulation process and decomposes in accord with the equation:[139]

$$3[AuCl_2]^- \rightarrow [AuCl_4]^- + 2Cl^- + 2Au$$

This would explain the absence of chloride in the coagulum from the sol.

That the charge on the particles formed in the presence of the several halides is probably not due primarily to direct adsorption of the halogen ion is further indicated by the fact that, for the same concentration of halogen, the tendency to form a stable gold sol by the Bredig process is in the order: chloride > bromide > iodide, whereas from solubility considerations and from the ease of deformability of iodide ion, one would expect the order of adsorbability of the ions by gold to be: iodide > bromide > chloride. The marked falling off in the tendency to form sols in going from chloride to bromide to iodide solutions is doubtless associated with the decreasing tendency to form complex salts of the type, $HAuX_4$ or $HAuX_2$ (where X = chlorine, bromine, iodine), in accord with the equations:

$$AuX_3 + HX = HAuX_4$$

and

$$AuX + HX = HAuX_2$$

This tendency is even less marked with sulfate than with iodide, which probably accounts for the failure to obtain stable sols by electrical dispersion in dilute sulfuric acid solutions. In dilute alkali solution it is unnecessary to postulate the formation of complexes such as $KAu(OH)_4$ or $HAu(OH)_4$, since, as already explained, one might expect fairly strong adsorption of the simple hydroxyl ions by the gold particles.

It is significant that the conditions of formation and the properties of gold sols formed by electrical dispersion in dilute alkali and in dilute hydrochloric acid are quite different. Thus, a higher concentration of alkali than of hydrochloric acid is required to form a stable sol; and the sol formed in the presence of alkali is instable on boiling and in the presence of carbon dioxide,[140] whereas that formed in the

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[139] Rose: Chem. News, **111**, 183, 196 (1915); Grube: Z. Elektrochem., **35**, 703 (1929).

[140] Eirich and Pauli: Kolloid-Beihefte, **30**, 113 (1930).

presence of hydrochloric acid is not affected by boiling or by carbon dioxide. This indicates that the adsorption of hydroxyl ions by the gold particles is not so strong as that of the complex $[AuCl_4]^-$ or $[AuCl_2]^-$ ions.

Since the sol formed by Zsigmondy's process is stable on boiling and in the presence of carbon dioxide, it is apparent that the stabilizing electrolyte in the Zsigmondy sol cannot be a pure hydroxy complex, $HAu(OH)_4$, as Pauli first assumed. As pointed out repeatedly, it seems altogether probable that the relatively high stability of the so-called "pure" Zsigmondy sol is not due so much to adsorption of hydroxyl or of a complex ion as to the presence of a small amount of protecting colloid formed by the action of dilute alkali on formaldehyde.

CHAPTER III

COLLOIDAL GOLD: PROPERTIES

The properties of colloidal gold will be considered under the following headings: size and shape of the particles; kinetic properties; electrical properties; color; mutual action between sols; and chemical properties.

SIZE AND SHAPE OF THE PARTICLES IN GOLD HYDROSOLS

Determination of Particle Size

Ultramicroscopic Method.—Probably the most satisfactory method of determining the size of colloidal particles consists in counting the number of particles in a given volume by the aid of the ultramicroscope[1] and analyzing for the total amount of disperse phase in a known volume. If n represents the number of particles per cubic centimeter of sol, m, the total amount of dispersed phase per cubic centimeter, and d, the density of the dispersed phase, then the volume v of a single particle is

$$v = \frac{m}{nd} \tag{1}$$

The method presupposes that the particles are quite uniform in size and that most of them are visible. The lower limit of particle size in gold sols that can be determined with the slit ultramicroscope is about 7.5 mμ in radius. With the immersion ultramicroscope,[2] particles from 3–4 mμ in radius may be observed.

The size of the invisible particles in very highly dispersed gold sols such as Faraday's sol (see page 38) can be determined by adding the sol to a suitable reduction mixture and allowing the particles to grow until they are large enough for observation with the ultramicroscope. If P_0 is the number of nuclei in 1 cc of the original sol and V_0 its

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[1] Siedentopf and Zsigmondy: Ann. Physik, (4) **10**, 1 (1903); Wiegner and Russel: Kolloid-Z., **52**, 1, 189 (1930).

[2] Zsigmondy: Physik. Z., **14**, 975 (1913).

volume; and if P_s is the number of particles in 1 cc of the final sol and V_s its volume, then

$$P_0 = \frac{P_s V_s}{V_0} \tag{2}$$

If the total amount of gold and P_0 are known, the size and weight of the single particle in the original sol can be calculated. By this procedure the size of gold particles as small as 2.6 mμ in diameter have been determined.

X-ray Method.—Scherrer[3] claims that the size of gold particles can be calculated from the breadth of the interference lines in the x-radiogram using the equation for a cubic lattice

$$B = 2\sqrt{\frac{ln\ 2}{\pi}}\cdot\frac{\lambda}{a}\cdot\frac{1}{\cos\theta/2} + b \tag{3}$$

in which B is the distance between the points on each side of the maximum blackening where the intensity of the radiation is reduced to half its value; a, the linear dimension of the particles considered as cubes; λ, the wave length of the x-rays; θ, the angle between the ray and the planes in the crystal; and b, the natural minimum breadth of the Debye-Scherrer diffraction line which is a constant depending on the apparatus and the size and absorption of the specimen. In a fine-grained sol prepared by Zsigmondy's method, Scherrer found the value of a to be 1.86 mμ as compared with Zsigmondy's value of 1.6 mμ obtained by osmotic-pressure measurements. This agreement would appear to be quite satisfactory, but the author is of the opinion that the values estimated from osmotic-pressure measurements are purely accidental and mean very little. Even with particles as small as 1 mμ radius and a sol as strong as 0.5%, the calculated osmotic pressure would be in the neighborhood of 1–2 mm of water. To measure accurately osmotic pressures of this order of magnitude and to be certain that they are not due to electrolyte impurities is expecting too much.

Sedimentation Method.—By determining the rate of settling of the gold particles under the effect of gravity and the radius of the particles, r may be readily estimated by the aid of Stokes' law. This states that the force of friction

$$W = 6\pi\eta r v \tag{4}$$

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[3] Zsigmondy's "Kolloidchemie," 5th ed., **1**, 77 (1925); Scherrer and Staub: Z. physik. Chem., **A154**, 309 (1931); *cf., also,* Brill and Pelzer: Z. Kryst., **72**, 398 (1930).

but since $$W = \frac{4}{3}\pi r^3(d_1 - d_2)g \tag{5}$$

Stokes' law is usually formulated

$$r^2 = \frac{9}{2}\frac{v\eta}{(d_1 - d_2)g} \tag{6}$$

where v is the velocity of settling; d_1, the density of the solid; d_2 and η, the density and viscosity, respectively, of the liquid; and g, the gravitational constant. The value of v can be measured fairly accurately if the particles are sufficiently large to settle relatively rapidly. When the particles are very fine, the rate of settling is negligibly slow. In such cases Svedberg and his coworkers[4] have increased enormously the settling rate by means of a centrifuge free from vibration and turning at a high velocity—a so-called ultracentrifuge. The extent of settling is followed by means of photographs taken automatically on a moving film at definite intervals, while the centrifuge is running. By this means the radius of the particles in a Faraday gold sol was found to vary from 1.7 to 2.5 mμ, the majority having radii between 2.0 and 2.5 mμ.

Burton and Reid[5] increased the settling rate in a copper sol by applying an alternating-current electric field so that the direction of migration was for alternate periods, with and opposed to gravity. By this means they were able to determine the particle size in sols containing particles so small that the Brownian movement masks the effect of gravity.

Diffusion Method.—The size of colloidal particles may be determined from measurements of the rate of diffusion as a result of the Brownian motion of the particles. The diffusion constant, D, of a colloid is given by the equation[6]

$$D = \frac{RT}{N}\cdot\frac{1}{f} \tag{7}$$

where N is the Avogadro constant; f, the frictional force acting on the dispersed particle by the molecules of the dispersion medium; R, the

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[4] Svedberg and Rinde: J. Am. Chem. Soc., **45**, 943 (1923); **46**, 2677 (1924): Svedberg and Nichols: **45**, 2910 (1923); **48**, 3081 (1926); **49**, 2920 (1907); Svedberg and Sjögren: **51**, 3594 (1929); **52**, 279, 5187 (1930); Svedberg: "Colloid Chemistry," 146, *et seq.* (1928); Nichols: Ind. Eng. Chem., Anal. Ed., **4**, 12 (1932).

[5] Phil. Mag., (6) **50**, 1221 (1925).

[6] Einstein: Ann. Physik, (4) **17**, 549 (1905); **19**, 371 (1906); Smoluchowski: Physik. Z., **17**, 557 (1916).

gas constant; and T, the absolute temperature. For a spherical particle $f = 6\pi\eta r$, in which η is the viscosity of the medium, and r, the radius of the particle. Hence

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r} \tag{8}$$

Using a specially designed diffusion apparatus to measure the diffusion coefficient D, Svedberg[7] calculated the radius of gold particles in a certain highly dispersed sol to be 1.29 mμ as compared with 1.33 mμ as estimated by the use of Zsigmondy's nuclear method, above described.

Ultrafiltration Method.—The attempt has been made to estimate the size of particles by ultrafiltration through membranes of graded pore size, the principle being that a particle will not be held back by a membrane containing pores larger than the colloidal particle. This method is probably unsatisfactory in most instances, and it would not be expected to work with colloidal gold because of the tendency of the particles to be adsorbed by the filtering membrane. For the same reason, the use of gold sols of different particle size to calibrate the pore size[8] in ultrafiltration membranes is of doubtful value. Zsigmondy[9] attempted to eliminate this adsorption factor as far as possible by stabilizing the gold sol with an excess of gum arabic. The difficulty with this procedure is that the protected sol can no longer be treated as if it consisted of pure gold particles of a definite size.

The Shape of Colloidal Gold Particles

The shape of the particles in gold sols cannot be determined by direct observation, but, since x-ray analysis[10] discloses that particles consist of crystals similar to those of gold in mass, the primary units are probably minute octahedra. Since in such crystals the axes are all of the same length, it is frequently permissible to consider them as spheres. Thus, as we have seen, the several methods differing in principle, for determining the particle size, give values which agree fairly well, and all assume the particles to be spherical. Also, in

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[7] "Colloid Chemistry," 97 (1928).

[8] Zsigmondy and Carius: Ber., 60, 1047 (1927).

[9] "Kolloidchemie," 5th ed., 1, 63 (1925).

[10] Scherrer: Zsigmondy's "Kolloidchemie," 3rd ed., 387 (1920).

determining the Avogadro constant from diffusion data, the assumption that the particles are spherical seems to be justified by the results obtained (see page 66). Furthermore, a satisfactory explanation of the color of red gold sols assumes that the particles must be approximately spherical.

On the other hand, there are a number of reasons for believing that the particles are not strictly spherical. Thus it has been shown that the light scattered at an angle of 90° to the direction of incidence is not completely polarized as it should be if the particles are perfect spheres, but contains some ordinary light.[11] Moreover, observations by Björnstahl[12] of the magnetic double refraction of the gold sols, and the double refraction produced in them by flow, indicate that the particles must contain a certain magnetic anisotropy. Bjornstahl[13] showed further that gold hydrosols possess an appreciable electrical double refraction. These observations indicate that the particles are not completely isodimensional but must be in the form of short rods or thick plates. This appears to be true especially if the particles are relatively large. Thus Svedberg[14] showed that the displacement of the colloidal particles as a result of their Brownian movement, as calculated from Einstein's equation (see page 64), agrees very well with the observed values provided the sol is highly dispersed; but the agreement is not so good if the sol is coarsely dispersed. With the latter the observed displacement is less than the calculated, suggesting that the gold particles in the coarse sols are rods or plates which offer greater resistance to diffusion than spheres. Finally, the blue color of certain sols and of defective gold ruby glass can be accounted for best by assuming an irregular growth of the particles.

In general, it may be said that the particles in colloidal gold which have been allowed to grow normally are regular octahedra, but under certain conditions rod-shaped or plate-like particles may develop.

KINETIC PROPERTIES

Since gold hydrosols lend themselves so well to ultramicroscopic observations, they have been used, probably more than any other colloidal systems, in investigations of Brownian movement, diffusion, and sedimentation in sols.

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[11] Diesselhorst and Freundlich: Physik. Z., **17**, 117 (1916).

[12] Phil. Mag., (6) **42**, 352 (1921).

[13] Bergholm and Björnstahl: Physik. Z., **21**, 137 (1920).

[14] "Colloid Chemistry," 2nd ed., 117 (1928).

Brownian Movement

The Einstein Equation.—Ultramicroscopic observations of the Brownian movement in gold sols first suggested that the zigzag motion of the particles is similar to molecular motion as conceived by the kinetic theory of gases. Since it has been established conclusively that Brownian movement is not due to external forces but results from bombardment of the dispersed particles by the molecules of the dispersion medium,[15] Einstein[16] assumed that suspended particles should behave like dissolved particles, exerting an osmotic pressure and diffusing through the dispersion liquid; in other words, that the gas laws should apply in the same way for suspended particles as for dissolved molecules.

In terms of the kinetic theory of gases, the temperature is determined by the kinetic energy, $\frac{1}{2}mv^2$, of the molecules, where m is the mass and v, the velocity of the molecules at that temperature. If the Brownian movement is a heat motion corresponding to the temperature of the sol, then $\frac{1}{2}mv^2$ must be the same for both the particles and the molecules of dispersion medium. In general, since m is considerably greater for suspended particles, their velocity will be correspondingly less at a given temperature than the velocity of the molecules. The latter is known from the kinetic theory of gases, and the size of a colloidal particle can be determined; hence, if the velocity of the particles is known, the size of the molecule can be calculated from the other data. But because of the extremely large number of collisions between the particles and the molecules of the dispersion medium,[17] it is impossible to follow the exact path of a particle with the eye or with a motion-picture camera. What can be determined, however, is the rectilinear displacement of the particles in unit time. Einstein showed that the displacement, A, of a particle with radius r, in the direction of a horizontal axis x, in the time t, is given by the expression

$$A = \sqrt{t}\sqrt{\frac{RT}{N}\cdot\frac{1}{3\pi\eta r}} \tag{9}$$

in which R is the gas constant; T, the absolute temperature; N, the Avogadro number; and η, the viscosity of the medium. It will be

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[15] Wiener: Pogg. Ann., **118**, 79 (1863); Gouy: J. phys., (2) **7**, 561 (1888); Compt. rend., **109**, 102 (1889).

[16] Ann. Physik, (4) **17**, 549 (1905); **19**, 289, 371 (1906); *cf.*, *also*, Smoluchowski: **21**, 756 (1906).

[17] *Cf.* Kruyt: "Colloids," 2nd ed., 148 (1930).

noted that this expression contains the quantity RT/N, which is connected with the kinetic energy of the particles, and the value $6\pi r\eta$ in Stokes' law (Equation 4), which denotes the ratio of the velocity to the force of friction for a particle moving in a liquid.

The Time Law in Brownian Movement.—For a given particle size and constant temperature,

$$\sqrt{\frac{RT}{N}\cdot\frac{1}{3\pi r\eta}}$$

is constant, hence

$$A = k\sqrt{t} \tag{10}$$

This relation, known as the Time Law in Brownian Movement, was established by Svedberg,[18] independently of the theoretical considerations of Einstein, from observations on gold sols which are summarized in Table V.

TABLE V

THE TIME LAW IN BROWNIAN MOVEMENT

Time in units of 1.48 seconds	r = 27mμ. A in μ		r = 52mμ. A in μ	
	Observed	Calculated	Observed	Calculated
1	3.1	3.2	1.4	1.7
2	4.5	4.4	2.3	2.4
3	5.3	5.4	2.9	2.9
4	6.4	6.2	3.6	3.4
5	7.0	6.9	4.0	3.8
6	7.8	7.6	4.5	4.2

Displacement in Brownian Movement.—Svedberg found also that the values of A for small gold particles as calculated from Einstein's equation, taking $N = 6 \times 10^{23}$, are in good agreement with the observed values, as shown by the results in Table VI. As already noted (see page 62), with large gold particles the observed displacements are always smaller than the calculated values, probably because the particles are not spheres as the Einstein equation assumes.

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[18] "Die Existenz der Moleküle," 124 (1912); Svedberg and Inouye: Arkiv Kemi, Mineral. Geol., 4, No. 19 (1911).

TABLE VI

DISPLACEMENT OF GOLD PARTICLES IN BROWNIAN MOVEMENT

Time in seconds	Displacement A in μ	
	Observed	Calculated
1	4.3	4.1
2	5.8	5.6
3	6.6	7.6
4	8.3	8.2

At constant temperature and with a given size of particles, the Einstein equation becomes

$$A = k\sqrt{\frac{t}{\eta}} \tag{11}$$

which Svedberg[19] found to apply especially with platinum sols. Also the relationships

$$A = k\sqrt{t}$$

$$A = k\frac{1}{\sqrt{r}}$$

and

$$A = k\frac{1}{\sqrt{\eta}}$$

which follow from the Einstein equation have been found to hold.[20]

The Avogadro Number.—The Einstein equation can be used also to calculate the Avogadro number, N, from the observed values of A, r, and η for the sol. With a gold sol containing highly dispersed particles, Svedberg and Inouye[21] obtained for N the value 6.2×10^{23}. Perrin,[22] working with relatively large gamboge and mastic particles varying in size from 0.212 to 5.5 μ, obtained values for N varying from 6.6 to 7.8×10^{23}. This means that, within the limits of experi-

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[19] Z. Elektrochem., **12**, 853, 909 (1906).

[20] Svedberg: Z. Elektrochem., **12**, 853, 909 (1906); Chaudesaigues: Compt. rend., **147**, 1044 (1908); Perrin: **149**, 477 (1909); Ann. chim. phys., (8) **18**, 5 (1909).

[21] Arkiv Kemi, Mineral. Geol., **4**, No. 19 (1911).

[22] Compt. rend., **147**, 475, 530, 594 (1908); **152**, 1165, 1380 (1911); Kolloid-Beihefte, **1**, 221 (1910); "Les atomes," Paris, 156 (1928).

mental error, N is independent of the size of the particles. In other words, the kinetic theory of gases holds irrespective of the particle size, the mean kinetic energy of all particles being the same at the same temperature.

Osmotic Pressure

From the kinetic point of view, the Brownian movement of suspended particles should give an osmotic pressure. The van't Hoff expression for the osmotic pressure, P, in a solution is

$$P = cRT$$

where c is the number of mols per unit volume. For a colloidal solution the expression for the osmotic pressure is

$$P = \frac{n}{N} RT \tag{12}$$

where n is the number of suspended particles in unit volume and N is the Avogardo number. Because of the relatively small number of particles in a sol of known dispersity, the observed value of the osmotic pressure is too low to verify the assumption that an equivalence exists between a suspended particle and a molecule. As we have seen (see page 59), Zsigmondy claims to have measured the osmotic pressure of a finely dispersed gold sol and calculated the particle size from the observations. Although particle size estimated in this way agrees fairly well with values obtained by other methods, the agreement is probably accidental.

Diffusion

In addition to osmotic pressure the Brownian movement of suspended particles should lead to diffusion. Einstein[23] and Smoluchowski[24] showed that this is related to the displacement, A, of the particles in the following way

$$D = \frac{A^2}{2t} \tag{13}$$

where D is the diffusion coefficient. Since

$$A = \sqrt{t}\sqrt{\frac{RT}{N} \cdot \frac{1}{3\pi r\eta}} \tag{9}$$

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[23] Ann. Physik, (4) **17,** 549 (1905); **19,** 371 (1906).

[24] Physik. Z., **17,** 557 (1916).

it follows that
$$D = \frac{RT}{N} \cdot \frac{1}{6\pi r\eta} \tag{8}$$

As already pointed out (see page 61), Svedberg used this equation for calculating the size of gold particles from diffusion measurements. He also tested the equation by diffusion measurements on gold sol containing particles of a known radius. And finally, from the observed diffusion with a sol containing particles 1.33 mμ in radius as determined by Zsigmondy's nuclear method, he calculated N, obtaining the value 5.8×10^{23}.

Sedimentation

The Perrin Equation.—In a colloidal solution the particles tend to settle under the influence of gravity. This tendency is opposed by the osmotic pressure and the diffusion occasioned by the Brownian movement. After a time these two opposing forces come to an equilibrium state, the so-called sedimentation equilibrium. Smoluchowski[25] pointed out that Laplace's so-called hypsometric formula, which is used to calculate the atmospheric pressure at a given height, must apply in the case of colloidal dispersions. Perrin[26] showed that this equation takes the form:

$$ln \frac{n_2}{n_1} = \frac{N}{RT} \cdot v(d_p - d_l)gh \tag{14}$$

in which n_2 and n_1 are the number of particles in equal volumes of two layers a distance of h apart; d_p and d_l, the density of the colloidal particles and of the dispersion medium, respectively; v, the volume of the particle; and g, the gravitational constant. Perrin[27] tested his equation by measuring the number and volume of the particles in sols of mastic and gamboge when sedimentation equilibrium was established. His counts were made with a microscope using a dark-field condenser so that the distance between the layers, h, was of microscopic dimensions. Within this narrow range the agreement between observed and calculated values of n was fairly good. He used this method for calculating N, the average value of a large number of determinations coming out to be 6.8×10^{23}.

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[25] Ann. Physik, (4) **21**, 756 (1906).

[26] Compt. rend., **146**, 968 (1908); Kolloid-Beihefte, **1**, 221 (1910).

[27] Compt. rend., **146**, 968; **147**, 530, 594 (1908); **152**, 1165, 1380 (1911).

Similar measurements on gold sols were made by Westgren[28] over a wider range as shown in Table VII. With particles 21 mμ in radius the equation holds over a range of 1100 μ or 1.1 mm. These observations and others are shown diagrammatically in Fig. 12, in which the log *n* at different values of *h* is plotted against *h*. For the sols with particles 20.5, 25.5, and 31.5 mμ in radius, the equilibrium was obtained by allowing the particles to diffuse up from a concentrated layer of sol at the bottom of the cell. For the sol with 50 mμ particles, the same equilibrium was obtained both by diffusion and by settling. The applicability of the equation in these cases over a considerable range is obvious.

TABLE VII

SEDIMENTATION EQUILIBRIUM IN GOLD HYDROSOL

Radius of Particles 21mμ

Height, *h* in μ	Number of particles, *n*	
	Observed	Calculated
0	889	886
100	692	712
200	572	572
300	428	460
400	357	369
500	253	297
600	217	239
700	185	192
800	152	154
900	125	124
1000	108	100
1100	78	80

Some values of *N* for gold sols obtained by Westgren by substituting in Perrin's equation are given in Table VIII. It will be noted that the mean value, 6.05×10^{23}, is very close to the generally accepted value of 6.06×10^{23} obtained by Millikan.

Limitations of the Perrin Equation.—Experiments by Burton[29]

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[28] Z. physik. Chem., **89**, 62 (1914); Z. anorg. Chem., **93**, 231 (1915); Thesis, Upsala (1915); Johnston and Howell: Phys. Rev., (2) **35**, 274 (1930).

[29] Burton and Bishop: Proc. Roy. Soc. (London) **100A**, 414 (1921); Burton and Currie: Phil. Mag., (6) **47**, 721 (1924).

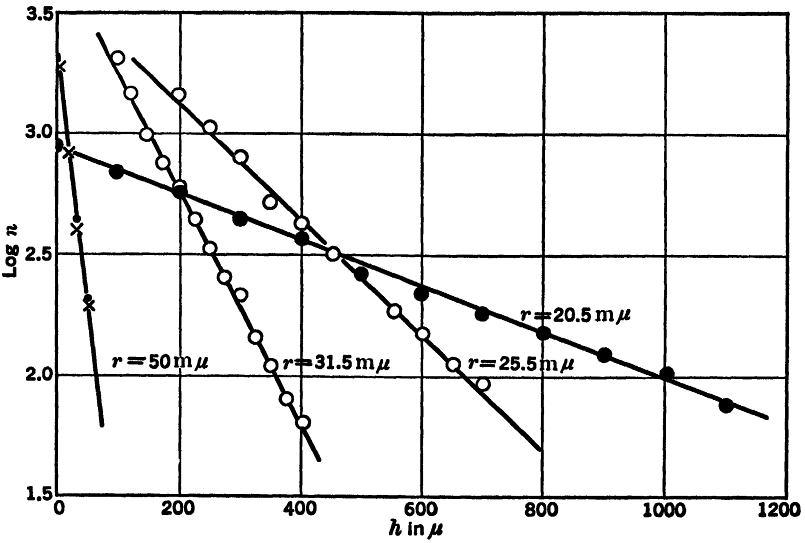

FIG. 12.—Sedimentation equilibria in gold sols.

TABLE VIII

AVOGADRO CONSTANT FOR GOLD SOLS CALCULATED BY MEANS OF PERRIN'S EQUATION

5.97×10^{23}	5.98×10^{23}	6.11×10^{23}
6.05	6.04	5.98
5 97	6 13	6.08
6 06	6.08	6.02
6.09	5.95	6.06
6.20	6.04	
		Average: 6.05×10^{23}

with a number of different sols, and by Porter and Hedges[30] with gamboge suspensions, have convinced them that the Perrin formula holds only over a relatively narrow range. Burton suggests that the concentration increases with increasing depth only up to a certain value and then remains practically constant. He assumes further that the charged particles in a sol tend to repel each other when their concentration gets too high, and he introduces a term in the equation to take care of this. Porter and Hedges, on the other hand, point out that Perrin's formula cannot hold because it assumes the validity

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[30] Trans. Faraday Soc., **18**, 91 (1922); **19**, 1 (1923); Barkas: **21**, 60 (1925).

of Boyle's law without considering the volume occupied by the particles. Possibly both of these factors must be taken into account, but in the light of Westgren's observations there is a tendency to question the validity of the experimental procedures of Burton and Porter rather than to admit that they represent real departures from an ideal sedimentation equilibrium.[31]

In this connection, observations on the spontaneous fluctuations in the number of gold particles[32] within a certain small volume communicatory with a large volume of sol give results demanded by the kinetic theory[33] for an ideal system with concentration as high as 7.2×10^9 particles per cc or as high as 4.49 g per liter. Since it is unlikely that discrepancies from ideal behavior should appear suddenly, there is no obvious reason why a marked departure from ideal behavior should follow at considerably higher concentrations. Moreover, in the light of the behavior of gold sols, there is no apparent reason for attributing the observed departures from an ideal sedimentation equilibrium in other sols to such internal agencies as volume of the particles and interaction between the particles.

Particle Weight

Since a colloidal particle suspended in a liquid behaves like a dissolved molecule, the so-called molecular weights of dispersed particles have been determined from measurements of osmotic pressure, diffusion, and sedimentation. Thus Perrin points out that the largest granules of mastic which follow the laws of perfect gases are visible in sunlight under a strong lens, the particles behaving as would the particles of a perfect gas with a gram molecular weight of 200,000 tons. Since the particles of a suspended substance may vary widely in size, it is obvious, from this point of view, that the same substance can have any number of molecular weights depending on the size of the dispersed particles. Moreover, different substances may have the same molecular weight, because a suspended particle of gold, for example, may weigh the same as a suspended particle of alumina. In other words, the so-called molecular weights of suspended sub-

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[31] Svedberg: "Colloid Chemistry," 2nd ed., 102 (1928); Fürth: Z. Physik, **40**, 351 (1926); Mason and Weaver: Phys. Rev., (2) **23**, 412 (1924); Weaver: Phys. Rev., (2) **27**, 499 (1926); Kraemer: Colloid Symposium Monograph, **5**, 81 (1928); Samuel: Ann. Physik, **5**, 678 (1930); *cf., however,* Laird: J. Phys. Chem., **31**, 1034 (1927).

[32] Westgren: Arkiv Mat. Astron. Fysik, **11**, Nos. 8 and 14 (1916); **13**, No. 14 (1918).

[33] Smoluchowski: Physik. Z., **13**, 1069 (1912).

stances are not specific and vary continuously with the degree of subdivision.

This point of view seems to contradict the usual concept of molecular weights as used by the chemist. The gram molecular weights determined from vapor density or change in vapor pressure are fixed values, specific for each substance. The absolute molecular weight, that is, the weight of a single molecule, is the gram molecular weight divided by the Avogadro number.

As Bancroft[34] points out, the two concepts of molecular weight are not so divergent as they seem. The molecular weight of a suspended particle is the weight of or a function of the weight of the individual particle. It varies continuously, therefore, with the particle size and is non-specific. On the other hand, the molecular weight of a gaseous or dissolved substance is the weight of a single molecule of that substance. Hence the weight of a single molecule is the lower limiting value which the weight of a suspended particle approaches continuously as the particle is continuously subdivided. The specificity comes in only at the limiting values, the weights of the single molecules.

Under the circumstances it would seem highly desirable to speak of the particle weight of suspended particles, using the term molecular weight in its time-honored sense to refer to the weight of a single molecule. The gram particle weight and the gram molecular weight would be the particle weight and molecular weight, respectively, multiplied by the Avogadro number.

ELECTRICAL PROPERTIES

Cataphoresis

The particles of colloidal gold are negatively charged, owing to preferential adsorption of anions, and move to the anode under electrical stress. Since the sols are so highly colored, the mobility of the particles can be followed by macroscopic observations in a U-tube.[35] The order of magnitude of the mobilities is similar to that of most ions other than hydrogen and hydroxyl. Thus the particles in a gold sol formed by electrical disintegration were found by Burton to move with a velocity of about 2.2 μ/second at a potential of 1 volt/cm.

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[34] J. Phys. Chem., **29**, 966 (1925).

[35] Whitney and Blake: J. Am. Chem. Soc., **26**, 1339 (1904); Burton: Phil. Mag., (6) **11**, 440 (1906); Galecki: Z. anorg. Chem., **74**, 174 (1912).

The cataphoretic velocity,[36] u, of the particles is given by the equation

$$u = \frac{\zeta HD}{4\pi\eta} \tag{15}$$

where ζ is the potential difference of the double layer, the so-called electrokinetic potential; H is the potential gradient in volts per centimeter; D and η are the dielectric constant and viscosity, respectively, of the medium. Since the size of the particle does not appear in the mobility equation, it would follow, if the equation applies, that for one and the same dispersed material the velocity under unit potential gradient would be independent of the particle size. In support of this, Thiessen and Heumann[37] showed that the mobility of the particles in 5 different sols was about 3.3 μ/second at 1 volt/cm for particles ranging in size from 4 to 80 mμ in radius, formed by reduction of chlorauric acid with phosphorus, formaldehyde, and hydroxylamine. On the other hand, a velocity of but 1.6 to 1.75 μ/second was obtained by Svedberg and Andersson[38] with particles 60 mμ in radius prepared by reduction of chlorauric acid with hydrogen peroxide in the presence of nuclei. The migration was followed ultramicroscopically, and an oscillating current was employed to eliminate the effect of polarization. As a matter of fact, it would seem to be purely accidental if the mobility of the particles should turn out to be the same in a series of sols prepared in different ways, since the charge is influenced greatly by the nature and amount of electrolytes present. Some observations by Briggs[39] on the change in mobility of a gold sol on adding electrolytes in varying concentrations are shown in Fig. 13 (*a*, *b*, *c*, *d*). It will be noted that the mobility falls off with increasing electrolyte concentration until flocculation takes place at the point indicated by an arrow. The significance of this will be discussed in the next section.

The Charge on the Particle

From Mobility Measurements.—Since gold particles have a mass much larger than that of an ordinary ion, it is obvious that a mobility

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[36] Perrin: J. chim. phys., **2**, 601 (1904); Freundlich: "Kapillarchemie," 229 (1909); Debye and Hückel: Physik. Z., **25**, 49 (1924) point out that for spherical particles the factor 4 in this equation should be 6.

[37] Z. anorg. Chem., **148**, 382 (1925); *cf.* Fuchs and Pauli: Kolloid-Beihefte, **25**, 195, 412 (1925).

[38] Kolloid-Z., **24**, 156 (1919).

[39] Briggs: J. Phys. Chem., **34**, 1326 (1930); *cf.*, *also*, Freundlich and Buchler: Kolloid-Z., **32**, 305 (1923).

of the order of magnitude of a small ion must result from the presence of a relatively large number of elementary charges on their surface. It is possible to calculate the particle charge by considering the particle with its double layer as a charged condenser. The potential difference of the double layer ζ is:

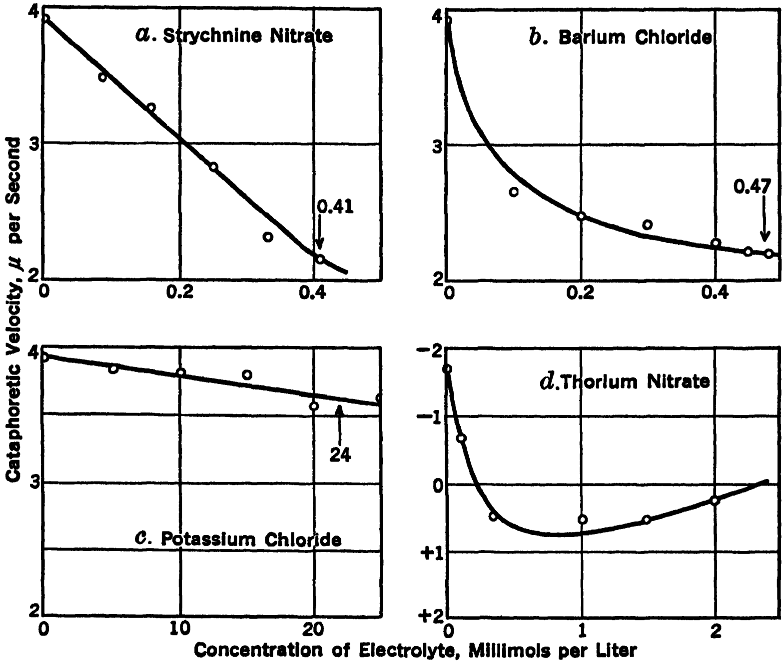

FIG. 13.—Effect of electrolytes on the cataphoretic velocity of the particles in gold sols.

$$\zeta = \frac{e(r_1 - r)}{Drr_1} = \frac{e\delta}{Dr(r + \delta)} \tag{16}$$

from which

$$e = \frac{\zeta Dr(r + \delta)}{\delta} \tag{17}$$

where e is the charge on a single particle; ζ, the electrokinetic potential; D, the dielectric constant; r, the radius of the inner sphere; r_1, the radius of the outer sphere; and $\delta = (r_1 - r)$, the thickness of the double layer. ζ from mobility measurements is approximately

0.07 volt; D for water is 81, and δ is of the order of magnitude of 5 mμ.[40] Using these values, von Hevesey[41] calculated the charge for gold particles of different sizes expressed as the number of electrons having a charge 4.7×10^{-10} electrostatic unit. The results are given in Table IX.

TABLE IX

Electric Charge on Particles of Varying Size

r of particle, mμ	e from $e = \frac{\zeta D r(r + \delta)}{\delta}$ Electrons
1.2	6
2.4	14
12.0	164
24 0	550
100.0	8,550
240.0	47,000

From Electrolysis Measurements.—Considering the colloidal particles to be ordinary ions, Wintgen[42] determines the amount of colloidal substance deposited by 1 faraday of current and designates this the electrochemical equivalent or equivalent aggregate of the colloid. The number of electrochemical equivalents of the colloid per liter is called the normality of the colloid, N. The value is obtained by applying Kohlrausch's law $1000K_m = N(u + v)$, where K_m, the specific conductance of the micelle, is estimated from the conductance of the colloidal system before and after ultrafiltration; v, the mobility of the colloidal particle, is determined from the migration measurements in a U-tube; u, the mobility of the cation (assumed to be H^+ ion), is known; and N is calculated. The number of charges on the individual particles, e, is calculated from the expression

$$e = \frac{AN}{n} \tag{18}$$

where N is the normality; A, the Avogadro number; and n, the number of particles in 1 liter of sol obtained by ultramicroscope count.

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[40] Stock: Anz. Akad. Wiss. Krakau, 635 (1912).

[41] Kolloid-Z., **21**, 129 (1917).

[42] Z. physik. Chem., **103**, 250 (1922); Kolloid-Z., **40**, 300 (1926).

From observations of this kind, Wintgen[43] estimates the number of charges per gold particle in 6 different dialyzed gold sols to be very large: 18,300 to 47,700; and in 5 undialyzed sols: 42,600 to 75,200. Fuchs and Pauli[44] modified Wintgen's procedure by determining the normality of the sol from electrometric titration of the hydrogen ion in the sol. The number of charges per gold particle in 9 different sols was estimated to be: 34,690 to 58,440.

These very large values for the number of charges per gold particle cannot be right, because of methodical and inherent errors in the measurements. Laing[45] showed that the fraction of the current carried by any charged body, whether ion, colloidal wall, or bubble, is equal to the ratio of its actual conductivity to the total conductivity of the system. That is

$$\text{fraction of current} = \frac{c_1 f_1}{\mu} \tag{19}$$

where c_1 is the concentration; f_1 is the conductivity of unit concentration; and μ is the sum total of all such cf terms for all constituents present. The bodily movement, n_1, differs from the above by a factor m which is the number of units to 1 electrical charge. Thus

$$\text{bodily movement} = n_1 = \frac{c_1 m_1 f_1}{\mu} \tag{20}$$

McBain[46] points out that the factor m was neglected by Wintgen. A further error is probably introduced by assuming that the only cations in the solution are hydrogen ions. Moreover, it is not certain that all the hydrogen ions in the intermicellar solution are compensated by anions adsorbed on the particle. Furthermore, if it is assumed that most of the hydrogen ions in the intermicellar liquid are in equilibrium with adsorbed anions, then the adsorption equilibrium will be disturbed by removing the hydrogen ions in electrometric titration so that the normality of the sol estimated from measurements of this kind cannot be right. Finally, Pauli points out that a great deal of the current may be carried by particles that are invisible in the ultramicroscope and so escape count. In view of these

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[43] Kolloid-Z., **40**, 300 (1926).

[44] Kolloid-Beihefte, **21**, 195 (1925); *cf.* Adolf and Pauli: Kolloid-Z., **34**, 29 (1924).

[45] J. Phys. Chem., **28**, 673 (1924).

[46] Colloid Symposium Monograph, **4**, 14 (1926).

errors in method, it is evident that Wintgen's and Pauli's values of the charge per particle in a gold sol may be 10 to 100 times too large.

Conductivity

Since the particles migrate under electrical stress, it is obvious that a sol should possess a certain conductivity independent of the presence of electrolytes. The conductivity, κ, in a pure sol can be calculated from Smoluchowski's equation

$$\kappa = \frac{n}{N} \frac{4\pi r\eta(r + \delta)u^2}{\delta} \tag{21}$$

in which n is the number of particles per unit volume; N, the Avogadro number; u, the mobility; η, the viscosity; and r and δ have the same significance as in the charge equation (17) above. For a gold sol containing particles of 10 mμ radius, a mobility of 5.2 μ/second, and a distance between charges $\delta = 5$ mμ, κ comes out to be 1.2×10^{-7}. Since the value due to the migration of the particles is so low, it is obvious that most of the conductivity in metallic sols results from impurities in the dispersion medium.[47] In general, the conductivity decreases with increasing purity of sol. In some cases the conductivity is even less than that of the dispersion medium. Thus, if mercury is dispersed in conductivity water by means of the oscillating arc, the conductivity of the resulting sol is less than that of the water[48] probably because of adsorption of the electrolyte impurities by the particles.

COLOR

The color of gold sols in transmitted light is usually red, violet, or blue, but may be yellowish brown, or brown. When viewed in the ultramicroscope, the particles in the red sols appear green, and in the blue sols yellow to reddish brown. The violet sols contain both green and yellow or brown particles.

The color of gold sols was at one time attributed to the presence of colored compounds. Although the blue of certain gold sols is due,

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[47] Nordenson: Kolloid-Z., **16**, 65 (1915); Wintgen and Hacker: **61**, 335 (1932). The latter investigators showed that the conductivity of the intermicellar solution in Zsigmondy's gold sol differs very little from the conductivity of the original sol. This furnishes additional evidence in support of the view that von Hevesey's estimation of the magnitude of the particle charge, as given in Table IX, is of the right order of magnitude and that Wintgen's and Pauli's values from electrolysis measurements are too high.

[48] Nordlund: Kolloid-Z., **26**, 121 (1920).

at least in part, to the presence of aurous oxide,[49] it is now known that the blue color is not necessarily connected with the presence of this or any other compound in the sol.[50] Moreover, the suggestion that the different colors are due to different allotropic modifications[51] of gold appears improbable in the light of Scherrer's observation (see page 50) that the x-ray pattern of colloidal gold particles is identical with that of gold in mass. It appears, therefore, that the variation in color of pure metal sols must be explained on physical rather than on chemical grounds.

Since the particles in blue sols are usually larger than those in red sols and since partial coagulation of red sols causes them to become blue, it is frequently assumed that the color of the sols is determined largely by the degree of subdivision of the particles. This is by no means the case, since both green and brown particles may have all possible dimensions from the smallest particles visible in the ultramicroscope up to 120 $m\mu$ in diameter, and over.[52] Moreover, in the coagulation of pure red sols, two or more green particles unite, giving a brown aggregate, and the sol appears blue. This color change is not due to the increased particle size resulting from the agglomeration since it occurs whether the particles in the original red sol are below the limits of visibility in the ultramicroscope or whether they fall well within the range of visibility. In the first case the secondary aggregates may be too small to be visible and may have a mass several hundred times smaller than primary particles which diffract green and give a red sol; yet the minute aggregates diffract brown, and the sol appears blue by transmitted light.

Tyndall Blue.—If very fine particles of a weakly absorbing material are suspended in a transparent solid, liquid, or gas, the particles scatter blue light more than red light; hence such a mass appears red by transmitted light and blue by reflected light. This blue of turbid media, known as Tyndall[53] blue, is observed with suspensions of mastic and sulfur, skimmed milk, tobacco smoke, etc. The blue of the sky is a Tyndall blue resulting from the scattering of the light by drops of liquid and particles of dust suspended in the air, or by the oxygen and nitrogen molecules themselves. The theory of this has been worked out by Lord Rayleigh,[54] who deduced that the intensity

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[49] Thiessen: Z. anorg. Chem., **134**, 393 (1924).

[50] *Cf.*, *however*, Pauli: Kolloid-Z., **28**, 50 (1921); Kautzky and Pauli: Kolloid-Beihefte, **17**, 294 (1923).

[51] Björnstahl: Phil. Mag., (6) **42**, 366 (1921).

[52] Zsigmondy: "Kolloidchemie," 5th ed., **2**, 19 (1927).

[53] Phil. Mag., (4) **37**, 384 (1869).

[54] Strutt: Phil. Mag., (4) **41**, 107, 274, 447 (1871); (5) **12**, 81 (1881); **47**, 375 (1899).

of the scattered light is directly proportional to the square of the size of the particles and inversely proportional to the fourth power of the wave length. The intensity of the scattered light, I, in the direction at right angles to the path of the incident light is given by the equation:

$$I = N\frac{9\pi^2 V^2 A^2}{\lambda^4 x^2}\cdot\left(\frac{n_1{}^2 - n^2}{n_1{}^2 + 2n^2}\right)^2 \tag{22}$$

where N is the number of particles in unit volume; V, the volume of the particles; A^2, the amount of energy falling on the particles; λ, the wave length; x, the distance between the source of light and the particles; n_1 and n, the refractive index of water and of the particle, respectively.

This equation for weakly absorbing, insulating particles does not apply for metallic conducting particles, as is evidenced by the variety and brilliance of the coloring in sols of the metals.

Mie's Theory of the Color of Metallic Sols.—Because of the inapplicability of Rayleigh's theory to metallic sols, attempts have been made to extend it. Thus Ehrenhaft[55] assumed that the particles in gold sols are perfect conductors and attributed the colors to optical resonance. The incorrectness of this view has been shown on both theoretical and experimental grounds.[56] Mie,[57] on the other hand, limited himself to spherical particles and explained a large number of experimental facts by introducing into Rayleigh's formula, instead of the ordinary indices of refraction, the complex indices of refraction of the metals. According to Mie, the scattering coefficient, k_s, which is obtained by multiplying the energy loss on one particle by the number of particles, is given by Rayleigh's formula:

$$k_s = N\frac{24\pi^3 V^2}{\lambda^4}\cdot\left(\frac{n_1{}^2 - n^2}{n_1{}^2 + 2n^2}\right)^2 \tag{23}$$

provided the particles are very small. For larger particles the respective refractive indices must be multiplied by factors a, b, c, d, which approach 1 as the volume of the particles become smaller.

For the absorption coefficient for dilute sols with very small particles, the equation, according to Mie, is:

$$k_a = NV\frac{6\pi}{\lambda}\cdot I_m\left(\frac{n_1{}^2 - n^2}{n_1{}^2 + 2n^2}\right)^2 \tag{24}$$

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[55] Ann. Physik, (4) **11**, 489 (1903).

[56] Pockels: Physik. Z., **5**, 153, 460 (1904); *cf.* Ehrenhaft: **5**, 387 (1904).

[57] Ann. Physik, (4) **25**, 377 (1908); Kolloid-Z., **2**, 129 (1907).

in which the symbol $I_m(\ )$ signifies that the imaginary part of the complex expression is to be taken. Mie has tested his calculations by comparison with Steubing's[58] measurements on gold sols, using the complex refractive indices obtained by Hagen and Rubens.[59] Mie's results are shown diagrammatically in Figs. 14 and 15 for 0.0025% red gold sols with particles of varying radius. It will be noted that the calculated results for both the scattering coefficient and the absorption coefficient for a sol containing particles of 18 mμ radius agree quite well with the observed values.[60]

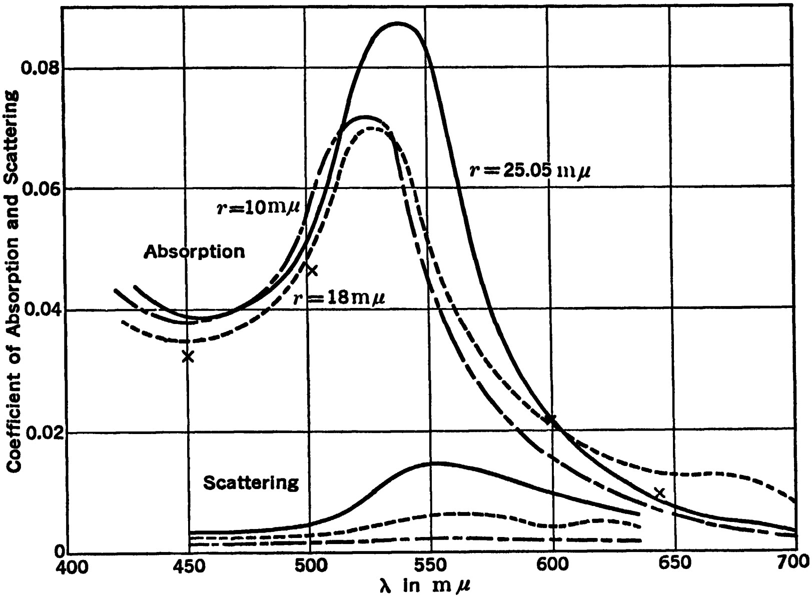

FIG. 14.—Absorption and diffraction coefficients for gold sols of different particle size. The x values were calculated by means of Mie's equation for particles 18 mμ in radius.

For the particle sizes under consideration it appears that the color is due chiefly to absorption of light rather than to scattering. The sols are red because of the strong absorption in the green (maximum at λ = 530 mμ).

Observations were made on blue sols formed by coagulation of particles with a radius of about 30 mμ. In this case the absorption

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[58] Ann. Physik, (4) **26**, 329 (1908).

[59] Ann. Physik, (4) **8**, 1, 432 (1903).

[60] *Cf.* Lange: Z. physik. Chem., **A132**, 27 (1928).

maximum was much flatter than in red sols and was displaced toward the red side of the spectrum; hence the blue color. Also, the scattering is relatively greater, radiating considerable light of a reddish brown color. This likewise accords with Mie's calculations.[61]

The conclusions from Mie's calculations are that red gold sols must contain approximately spherical particles of radius under 40 mμ that scatter little light, whereas sols with large particles are blue and radiate more strongly. The reason for this is that gold has an absorption maximum in the green and a reflection maximum in the yellow; and the absorption predominates in the sols with finer particles.

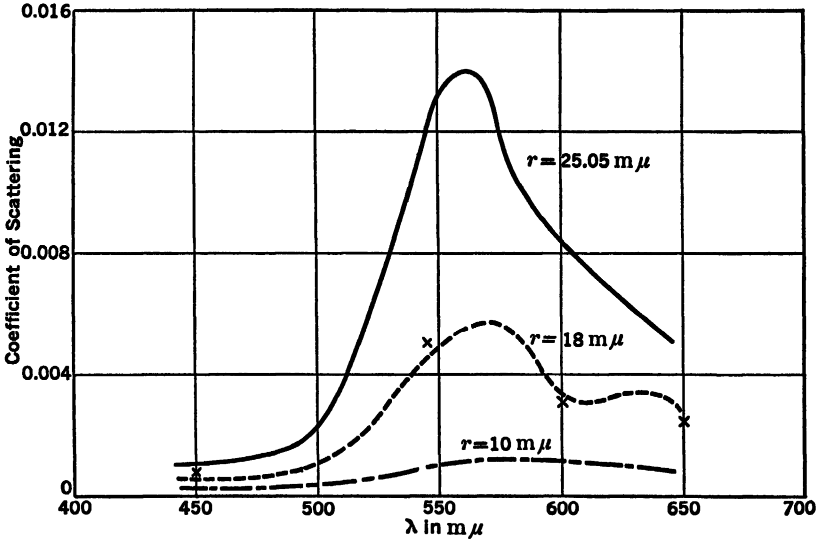

FIG. 15.—Diffraction coefficients of gold sols of different particle size. The *x* values were calculated by means of Mie's equation for particles 18 mμ in radius.

Ostwald's[62] rule that the absorption maximum moves toward shorter wave lengths as the degree of dispersity increases is not generally applicable to metallic sols (see, however, page 331).

Limitations of Mie's Theory.—Mie's theory is obviously not a complete theory of the color of metallic sols, since, as has been pointed out, primary particles and aggregates smaller than 40 mμ radius may be brown and therefore give blue sols. It should be remembered that Mie's theory assumes that the particles are spherical masses of com-

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[61] *Cf.*, *also*, Pihlblad: Dissertation, Upsala (1918).

[62] Kolloid-Beihefte, 2, 447 (1911).

pact metal. This is not a necessary condition, and one might expect divergence from the theory. From the standpoint of the theory, if primary particles or aggregates of gold below 40 mμ in radius are brown, it means either that the shape is not spherical or that the entire space occupied by the particle is not metal. With reference to the primary particles, there is considerable evidence to support the view that they are not necessarily spherical or isodimensional. Thus we have seen that certain gold sols show double refraction in both magnetic and electric fields (see page 62). Svedberg[63] observed dichroism in certain gold-gelatin films which he attributed to a difference in the distance between the particles in the two directions. He assumed the particles to be long and flat, or leaf shaped. In support of this, Ambronn and Zsigmondy[64] showed that if metal particles are similarly oriented by spreading out the gelatin to form gold- or silver-gelatin films, the color will be blue if the vibrations of the transmitted light are parallel to the direction of the distension, and red if the vibrations are at right angles to the distension. Finally, Siedentopf[65] believed that the color of the particles is influenced by their shape, since the color changed from green to brown when pressed between the cover glass and the platform of the cardioid ultramicroscope. Hence it would appear that the shape of the particle is nonspherical[66] in blue sols containing very finely divided primary particles.

The blue sols formed by agglomeration of red sols consist of aggregates of small green particles which appear brown irrespective of how small they are. In this case, the particles do not melt into one another as drops of liquid, but form a loose mass instead. Moreover, there is no reason for assuming that the agglomerates, however small, are spherical in shape. Probably the loose structure and the shape, rather than the size, determine the color of such complexes.

Gold sols which appear brown rather than red or blue in transmitted light are sometimes obtained when stannous chloride is added to chlorauric acid in the preparation of purple of Cassius, the brown color first formed changing gradually to red. Similarly, brown sols may result in the reduction of chlorauric acid with excess phosphorus; and gold ruby glass containing a considerable quantity of lead or tin

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[63] Arkiv Kemi, Mineral. Geol., **4**, No. 8, 19 (1911).

[64] Ber. Verhandl. sächs. Akad. Wiss., **51**, 13 (1899); Ambronn: **48**, 613 (1896); Z. wiss. Mikroskop., **22**, 349 (1905).

[65] Ber. deut. physik. Ges., **12**, 6 (1910).

[66] *Cf.* Gans: Ann. Physik, (4) **37**, 881 (1912).

solidifies to a dark yellow or brown mass. Zsigmondy[67] believes that the particles in such brown sols are not pure gold[68] but are mixtures with stannic oxide, lead oxide, phosphorus, etc.

Summary.—From the above considerations, it appears that both red and blue gold sols may contain particles of all possible dimensions from the smallest visible in the ultramicroscope up to 120 mμ in diameter, and over. In general, however, the sols are red by transmitted light if the particles are spherical and smaller than 80 mμ in diameter; and are violet to blue by transmitted light (*a*) if they contain spherical particles larger than 80–100 mμ in diameter, (*b*) if the particles are distinctly non-spherical, irrespective of the size, (*c*) if the particles are agglomerates, irrespective of the size, (*d*) if the sol contains some aurous oxide or hydroxide.

COAGULATION

Coagulation by Electrolytes

Precipitation Values.—The addition of electrolytes to unprotected red gold sols in concentrations above a certain limiting value causes flocculation of the particles into secondary aggregates, accompanied by a change in color to violet or blue and a slight clouding. After a time the gold settles out as a blue-black, fine-powdered precipitate. Scherrer and Staub[69] showed by x-ray examination that the unprotected primary particles coalesce to form much larger primary particles during coagulation.

The coagulation process is readily followed in the ultramicroscope. The green primary particles decrease in number more or less rapidly, and in their place brown aggregates appear which show up brighter as they grow larger. The color change from red to violet on adding electrolytes serves as such a good indicator of coagulation that the precipitation value of electrolytes for red gold sols is usually taken as that concentration which will just cause a slight violet appearance in a given time. The precipitation values shown in Table X[70] are the final concentrations of the several electrolytes which give a violet tinge to the sol when 5 cc of electrolyte is mixed with 5 cc of a sol prepared by reduction of chlorauric acid with hydrogen peroxide (see page 34).

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[67] "Kolloidchemie," 5th ed., **2**, 19 (1927).

[68] *Cf.* Svedberg: Z. physik. Chem., **65**, 624; **66**, 752; **67**, 249 (1909).

[69] Z. physik. Chem., **A154**, 309 (1931).

[70] Freundlich and Buchler: Kolloid-Z., **32**, 305 (1923).

TABLE X

Precipitation Values of Electrolytes for Gold Hydrosol

Electrolyte	Precipitation value, millimols/liter	Electrolyte	Precipitation value, millimols/liter
LiCl	50.0	Strychnine nitrate	0.066
NaCl	30.0	NaCNS	25.0
KCl	30.0	Na formate	30.0
RbCl	45.0	Na acetate	35.0
$AlCl_3$	0.25	Na propionate	40.0
Quinine hydrochloride	0.005	Na valerianate	35.0
$NaNO_3$	25.0	Na salicylate	40.0
KNO_3	20.0	0.5 Na_2SO_4	29.0
$Ca(NO_3)_2$	1.0	0.5 K_2SO_4	28.0
$Ba(NO_3)_2$	1.0		
$Ce(NO_3)_3$	0.2		

The Critical ζ-Potential.—Referring to Fig. 13, it will be noted that the addition of electrolytes to the sol causes a decrease in the mobility of the particles to the point where agglomeration and precipitation take place. This decrease in mobility results from a lowering of the electrokinetic potential which for cubical particles is related to the mobility by the equation

$$\zeta = \frac{4\pi\eta u}{HD} \qquad \text{(25) from (15)}$$

For the several electrolytes which cause flocculation in low concentration, the critical velocity for the sol under observation is approximately 2.15 μ/second, corresponding to a ζ-potential of 30.5 millivolts. The ζ-potential below which coagulation takes place is called the critical potential,[71] and the concentration of electrolyte corresponding thereto is the precipitation value. It is apparent that the stability of the sol is so low that coagulation results before the potential is reduced to zero.

Referring to curve *c*, Fig. 13, it will be seen that coagulation is reached with potassium chloride when the mobility of the particles and hence the calculated ζ-potential is higher than with the other electrolytes. This is the usual behavior with electrolytes that effect

[71] Hardy: Z. physik. Chem., **33**, 385 (1900); Powis: **89**, 186 (1915); J. Chem. Soc., **109**, 734 (1916).

coagulation only in relatively high concentrations.[72] Kruyt accounted for this anomalous behavior by pointing out that the calculation of ζ-potential from u by equation (25) is permissible only in case D, the dielectric constant, is known. With weak solutions of electrolytes, it is permissible to assume that D is the same as for water; but with the relatively high concentrations of electrolytes such as potassium chloride which must be used to effect coagulation, D is higher than it is for pure water,[73] although the exact value is undetermined. To assume that it is the same as for pure water gives a calculated ζ-potential higher than the correct value. It is not a question of the valence of the cation, for an electrolyte with a univalent cation, such as strychnine nitrate, which coagulates in low concentrations, gives a normal ζ-potential.

The difficulty with Kruyt's explanation is that it will not account for the higher critical ζ-potential of platinum sol with sodium chloride which coagulates at the low concentration of 4.0 milliequivalents per liter (see page 191).

Adsorption and Schulze's Valency Rule.—The mechanism by which the charge on the particles is lowered to the critical potential on the addition of electrolytes is as follows: The particles of gold sol formed in the presence of dilute sodium chloraurate solution, say, owe their charge to the preferential adsorption of the anion $[AuCl_4]^-$ or $[AuCl_2]^-$ which constitutes the inner layer of the double layer, the cation making up the diffuse outer layer as represented graphically in Fig. 16*a* (see also Fig. 11); a portion of the cations in the outer layer are held so close to the inner layer that they are an integral part of the micelle; but a portion (shown beyond the dotted circle) have sufficient osmotic pressure that they are really a part of the intermicellar solution. On the addition of a small amount of electrolyte with a multivalent cation such as barium chloride or aluminum chloride, the ζ-potential is lowered, owing to the strong adsorption of the multivalent ion. In other words, the multivalent ions go into the outer layer displacing more weakly adsorbed cations and orient themselves close to the inner layer as shown in Fig. 16*b*. In this way the thickness of the double layer is reduced, and the charge on the particle is correspondingly diminished. The critical concentration of aluminum

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[72] *Cf.* Freundlich and Zeh: Z. physik. Chem., **114**, 65 (1925); Kruyt and van der Willigen: **130**, 170 (1927); Kruyt and Briggs: Proc. Roy. Soc., Amsterdam, **32**, 384 (1929); Briggs: J. Phys. Chem., **34**, 1326 (1930).

[73] Fürth: Physik. Z., **25**, 676 (1924); Walden, Ulich, and Werner: Z. physik. Chem., **116**, 261 (1924); Walden and Werner: **124**, 405 (1926).

chloride necessary for rapid coagulation is less than that of barium chloride since aluminum ion is more strongly attracted to the negative surface layer, in other words, is more strongly adsorbed.

From the above considerations, one might expect a tetravalent or trivalent ion to be more strongly adsorbed than a bivalent ion and the latter in turn to be more strongly adsorbed than a univalent ion, with the result that the precipitating power of electrolytes with precipitating ions of varying valence will be in the order: tetravalent > trivalent > bivalent > univalent. This is the valency rule of Schulze.[74] If this were a quantitative statement, it would mean that the valency of an ion is the only thing which determines its adsorption and hence its precipitating power. Actually, the rule is only qualitative, at best.[75] Thus by referring to Table X it will be seen that the precipitating power of the univalent quinine and strychnine cations for gold sols is greater than that of trivalent aluminum or cerium and of bivalent calcium or barium. This means that these organic cations are more strongly adsorbed than other ions of the same and higher valence and so reduce the ζ-potential to the critical value at lower concentrations.

For many years, Freundlich[76] held the erroneous view that the adsorption of equivalent amounts of ions of varying valence is necessary to lower the charge to the critical coagulation value. More than ten years ago this was found[77] not to be the case; and recently it was demonstrated[78] that, in general, the adsorption of a smaller amount of trivalent than of bivalent ion is necessary to neutralize the charge to the critical value. The reason is that the more strongly adsorbed trivalent ion is attracted closer to the inner layer than the bivalent ion, so that less of the former needs to be adsorbed in order to effect a given lowering of the charge. Anderson[79] points out that the activity, and not the concentration of the ion, determines the precipitating action.

Blake[80] detected a small amount of barium in the coagulum after

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[74] J. prakt. Chem., (2) **25**, 431 (1882); **27**, 320 (1883); *cf.* Linder and Picton: J. Chem. Soc., **67**, 63 (1895); Hardy: Z. physik. Chem., **33**, 385 (1900).

[75] Bancroft: J. Phys. Chem., **19**, 363 (1915).

[76] Z. physik. Chem., **73**, 408 (1910); *cf., however,* Freundlich, Joachimsohn, and Ettisch: **A141**, 249 (1929).

[77] Weiser and Sherrick: J. Phys. Chem., **23**, 205 (1919); Weiser and Middleton: **24**, 30, 630 (1920); Weiser: **25**, 399 (1921).

[78] Weiser: J. Phys. Chem., **35**, 1368 (1931).

[79] Trans. Faraday Soc., **19**, 623 (1923).

[80] Am. J. Sci., (4) **16**, 381 (1903); Z. anorg. Chem., **39**, 69 (1904).

precipitating colloidal gold with barium chloride. This was denied by Kautzky and Pauli,[81] but Freundlich[82] working with a relatively concentrated sol showed that appreciable amounts of cations of varying valence were carried down by the precipitate. Freundlich was troubled by the fact that the cations were not adsorbed in equivalent amounts at the respective precipitation values, but, as pointed out above, we now know that the adsorption values should not be equivalent.

Not only are precipitating ions of varying valence adsorbed in different amounts, but also ions of the same valence show considerable variation in adsorbability and hence in precipitating power. For the common inorganic cations of the same valence, those which are the least hydrated and have the highest mobility have the greatest precipitating power. Thus Westgren[83] found univalent cations to

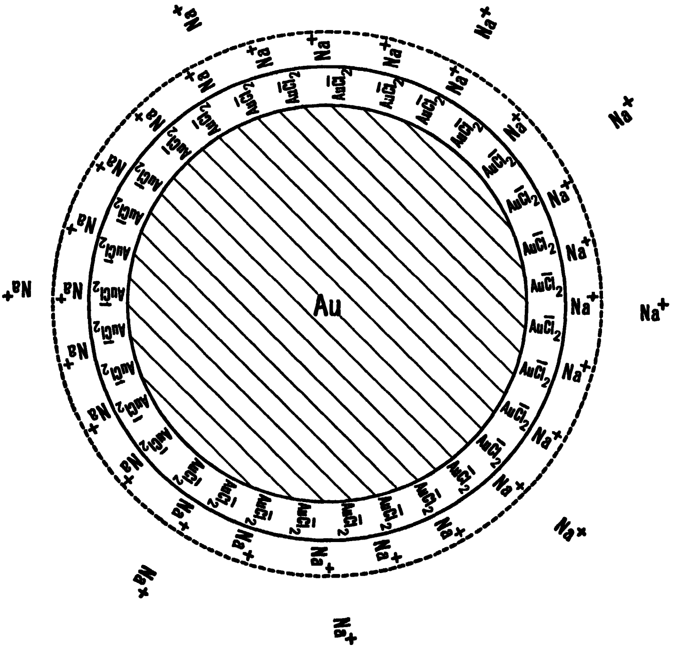

FIG. 16*a*.—Diagrammatic representation of the constitution of a colloidal gold micelle before the addition of barium chloride to the sol.

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[81] Kolloid-Beihefte, **17**, 294 (1923).
[82] Freundlich, Joachimsohn, and Ettisch: Z. physik. Chem., **A141**, 249 (1929).
[83] Arkiv Kemi, Mineral. Geol., (6) **7**, 19 (1918).

effect coagulation of colloidal gold in the order: hydrogen > potassium > sodium > lithium, which is the order of increasing hydration and decreasing mobility. In support of this view, Wiegner[84] prepared several gold hydrosols by the Zsigmondy method, following the same procedure in every case with the exception that different alkali carbonates were added to the chlorauric acid solution before reduction with formaldehyde. The stability of the sols varied with the alkali carbonate used in the order: lithium > sodium > potassium > rubidium > cesium. This indicates that the highly hydrated lithium ion is the least strongly adsorbed and therefore has the lowest precipitating power, so that a gold sol formed in the presence of lithium is more stable than one formed in the presence of any other alkali

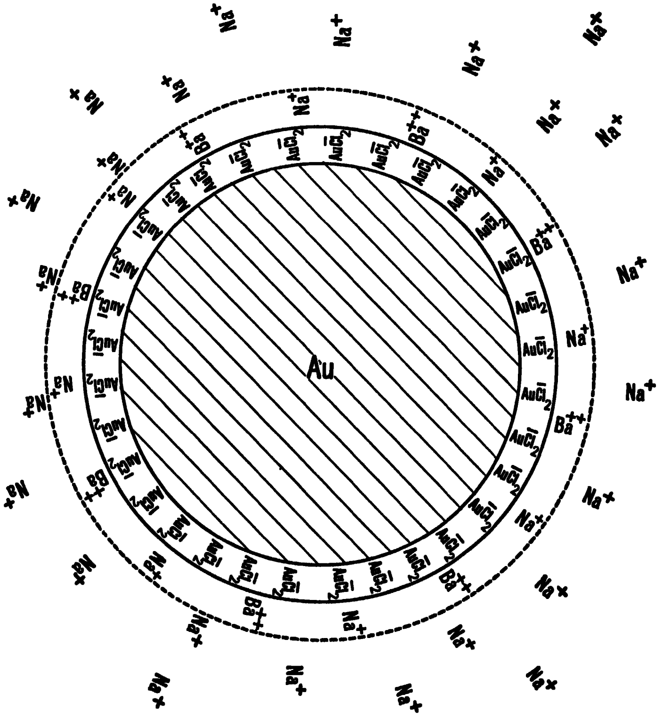

FIG. 16*b*.—Diagrammatic representation of the constitution of a colloidal gold micelle after the addition of barium chloride to the sol.

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[84] Zsigmondy and Thiessen's "Das kolloide Gold," 137 (1925); *cf*. Tuorila: Kolloid-Beihefte, **22**, 191 (1926).

cation. Arranged in the order of their precipitating power for colloidal gold, the divalent alkaline earth cations are: barium > strontium > calcium > magnesium, which is likewise the order of increasing hydration. Apparently the attraction of the negative inner layer for the ions with a relatively thick water envelope is less than for the weakly hydrated ions; hence, for the same concentration, the thickness of the double layer is greater and the reduction in charge is less, the greater the hydration of the cation of a given valence. For the common cations of varying valence, Mukherjee[85] gives the following order of precipitating power on gold sol: thorium > aluminum > barium > strontium > calcium > magnesium > hydrogen > cesium > rubidium > potassium > sodium > lithium.

It must be emphasized that one should speak of the precipitating power of an electrolyte and not of an ion. Thus the anions which have the same charge as the gold particles, the stabilizing ions, tend to be adsorbed and thereby to increase the negative charge on the particles. Accordingly, the precipitating power of different electrolytes varies with the adsorbability of the stabilizing ions. By referring once more to Table X, it will be seen that the precipitating power of the several sodium salts for gold sol is in the order: thiocyanate > sulfate, chloride, formate > acetate, valerianate > propionate, salicylate. This means that, because of the relatively stronger adsorption of salicylate than of chloride, more of the sodium salt of the former than of the latter must be added to cause coagulation.

Cone, Tartar, and Taylor[86] report that the stability of a Zsigmondy gold sol toward sodium chloride is increased by bubbling nitrogen, oxygen, and especially hydrogen, through the sol. The magnitude of the charge on the particles apparently does not change. Since a turbid brownish sol becomes brighter red on bubbling hydrogen through it, the increase in stability may be due in part to disintegration of larger aggregates into smaller ones. The phenomenon should receive further study.

Reversal of Charge. Irregular Series.—If a small amount of electrolyte with a very strongly adsorbed cation and a weakly adsorbed anion, such as thorium nitrate, is added to a neutral gold sol, the ζ-potential is reduced to the critical value and coagulation takes place. On further addition of electrolyte the strong adsorption of tetravalent thorium ion or of hydrous thorium oxide lowers the charge on the particles to zero and then reverses the charge with the formation of a

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[85] Faraday Society Report on Colloids, 103 (1921).

[86] J. Phys. Chem., 36, 735 (1932).

positively charged gold sol. (See Fig. 13 (*d*), page 73.[87]) With still more electrolyte the critical potential of the positively charged sol is reached, this time owing to adsorption of the nitrate ion, and coagulation takes place once more. A typical example of this behavior is given in Table XI.[88] Similar so-called irregular series are obtained with ferric, aluminum, lanthanum, and thorium chlorides.[89] There are thus two zones of coagulation, one of a negative sol and the other of a positive sol; this is shown diagrammatically in Fig. 17. As already noted, the reversal in charge on the particles in the presence of salts which hydrolyze appreciably is sometimes attributed to the formation of a positively charged hydrous oxide-gold adsorption complex.[90] Kruyt[91] showed to his own satisfaction that this was not the case; but the author is not convinced (see page 191).

TABLE XI

ACTION OF $Th(NO_3)_4$ ON GOLD SOL

$Th(NO_3)_4$, millimols/liter	Color after 5 minutes	Remarks
0–0.00084	Red	Sol negative
0.00086–0.00088	Red to blue	Sol negative
0 00090	Blue	Precipitation value of negative sol
0.00090–0.0028	Blue	
0.0030	Violet blue	End of first precipitation zone
0.0040	Red	Sol positive
0.0040–15.0	Red	Sol positive
17–19	Violet	Sol positive
20	Blue	Precipitation value of positive sol

Velocity of Coagulation—Smoluchowski's Theory.—Colloidal gold is a particularly satisfactory preparation for studying the general kinetics of the coagulation process. The velocity of coagulation has

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[87] Freundlich and Buchler: Kolloid-Z., **32**, 305 (1923).

[88] Kruyt and van Arkel-Adriani: Rec. trav. chim., **39**, 609 (1920).

[89] Mayanagi: Kolloid-Z., **39**, 319 (1926); Kermack and Voge: Proc. Roy. Soc., Edinburgh, **45**, 90 (1925); Boutaric and Dupin: Bull. soc. chim., (4) **45**, 28 (1929).

[90] Kermack and Voge: Proc. Roy. Soc., Edinburgh, **45**, 90 (1925); *cf.* Friedemann and Neisser: Münch. med. Wochschr., **51**, No. 11 (1903); Buxton and Teague: Z. physik. Chem., **57**, 72, 79 (1904); Herstad: Kolloid-Beihefte, **8**, 414 (1916).

[91] Kruyt and van der Spek: Kolloid-Z., **25**, 17 (1919); Kruyt and van Arkel-Adriani: Rec. trav. chim., (4) **39**, 609 (1920).

been followed in a number of different ways. Zsigmondy[92] made direct visual observation of the time required for the color to change from red to blue; Hatschek[93] used a color comparator and Mukherjee[94] a spectrophotometer for this purpose; and Galecki[95] made an ultramicroscopic count of the number of particles. In Fig. 18 are plotted Zsigmondy's observations of the time for the appearance of the easily distinguished violet-red color in the presence of varying amounts of strontium chloride. Galecki's observation of the change in mobility of the particles is also indicated in the figure. The same type of curve was obtained with several electrolytes with precipitating ions of varying valence. The observations show that concentrations of electrolytes considerably below the precipitation value cause no visible change. On gradually increasing the concentration, a zone of slow coagulation is reached where a small addition causes a rather large decrease in coagulation time, as shown by the almost horizontal portion of the curve. With still more electrolyte, the so-called precipitation value is attained above which is the zone of rapid coagulation, the vertical portion of the curve. In the latter zone, the time

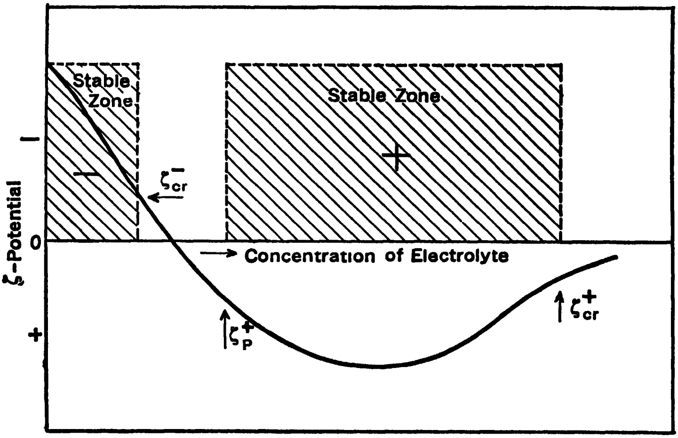

FIG. 17.—Diagram showing the existence of two coagulation points with a stable zone between. ζ^{-}_{cr} and ζ^{+}_{cr} are the critical potentials for the negative and positive sol, respectively. ζ^{+}_{p} is the potential at which the particles are peptized as a positive sol.

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[92] Z. Elektrochem., **23**, 148 (1917); Z. Physik, **92**, 600 (1918).

[93] Trans. Faraday Soc., **17**, 499 (1921).

[94] Mukherjee and Papaconstantinou: J. Chem. Soc., **117**, 1563 (1920).

[95] Z. anorg. Chem., **74**, 174 (1912); Reissig: Ann. Physik, (4) **27**, 186 (1908).

for the color change is independent of the electrolyte concentration and also of the nature and valence of the precipitating ion. The sol under consideration, in which the mobility of the particles was 1.35 μ/second, started to exhibit slow coagulation at about

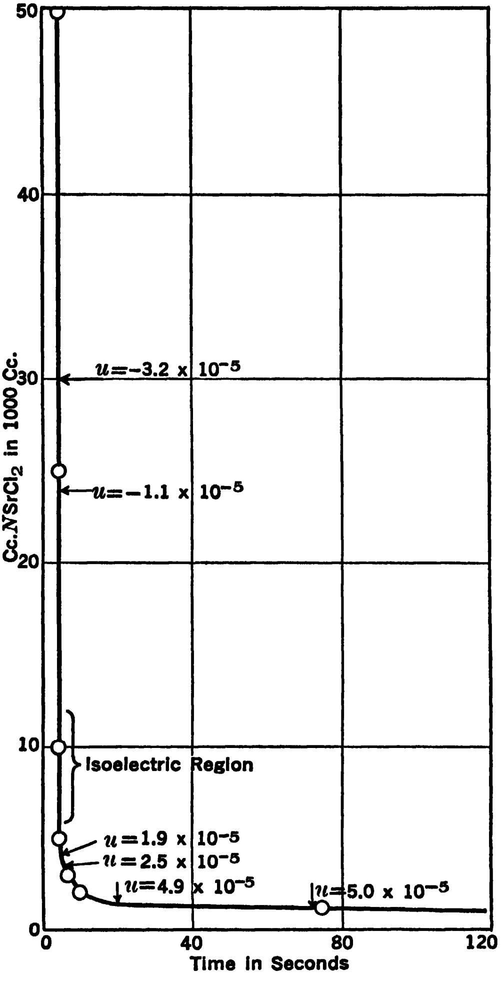

FIG. 18.—Effect of concentration of strontium chloride on the time of coagulation of gold sol.

0.50 μ/second and rapid coagulation at 0.18 μ/second. As already noted (see page 83), the isoelectric zone where the particles have zero charge lies entirely within the zone of rapid coagulation.

Smoluchowski assumes that, in the case of rapid coagulation of particles of equal size and of radius r, one particle becomes permanently fixed to another when the two approach within a certain minimum distance defined as the radius R of the sphere of action. If $R > 2r$ as shown in Fig. 19 the sol is more or less stable, whereas agglomeration takes place whenever the centers of the particles are at a distance less than R, that is, when $R < 2r$.

Starting with this assumption, Smoluchowski[96] deduced the equation for the decrease in number of particles with the time for different stages of coagulation as a function of the radius of action, the diffusion constant, and the original number of particles per unit volume.

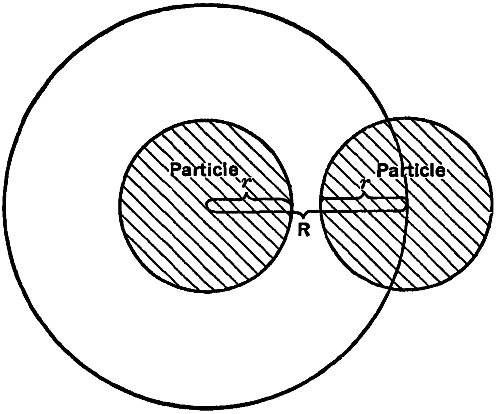

FIG. 19.—The sphere of action in the coagulation process.

The simplest equation which gives the rate of disappearance of primary particles is

$$n_1 = \frac{n_0}{(1 + \beta t)^2} \tag{26}$$

where n_0 is the number of primary particles in unit volume at zero time; n_1, the number of primary particles at time t; and β, a constant which is equal to $4DRn_0$ where R is the radius of action and D the diffusion constant given by Einstein's equation (8). For the total number of particles, Σn, present at a given time the equation is

$$\Sigma n = \frac{n_0}{1 + \beta t} \tag{27}$$

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[96] Physik. Z., **17**, 587 (1916); Z. physik. Chem., **92**, 129 (1917).

It is possible to test this equation by direct observations on gold sols since the primary particles appear green in the ultramicroscope, and the aggregates, brown. Moreover, by adding a protecting colloid, such as gelatin or gum arabic, the coagulation can be readily stopped after a given time interval and the particle count made. Some typical data from Zsigmondy[97] are given in Table XII.

TABLE XII

DECREASE IN NUMBER OF PRIMARY PARTICLES IN THE COAGULATION OF GOLD SOL

t, seconds	n_1 observed	n_1 calculated
0	1.97	1.97
2	1.35	1.65
5	1.19	1.31
10	0.89	0.93
20	0.59	0.54
40	0.29	0.25

Westgren and Reitstötter[98] observed the change in the total number of particles with four different sols containing particles of radius 76, 96, 120, and 152 mμ, respectively, and used these values to calculate the R/r ratio. Some typical data are given in Table XIII.

TABLE XIII

R/r VALUES FOR GOLD SOL WITH PARTICLES 96 mμ IN DIAMETER

t, seconds	$\Sigma_n \times 10^{-8}$ per cc	R/r
0	5.22	0.00
60	4.35	2.56
120	3.63	2.81
180	3.38	2.33
300	2.75	2.33
420	2.35	2.31
600	1.95	2.16
900	1.48	2.19
		2.35

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[97] "Kolloidchemie," 5th ed., 1, 155 (1925).

[98] Z. physik. Chem., 92, 750 (1918).

Since the range of the R/r values of a large number of observations is not far from 2, it follows that the sphere of action is about double the particle size, which means that the gold particles must come almost in contact before agglomeration takes place.

The Smoluchowski theory has been tested by a number of other investigators, and the above results have been confirmed[99] for the rapid coagulation process. It is significant that the theory holds for the rapid coagulation of gold particles in a molten borax bead at a temperature of 900°, showing that the radius of action of colloidal gold particles is independent of the temperature and the properties of the dispersion medium.[100] Moreover, the change in rate of coagulation with the temperature was found to be due to the change in viscosity with the temperature in accord with Smoluchowski's theory.[101]

Although they interpret the facts fairly satisfactorily for rapid coagulation of monodisperse sols, that is sols having particles all of the same size, Smoluchowski's equations do not hold in the zone of slow coagulation or with polydisperse sols. Müller[102] has extended the theory to take care of the rapid coagulation of polydisperse sols, and Smoluchowski has attempted to modify his equation to represent the slow coagulation process. One reason that the equation does not apply to slow coagulation is that, in this zone, only a fraction ϵ of the collisions are effective and lead to the formation of agglomerates. The number of effective collisions is greater the lower the charge and hence the greater the electrolyte concentration. He therefore introduces the factor ϵ into the original equation, which thus becomes

$$n_1 = \frac{n_0}{(1 + \epsilon\beta t)^2} \qquad (28)$$

This equation has been found by Westgren[103] and by Tuorila[104] to

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[99] Kruyt and van Arkel: Rec. trav. chim., (4) **39**, 656 (1920); Kolloid-Z., **32**, 29 (1923); Hatschek: Trans. Faraday Soc., **17**, 499 (1921); Anderson: **19**, 623 (1923); Mukherjee and Papaconstantinou: Phil. Mag., (6) **44**, 305 (1922); Wiegner: Z. Pflanzenernähr Düngung, B, **11A**, 185 (1928); Garner and Lewis: J. Phys. Chem., **30**, 1401 (1926).

[100] Ehringhaus and Wintgen: Z. physik. Chem., **104**, 301 (1923).

[101] Lachs and Goldberg: Kolloid-Z., **31**, 116 (1922); Garner and Lewis: J. Phys. Chem., **30**, 1401 (1926); Davies: **33**, 274 (1929); Butler: **34**, 656 (1930).

[102] Kolloid-Z., **38**, 1 (1926); Wiegner and Tuorila: **38**, 3 (1926); Turoila: Kolloid-Beihefte, **22**, 191 (1926).

[103] Westgren and Reitstötter: Z. physik. Chem., **92**, 750 (1918).

[104] Kolloid-Beihefte, **22**, 191 (1926).

apply more or less satisfactorily for the slow coagulation of monodisperse sols, and Smoluchowski[105] claims that his modified theory interprets satisfactorily the observations on slow coagulation by Paine,[106] Freundlich and Ishizaka,[107] and Gann[108] with sols other than gold. On the other hand, some measurements on the slow coagulation of selenium sols by Kruyt and van Arkel[109] show that the modified Smoluchowski equation does not hold.[110]

Coagulation by Radiations

With certain gold sols, radiations such as x-rays and ultraviolet light have a coagulating action similar to that of a small amount of electrolyte. Thus Galecki[111] observed that the number of particles in a Zsigmondy sol decreased with the length of time of exposure to x-rays; but there was no change in color of the sols. Pietravalle[112] failed to observe any coagulating action of x-rays on a salt-free sol, but the radiation seemed to increase the coagulating power of salts. The α-particles from radium have only a slight effect at the outset, but after a short period of inhibition, flocculation takes place similar to that induced by electrolytes.[113]

The action of ultraviolet light on certain gold sols is especially interesting. Nordenson,[114] in Svedberg's laboratory, showed that the light has a slow action, similar to that of weak electrolytes, on sols formed by reduction with hydrogen peroxide. This was confirmed and extended by Beaver and Muller,[115] who observed that red sols which are rendered blue and unstable by ultraviolet light are repeptized to stable red sols by prolonged action of the light. This holds for sols formed by reduction with hydrogen peroxide, tannin, quinol, catechol, resorcinol, and pyrogallol, but not for sols prepared by reduction with hydrazine, phosphorus, formaldehyde, and acetylene or for Bredig gold sols. Moreover, it was found that blue and some-

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[105] Z. physik. Chem., **92**, 129 (1918).

[106] Kolloid-Beihefte, **4**, 24 (1912); Kolloid-Z., **11**, 115 (1912).

[107] Kolloid-Z., **12**, 230 (1913); Z. physik. Chem., **85**, 398 (1913).

[108] Kolloid-Beihefte, **8**, 63 (1916).

[109] Rec. trav. chim., (4) **39**, 656 (1920); **40**, 169 (1921); Kolloid-Z., **32**, 29 (1923).

[110] *Cf.* Anderson: Trans. Faraday Soc., **19**, 623 (1923).

[111] Kolloid-Z., **10**, 149 (1912).

[112] Chem. Zentr., II, 1017 (1925); *cf.* Bhatnagar, Gupta, Mathur, and Mathur: Z. Physik, **56**, 684 (1929).

[113] Maisin: Ann. soc. sci. Bruxelles, **48B**, 48 (1928).

[114] Z. physik. Chem., **90**, 603 (1915).

[115] J. Am. Chem. Soc., **50**, 304 (1928).

what instable sols formed with the first series of reducing agents are rendered red and stable by prolonged exposure to ultraviolet light.

To account for this behavior, it is assumed that light of one wave length acting on certain sols causes the stabilizing ions, say the $[AuCl_2]^-$ ions in a red sol formed by reduction with hydrogen peroxide, to leave the layer surrounding the particle and enter the intermicellar solution. This raises the conductivity and the refractive index of the sol but decreases its stability so that it turns blue. This effect cannot continue without limit since the change to a blue color is accompanied by a decrease in absorption in the ultraviolet. A return to something approaching the original equilibrium conditions then takes place on prolonged exposure with an accompanying decrease in conductivity and refractive index and a change to the red color. Thus the theory postulates two effective frequencies of radiation, one that turns the red sol blue and the other which turns it back to red. Observations on refractive index, conductivity, and chloride ion concentration in a sol reduced with hydrogen peroxide at different stages of the exposure to ultraviolet light support the view that there is more unadsorbed chloride ions in the blue sols than in the red. Moreover, spectrograms show that the original and final red states are different in that the latter which are light stable no longer absorb the effective radiation which changes the original red sol to blue.

MUTUAL ACTION OF COLLOIDAL GOLD WITH OTHER COLLOIDS: BIOLOGICAL APPLICATIONS

Mutual Coagulation

Suitable mixtures of colloids of opposite charge undergo complete mutual coagulation. An interesting example of this phenomenon is the mutual coagulation of positively charged colloidal gold and negatively charged colloidal stannic oxide. It will be recalled that an experiment of this kind enabled Zsigmondy to establish the nature of purple of Cassius (see page 47). A similar behavior was observed on treating colloidal gold with the positive hydrous oxide sols of iron, thorium, cerium, zirconium, chromium, and aluminum.[116]

Mechanism.—A study of the mechanism of mutual coagulation led Weiser and Chapman[117] to conclude that four factors may enter into the process and determine the width of the mutual coagulation zone: mutual electrical neutralization of particles of opposite charge;

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[116] Biltz: Ber., 37, 1095 (1908).

[117] J. Phys. Chem., 35, 543 (1931).

mutual adsorption of particles that is independent of the charge; the presence of precipitating ions as impurities in the sols; and inter action between the stabilizing ions with the formation of insoluble or unionized products.[118] On either side of the mutual coagulation zone, the colloid in excess reverses the charge and adsorbs the particles of the other sol, giving a mixed sol whose stability is determined by the charge on the aggregates, which, in turn, is dependent on the relative amounts of the two constituents present.

If a hydrophilic colloid such as gelatin is added to a gold sol prepared by reduction in an alkaline medium, not only is there no precipitation but the gold sol is strongly protected against the precipitating action of electrolytes. On the other hand, when gelatin is added to an acid gold sol there is no protective action but mutual precipitation takes place. The difference in behavior is accounted for by the fact that hydrophilic colloids like gelatin change their charge with the hydrogen ion concentration of the medium. Thus gelatin particles are positively charged in a medium of pH less than 4.7, the isoelectric point of gelatin, and negatively charged at a pH greater than 4.7. Hence, in a sufficiently acid gold sol the gelatin particles are positively charged and so coagulate the negative gold, whereas in an alkaline or neutral sol they are negatively charged and stabilize the gold sol.[120] If an excess of gelatin above the coagulation concentration is added to the acid gold sol, the charge on the gold particles is reversed and the sol is stabilized by an adsorbed gelatin film.

The U-number.—The number of milligrams of colloidal substance required to bring about a color change from red to blue in 10 cc of Donau's gold sol or Zsigmondy's gold sol to which is added 3.8 cc of 0.1 N HCl in 100 cc of sol, is called by Zsigmondy[121] the "Umschlagezahl" or U-number of the substance. The U-numbers for several substances obtained by Gann[122] are given in Table XIV. U-numbers were determined also for a number of polypeptides and amino acid salts as well as for several series of basic dyes, alkaloids, amine hydrochlorides, etc. With many of these substances, the coagulation process is a true electrolyte precipitation by organic

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[118] *Cf.* Lottermoser: Kolloid-Z., **6**, 78 (1910); Thomas and Johnson: J. Am. Chem. Soc., **45**, 2532 (1923).

[119] *Cf.* Billitzer: Z. physik. Chem., **51**, 145 (1905); Reinders and Bendien: Rec. trav. chim., (4) **47**, 977 (1828).

[120] *Cf.* Reinders: Chem. Weekblad, **22**, 481 (1925).

[121] Z. Elektrochem., **22**, 102 (1916); Z. anorg. Chem., **96**, 265 (1916).

[122] Kolloid-Beihefte, **8**, 251 (1916).

TABLE XIV

U-NUMBERS

Substance	U-number	Substance	U-number
Gelatin	0.002–0.004	Erepton	0.02–0.03
Witte's peptone	0.002–0.004	Glycocoll	80
Heteroalbumoses	0.002–0.004	Alanine	12–14
Protoalbumoses	0.002–0.0035	Leucine	40
Deuteroalbumoses A	0.0025–0.004	Leucylglycin	20
Deuteroalbumoses B	0.002–0.003	Asparaginic acid	20
Deuteroalbumoses C	0 002–0.0035	Glutamic acid	2.5–3.0
Peptone	0.04–0.06	Histidine hydrochloride.	0.1–0.16

cations in molecular solution; with others, as in certain of the basic dyes, the cations are colloidal aggregates of the simple ions. The U-numbers for acid gold sols prepared in different ways were found to be almost the same with a given substance provided the excess of free acid in the sols was kept approximately constant.

Protective Action

Gold Number.—In the preceding section it was pointed out that a negatively charged hydrophilic or "water soluble" sol will protect a gold sol against the action of electrolytes. This protective action varies widely with different substances, and Zsigmondy devised what he calls the "gold number" as a means of measuring the relative protective power. The "gold number" is defined as the number of milligrams of protecting colloid added to 10 cc of Zsigmondy's gold sol which just fails to prevent the change in color from red to blue on the addition of 1 cc of 10% sodium chloride solution. The gold number varies with the size of the gold particles,[123] and Zsigmondy recommends that the sol be prepared by the nuclear method in such a way that it contains particles approximately 25 mμ in diameter. The gold number is greater the finer the particles, that is, the greater the extent of surface.

The gold number is determined about as follows: After determining the approximate concentration of protecting colloid required, 0.01, 0.1, and 1.0 cc portions are put into the beakers and 10 cc of gold sol added to each. After shaking 3 minutes, 1.0 cc of 10% sodium

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[123] Menz: Z. physik. Chem., **66**, 129 (1909); Prosch: Z. deut. Öl Fett-Ind., **42**, 412 (1922).

chloride is added to each. If the color changes in the first beaker and not in the others, the gold number lies between 0.01 and 0.1 cc of the protecting colloid. By repeating with concentrations between these limits more exact values are obtained. The gold numbers found in this way by Zsigmondy[124] and by Gortner[125] for several hydrophilic colloids are given in Table XV.

TABLE XV

GOLD NUMBERS

Substance	Gold numbers	
	Zsigmondy	Gortner
Gelatin	0.005–0.01	0.005–0.0125
Casein	0.01	
Egg albumin		0.08–0.10
Protalbinic acid	0.03–0.08 (Na salt)	0.15–0.20
Lysalbinic acid	0.02–0.06 (Na salt)	0.10–0.125
Gum arabic	0.15–0.5	0.10–0.125
Dextrin	6–20	
Dextrin (British gum)		125–150
Soluble starch		10–15
Potato starch	about 25	
Sodium oleate	0.4–1.0	2–4

The gold number gives only a rough indication of the protective action, since it is influenced by a number of factors. Mention has been made of the effect of the size of particles in the gold sol. The *p*H value must be controlled also. Thus Tartar and Lorah[126] obtained a constant value for gelatin only between a *p*H value of 8 and 5; below *p*H = 4.7 the protective action decreased very rapidly with increase in the hydrogen ion concentration. Moreover, the degree of dispersion of the protecting colloid has a marked effect, as shown by observation on gelatin by Menz[127] and Elliott and Sheppard.[128] Thus it was found that the protective action increased with decreasing concentration on account of the greater dispersity at

[124] Z. anal. Chem., **40**, 698 (1901).

[125] J. Am. Chem. Soc., **42**, 595 (1920).

[126] J. Phys. Chem., **29**, 792 (1925).

[127] Z. physik. Chem., **66**, 129 (1900).

[128] Ind. Eng. Chem., **13**, 699 (1921).

higher dilution. Also, the protective action of gelatin sols was observed to decrease with age, probably because of an increase in particle size.

Elliott and Sheppard attempted to use the gold number for the purpose of grading gelatins, but the values vary so little with different samples that the method is of slight value. The method has been used to give a qualitative measure of the degree of purity of such substances as gum arabic[129] and dextrin,[130] and to distinguish between different proteins such as the globulins, crystalline albumin, and non-crystalline albumin obtained by the fractional precipitation of egg white[131] and the several albumoses formed by digestion of egg white (Zunz).[132]

Anomalous Behavior.—Contrary to expectations, Zsigmondy obtained a fraction from the non-crystalline albumins of egg white which coagulated rather than protected his alkaline gold sol. Zunz likewise obtained a series of albumoses by digestion of egg white which had a precipitating rather than a protecting action on alkaline gold sol. Krebs[133] found that only acid gold sols are coagulated by blood serum; but Reznikoff[134] showed that serum albumin has a distinct precipitating action on Zsigmondy's sol at certain concentrations. Reznikoff points out further that the action of proteins is characteristic for each one, stabilizing or sensitizing colloidal gold to different degrees depending on its nature. Of particular significance in this connection is the observation of Menz,[135] which was confirmed by Zsigmondy and Joel,[136] that gelatin sols will precipitate Zsigmondy's alkaline gold sols under certain conditions when the gelatin particles are relatively large, but exhibit no precipitating action if the particles are fine. Some observations are recorded in Table XVI. A 1% chloride-free French gelatin was kept for 2 days at 15°, and just before adding to the sol, it was diluted 100-fold. This ensured a coarsely dispersed gelatin which was added to the gold sol in varying amounts. It will be noted that a relatively large

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[129] Zsigmondy: Z. anal. Chem., 40, 718 (1901).

[130] Heumann: Zsigmondy-Thiessen's "Das kolloide Gold," 179 (1925).

[131] Schulz and Zsigmondy: Hofmeister's Beiträge Physiol. Path., 3, 137 (1902).

[132] Arch. intern. Physiol., 1, 427 (1904); 5, 111, 245 (1907); Bull. Soc. Roy. Sci. med. nat., 64, 174, 187 (1906).

[133] Biochem. Z., 159, 311 (1925).

[134] J. Lab. Clin. Med., 8, 92 (1922); *cf.* Wernicke and Modern: Rev. soc. argentian biol. 2, 143 (1926); Spiegel-Adolf: Biochem. Z., 180, 395 (1926).

[135] Z. physik. Chem., 66, 136 (1909).

[136] Z. physik. Chem., 113, 299 (1924).

TABLE XVI

ACTION OF COARSELY DISPERSED GELATIN ON ZSIGMONDY'S GOLD SOL

Gelatin in 1 cc of distilled water, mg	Gold sol, cc	Color	
		Without NaCl	After adding 5 cc 10% NaCl
0.1	5	Red	Red
0.05	5	Red	Red
0.025	5	Red	Red
0.012	5	Red	Red
0.006	5	Red	Violet red
0.003	5	Violet red	Blue
0.0015	5	Violet	Blue
0.0007	5	Blue violet	Blue
0.00035	5	Violet	Blue
0.00017	5	Violet red	Blue
0.00008	5	Red	Blue
0.00004	5	Red	Blue

amount of the coarsely dispersed gelatin stabilizes the sol against the action of electrolytes; then follows a region in which the agglomeration takes place in the absence of electrolyte; and finally, at very low concentration, there is no apparent effect. A probable explanation of this behavior is given in the next section.

Theory of Protective Action.—Since it has been demonstrated conclusively that gold adsorbs gelatin strongly,[137] the protective action of hydrophilic colloids such as gelatin on hydrophobic sols such as gold is due in the first instance to mutual adsorption of colloids of the same sign. Mutual coagulation takes place in a critical range if the sols are of the opposite sign; but if the protecting colloid is added in excess of the mutual coagulation concentration, the charge on the hydrophobic sol is reversed and is then protected by mutual adsorption.[138] Three possibilities arise in a typical case such as Zsigmondy's alkaline gold sol and gelatin: (1) assuming a constant gelatin concentration, if the particles of gelatin are smaller and more numerous than the gold particles the mutual adsorption will result

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[137] Zsigmondy: Z. anal. Chem., **40**, 713 (1901); Mines: J. Physiol., **43**, 22 (1912); Kolloid-Beihefte, **3**, 191 (1912); Beans and Beaver: referred to by Thomas in Bogue's "Colloidal Behavior," **1**, 359 (1924).

[138] *Cf.* Uhlenbruck: Klin. Wochschr., **5**, 710 (1926); Reinders and Bendien: Rec. trav. chim., (4) **47**, 977 (1928).

in the formation of a protecting film of gelatin on gold (see Fig. 20*a*), thereby minimizing the coagulating action of electrolyte; (2) if the particles of gelatin and gold are of the same size, an arrangement similar to that in (1) is possible, but in this case there are fewer particles to be distributed over the gold surface and, in consequence, a lower protection prevails; (3) if the gelatin particles are much larger than the gold particles, the latter are adsorbed on the surface of the protecting colloid as shown diagrammatically in Fig. 20*b*.

In case (3), if the number of gold particles is very great relatively to the number of gelatin particles, the former may be crowded so close on the surface of the latter that it amounts to an agglomeration and the sol changes in color from red to blue. This probably accounts for the observed coagulating action of coarsely dispersed gelatin of a certain concentration on gold sol, as noted in Table XVI. An analogous behavior was observed with globulin from egg, edestin, egg white, and blood serum.[139] Globulin and edestin cause coagulation only in the presence of sufficient electrolyte, such as sodium chloride, to cause peptization. Egg white and blood serum contain the necessary electrolyte for peptization in water. The action of these substances toward colloidal gold resembles Lange's gold sol reaction which will be considered next.

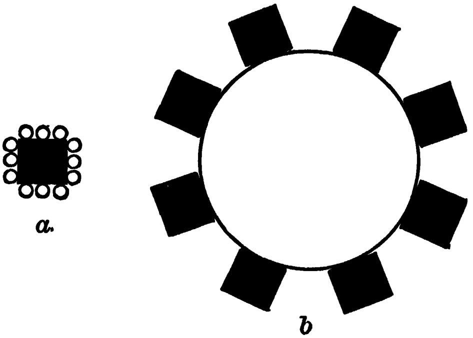

FIG. 20.—Diagrammatic representation of colloidal gold particles of a given size: (*a*) surrounded by smaller gelatin particles, (*b*) attached to larger gelatin particles (after Zsigmondy).

Biological Applications

Lange's Gold Sol Reaction.—As noted in the preceding section, the reaction toward colloidal gold may be used to characterize certain albuminous bodies and their degradation products. Probably the most important application of the action of proteins with colloidal gold is Lange's so-called gold sol reaction of the cerebrospinal fluid,[140] which is used in the diagnosis of certain diseases. In this test, observa-

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[139] Joël: "Das kolloide Gold in Biologie und Medizin," Leipzig, 28 (1925).

[140] Z. Chemotherap., 1, 44 (1913).

tions are made of the effect of mixing varying amounts of the spinal fluid with a constant amount of gold sol. Lange's method of procedure is as follows: The fluid, which must be free from blood, is diluted in the ratio of 1 : 10 with 0.4% sterile sodium chloride solution. A series of 10 test tubes is then prepared, in the first of which is placed 1 cc of the 1 : 10 fluid; in the next, 1 cc of 1 : 20; in the third, 1 cc of 1 : 40; and so on. To each of the tubes is added, rapidly, 5 cc of bright red neutral gold sol, the mixtures shaken thoroughly, and observations made after 5 minutes, 30 minutes, and 24 hours. A normal spinal fluid does not change a satisfactory sol, except that sometimes the first tube takes on a purple or reddish-violet color. A pathological fluid, on the other hand, coagulates the sol to different degrees at different concentrations. If the several colors after 24 hours are plotted as ordinate against the concentrations of the spinal fluid as abscissa, a curve is obtained which is more or less characteristic for certain types of disease. The colors are numbered as follows: Cherry red, 0; bluish red, 1; reddish blue, 2; deep blue, 3; pale blue, 4; colorless, indicating complete coagulation, 5.

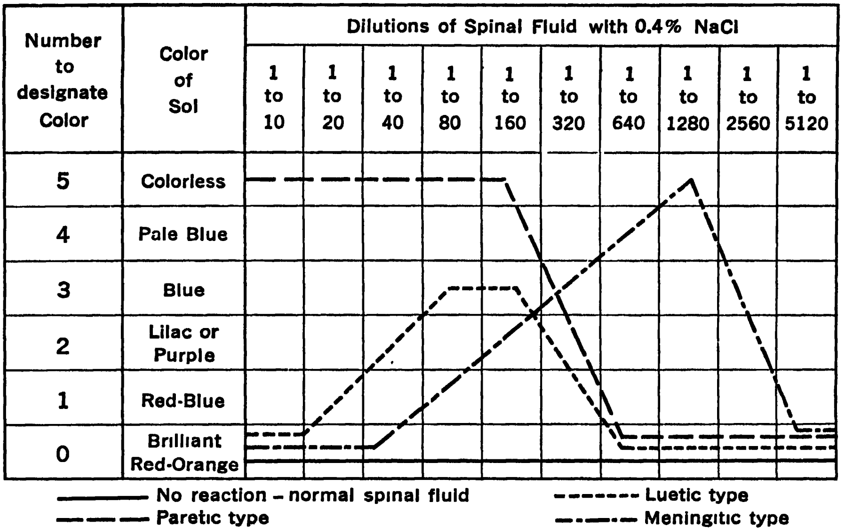

FIG. 21.—Reaction types of spinal fluid with colloidal gold. (Haden.)

Three types of curves are obtained which have been found to have clinical significance (see Fig. 21). At the left is the paretic zone where the reaction in the first five or six tubes is of the 5 type. From there the color values fall off rapidly to 0. This type of curve is significant of dementia paralytica. The middle zone is known as the luetic zone. Here, the change starts at 0, rises as high as 3 to 4 in the fourth and fifth tubes, and then returns to 0. This type of curve is given by patients suffering from neurosyphilis of the non-parenchymatous type but is not an exclusive diagnosis of this condition, since a curve of similar character is obtained in other conditions. The zone at the right where the maximum color change occurs in the higher dilutions is the meningitic zone. Spinal fluids giving this type of curve indicate suppurative or tuberculosis meningitis.

It is needless to point out that Lange's gold sol reaction is a complicated one. The theory of the process has been considered by Schmitt[141] in an extensive monograph in which he gives 228 references. He concludes that the precipitation and protective reactions of the cerebrospinal fluid depend on the quantity of the interacting substances, their particle size, charge, and the *p*H value. Four types of coagulation may come in: (1) adsorptive coagulation of colloids of like sign uninfluenced by electrolytes, like that in the middle portion of the third column of Table XVI; (2) the same as (1) influenced by electrolytes; (3) coagulation at the isoelectric point; and (4) mutual coagulation of colloids of opposite sign.

A consideration of the various diagnostic complications, in using Lange's test, which arise as a result of various pathological conditions affecting the composition of the spinal fluid, goes beyond the scope of this book. Nor does it seem advisable in this place to survey the various suggestions that have been made to improve on Lange's technique. These points have been taken up critically in a monograph by Joël.[142]

It is at once apparent that the colloidal gold used in diagnosis must be of such a character that it will exhibit a normal behavior with normal fluids and the typical curve for a typical pathological condition. The most satisfactory preparations appear to be neutral sols obtained by Zsigmondy's method or some modification thereof.[143]

Gold Number of Serum and Urine.—Lange's gold sol reaction is

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[141] Kolloid-Beihefte, **26**, 58 (1928).

[142] "Das kolloide Gold in Biologie und Medizin," Leipzig (1925).

[143] Lederer: Chem. Abstracts, **16**, 4225 (1925); Mellanby and Amoyl-Davies: Brit. J. Exptl. Path., **4**, 132 (1923); Grey: Biochem. J., **18**, 448 (1924); Manhems and Bernhard: J. Lab. Clin. Med., **11**, 235 (1925); Kilduffe and Hersolm: **12**, 810 (1927); Nicol: J. Soc. Chem. Ind., **46**, 179 T (1927); Rebiere: Colloides biol. chim. therap., **1**, 213, 229 (1928); Fowweather: Brit. J. Exptl. Path., **9**, 161 (1928).

of no value in distinguishing between normal and syphilitic blood serum. The gold number of a serum was likewise found by Reitstötter[144] to give no specific information in the diagnosis of infections. Thus, various antitoxic sera possess the same protecting power as normal sera. Of the serum proteins, albumin has the least protecting power, euglobulins the greatest, and paraglobulins an intermediate value. Such sera as tetanus serum, swine fever serum, dysentery serum, and others which contain little or no albumin but chiefly globulins, may have a protecting action 10 times as great as the normal albumin-holding serum. The changes in serum during immunization result in a diminution of the albumin content which increases the protecting power. Accordingly, the gold number of sera, though indicating nothing specific, is of value in the diagnosis of infections to the extent that it demonstrates the presence of pathological changes in the diseased organism.

Attempts have been made to use the gold number in testing pathologic urine. The urine contains protecting colloids[145] which usually escape notice because of the predominating precipitating action of the electrolytes present in the liquid. But by dialysis, shaking out with benzol, or precipitating with alcohol,[146] the colloids may be separated from most of the electrolyte and the gold number determined. Ottenstein[147] found, however, that the protective action of the colloids from pathologic urines was not sufficiently characteristic to be of much value in diagnosis. The gold numbers of well-dialyzed sols from normal urines were found to range from 3.5 to 7; in pathologic urines, fluctuating values both below and above the normal were obtained that were not characteristic for any one disease with the exception that the values were generally lower than normal in tuberculosis.

The protecting power of albumin is greater than that of the proteoses and peptones formed by the action of the gastric ferments. Hence the breaking down of albumin during digestion can be followed readily by means of the gold number.[148]

Fixation by Organisms.—Zsigmondy[149] showed that mold forms colonies in certain gold solutions. A further investigation of the

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[144] Z. Immunität., **30**, 468 (1920); Kolloid-Z., **28**, 20 (1921).

[145] Lichtwitz and Rosenbach: Z. physiol. Chem., **61**, 112 (1909); Lichtwitz: **64**, 144 (1910).

[146] Salkowsky: Berlin klin. Wochschr., Nos. 51–52 (1905).

[147] Biochem. Z., **128**, 382 (1922).

[148] Uhlenbruck: Klin. Wochschr., **5**, 710 (1926).

[149] Ann., **301**, 29 (1898).

phenomenon by von Plotho[150] disclosed that various types of bacteria, algae, fungi, and higher plants as well as the protozoa, amoeba and paramecium, fix gold particles on their surface. The fixation is the result of mutual adsorption of oppositely charged bodies. This is evidenced by the fact that the fixation takes place only in acid solution in which the surface charge on the organism is positive, hence the opposite of that on the gold particles. Moreover, the presence of protecting colloids in the gold sol cuts down the adsorption and consequent fixation of the gold by the organism; if too much protecting colloid is present, no gold is taken up.

In this connection von Bresslau[151] was able to show that, under certain stimulation, protozoa secrete a slimy material which he named tektin. Ordinarily this could not be detected since it possesses a refractive index identical with that of water. But in contact with finely divided gold sol, the tektin takes up the gold particles and its presence is manifested in the microscope.

In the higher organisms, colloidal gold behaves in many respects like the vital stains. Thus Schulemann[152] found that colloidal gold injected under the skin, into the peritoneum, and in the blood vessels, distributes itself in the cells of the organism like dyes and exhibits a similar metachromatism which is due to partial coagulation of the colloid in the cells. Voight and Fritz[153] injected colloidal gold intravenously into dogs and studied the histological appearance of the kidney tissues in which the gold was largely deposited.

CHEMICAL PROPERTIES

Chlorine and potassium cyanide in the presence of oxygen react readily with the finely divided particles of colloidal gold. Peskoff[154] studied the kinetics of the solution and showed that it was neither a typical heterogeneous nor a molecular process, but a heterogeneous process modified by the relatively larger surface of smaller particles and by the Brownian movement. Ozone reacts with Faraday's colloidal gold to some extent and flocculates it.[155] It is not known whether the flocculating action is due to a gold salt resulting from the oxidation or to some oxidation product of the impurities in the sol.

[150] Biochem. Z., **110**, 1, 33 (1920).

[151] Joël's "Das kolloide Gold in Biologie und Medizin," 103 (1925).

[152] Biochem. Z., **80**, 111 (1917).

[153] Biochem. Z., **120**, 303 (1921).

[154] Kolloid-Z., **32**, 24, 232 (1923).

[155] Riesenfeld and Haase: Z. anorg. Chem., **147**, 188 (1925).

The gold in a gold sol does not amalgamate with mercury when shaken with the latter element.[156] Pauli[157] attributes this to the presence of a film of oxide on the surface; but Zsigmondy[158] points out that there is no action with his gold sol which is free from oxygen compounds. He explains the failure to amalgamate to an electrical charge of like sign on the two elements. Although this may be true, it seems more probable that the observed behavior is due primarily to a film of formaldehyde condensation products on the particles in the Zsigmondy sol (*cf.* pages 32–34). If the metal is shaken for a long time with the sol, coagulation results, owing partly to some solution of the mercury giving Hg^{++} ion which discharges the particles by adsorption, and partly to the reduction in stability of the sol as a result of the stirring.[159]

If gold or silver sol and either arsenic trisulfide or antimony trisulfide sol are mixed in the dark, there is little apparent change since the colloidal particles in the two sols have the same sign. In direct sunlight, however, the sulfides hydrolyze giving sulfide which attacks the metals forming metallic sulfides, accompanied by a series of marked color changes.[160]

Certain sols are very sensitive to the action of ammonia, which causes them to change in color and coagulate. This is true, for example, of Faraday's gold sol, but not of Zsigmondy's sol when properly prepared. Thiessen[161] showed that the coagulating action on certain sols is due to the presence of gold fulminate which is formed by interaction of ammonia with gold oxides or other unreduced compounds of gold. He therefore takes the action of a gold sol with ammonia as the criterion of the presence or absence of unreduced gold in the sol.[162]

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[156] Zsigmondy: Ann., **301**, 36 (1898).

[157] Kolloid-Z., **28**, 50 (1921).

[158] Zsigmondy-Thiessen: "Das kolloide Gold," 164 (1925).

[159] Freundlich and Basu: Z. physik. Chem., **115**, 203 (1925).

[160] Bhatnagar, *et al.*: J. Indian Chem. Soc., **4**, 209 (1927).

[161] Z. anorg. Chem., **134**, 357 (1924).

[162] *Cf., however,* von Weimarn: Kolloid-Z., **45**, 203 (1928).

CHAPTER IV

COLLOIDAL SILVER

Silver, like gold, was obtained in the colloidal state long before this state of matter was recognized. Thus, glass colored with colloidal silver was used in the cathedral of Limoges, which dates from the middle of the fourteenth century. Silver in the form of a hydrosol, first described by H. Rose[1] more than a century ago, was obtained by conducting phosgene into a solution of a silver salt; and, at the same time, Frick[2] prepared a silver "purple" similar to gold purple of Cassius. Recently Voigt[3] synthesized the former in the same way as Zsigmondy did the latter by the mutual coagulation of stannic oxide sol and the metal sol. The so-called silver "sub-citrate" and "sub-oxide" obtained by Wöhler[4] in 1839 were recognized almost half a century later by Newberry[5] and Muthmann[6] to be hydrosols of silver. Carey Lea's[7] so-called allotropic modification of silver formed by the interaction of silver nitrate and ferric citrate, which was described in 1889, was recognized by Prange[8] a year later as colloidal silver. About the same time Bredig[9] prepared the hydrosol by electrical disintegration; and a few years later Kohlschütter[10] described the preparation of the hydrosol by reduction of a solution of the hydroxide with hydrogen.

FORMATION OF SILVER SOLS

Pure stable hydrosols of silver are much more difficult to prepare than the corresponding gold and platinum hydrosols. Pure sols are instable unless they are quite dilute. Concentrated sols are therefore obtained only in the presence of a suitable excess of protecting electrolyte or colloid. The most common methods of formation are:

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[1] Pogg. Ann., **14**, 183 (1828).

[2] Pogg. Ann., **12**, 285 (1828).

[3] "Das kolloide Silber," 61 (1929).

[4] J. prakt. Chem., (1) **18**, 182 (1839).

[5] Chem. News, **54**, 57 (1886).

[6] Ber., **20**, 983 (1887).

[7] Am. J. Sci., (3) **37**, 476 (1889).

[8] Rec. trav. chim., **9**, 121 (1890).

[9] Z. Elektrochem., **7**, 161 (1900).

[10] Z. Elektrochem., **14**, 49 (1908).

reduction of silver salts with or without protecting colloids and electrical disintegration of metallic silver.

Reduction with Hydrogen

Kohlschütter's Sol.—To prepare the sol commonly referred to as Kohlschütter's[10] sol, a saturated solution of silver oxide containing an excess of the solid is placed in a round-bottom flask preferably of resistance glass and after warming to 50°–60°, hydrogen gas is bubbled through the solution. At temperatures below 50° the reduction is quite slow, and above 60° the resulting sol may be instable. In 8–10 hours from 0.5 to 1 liter of a highly colored sol is formed. A silver mirror is precipitated on the glass simultaneously with the sol formation.

The reduction apparently takes place at the surface of the container since the size and shape of the particles and hence the color of the sol varies with the nature of the vessel. According to Kohlschütter no sol is formed in a platinum vessel, all the silver depositing as crystals on the walls. With Thuringen soft glass or quartz he obtained yellowish brown sols; with Jena glass, the color was red, reddish brown, violet, or blue. Taylor[11] reports that a filtered saturated solution of silver oxide in Jena glass gives a perfectly clear intense yellow sol in 20–50 minutes at 60°. The solubility of the glass is not the important thing in determining the nature of the sol since sols having the same color are obtained by reduction in Jena glass of a solution of silver oxide in pure water and in water previously shaken with broken soft glass.

The silver sols prepared as above described contain relatively large amounts of unreduced oxide or hydroxide. This may be removed by dialysis, but the sol is likely to coagulate during the process. Fortunately, the purification is readily accomplished by passing hydrogen through the sol contained in a platinized platinum vessel protected from air with a bell jar. By this procedure the excess silver deposits on the vessel and the conductivity of the sol may be reduced to $4–8 \times 10^{-6}$ mho, which is approximately one-tenth that of the original sol, without any appreciable change in its appearance. The use of carbon monoxide as reducing agent gives a much less stable sol than is obtained with hydrogen.

Erlach and Pauli[12] observed that a sol prepared by Kohlschütter's method using hydrogen from a Kipp generator always contained sulfur

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[11] "Chemistry of Colloids," 188 (1923).

[12] Kolloid-Z., 34, 213 (1924).

which came from hydrogen sulfide present in the hydrogen. Starting with pure silver oxide and pure electrolytic hydrogen there was said to be no sol formation in a clean hard-glass container; but if a trace of potassium carbonate, sodium hydroxide, or ammonium hydroxide was added to the silver oxide solution, a stable sol resulted. It is apparent therefore that sulfur as impurity is not essential to sol formation in the presence of alkali. Pauli attributed the effect of alkali to the formation of an argentate such as NaAgO which serves as the stabilizing electrolyte. The stabilizing effect of a trace of hydrogen sulfide was attributed to the formation of a silver complex, but it is not obvious what this would be or how it would form (see page 123).

Pauli's explanation of the necessity for sol formation of having either alkali or hydrogen sulfide in the reducing solution is inadequate since it is based on erroneous experimental results. Pauli was unable to prepare a sol with pure silver oxide solution and pure hydrogen, and, as we shall see, he was unable to prepare a stable sol by the Bredig method in pure water. Best and Cox[13] had no difficulty with the latter preparation when they hit upon the right conditions, and Roy in the author's laboratory never failed to get a yellow sol in a Pyrex vessel at 50° by the action of purest hydrogen on a pure silver oxide solution that had not been ultrafiltered. In every case a portion of the reduced silver was deposited on the walls of the glass vessel. When the silver oxide solution was ultrafiltered to remove nuclei, no sol formation whatsoever was observed, but all the silver was deposited on the walls. With thoroughly cleaned, clear quartz test tubes and a quartz inlet tube for the hydrogen there was no deposition on the walls and a very dilute sol was obtained provided the oxide was not ultrafiltered. On the other hand, if the solution was ultrafiltered no reduction was observed even after 3 days in contact with hydrogen at 50°. From these observations it is apparent that silver oxide solution is not reduced by hydrogen at 50°–60°. Sol formation results from reduction of solid particles of the suspended oxide or the oxide adsorbed on the walls of the glass vessel.

The hydrogen used in the above experiments was formed by the action of pure zinc amalgam on dilute acid, passed slowly over stick sodium hydroxide, and finally washed with water.

Muthmann's Sol.—Wöhler[14] obtained a red soluble substance which he believed to be silver sub-citrate, by the partial reduction

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[13] J. Chem. Soc., 2727 (1929).

[14] J. prakt. Chem., (1) **18**, 182 (1839).

of silver citrate with hydrogen at 100°. Newberry[15] showed, however, that a sub-citrate of silver does not exist, the red color of the reduced substance and of its solution in water being due to finely divided silver. About the same time, Muthmann[16] prepared a fairly concentrated sol by peptizing the reduction product from silver citrate with ammonium hydroxide, and dialyzing. This is sometimes referred to as Muthmann's sol. By dissolving gum arabic in the sol and treating with alcohol a reversible coagulum results.

Reduction with Phosphorus

Kohlschütter's sol usually contains particles of widely varying size. To prepare sols with particles of uniform size, it is common practice with silver,[17] as with gold, to carry out the reduction in the presence of a nuclear solution. Voigt and Heumann[18] prepared a fairly satisfactory nuclear solution in the following way: A saturated solution of freshly precipitated and thoroughly washed silver oxide is first made up and ultrafiltered once or twice to free from any colloidal oxide. To 24 cc of the solution containing 0.005% silver are added 120 cc of pure water and 1 cc of an ether solution of phosphorus prepared by diluting the saturated solution with 5 times its volume of ether. To get the most finely divided particles, 1–2 drops of an 0.18 N sodium carbonate solution are added to the silver solution followed by the addition of 1 cc of a phosphorus solution prepared by diluting the saturated solution 20 times with ether. The mixture, which is brown-yellow at first, soon becomes a beautiful clear yellow. The particles are too small to be seen with the ultramicroscope but they act as nuclei in silver reduction mixtures. Electrolytic titration discloses that only 9% of the silver is present as ion in a freshly formed sol, but this rises to almost 40% in 24 hours. It is important therefore to use only freshly prepared sols as nuclear solutions.

Galecki[19] prepared a somewhat less pure nuclear solution by mixing 1.5 cc of 0.1% silver nitrate and 0.5 cc of ammonium hydroxide (d = 0.925) with 100 cc of water and adding to the boiling solution 5–6 cc of an ether solution of phosphorus, dropwise, with constant stirring.

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[15] Am. Chem. J., **8**, 196 (1886); Bailey and Fowler: J. Chem. Soc., **51**, 416 (1887)

[16] Ber., **20**, 983 (1887).

[17] Zsigmondy: Z. physik. Chem., **56**, 65 (1906); Nachr. Ges. Wiss. Göttingen Math-Physik. Klasse., 11 (1916); Börjeson: Kolloid-Z., **27**, 18 (1920).

[18] Z. anorg. Chem., **164**, 409 (1927); **169**, 140 (1928).

[19] Z. anorg. Chem., **170**, 45 (1928).

Reduction with Hydrazine

Gutbier[20] prepared a relatively stable silver sol by dissolving 1–2 g of silver nitrate in 1 liter of distilled water, neutralizing exactly with dilute sodium carbonate, and adding a few drops of 1–2000 hydrazine hydrate. The reaction takes place at room temperature, and the sol is sufficiently stable to be purified by dialysis and concentrated somewhat without coagulation. Hydroxylamine hydrochloride gives a less satisfactory sol.

A sol which is free from foreign electrolyte may be obtained by adding 4 cc of a 0.06% solution of hydrazine hydrate to 50 cc of silver oxide solution containing 0.001% silver. This sol is a clear bright yellow with greenish blue particles.[21]

Hydrazine is a satisfactory reducing agent for preparing a sol by reduction of an ammoniacal silver solution. Neureiter and Pauli[22] precipitate 0.6 g of silver nitrate with hydrochloric acid, wash the silver chloride thoroughly, suspend it in water, and dissolve it with 15 cc of 20% ammonium hydroxide. After diluting to 1 liter the mixture is reduced with 15 cc of hydrazine hydrate solution prepared by adding 2 cc of the commercial 50% preparation to 1 liter of water. The particles adsorb chloride which cannot be removed even by prolonged dialysis. The kinetics of the reduction process has been studied by Jablczyński and Kobryner.[23]

To prepare a uniform sol with particles of approximately the same size and color, Voigt and Heumann[21] recommend the following procedure: To 50 cc of a freshly prepared and ultrafiltered solution of silver oxide containing 0.001% silver are added 0.4 cc of 0.18 *N* sodium carbonate, 40 cc of nuclear solution freshly prepared as above described, and 4 cc of 0.0055% solution of hydrazine sulfate or of 0.06% hydrazine hydrate. Reduction takes place at once with the formation of a bright yellow, clear sol with greenish blue particles of uniform size.

The uniform sol formed by the above procedure, and others to be described using different reducing agents, is entirely satisfactory for purposes where the number and size of the particles are not important. In the preparations there is, however, no relationship between the amount of nuclear solution added and the size of the particles. There are two reasons for this: In the first place, an excess of phosphorus

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[20] Kolloid-Z., **4**, 308 (1918).

[21] Voigt and Heumann: Z. anorg. Chem., **164**, 409 (1927).

[22] Kolloid-Z., **33**, 68 (1923); Fried and Pauli: **36**, 138 (1925).

[23] Roczniki Chem., **9**, 704 (1929).

must be used in preparing the nuclear solution, and the excess cannot be oxidized, as in the case of gold nuclear solutions, without oxidizing the silver also. This excess phosphorus furnishes additional nuclei on adding the nuclear solution to the reduction mixture. A second difficulty is that the addition of sodium carbonate to the silver oxide solution either directly or with a nuclear solution gives finely divided silver carbonate particles which act as nuclei.[24] It would seem that this latter difficulty might be avoided by using sodium hydroxide instead of sodium carbonate. Voigt and Heumann[21] get around both difficulties in one of two ways: first, by using a nuclear solution of gold instead of silver; and second, by using a nuclear solution of silver which contains but a trace of phosphorus or sodium carbonate. The latter is obtained by adding 20 cc of the nuclear solution above described to 25 cc of silver oxide containing 0.001% silver and reducing with hydrazine hydrate in the absence of sodium carbonate. The particles in this sol are mostly amicroscopic in size, and since the amount employed in making sols of graded particle size is so small, the detrimental effect of phosphorus and carbonate is reduced to a minimum.

Reduction with Formaldehyde

The reducing agent so commonly used in preparing colloidal gold may be employed in preparing colloidal silver.[25] Voigt and Heumann[26] recommend the following procedure: To 50 cc of an ultrafiltered solution of silver oxide containing 0.001% silver are added 0.2 cc of 0.18 *N* sodium carbonate and 0.5 cc of formaldehyde solution prepared by diluting 2 cc of commercial formalin with 100 cc of water. On heating to 50°–60°, rapid and complete reduction takes place, giving a yellow sol with particles of various sizes and colors. By carrying out this process in the presence of 20 cc of silver nuclear solution, at room temperature or at the boiling point, Voigt obtained a sol with particles of two different sizes but of the same color. This was probably due to the formation of a few nuclei of silver or silver carbonate in addition to those already present in the nuclear solution.

A very stable sol is obtained by a method which von Weimarn[27] found so successful for preparing colloidal gold (*cf.* page 32): To 500 cc of a 0.001 *N* silver nitrate solution is added 10 cc of a mixture

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[24] Voigt and Heumann: Z. anorg. Chem., **169**, 140 (1928).

[25] *Cf.* Pickles: Chem. News, **117**, 358 (1918); Galecki: Z. anorg. Chem., **170**, 45 (1928).

[26] "Das kolloide Silber," 34 (1929).

[27] Kolloid-Z., **33**, 81 (1923).

of 1 cc of formaldehyde and 9 cc of 0.2 *N* potassium hydroxide. The sol is formed at once, and after boiling for an hour or more it is quite stable, standing for a year without coagulation.[28] Slow evaporation to dryness gives a precipitate that is repeptized by water. The stabilizing agent in this case, as in the case of colloidal gold, consists of formoses resulting from the interaction of formaldehyde and alkali.

In addition to formaldehyde other aldehydes,[29] ketones, and phenols[30] have been used as reducing agents in preparing silver hydrosol.

Reduction with Hydrogen Peroxide

To 50 cc of silver oxide solution containing 0.001% silver are added 2 cc of 0.18 *N* sodium carbonate, 25 cc of silver nuclear solution, and 0.2 cc of hydrogen peroxide solution diluted to 1 part in 1000.[21] The reaction takes place rapidly, giving a clear sol containing bluish particles that are not uniform in size. This is probably due to the excess phosphorus added with the relatively large amount of nuclear solution; but the preparation is less satisfactory with less nuclear solution and is very poor with no nuclear solution. The most uniform sol results with hydrogen peroxide if a small amount of gold nuclear solution is employed. The particle size is smaller the larger the amount of nuclear solution, and the color of the sol goes from golden yellow to greenish with increasing particle size as shown in Table XVII.

TABLE XVII

UNPROTECTED SILVER SOLS OF UNIFORM PARTICLE SIZE

Solutions mixed in cc				Color	
Ag_2O 0.001%	Na_2CO_3 0.18 *N*	Au nuclear solution	H_2O_2 1 : 1000	Of sol	Of particles
50	0.3	1.0	0.5	Golden yellow, clear	Chiefly blue, very small
50	0.3	0.5	0.5	Brown yellow, clear	Chiefly blue, very small
50	0.3	0.2	0.5	Brown yellow, clear	Chiefly blue, very small
50	0.3	0.1	0.5	Brownish, cloudy	Variegated, many blue
50	0.3	0.05	0.5	Greenish brown, cloudy	Variegated, some blue

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[28] Von Weimarn: Kolloid-Z., **36**, 55 (1925).

[29] Castoro: Kolloid-Z., **6**, 283 (1909).

[30] Henrich: Ber., **36**, 609 (1903); Garbowski: **36**, 1215 (1903).

Reduction by Light

It was first observed by Svedberg[31] that a dilute silver sol is formed by immersing a piece of silver in water or alcohol and exposing it to ultraviolet light. Nordenson[32] showed that the silver dissolves as silver hydroxide or organic salt which is subsequently reduced, giving a sol. The dissolution process is accelerated by light, but if water or alcohol which has stood in contact with silver in the dark is illuminated with ultraviolet light, some silver particles are formed. Because of this solubility of silver in water and the ease of reduction by light or organisms, Nordenson points out that a silver condenser should not be used in preparing pure water for colloidal work.

Galecki[33] exposed his silver nuclear solution to ultraviolet light and observed an initial discoloration of the sol accompanied by an increase in conductivity owing to the formation of silver ion. Longer illumination resulted in the reprecipitation of the silver as a sol and an accompanying decrease in conductivity.

A solution of silver hydroxide prepared with very pure water and ultrafiltered in the dark does not give a precipitate or sol when exposed to ultraviolet light.[34] This means that nuclei must be present for the reduction to take place. In the presence of gum arabic a clear, yellow brown sol is obtained; but a few minutes' exposure in the presence of gold nuclei gives a cloudy light gray sol as a result of the simultaneous reducing and coagulating action of the light.[35]

Illumination of dilute silver nitrate solution containing gum arabic in a Jena glass vessel gives a black precipitate; in a uviol glass vessel, a black precipitate together with a small amount of the sol; and in a quartz vessel, an almost clear sol.[36] Even in the latter case microscopic crystals are first formed which are disintegrated with sol formation by longer exposure to light. Moreover, the precipitates formed in Jena and uviol glass are peptized by exposure to light in a quartz vessel. It is probable that the peptization consists in a solution of larger silver particles and subsequent reduction

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[31] Kolloid-Z., **6**, 129 (1910); *cf.* Kimura: Mem. Coll. Sci. Eng. Kyoto Imp. Univ., **5**, 211 (1913).

[32] Kolloid-Beihefte, **7**, 110 (1915).

[33] Galecki and Spychalski: Z. anorg. Chem., **177**, 337 (1928); Kolloid-Z., **53**, 338 (1930).

[34] Voigt: Kolloid-Z., **43**, 30 (1927).

[35] *Cf.* Kraemer: Colloid Symposium Monograph, **2**, 57 (1925); Janek and Jirgensons: Kolloid-Z., **41**, 40 (1927); Wiegel: Z. wiss. Phot., **24**, 316 (1927); Lal and Ganguly: J. Indian Chem. Soc., **7**, 513 (1930).

[36] Voigt: Kolloid-Z., **45**, 319 (1928).

to sol under the influence of the light which penetrates quartz but not glass.

Decomposition of Silver Trinitride

When a suspension of silver trinitride is boiled, the following reaction takes place:

$$2AgN_3 \rightarrow 2Ag + 3N_2$$

with the formation of a violet silver sol.[37] Since no foreign electrolyte is added, it is probable that the stabilizing agent is silver hydroxide formed by hydrolysis of the trinitride.

Electrical Synthesis

Arcing Process.—The electrical methods of Bredig and Svedberg described in Chapter I are widely used in the preparation of hydrosols and organosols of silver. (For the preparation of colloidal silver with the enclosed arc, see page 11.) It is claimed by Pauli and Perlak[38] that silver, like gold, cannot be obtained as a stable hydrosol by arcing under pure water but that a small amount of silver oxide or alkali hydroxide must be dissolved in the water. Best and Cox[39] found, however, that stable silver sols are formed by arcing in water of initial specific conductivity of $0.4–0.5 \times 10^{-6}$ mho, protected from the carbon dioxide of the air. The best results are obtained by passing a direct current of 5–6 amperes at 200 volts for 40–55 minutes, keeping the water at a temperature of 15°–40°. In case of too long or too short arcing, the sols precipitate within a few hours or days,[40] whereas under the favorable conditions above described, the sols remain stable over a period of at least 10 months. The reason for the stability is that silver hydroxide is produced during the arcing process,[41] and this, by itself or by forming an argentate, furnishes the stabilizing electrolyte for the sol. If the arcing is too short, too little hydroxide is formed and the sol is instable; if the arcing is too prolonged, the precipitation concentration is approached and the sol is instable. Pauli and Perlak set the minimum concen-

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[37] Wöhler and Krupko: Ber., **46**, 2045 (1913).

[38] Kolloid-Z., **39**, 195 (1926); *cf., also*, Woodard: J. Phys. Chem., **34**, 138 (1930).

[39] J. Chem. Soc., 2729 (1929).

[40] *Cf., also*, Woodard: J. Phys. Chem., **34**, 138 (1930).

[41] Kohlschütter: Z. Elektrochem., **14**, 49 (1908); Paul: **18**, 521 (1912); Rebiere: Compt. rend., **148**, 354 (1909); **154**, 1540 (1912); Treadwell, Janett, and Blumenthal: Helv. Chim. Acta, **6**, 513 (1923); **8**, 89 (1925); Schlee: Biochem. Z., **148**, 383 (1924); Schlee and Thiessenhusen: **151**, 27 (1924); Z. angew. Chem., **37**, 837, 855 (1924).

tration of silver hydroxide for preparing a stable sol, in this medium, at 6×10^{-6} *N*.

Bredig silver sols apparently form most easily in the presence of a small amount of alkali. According to Pauli and Perlak,[38] if the dispersing liquid is 1×10^{-5} *N* potassium hydroxide, the resulting sol is stable for several days. The stability and silver content of the sol increase with increasing amounts of alkali only up to a certain concentration. With 5×10^{-4} *N* potassium hydroxide a permanently stable sol results containing 0.05 g silver per liter. Increasing the alkali concentration to 4×10^{-3} *N* lowers the silver content of the sol but not its stability. In 5×10^{-3} *N* potassium hydroxide, an instable sol is obtained; and in 5×10^{-2} *N* potassium hydroxide there is no sol formation. Woodard[40] showed that, in general, the stability of Bredig's silver sol is determined by the nature of the anion in the arcing solution. Relatively concentrated stable sols are formed in dilute solutions of sodium carbonate and potassium hydroxide; dilute but stable sols in solutions of hydrochloric acid, sodium chloride, ammonium chloride, sodium thiocyanate, and sodium sulfide; but no sols in acetic acid and sulfuric acid and only transient ones in sodium nitrate and sodium acetate. From this it would appear that only those electrolytes in small amounts which are capable of forming moderately insoluble silver compounds are effective stabilizing agents. This would be expected in view of the fact that the anions of such compounds are, in general, the most strongly adsorbed by silver.

Long[42] has patented a procedure for making a silver sol for therapeutic purposes, which consists in passing an oscillating arc of a frequency of 100,000 to 850,000 per second between silver electrodes. It is not apparent in what way this process differs from Svedberg's oscillating-arc process (see page 12).

Electrolysis.—Lottermoser and Bausch[43] prepared dilute impure silver sols by alternating-current electrolysis for 8 hours of 0.005 to 0.2 *N* sodium hydroxide or 0.05% to 2% sodium silicate, with silver electrodes of 1 cm^2 area. In the last analysis this is really an arcing process since an audible and visible sparking effect at the electrode surface is responsible for the sol formation. A sol is formed without arcing by direct-current electrolysis of a sufficiently dilute silver nitrate solution.[44] Thus Billitzer[45] prepared a sol by electrolyzing

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[42] Brit. Pat., 212,442 (1923).

[43] Z. Elektrochem., **32**, 87 (1926); *cf., also,* Jirsa: **25**, 146 (1919); Kolloid-Z., **40**, 28 (1926).

[44] Kohlschütter: Kolloid-Z., **12**, 289 (1913).

[45] Ber., **35**, 1929 (1902).

$N/300$ aqueous silver nitrate at a high current density; better results were obtained in alcohol as solvent.[46]

Reduction with Protecting Colloids

Because of the importance of silver hydrosols as medicinal agents, a wide variety of protecting colloids have been used in their preparation, and many of the preparations have been patented and sold under such names as collargol, lysargin, argyrol, dispargin, protargentum, solargentum, protargol, etc. In some cases the protecting colloid exerts a reducing action; in others, the reduction is accomplished by a suitable agent after the addition of the protecting colloid to the silver solution. As in the case of colloidal gold, the two general methods will be considered separately.

Among the substances which exhibit the property both of reducing agents and protecting colloids, in the preparation of silver hydrosol, are ferrous citrate containing colloidal material, dextrin, tannin, and sodium protalbinate and lysalbinate.

Reduction with Ferrous Citrate. Carey Lea's Sol.—The hydrosol prepared by the classic procedure of Carey Lea[47] is one of the most widely used sols of silver. It is prepared by precipitation from concentrated solutions followed by peptization by washing out the agglomerating electrolytes (see page 16). In one beaker is placed 200 cc of 10% silver nitrate; and in a second beaker, 200 cc of 30% ferrous sulfate, 280 cc of 40% sodium citrate, and 50 cc of 10% sodium hydroxide.[48] The contents of the two beakers are thoroughly mixed and the precipitate is allowed to settle or is thrown down by the aid of a centrifuge. After removing the supernatant solution and shaking up with water, a blood red sol is formed which is purified, preferably by coagulation with as small an amount of ammonium nitrate as possible, the supernatant solution removed, and the process repeated. After several repetitions the precipitate is transferred to a filter paper and washed with 95% alcohol. The dry precipitate, which is readily dispersed in water, contains approximately 98–99% of silver and 1–2% of a ferrous oxide-sodium citrate complex which acts as a protecting colloid.

The Carey Lea sol contains particles of widely varying sizes, but Odén[49] showed that a given sol may be divided into a series of 6 or 8 sols each of which contains particles of approximately the same

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[46] Nordenson: Kolloid-Beihefte, 7, 130 (1915).

[47] Am. J. Sci., (3) 37, 476 (1889).

[48] *Cf.* Voigt: "Das kolloide Silber," 26 (1929).

[49] Z. physik. Chem., 78, 682 (1912).

size, by fractional coagulation with ammonium nitrate solutions varying in concentration from 0.08 *N* to 0.25 *N*, followed by repeptization of the several fractions by washing. The largest particles in the original sol are thrown down by the lowest electrolyte concentrations; the smallest particles require the highest concentrations.

Carey Lea's hydrosol may be converted into an alcosol by dialyzing with absolute alcohol or by precipitation with alcohol and repeptizing the partially dried precipitate in alcohol.[50] Schneider[51] reports that a 0.3% silver alcosol is precipitated at once by adding isopropyl, primary and secondary butyl, trimethyl, and heptyl alcohols, octane, and formaldehyde; but is not affected by propyl or isobutyl alcohol or glycerin. These observations should be confirmed and an explanation of the behavior formulated.

Reduction with Dextrin.—On adding 28 g of silver nitrate in a little water very slowly to a solution of 40 g of dextrin and 40 g of sodium hydroxide in 2000 cc, Carey Lea[47] obtained a precipitate which is readily peptized, giving a black sol. It may be purified by precipitation with a small amount of basic sodium phosphate and subsequent washing. The precipitate is copper-red in color, but after repeated washing on the filter it assumes a Nile green color and then peptizes to a sol possessing a reddish color.

A silver sol results on filtering a boiling hot suspension of silver oxide in water through a filter paper, cooling the filtrate, reheating to 80°–90°, and holding at this temperature until there is no further color change.[52] The reducing agent in this case is probably some dextrin-like material extracted from the filter paper.

Luppo-Cramer prepared a very satisfactory nuclear sol by mixing 10 cc of 10% dextrin, 10 cc of 10% sodium hydroxide, and 7.5 cc of 10% silver nitrate with 22.5 cc of water. After standing 30 minutes the mixture is diluted to 1500 cc. The resulting nuclear sol is optically empty. In transmitted light it is brown red in color, but in thin layers or higher dilution it is pure yellow.

Reduction with Tannin.—Wo. Ostwald prepared a dilute, red-brown silver sol by adding a few drops of freshly prepared tannin solution to 0.0001 *N* silver nitrate containing a very little sodium carbonate.[53] Carey Lea prepared a perfectly clear concentrated sol by adding in small portions 24 g of silver nitrate dissolved in a little water, to a solution of 72 cc of 4% tannin in 1200 cc of water.

[50] Schneider: Ber., **25**, 1281 (1892).

[51] Z. anorg. Chem., **7**, 339 (1894).

[52] Rock and Klosky: J. Phys. Chem., **33**, 143 (1929); Briggs: **34**, 1330 (1930).

[53] *Cf.* Pieroni: Gazz. chim. ital., **43** I, 197 (1913).

Reduction with Sodium Protalbinate and Lysalbinate.—Paal's[54] method of forming colloidal silver using the alkali degradation products of albumin is similar to the method for colloidal gold. To the aqueous solution of the protecting colloid in excess alkali is added a dilute solution of silver nitrate, and the mixture is heated on the water bath until reduction is complete.

Among the other reducing agents which exert a protecting action on colloidal silver are glycocholic and gallic acids, adrenalin,[55] starch viscose,[56] dimenthyl-*p*-phenylenediamine,[57] gum tragacanth,[58] gum arabic,[59] and degradation products of cellulose.[60]

Reduction in the Presence of Protecting Colloids

Of the protecting colloids which have been used in conjunction with the reducing agents in preparing stable silver hydrosols, the following may be mentioned: gelatin in ammoniacal silver nitrate with acrolein as reducing agent;[61] gelatin with chloroform;[62] gelatin with hydroquinone;[63] protein salts,[64] gelatin,[65] gum arabic,[66] various plant extracts,[67] 3.3′ diamino 4.4′ diazo-oxyarsenobenzolmethylenesulfoxalate[68] with hydrazine hydrate; methyl or ethyl cellulose or starch with ammonium formate;[69] acetate of diethylaminoethyl-

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[54] Ber., **35**, 2225 (1902); *cf.* Gerasimov: J. Russ. Phys.-Chem. Soc., **48**, 251 (1916); Lottermoser: J. prakt. Chem., **71**, 299 (1905).

[55] Richter: German Pat., 345,756, Kl, 12n (1921).

[56] Richter: German Pat., 345,717, Kl, 12n (1921).

[57] Richter: German Pat., 342,212, Kl, 12n (1921).

[58] Wüterich and Gutbier: Kolloid-Z., **32**, 331 (1923).

[59] Garard and Duckers: J. Am. Chem. Soc., **47**, 692 (1925).

[60] Von Weimarn: Repts. Imp. Ind. Research Inst., Osaka, Japan, **5**, No. 18, 7 (1925).

[61] Castoro: Kolloid-Z., **6**, 283 (1909).

[62] Morávek: Chem. Listy, **19**, 195 (1925).

[63] Lüppo-Cramer: Kolloid-Z., **7**, 99 (1910).

[64] Neureiter and Pauli: Kolloid-Z., **33**, 67 (1923).

[65] Gutbier, Huber, and Zweigle: Kolloid-Z., **30**, 306 (1922).

[66] Gutbier: Z. anorg. Chem., **32**, 350 (1902); Gutbier and Hofmeier: **45**, 77 (1905); Gutbier: Kolloid-Z., **4**, 300 (1909).

[67] Gutbier, Wolf, and Kiesz: Kolloid-Z., **30**, 31 (1922); Gutbier and Wagner: **19**, 280, 287 (1916); Janek: **41**, 242 (1927); Gutbier: Kolloid-Z., **9**, 175 (1911); Gutbier, Huber, and Kuhn: **18**, 57, 263 (1915); Gutbier and Weise: **19**, 230 (1916); Gutbier and Weingärtner: Kolloid-Beihefte, **5**, 244 (1913); Miller and Hibbard: Plant Physiol., **1**, 409 (1926).

[68] Binz: German Pat., 417,973 Kl, 12q (1925).

[69] Lilienfeld: German Pat., 388,369, Kl, 12q (1924).

monamide of oleic acid with H_3PO_2 and sodium acetate;[70] hydrous stannic oxide or silica with formaldehyde.[71]

A stable, yellow-red alcosol is obtained by reduction of a dilute alcoholic solution of silver nitrate with alcoholic formaldehyde rendered alkaline with ammonia.[72] This sol serves as a nuclear sol in the preparation of blue and green alcosols by reduction of a collodion-silver nitrate solution with alcoholic glycine.

COLLOIDAL SILVER IN SOLIDS: PHOTOHALIDES

In the first paragraph in this chapter attention was called to two examples of colloidal silver in a solid dispersion medium both of which have been known for a long time: glass colored by colloidal silver, and silver "purple," a dispersion of silver in stannic oxide analogous to gold purple of Cassius. To this same class of substances belong the photohalides, the name given by Carey Lea to the colored products formed by the action of light on silver halides. Carey Lea[73] was the first to prepare these substances by incomplete chemical reduction of silver halide with such reducing agents as ferrous oxalate and pyrogallol. The converse of this process, namely, the incomplete oxidation of silver by halogen, will also give photohalides. Thus Baur[74] prepared a colloidal photochloride by treating a silver sol with an amount of chlorine water insufficient to effect complete oxidation.

Carey Lea believed the photohalides to be lakes or adsorption compounds of the normal halide and a sub-halide or an allotropic form of silver. It is now known that the sub-halides assumed by Carey Lea do not exist and that his allotropic silver is colloidal silver. Conclusive evidence that the photohalides are dispersions of silver in silver halide is given by methods of preparation in which silver halide is allowed to act directly with colloidal silver. For example, Carey Lea boiled freshly precipitated silver chloride with finely divided silver and obtained a red precipitate. Similar preparations are obtained by allowing silver to act on molten silver chloride;[75] by

[70] U. S. Pat., 1,527,869 (1925).

[71] Küspert: Ber., 35, 2815, 4066 (1902); Dumanskii and Shershnev: J. Russ. Phys-Chem., Soc., 60, 1593 (1928).

[72] Formstecher: Phot. Ind., 30, 6 (1932).

[73] Am. J. Sci., (3) 33, 349 (1887).

[74] Z. physik. Chem., 45, 619 (1903).

[75] Lorenz: Z. Elektrochem., 7, 281 (1900); Lorenz and Eitel: Z. anorg. Chem., 91, 57 (1915); "Pyrosole" (1926).

allowing colloidal silver to act upon flakes of silver chloride;[76] and by allowing silver chloride to crystallize from an ammoniacal solution containing colloidal silver.[77]

The photohalides possess certain of the properties of silver hydrosol, such as their wide diversity of color and their strong coloring power even in low concentrations. Carey Lea obtained photochlorides which he described as pale flesh, pale pink, rose, copper, red-purple, dark chocolate, and black. For a long time there was opposition to the view that the various colors were due to dispersed silver since the metal was dissolved out of the photohalide by nitric acid only with great difficulty. Lüppo-Cramer[78] showed, however, that the silver was dissolved out if the particles were quite fine, but that little or no silver was removed if the particles were sufficiently coarse. He demonstrated further[79] that the silver in photobromides prepared by mutual coagulation of silver and silver bromide sols was protected by the silver bromide in much the same way as gold in purple of Cassius is protected by stannic oxide from the solvent action of mercury (see page 47).

The elucidation of the nature of the photohalides is of particular importance for the theory of the photographic process. Thus through the work of a number of people, notably Lorenz[75] and Luppo-Cramer,[80] it has been shown that the so-called "latent image" is an early stage of photohalide formation and consists therefore of silver extremely highly dispersed in silver halide and adsorbed thereby.[81] The silver particles furnish the nucleus for the subsequent development by suitable chemical reducing agents.

COMPOSITION OF SILVER HYDROSOLS

Sols Formed by Reduction

Kohlschutter's sol, formed by reduction of silver oxide with hydrogen and purified by the deposition of the excess silver on platinized platinum, always contains some silver hydroxide. Preferential adsorption of the hydroxyl ion by the particles would give a negatively charged sol with silver ion as the contra ion in the diffuse outer portion

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[76] Günther: Lüppo-Cramer's "Kolloidchemie et Photographie," 2nd ed., 26 (1921).

[77] Reinders: Z. physik. Chem., 77, 213 (1911).

[78] "Photographesche Probleme," 62 (1907).

[79] "Kolloidchemie et Photographie," 2nd ed., 26 (1921).

[80] "Kolloidchemie et Photographie," 2nd ed. (1921).

[81] Bancroft: J. Phys. Chem., 17, 93 (1913).

of the double layer surrounding the particles. This explanation of the origin of the charge on the silver particles is apparently not sufficiently complex for Pauli, who demands a complex stabilizing electrolyte of some kind with the complex ion on the surface of the particle. Pauli[82] suggests the formation of a complex in accord with the equation:

$$AgOH + Ag_2O \rightarrow Ag_3O^+ + OH^-$$

but this does not help since the complex ion is the cation and so would charge the particle positively if it were on its surface. A second suggestion is an autooxidation in accord with the equation:

$$2Ag_2O \rightarrow Ag_3O^+ + AgO^-$$

The difficulty with this is that the solution is quite basic; hence the first of the above reactions predominates to such an extent that the formation of an appreciable amount of the complex negative ion by the second reaction is improbable. Pauli got out of this difficulty temporarily by observing that a sol is formed in the presence of hydrogen sulfide, alkali, or ammonia as impurity but is not formed with pure silver oxide and hydrogen. This suggests that the stabilizing electrolyte is an argentate or sulfargentate such as NaAgO or NaAgS in which the silver is in the complex anion. As has been pointed out (*cf.* page 110), this might be all right if the facts were as stated; but Best and Cox[83] prepared a stable sol by the Bredig method in the absence of either sulfur or base other than silver hydroxide formed during the arcing process, and Roy obtained a silver sol by reduction of an unfiltered solution of pure silver oxide with very pure hydrogen.

During dialysis with parchment membranes of the sols formed (1) with hydrogen containing sulfur, and (2) with pure hydrogen but with added base, Erlach and Pauli[82] observed that the original basic solution became weakly acid. This is attributed to membrane hydrolysis and to exchange of hydrogen for the alkali cation during preliminary purification by reduction with hydrogen in a platinum dish. Pauli says: "In the Kipp sols the silver ions and in the electrolyte sols the alkali ions are exchanged for hydrogen ions as the contra ions."[84]. The admission that silver ions are the contra ions in the sulfur-containing sol raises the question as to why silver ions

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[82] Erlach and Pauli: Kolloid-Z., 34, 213 (1924).

[83] J. Chem. Soc., 2729 (1929).

[84] Pauli and Valko: "Elektrochemie der Kolloide," 485 (1929).

may not be the contra ions in a sol containing no sulfur. Pauli claims that what the author terms the stabilizing ion in the sulfur-containing sol is a sulfargentate ion, but he does not state how such an ion would form. If it is the AgS^- ion analogous to AgO^- ion, and Ag^+ is the contra ion, the stabilizing electrolyte would be AgAgS, which is Ag_2S. Since Pauli rules out as improbable that Ag_2O should dissociate into Ag^+ and AgO^-, it is not obvious why the highly insoluble Ag_2S should give any appreciable amount of Ag^+ and AgS^- ions. As a matter of fact, the presence of sulfur is unnecessary for forming a sol, although hydrogen sulfide in the hydrogen may facilitate the sol-formation process by giving a trace of silver sulfide, the surface of which favors the reduction.

Coming back to the slight acidity of the well-dialyzed sols, it is by no means certain that this results chiefly from membrane hydrolysis. Acid may be extracted from the membrane or fermentation of carbohydrates may be a factor in determining the *p*H value of the dialyzed sol. Indeed, Fried and Pauli[85] observed that the sols extract from fresh parchment sufficient carbohydrate, which acts as a protector, to give reversible sols; but from a used parchment, less carbohydrate is extracted and the resulting sols are irreversible.

The particles in a silver hydrosol, formed by reduction of ammoniacal silver chloride with hydrazine hydrate followed by dialysis, always contain a trace of silver chloride.[86] The contra ion is ammonium, which is said to be replaced by hydrogen during prolonged dialysis owing to membrane hydrolysis. Here again it is not certain what happens during several weeks' contact of the sol with parchment.

It may be mentioned in passing that silver nitrate is apparently not adsorbed by silver sponge.[87] The alleged adsorption reported by Euler and Hedelius[88] was due to the presence of zinc in the silver.

Bredig's Sol

The Bredig sol prepared by the method of Best and Cox consists of silver particles with silver hydroxide in the intermicellar solution. Since a Kohlschütter sol can be obtained with pure silver oxide and hydrogen, it is reasonable to suppose that in both types of sols the stabilizing ion is OH^- ion adsorbed directly on the surface of the silver particles or on a film of oxide which is probably on the particle surface,

[85] Kolloid-Z., 36, 138 (1925).

[86] Neureiter and Pauli: Kolloid-Z., 33, 68 (1923).

[87] Tartar and Turinsky: J. Am. Chem. Soc., 54, 580 (1932).

[88] Arkiv Kemi, Mineral Geol., 7, No. 31, 1716 (1920).

as in the case of dispersed platinum (see page 178). The greater ease with which sols of both types are formed in the presence of added alkali may well be due, as Pauli suggests, to the formation and relatively stronger adsorption of argentate ion than of hydroxyl ion.[89]

PROPERTIES OF COLLOIDAL SILVER

Stability of Silver Hydrosols

Coagulation by Electrolytes.—Unprotected silver sols are quite sensitive to electrolytes. For this reason the sols employed for therapeutic purposes are, for the most part, protected by hydrophilic colloids. Many of the protected preparations kept in the dry state for indefinite periods are still peptized by water.

The precipitating action of a variety of electrolytes on two Carey Lea silver sols is given in Table XVIII.[90] Although these sols are usually classified among the protected sols, it is apparent that their behavior toward electrolytes with precipitating ions of varying valence is much the same as for typical hydrophobic negative sols.

TABLE XVIII

PRECIPITATION OF CAREY LEA'S SILVER SOLS BY ELECTROLYTES

Electrolyte	Precipitation concentration, millimols/liter	
	Sol 1	Sol 2
$NaNO_3$	51.0	......
KNO_3	41.0	......
NH_4NO_3	36.0	40.0
KOH	.....	26.0
$AgNO_3$	11.0	......
Strychnine Nitrate	3.1	......
$Sr(NO_3)_2$	0.63	0.54
$Ba(NO_3)_2$	0.46	......
$FeSO_4$	.....	0.51
$Pb(NO_3)_2$	0.27	......
$Al(NO_3)_3$	.....	0.067
$\frac{1}{2} Al_2(SO_4)_3$	0.19	0.058
$LaNO_3$	.....	0.035
$\frac{1}{2} Fe_2(SO_4)_3$	.....	0.023
$Th(NO_3)_4$	0.15	......

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[89] *See, also,* Löffler and Pauli: Kolloid-Z., **60**, 146 (1932).

[90] Freundlich and Loening: Kolloid-Beihefte, **16**, 1 (1922); *cf., also,* Lottermoser and Meyer: Z. prakt. Chem., (2) **56**, 241 (1897); **57**, 540 (1898).

The rate of coagulation of a Kohlschütter silver sol by sodium chloride can be represented by Smoluchowski's equation for rapid coagulation, but, as is generally true, the divergences are quite large for slow coagulation.[91]

Dörinckel[92] and Rabinerson[93] investigated the mutual coagulation of colloidal silver and ferric oxide, which are oppositely charged.

Action of Hydrophilic Colloids.—Gum arabic and saponin in all concentrations exert a protective action toward electrolytes. Other hydrophilic colloids such as gelatin and casein exert a sensitizing effect in very low concentrations just as they do on colloidal gold, and for the same reason (see page 97); but in high concentrations they have a marked protective action.

Charge Reversal.—Like colloidal gold, Carey Lea's sol is readily reversed in the presence of a small excess of thorium nitrate,[94] assuming the properties of a typical positive colloid. A Bredig sol likewise undergoes charge reversal in the presence of a suitable excess of aluminum sulfate or ferric sulfate. According to Malarski,[95] if the reversed sol is filtered through a paper filter, it assumes its original charge. This is probably due to adsorption of the reversing electrolyte by the paper.

Since the surface of the particles of colloidal silver like colloidal platinum is covered with a film of oxide, it is probable that the mechanism of the charge reversal is similar in the two cases (see the discussion of this phenomenon on page 191).

Color

The property of exhibiting a wide variety of colors is probably the most outstanding characteristic of colloidal silver. Thus both protected and unprotected hydrosols and photohalides have been obtained in all shades of yellow to brown; in different shades of clear red, vermilion, dark red, and violet; and in a variety of tones of green and blue, blue-gray and black. The variety of colors is much greater than can be obtained with colloidal gold, which exhibits colors only from shades of red through violet to blue. As in the case of other metallic sols, the color for a given concentration of silver is determined by (1) the size of the primary particles, (2) the shape of

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[91] Steacie: J. Phys. Chem., **34**, 1848 (1930).

[92] Z. anorg. Chem., **67**, 161 (1910).

[93] Kolloid-Z., **39**, 112 (1926).

[94] Freundlich and Buchler: Kolloid-Z., **32**, 305 (1923).

[95] Kolloid-Z., **23**, 113 (1919).

the primary particles, and (3) the size and nature of the agglomerates. These will be considered in order, as they influence the color of silver sols.

Particle Size.—Frequent reference is made by Carey Lea to the striking variations in color during the preparation of sols by his method. As already noted, Odén[96] separated the polydisperse Carey Lea sol into a number of more nearly monodisperse sols by fractional precipitation with ammonium nitrate. The color of the several fractions varied from reddish brown to yellow with increasing degree of dispersion. By treating with varying amounts of 9% hydrogen peroxide, Wiegel[97] obtained sols varying in color from orange-yellow and shades of red, to shades of violet or blue. The change is due to increase in particle size as a result of dissolution of smaller particles and reprecipitation on larger ones in accord with the mechanism:

Solution of Ag　　　　　　　　　　Reprecipitation of Ag

$$H_2O_2 + Ag \longrightarrow AgOOH \xrightarrow[\text{on surface of precipitate}]{+\,Ag} Ag_2O_2 \xrightarrow[\text{of precipitate}]{\text{on surface}} 2Ag + O_2$$

Particles which separate out from the sol are well-formed crystals of silver.

An important quantitative study of the effect of particle size on color has been made by Schaum,[98] who prepared quite uniform, easily reproducible monodisperse sols by "developing" a solution of silver nitrate and sodium sulfite with a solution of *p*-phenylenediamine and sodium sulfite in the presence of gelatin and of a silver nuclear solution. The final size of the particles for a given amount of reactants was found to depend on the concentration of the nuclear solution. In preparing a series of sols, two solutions were made up as follows: (*A*) 18 g $Na_2SO_3 \cdot 7H_2O$ and 0.75 g $AgNO_3$ in 100 cc water; (*B*) 2 g $Na_2SO_3 \cdot 7H_2O$ and 2 g *p*-phenylenediamine in 100 cc water. To solution *B* was added a small amount of nuclear solution and gelatin, followed by the dropwise addition of solution *A*. The solutions mixed and the color of the sol particles in a series of sols, are given in Table XIX. It will be noted that the color of the sol varies from yellow to blue-green and of the particles from blue-violet to yellow with decreasing number of nuclei in the reducing solution, that is,

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[96] Z. physik. Chem., **78**, 699 (1912).

[97] Kolloid-Z., **47**, 323 (1929); **51**, 112 (1930).

[98] Schaum and Lang: Kolloid-Z., **28**, 243 (1921); Schaum and Marx: **31**, 64 (1922).

with increasing particle size. It will be noted, further, that the color in reflected light is complementary except with the coarser dispersions where the turbidity of the sols affects the observations.

TABLE XIX

COLOR OF PROTECTED SILVER SOLS OF VARYING PARTICLE SIZE

Sol No.	Solutions mixed				Transmitted color of dilute sol	Appearance of particles in the ultramicroscope
	Nuclear liquid	1% gelatin	*B*	*A*		
1	2 cc Lüppo-Cramer's	9.2	0.2	0.4	Yellow	Very faint blue-violet
2	5 cc Sol 1	4.5	0.1	0.2	Yellow-orange	Faint blue-violet
3	5 cc Sol 2	4.5	0.1	0.2	Orange	Brighter blue-violet
4	5 cc Sol 3	4.5	0.1	0.2	Orange-red	Mostly blue; some blue-green, and a few orange
5	5 cc Sol 4	4.5	0.1	0.2	Red-violet	No blue; mostly blue-green, orange, and red
6	5 cc Sol 5	4.5	0.1	0.2	Blue-violet	Orange and yellow
7	5 cc Sol 6	4.5	0.1	0.2	Blue-green	Only yellow and white

Starting with 0.1 cc of nuclear solution in solution *B* containing a small amount of gelatin, and adding dropwise during 15 minutes 6 cc of solution *A*, it is possible to pass through the entire color scale: yellow, yellow-red, purple, violet, blue, and blue-green. A reversal of this scale of colors may be accomplished by slowly dissolving larger particles by the following procedure:[99] A blue sol is prepared by adding 1.5 cc *M*/20 magnesium sulfate to 2 cc of Lüppo-Cramer's nuclear solution diluted with 2 cc of water and allowing to stand. After attaining a blue color, an equal amount of 10% gelatin is added and allowed to solidify. The gel is then covered with a concentrated solution of ammonium hydroxide, potassium cyanide, or sodium thiosulfate. After a few days, the color variation from the bottom to the top of the jelly is: blue, blue-violet, red, violet-red, orange, yellow, colorless.

On the basis of Mie's theory of the color of metallic turbid media (*cf.* page 78), Müller[100] determined what should be the color trans-

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[99] Schaum and Marx: Kolloid-Z., 31, 64 (1922).

[100] Ann. Physik, (4) 35, 500 (1911).

mitted by a metallic sol containing particles assumed to be spheres of a given diameter. In Table XX are given the diameters of particles corresponding to a given color on the basis of Mie's theory and Schaum and Lang's[101] observations on two series of silver sols prepared as described above. It will be noted that the agreement is fairly good.[102] Similar qualitative relationships obtain with unprotected silver sols as shown by the observations of Voigt and Heumann, to which reference has already been made (see page 114).

TABLE XX

RELATION OF PARTICLE SIZE TO COLOR IN PROTECTED SILVER SOLS

Transmitted color	Diameter of particles in mμ		
	Theoretical from Mie's theory	Observed with	
		Series I	Series II
Yellow-orange	...	...	60
Orange	80	70	...
Orange-red	...	...	90
Red	100	90	...
Purple	120	110	120
Violet	...	...	150
Blue-violet	140	137	...
Blue	160	...	...
Blue-green	180	[180]	[180]

Shape of Particles.—Mie's theory of the color of metallic colloids is based on the assumption that the particles are perfect spheres. That they apparently do approximate this shape is indicated by the similarity between the observed and calculated diameters corresponding to a given color as given in Table XX. Feick[103] showed, however, that Mie's theory does not apply rigidly to silver sols. This would be expected in view of the fact that the particles are not quite spherical,[104] exhibiting distinct double refraction in an electrical field.[105]

[101] Kolloid-Z., **28**, 243 (1921).

[102] *Cf., also,* Pihlblad: Kolloid-Z., **9**, 156 (1911).

[103] Ann. Physik, (4) **77**, 673 (1925).

[104] Szegvari: Z. physik. Chem., **112**, 277, 295 (1924); Gans: Physik. Z., **13**, 1185 (1913).

[105] Bergholm and Björnstahl: Physik. Z., **21**, 137 (1920).

Form of Agglomerates.—Closely related to both size and shape of primary particles are the form of the aggregates and the density of the packing of the aggregates of primary particles in certain sols. The importance of this factor on color is indicated in a striking way by some observations of Hamburger[106] on silver precipitates formed by evaporation and subsequent condensation in a high vacuum (*cf.* page 71). The precipitates were clear yellow at first, becoming orange, red, violet, and finally blue as the vaporization and condensation with accompanying particle growth were continued. The red, violet, and blue precipitates were resolvable in the ultramicroscope; the yellow and orange precipitates, composed of smaller particles, were not resolvable. Although these observations indicate the importance of particle size for color, Hamburger emphasized that the form and density of aggregates of primary particles must not be overlooked. Thus when a cold precipitate formed in a high vacuum was opened to the air there was always a deepening of the color in the direction: yellow to red to blue. Since the precipitates were cold, this could not be attributed to growth of primary particles but was probably due to a closer packing of the particles under atmospheric pressure. In support of this, Hamburger showed that the deepening in color on opening to the air was retarded by covering the precipitate with Canada balsam which prevented the packing of the particles into aggregates.

The importance of agglomeration of primary particles on the color of silver sol is well illustrated by observations of the color change during electrolyte coagulation. Table XXI gives some data taken from Voigt and Heumann's[107] observations of color change on adding 0.2 cc of $N/10$ electrolytes to 10 cc of sol diluted to 20 cc. Sol 1 was prepared by adding 20 cc of 0.06% hydrazine hydrate to 125 cc of 0.001% silver oxide solution containing 0.5 cc of gold nuclear solution; Sol 2 was obtained by adding a mixture of 20 cc of silver nuclear solution (with phosphorus) and 1.5 cc of 1 : 50 formaldehyde, to 125 cc of 0.001% silver oxide containing 5 cc of 0.18 N sodium carbonate.

It is apparent that the color transformations which yellow silver sols undergo during electrolyte coagulation are more complex than is observed with red gold sols. In the latter, the color changes are always from red through violet to blue; in the former, the color may go from yellow through rose to violet, or from yellow through greenish

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[106] Kolloid-Z., **23**, 177 (1918).

[107] Z. anorg. Chem., **173**, 27 (1928); *cf.* Schaum and Marx: Kolloid-Z., **31**, 64 (1922).

TABLE XXI

COLOR CHANGE DURING COAGULATION OF SILVER SOLS WITH ELECTROLYTES

Electrolyte	Sol 1	Sol 2
$PbCl_2$.....	Yellow, rose, red, gray-red	Yellow, rose-yellow, cloudy yellow-rose
Na_2SO_4.....	Yellow, yellow-green, green	Yellow, rose, yellow-rose, rose-violet
$NaNO_3$.....	Yellow, dirty yellow-green....	Yellow, rose-yellow, rose, rose-violet
NH_4CNS...	Yellow, gray-yellow, gray.....	Yellow, clear yellow, gray-yellow, greenish yellow
KBr........	Yellow, green, gray-green	Yellow, clear rose-yellow, cloudy gray
NaCl	Yellow, light green, dirty gray	Yellow, clear rose-yellow, cloudy gray
NH_4NO_3...	Yellow, green, gray-green.....	Yellow, rose, yellow, rose, violet-rose
$NaNO_2$.....	Yellow, yellow-green, olive green, gray green	Yellow, rose-yellow, rose, rose-violet
Na_2HPO_4...	Yellow, rose, red, violet, bluish gray	Yellow, rose-yellow, rose, rose-violet
$Al_2(SO_4)_3$...	Yellow, rose-yellow, gray	Yellow, rose-yellow, gray-yellow

yellow to green, or from yellow through brownish red to greenish brown. With a given silver sol the variation in the color changes during coagulation is probably associated with the form and the closeness of packing of primary particles in the aggregates.

Chemical Properties

The particles in silver sol have been found by x-ray analysis to be made up of minute crystals of the metal.[108] Indeed, amorphous silver has been prepared only by a special procedure which consists in allowing a stream of molecules of silver and naphthalene to strike against a drum revolving at 8000 r.p.m., cooled to the temperature of liquid air. An x-radiogram of the silver powder obtained by dissolving out the naphthalene shows only a general darkening, but diffraction lines appear after the powder is warmed.

Colloidal silver particles are readily dissolved by relatively low concentrations of silver solvents; ozone oxidizes the element to oxide.[109] A mixture of unprotected, negatively charged sols of silver and arsenic trisulfide react with each other.[110] If the action takes

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[108] Scherrer: Zsigmondy's "Kolloidchemie," 3rd ed., 407 (1920); Gross: Umschau, **34**, 510 (1920); Freundlich: Ber., **61**, 2219 (1928).

[109] Riesenfeld and Haase: Z. anorg. Chem., **147**, 188 (1925).

[110] Freundlich and Moor: Kolloid-Z., **36**, 17 (1925).

place in the dark, it is accompanied by color changes through greenish brown to lilac; in the light, the color change is through green and blue to a golden yellow. A chemical process involving oxygen takes place, and silver thioarsenite is formed. In the presence of gelatin the particles are prevented from coming together and there is no interaction between the adsorbed stabilizing ions and no color changes.

Under the influence of ultraviolet light, nuclear silver sols are decolorized by the solvent action of hydrogen peroxide formed by the action of the light. The reaction is of the first order.[111]

APPLICATIONS OF COLLOIDAL SILVER

Medicinal Use

Bactericidal Action of Metals.—The therapeutic effect of certain of the metallic elements, especially of mercury and silver, has been known for a long time. Thus Izar[112] reports that even the Macedonians covered wounds with silver plates, and in parts of Italy erysipelas is still treated in the same way. If the use of finely divided mercury in the form of blue ointment is excepted, the introduction of colloidal silver by Crede[113] in 1896 marks the beginning of the use of colloidal metals as therapeutic agents; and at the present time, silver is probably the most important of the metals to be employed for this purpose.

At the outset, Crede used Carey Lea's dextrin sol; but at the present time there is a wide variety of commercial products on the market which are given names indicative of the method of preparation or of the protecting colloid which is added to ensure their stability. Some of the sols most frequently encountered, together with the protecting colloid each contains, are the following: "argentum Crede" or collargol (dextrin); lysargin (sodium lysalbinate); protargol (sodium protalbinate); argyrol (vitellin from egg yolk); dispargin (acid degradation product of gluten); sophol (nucleic acids and formaldehyde); and electrargol, an electrically dispersed sol protected by gelatin.

The toxic action of colloidal metals on microorganisms is indicated by their action on certain protozoa as reported by Filippi;[114] see Table XXII. The superior toxic action of colloidal silver is apparent from these observations. It is significant that the lethal thresholds

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[111] Galecki and Spychalski: Kolloid-Z., **53**, 338 (1930); *see* page 127.

[112] Z. klin. Med., **68**, 516 (1909).

[113] Apoth. Ztg., **11**, 165 (1896).

[114] Arch. ital. biol., **50**, 175 (1908); **51**, 447 (1909).

TABLE XXII

ACTION OF COLLOIDAL METALS ON PROTOZOA

Sol	Lethal Concentration of Metal for	
	Paramecium	Vorticella
Ag	1 : 450,000	1 : 170,000
Hg	1 : 390,000	1 : 92,000
Cu	1 : 70,000	1 : 36,000
Ni	1 : 24,000	1 : 9,500
Pd	1 : 6,500	1 : 5,200
Au	1 : <4,000	1 : 4,000
Pt	1 : <4,000	1 : <4,000

for salts of the same metal are similar for the same dilution and the same content of metal.

Colloidal silver has no effect on molds but it exhibits a strong bactericidal action on such bacteria as *B. anthrax*; *B. coli*; *Staphylococcus pyogenes*, *aureus*, and *albus*; *B. dysenteria*; etc.[115]

In considering the therapeutic action of colloidal metals generally, it is necessary to take into account the possible effect of three constituents in such sols: the ions, the metals, and the protecting colloid. These will be considered in order.

Effect of Ions.—The therapeutic action of silver sol and of metallic sols, generally, appears to be due in large measure to the metallic ions present in the sol.[116] This was recognized definitely by Paul,[117] who showed that different silver sols give silver ions in different amounts on dilution, and attributed the varying bactericidal action of the technical preparations to their varying tendency to give silver ion. This has been demonstrated repeatedly in more recent years. For example, Sollmann and Pilcher[118] tested four dilutions of protargol, argyrol, collargol, and silver nitrate for their antiseptic properties against 2% yeast in 10% cane sugar solutions, taking the quantity of gas liberated as a measure of the antiseptic action. It was found that the antiseptic efficiency in this case resided wholly

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[115] Henri and Cernovadeanu: Compt. rend. soc. Bio., **61**, 122 (1906).

[116] Ascoli and Izar: Biochem. Z., **5**, 394; **6**, 192 (1907); **7**, 142; **10**, 356; **14**, 491 (1908); **17**, 361 (1909).

[117] Mitt. Bayr. Moorkulturanstalt, No. 2 (1908).

[118] J. Lab. Clin. Med., **10**, 38 (1924).

in the liberation of silver ions by the several preparations. The silver ion content of argyrol and silvol increased with age, and this was paralleled by an increase in its antiseptic value and its irritating action. The obvious conclusion from these observations is that any advantage colloidal silver possesses over silver nitrate must depend upon demulcent qualities which serve to diminish the irritating effect of silver ion.

Because of the toxicity of silver ion and its varying concentration in sols, it is important that different preparations be subjected to rigid tests before use, especially in intravenous injection.[119]

Effect of the Metal.—It is uncertain whether the silver itself has any therapeutic effect independent of its ability to form ions. The metal may act indirectly by stimulating the formation of antibodies or by intensifying the metabolic processes, thereby destroying the source of infection in some way. It is more likely, however, that the metal acts directly on the bearer of the infection. This is indicated by the fact that injected metal is stored[120] in the reticular endothelium of glands, bone marrow, and in the phagocytes, that is, in the same places that the bacteria congregate. It seems probable, therefore, that the metal in close contact with the bacteria acts either to destroy them completely or to retard their development.[121] It is impossible to say definitely to what extent these effects are due to the solubility of the silver in the tissue fluids. That this would seem to be an important factor is suggested by the fact that the more finely divided the silver the stronger is its bactericidal action.

Effect of the Protecting Colloids.—The presence of the protecting colloid in silver sols is undoubtedly of importance since different results are obtained depending on whether the stabilizer is a carbohydrate or a protein.[122] Moreover, the protecting colloid may exhibit a therapeutic effect in the absence of colloidal silver. For example, protein bodies such as milk and casein are injected like colloidal metals in the treatment of certain septic processes. If the results are similar with the two agents, it is logical to ascribe at least a part of the action of the colloidal metal to the protein component.

The combination of colloidal silver and protecting colloid may exert an influence that is different from either taken separately.

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[119] *Cf.* Voigt: "Das kolloide Silber," Chapter 14 (1929); *cf.* Shouse and Whipple: J. Exptl. Med., **53**, 413 (1931); Shouse and Warren: **53**, 437 (1931).

[120] Voigt: Biochem. Z., **63**, 409 (1914); **68**, 477 (1915); **73**, 211 (1916); Virchow's Arch., **257**, 851 (1925).

[121] Koller: Schweiz. med. Wochschr., No. 43 (1919).

[122] *Cf.* Nissen: Z. ges. exptl. Med., **28**, 193 (1922).

For example, Voigt[123] is of the opinion that certain protecting colloids increase the solubility of silver and so recommends detailed animal experimentation before using combinations of silver and hydrophilic colloids. Similarly, Assmann[124] reports the absence of any disinfecting action of collargol or lysargin on intestinal bacteria. On the other hand, a mixture of the colloids with officinal gum arabic solution, in the ratio of one of the former to four of the latter, diminishes the bacteria count quite appreciably. Also, Ascoli and Izar observed a marked rise in uric acid elimination on injection of a protected silver sol containing 0.03% gelatin, whereas no such effect was obtained with the colloid in the absence of gelatin. These examples and many others which might be mentioned[125] merely emphasize the importance of careful control in the use of such medicinal agents as protected silver sol. It is safe to say that no two preparations are exactly alike, and their indiscriminate use without control[126] is not recommended.

Mode of Application.—Silver hydrosol is most frequently applied by intravenous injection, but in some illnesses it is used in an enema or as an ointment. When injected into the blood stream, the silver is said to precipitate selectively on inflamed tissue.[127] It has been employed with more or less favorable results in a large number of infectious diseases, among which may be mentioned the common cold, conjunctivitis, pneumonia, inflammatory rheumatism, erysipelas, typhoid and paratyphoid, appendicitis, furunculosis, phlegmons, anthrax, cerebrospinal meningitis, scarlatina, dysentery, diphtheria, grippe, gonorrhea, syphilis, etc. The reports of clinicians on the therapeutic effect in the several illnesses are quite conflicting. This would be expected in view of the varying nature of the hydrosols that are employed.

Silver Mirrors

The deposition of silver on glass in the form of a mirror is a colloid chemical process which has been studied in detail by Kohlschütter.[128] The method consists in the reduction of silver solutions at a suitably slow rate from complex silver compounds in the presence of certain high molecular or colloidal substances which act as protecting agents,

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[123] Z. ges. exptl. Med., **52**, 33 (1926); *cf.* "Das kolloide Silber," Chapter 14 (1926).

[124] Z. Tiermed., **15**, 121 (1907).

[125] *Cf.* Voigt: "Das kolloide Silber," Chapter 13 (1929).

[126] *Cf.* Voigt: "Das kolloide Silber," Chapter 15 (1929).

[127] Koller-Aeby: Kolloid-Z., **53**, 101 (1930).

[128] Kolloid-Z., **12**, 285 (1913); Kohlschütter and Fischmann: Ann., **387**, 86, 88 (1911).

The mirror consists of finely divided silver particles deposited close to each other.

The technical manufacture of silver mirrors is carried out by a variety of processes in most of which ammoniacal silver nitrate is used. After a comprehensive study of the methods of preparation, Silverman and Howe[129] used a mixture of reagents in the following proportion for rapid deposition in the cold: 20 cc of 0.2 *M* silver nitrate are mixed with 0.5 cc of 80% methyl alcohol; to this 0.5 cc of 40% formaldehyde is added, and the whole mixed thoroughly before adding to the vessel to be silvered.

A slow cold process which gives specially good mirrors was also developed, based on the following principles: (1) low concentration of reducing agent, formaldehyde, which serves to lengthen the reaction time; (2) low concentration of silver nitrate, which results in high deposition percentage; (3) addition of sugar, which acts as a protecting agent to give even mirrors; (4) addition of methyl alcohol, which results in a high deposition efficiency. The mixture is in the following proportions: 165 cc of 0.37 *M* silver nitrate; 1 cc of *M* sucrose; 0.5 cc of 80% methyl alcohol; and 2 cc of 0.8% formaldehyde.

In hot processes, cane sugar is the most satisfactory reducing agent.

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[129] Ind. Eng. Chem., 9, 1032 (1917).

CHAPTER V

COLLOIDAL COPPER AND MERCURY

COLLOIDAL COPPER

Copper is obtained in the colloidal state as sol and gel, and in a highly dispersed form for use as a contact catalyst and as a condensing agent in organic chemistry. The preparation and properties of the sols will be considered first.

FORMATION OF COPPER SOLS

As compared with silver sols, copper sols are in general more difficult to prepare and are less stable in the absence of protecting colloids. Accordingly most copper sols are protected.

Reduction without Protecting Colloids.—Gutbier[1] reduced a dilute solution of copper sulfate with hypophosphorous acid at a temperature of 70°–80°. The resulting reddish brown sol was so instable that it could not be dialyzed without coagulation. Meyer[2] added sodium hydrosulfite to a very dilute solution of copper sulfate and after gentle warming obtained a beautiful red copper sol. The preparation was not very stable, coagulating spontaneously on standing for some time at room temperature or on heating.

Barnard[3] allowed 5% copper sulfate to drop into a 50% solution of hydrazine hydrate until a deep golden color was obtained. If a well-cleaned glass article is placed in the reducing agent before adding the copper salt, a thin adhering film of metallic copper is deposited on which a thick film of the metal may be plated electrolytically. This is a satisfactory method of plating copper on glass.

Reduction with Protecting Colloids.—A hydrosol of copper is obtained by adding a weakly alkaline solution of stannous chloride to a solution of copper chloride in alkali citrate or tartrate. The resulting precipitate is peptized by washing, giving a reddish brown sol, the particles of which are a copper-stannic oxide adsorption

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[1] Z. anorg. Chem., **32**, 355 (1902).

[2] Z. anorg. Chem., **34**, 60 (1903).

[3] Science, **66**, 330 (1927).

complex resembling purple of Cassius. As would be expected, the sol possesses the properties of the more hydrophilic colloid rather than those of the metal.

Copper sols result by reduction with hydrazine hydrate of a colloidal solution of copper hydroxide prepared by adding copper sulfate to a solution of sodium protalbinate or lysalbinate.[4] With high concentrations in the cold, a relatively instable blue sol results; but by heating a mixture containing not more than 25% copper and a small amount of ammonia, a highly stable sol, red by transmitted light and black by reflected light, is obtained. Evaporation of the liquid out of contact with air gives a solid red powder which is peptized by shaking with water. Red colloidal copper that can be peptized by water is obtained also by reduction with hydrogen at 200°, of copper oxide formed in the presence of sodium protalbinate or lysalbinate. If the instable blue sol mentioned above is coagulated by dilute sulfuric acid, copper-red flocks are obtained which may be washed in an atmosphere of carbon dioxide and dried in a vacuum. This red powder is peptized by dilute alkali, giving a blue sol once more.[5]

Copper sol also results by reduction of ammoniacal copper sulfate with hydrazine hydrate in the presence of gum arabic[6] or of island moss.[7]

A novel method of preparing a stable copper sol consists in suspending freshly prepared pure white cuprous chloride in a solution of 10% casein in 2% sodium hydroxide. After a time, a ruby-red to black-red sol results which is said to be useful as a ray filter since it transmits only red light of a definite wave length.[8]

Electrical Methods.—Relatively stable olive-green to brown-green hydrosols are readily prepared by passing an arc between copper wires under water, according to Bredig's method.[9] Burton[10] obtained a methyl alcosol by the Bredig method, but it was contaminated with carbon. With the oscillating arc a relatively pure copper etherosol and isobutyl alcosol were made by Svedberg (see page 162). The former was black and the latter greenish black in transmitted light.

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[4] Paal and Leuze: Ber., **39**, 1550 (1900); Gerasimov and Matveev: J. Russ. Phys-Chem. Soc., **62**, 839 (1930).

[5] Paal and Amberger: Ber., **38**, 1398 (1905).

[6] Gutbier and Hofmeier: Z. anorg. Chem., **44**, 227 (1905).

[7] Gutbier and Sauer: Kolloid-Z., **25**, 145 (1919).

[8] German Pats., 383,098 and 325,957.

[9] Ehrenhaft: Anz. Akad. Wiss. Wien, **39**, 241 (1902); Sitzber. Akad. Wiss. Wien, **112**, 182 (1903); *cf.* Billitzer: Ber., **35**, 1933 (1902).

[10] Phil. Mag., (6) **11**, 472 (1906).

COMPOSITION AND PROPERTIES OF COPPER SOLS

Composition

Copper sols formed by Bredig's method have been shown by x-ray analysis to be coated with a layer of copper oxide.[11] Both hydroxide and oxide have been detected chemically in this sol, the ratio $Cu(OH)_2/CuO$ decreasing with the time of passing the arc and with increasing *p*H value of the solution.[12] The conductivity of copper sols is distinctly lower than that of either silver or platinum sols. Evans[13] obtained values of 0.30–0.50 mho/cc, which were less than that of the conductivity water. This was attributed to adsorption of ions by the gelatinous copper hydroxide on the surface of the particles. According to Murray,[14] the conductivity of Bredig's copper sols is probably due largely to the saturated solution of copper hydroxide formed during the arcing process.

The positive charge on the particles of Bredig sols is due to preferential adsorption of copper ions by the oxide or hydroxide layer surrounding the particles. The hydroxyl ions are the contra ions which constitute the diffuse outer portion of the double layer.

No definite information is available concerning the composition and constitution of the relatively impure protected sols formed by reduction processes.

Stability of Sols

Effect of Radiations.—As already noted, chemically prepared copper sols formed in the absence of protecting colloids are quite instable. The Bredig sols are fairly stable at ordinary temperatures, but they are easily coagulated by the addition of electrolytes, by subjecting them to x-rays or the β-rays from radium, and by raising the temperature. Crowther[15] attributes the discharging action of the radiation to negative ions produced in the dispersing solvent by the ionizing agents. The action is therefore confined to positively charged sols. Moreover, since the negative ion produced by the ionizing agent appears to be the only active agent in the process, the effect is independent of the source of the ionizing radiation.

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[11] Freundlich: Ber., **61**, 2219 (1928).

[12] Podrouzek: Chem. Listy, **20**, 403 (1926).

[13] Trans. Faraday Soc., **24**, 409 (1928).

[14] J. Chem. Soc., 1235 (1928).

[15] Phil. Mag., (7) **7**, 86 (1929); Crowther and Fairbrother; **4**, 325 (1927); *cf.* Bhatnagar, *et al.*; Z. Physik, **56**, 684 (1929).

Effect of Heat.—For a colloid like Bredig's copper sol to be stable, the particles must be sufficiently small that the Brownian movement keeps them from settling under the influence of gravity, and the charge on the particles must be sufficiently large that collisions do not result in coalescence of the particles to form larger aggregates. The mutual repulsion of oppositely charged particles does not come in until the particles are quite close together. Since it is now generally recognized that the outer layer of the electrical double layer is quite diffuse and may be several molecular diameters in thickness, the close approach of two particles will result in an overlapping of the outer layers so that the particles will possess an effective charge relative to one another and consequently will repel one another. But if the charge is sufficiently low or the Brownian movement sufficiently intense, the particles may touch and form an agglomerate in spite of the repulsion. One would expect the frequency of the effective collisions to be increased by lowering the charge on the particles by the addition of electrolytes or by increasing the intensity of the Brownian movement. The effect of electrolytes on the particle charge of hydrosols and hence on their stability has received extended study, and the effect of temperature alone on organosols has been considered by Svedberg and Inouye.[16] Recent investigations by Burton and his pupils[17] on a Bredig copper hydrosol show that, if samples of the sol are maintained at different high temperatures for a definite time interval, there exists one temperature below which the samples do not coagulate in a given time and above which they do coagulate. This temperature has been termed the "coagulation temperature" for the sol.

In the actual experiments the samples of sol were placed in a copper tube and sealed in a glass tube which was immersed in an electrically heated bath for a given time interval. Observations were made of the presence or absence of coagulation 24 hours after heating. Some results are given in Fig. 22. It is apparent that coagulation may be brought about by temperature alone. Moreover, the coagulation temperature decreases with increasing time of heating when the particle charge in each case is the same. Since the curve becomes asymptotic with the axis of time, the sol might be expected to remain stable indefinitely at room temperature. Finally, it was found that, by varying the charge on the particles by adding different amounts

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[16] Kolloid-Z., **9**, 153 (1911).

[17] Reid and Burton: J. Phys. Chem., **32**, 425 (1928); Deacon: **34**, 1105 (1930); Burton and Deacon: Colloid Symposium Monograph, **6**, 77 (1928).

of potassium chloride, the coagulation temperature decreases with decreasing charge for the same time of heating.

In every case, heating the sol speeds up the process of coagulation so that eventually all the heated samples coagulate. The reason is that multiple particles are formed during the heating process, the more the higher the temperature, and that these agglomerates act as coagulation nuclei for smaller particles.[18]

The reason for the horizontal position of the curve in Fig. 22 is not at once apparent. It is suggested that at a temperature of 155° the cupric oxide or hydroxide on the particles is reduced to the cuprous state, thus disturbing the charge on the particles. If this be true, it is not obvious why the portions *A* and *B* apparently belong to the same smooth curve.

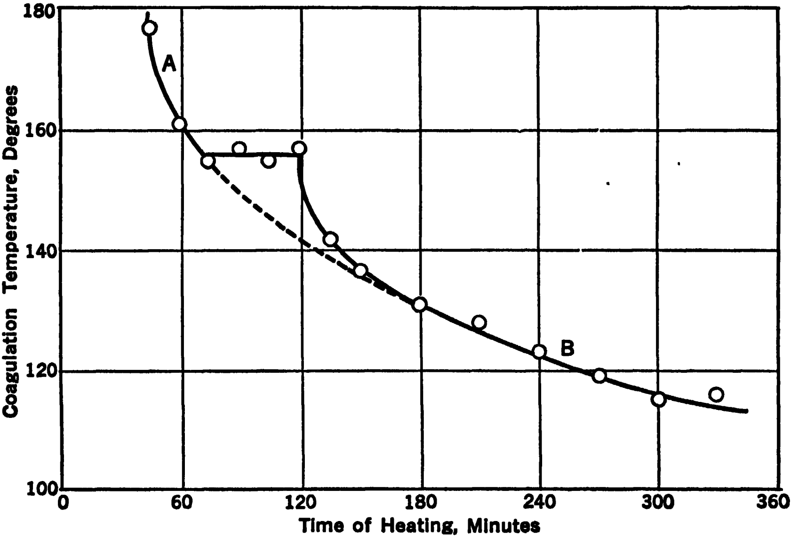

FIG. 22.—Effect of heat on the coagulation time of colloidal copper.

Effect of Electrolytes and Non-electrolytes on Organosols.—An alcosol of copper prepared by Bredig's method is sensitized and ultimately coagulated[19] by solutions of salts in various organic media miscible with alcohol, such as acetone, ether, and glycerin. The order of precipitating power of the salts is: lithium chloride < ammonium bromide < strontium chloride < mercuric chloride < aluminum chloride, which is the same as for a negative hydrosol. This

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[18] Wiegner: Kolloid-Z., **8**, 227 (1911); Galecki: Z. anorg. Chem., **74**, 174 (1912); Müller: Kolloid-Beihefte, **26**, 257 (1928).

[19] Yajnik, Goyle, and Bhan: J. chim. phys., **27**, 386 (1930).

indicates that copper dispersed in ethyl alcohol is negatively charged. For a zinc sol in acetone, the cation is likewise the precipitating ion, the order of precipitating power of salts being: lithium chloride < sodium iodide < calcium nitrate < mercuric chloride < antimony trichloride. The coagulating action is due both to the lowering of the charge on the particle by the electrolyte and to the change in the solvation of the particle in the presence of the added non-electrolyte.[20]

Color

Like silver, colloidal copper exists in a wide variety of colors. Thus Paal and Steyer[21] obtained sols of the following colors: reddish brown, blue, ruby red, brown, olive, and green. Copper is used in place of gold in the preparation of a cheaper grade of ruby glass. In true copper ruby glass the particles are of ultramicroscopic dimensions; in opaque copper-red hematinon, they are microscopically visible; and in aventurine glass, they exist as spangles visible to the naked eye. From analogy with gold ruby glass one would expect the color of copper ruby glass to be due to colloidal copper. Williams[22] subscribes to this view, but Seger[23] attributes the color to colloidal cuprous oxide or copper silicate. Stokes[24] argues against the red color being due to colloidal copper on the ground that the most finely divided copper is blue; but his argument is not valid since it is the coarser particles which are blue. It is difficult to distinguish between colloidal copper and cuprous oxide in glass; but if the color is due to a copper silicate in solution, the glass should not scatter light as would a colloidal coloring agent.

Pharmacological Action

As already noted (see page 133), both colloidal silver and mercury are better bactericides than colloidal copper. The germicidal action of Bredig copper sol has been shown to be due exclusively to copper ions from cupric oxide and cupric carbonate formed in the presence of atmospheric gases.[25] Colloidal copper has been suggested

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[20] *Cf.* Weiser and Mack: J. Phys. Chem. **34**, 101 (1930).

[21] Kolloid-Z., **30**, 88 (1922).

[22] Trans. Am. Ceram. Soc., **16**, 284 (1914).

[23] "Collected Writings," **2**, 731 (1902); Zulkowski: J. Soc. Chem. Ind., **16**, 441 (1897).

[24] "Mathematical and Physical Papers," **4**, 245 (1904).

[25] Kusunoki: J. Biochem. (Japan) **3**, 1 (1923).

for use in the treatment of cancer, but it has little apparent destructive action on tumor tissue.[26]

SOLID FORMS OF COLLOIDAL COPPER

Copper Gel.—By electrolyzing in the cold a neutral or feebly basic 10% solution of copper acetate, Schutzenberger[27] obtained an extremely brittle, bronze-colored deposit which was very readily oxidized, had a higher electrical resistance than copper, and a specific gravity of 8 to 8.2, which is appreciably lower than that of the metal in mass. The deposit became like ordinary copper if heated rapidly to 100° or allowed to stand for some time in contact with dilute sulfuric acid. Schutzenberger believed this preparation to be an allotropic form of copper, and Benedicks[28] regarded it as a solid solution of acetic acid in ordinary copper. Briggs[29] showed, however, that the deposit was in reality a gel of the normal metal consisting of finely divided particles which were prevented from agglomerating into a dense mass by adsorption of a protecting film of gelatinous hydroxide or basic acetate from the partly hydrolyzed solution.

Briggs electrolyzed solutions of copper propionate, acetate, or formate in the presence of gelatin and obtained a finely divided deposit of gelatin-copper which underwent a striking "development" on immersion in a copper salt of a weak acid such as the acetate or propionate. The color changed from the original pale brown, through reddish purple, purple, and finally blue. The blue coloration was attributed to adsorption from the solution by the colloidal copper, of hydrous copper oxide or hydroxide, giving a colloidal copper-copper oxide adsorption complex similar to the gold-stannic oxide mixture, purple of Cassius.

Organic Condensing Agent.—Colloidal copper for use as a condensing agent is prepared by shaking zinc dust through a fine sieve into a thoroughly agitated, cold, saturated copper sulfate solution. The precipitate of finely divided copper is treated with dilute hydrochloric acid to remove any zinc, and finally is washed thoroughly with water.[30]

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[26] Weil: J. Am. Med. Assoc., **61**, 1034 (1913).

[27] Compt. rend., **86**, 1265, 1398 (1878).

[28] Metallurgie, **4**, 33 (1907).

[29] J. Phys. Chem., **17**, 281 (1913).

[30] Cohn: "Arbeitsmethoden organisch-chemische Laboratorium," 360 (1903).

COLLOIDAL MERCURY

The importance of mercury and its salts as therapeutic agents was not recognized until comparatively recent times, although Parcelsus, in the sixteenth century, introduced widely the use of colloidal mercury as a medicine in the form of blue ointment, a preparation formed by triturating mercury with fats. Mercury in bulk has comparatively little therapeutic action. Its efficacy in the colloidal state is probably due to the presence of more or less oxide which yields mercury ions, the real bactericide. In recent times, investigations on the colloidal metal has been concerned largely with the formation of hydrosols which may be used as antiseptics and disinfectants.

FORMATION OF MERCURY SOLS

Reduction Methods

Sols formed by reduction methods, even under the most favorable conditions, are relatively instable in the absence of suitable protecting colloids. Thus Weinmayr[31] reduced a solution of mercuric chloride by hydrogen peroxide in the presence of a gold nuclear solution. Although this might be expected to yield a stable sol with small, relatively uniform particles, the preparation soon became cloudy and precipitated.

Lottermoser's Sol.—A satisfactory stable sol was first prepared by Lottermoser[32] by reduction of mercurous salts with stannous salts. By using 5–10% solutions of stannous nitrate and mercurous nitrate, containing enough nitric acid to prevent precipitation, a clear, red-brown sol results which soon precipitates in the strong acid solution. By neutralizing the acid with sodium hydroxide, a fine black mass is thrown down from which the excess electrolyte is removed by filtration. The precipitate is readily peptized by water and retains this property even after washing with alcohol[33] and drying in vacuum.

From the point of view of ease of preparation and stability, Lottermoser's preparation has not been improved upon.[34] It is in reality a mercury "purple" in which the protecting agent is the relatively inert and highly stable hydrous stannic oxide.

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[31] German Pat., 217,724 (1910).

[32] J. prakt. Chem., (2) 57, 484 (1898); 72, 39 (1915); U. S. Pat., 685,477 (1901).

[33] *Cf.* Schneider: Ber., 25, 1281 (1892).

[34] *Cf.* Feick: Kolloid-Z., 37, 260 (1925).

Paal's Sol and Similar Preparations.—Paal[35] reduced mercuric oxide with hydrazine hydrate in the presence of his protecting sodium protalbinate and lysalbinate, in much the same way as he prepared the corresponding silver and copper sols. Other protecting colloids which give more or less satisfactory preparations using suitable reducing agents are plant extracts,[36] gelatin,[37] dextrin, gums and gluten,[38] soap,[39] casein,[40] and glycogen.[41]

Rhythmic bands of mercury in the form of drops about 0.0001 cm in diameter result on allowing dilute mercurous nitrate to diffuse into 3% agar containing 0.5% sodium formate.[42]

Mechanical Methods

If a very fine stream of mercury is ejected forcibly against a glass wall under water containing 2.5×10^{-3} *N* potassium citrate, only a very dilute, coarsely dispersed sol is obtained.[43] On the other hand, if the dilute citrate solution is forced to rise through mercury, thin mercury lamellae are produced when the surface of the metal is reached, and the bursting of these lamellae gives a sol containing droplets smaller than in any other mercury sol yet prepared. Similar results are obtained by shaking mercury with the dilute citrate solution, the optimum concentration for making the strongest sols being between 2 and 7×10^{-3} *N*. After the larger particles settle out, the resulting reddish brown sol is highly stable. Nordlund reports that a sol formed by shaking shows no trace of coagulation after standing a month. Other dilute solutions such as sodium tartrate and ammonium sulfate may be substituted for citrate, but the resulting sols are much less stable.

More or less stable sols can be formed by shaking mercury with other liquids such as ether and turpentine; and solid or semi-solid sols result by triturating with sulfur, antimony sulfide, sugar, grease, etc.

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[35] Ber., **35**, 2219 (1902); *cf.* Hoffmann: German Pat., 185,600 (1907); Amberger: Kolloid-Z., **8**, 88 (1911); **18**, 97 (1916); German Pats., 178,520 (1905); 186,061; 186,138 (1907).

[36] Gutbier and coworkers: Kolloid-Z., **19**, 33, 291 (1916); **20**, 83, 123 (1917); **25**, 97 (1919).

[37] Lobry de Bruyn: Rec. trav. chim., **19**, 240 (1900); Westgren: Z. physik. Chem., **83**, 151 (1913); Feick: Kolloid-Z., **37**, 257 (1925).

[38] German Pat., 286,414 (1915).

[39] Roth: German Pat., 228,139.

[40] Busch: German Pat., 189,480 (1907).

[41] Hugounenq and Loiseleur: Compt. rend., **182**, 851 (1926).

[42] Davis: J. Am. Chem. Soc., **39**, 1312 (1917).

[43] Nordlund: Kolloid-Z., **26**, 121 (1920).

A sol which required 1.5 months to settle completely was prepared by grinding mercury for a long time with glucose and dissolving out the glucose with water.[44]

Pharmaceutical Preparations.—In Table XXIII are listed some of the more important therapeutic preparations of colloidal mercury referred to in the United States, and British pharmacopoeias. In every case the mercury is reduced to the colloidal state by trituration.

TABLE XXIII

PHARMACEUTICAL PREPARATIONS OF COLLOIDAL MERCURY

Name	Dispersion medium	Colloidal Hg in %	Use
Mercury ointment (blue ointment)..........	Suet, lard, and vaselin	30	Against cutaneous parasites
Mercury ointment (Scott's dressing)....	Lard and camphor	12	In synovitis
Mercury ointment. ...	Lard and suet	50	For inunction
Mercury mass (blue mass)	Licorice root and confection of roses	33	Similar to calomel
Mercury plaster.......	Lead plaster base	33	Against glandular enlargements
Mercury with chalk....	Chalk and honey	38	In infantile paralysis

Thermal Methods

If mercury is boiled vigorously and the vapors conducted into water containing ice, a brownish red sol is obtained[45] which coagulates within 24 hours. The simultaneous condensation of water and mercury vapor to give sols according to the method of Roginsky and Schalnikoff[46] has been described in Chapter I.

Electrical Methods

The Bredig method for the preparation of a stable mercury sol was first used successfully by Billitzer,[47] who employed a rigid cathode of zinc, cadmium, or iron on which a layer of mercury was electroplated.

[44] Von Weimarn and Utzino: Alexander's "Colloid Chemistry," **1**, 659 (1926).

[45] Nordlund: Kolloid-Z., **26**, 121 (1920); Gutbier: Z. anorg. Chem., **158**, 99 (1926).

[46] Kolloid-Z., **43**, 67 (1927); Tomaschewsky: **54**, 79 (1931).

[47] Ber., **35**, 1929 (1902).

The resulting sol was relatively pure, but the metal content was low. A sol may be formed by passing an arc between two fine streams of mercury under water.[48] To obtain a high degree of dispersion, it is apparently important to employ a low current density.

Nordlund[49] prepared concentrated sols using either the direct- or oscillating-current arc under conductivity water between one flowing and one stationary mercury electrode. The former was a stream of mercury 0.4–0.8 mm in diameter, and the latter was a pool of the element in the bottom of a flask. The distance between the electrodes was regulated so that a current of 2.8 amperes at 220 volts was obtained. The temperature was kept down by passing ice water through a coil immersed in the water. With the direct current, stable 4% mercury sols, and with the oscillating current, 0.5% mercury sols, were obtained at the rate of 8 minutes for each 100 cc of water.

A salve similar to blue ointment may be prepared by passing an arc between mercury electrodes immersed in molten vaselin, lanolin, etc.[50] An isobutyl alcosol prepared by means of an oscillating discharge at $-80°$ was quite instable, coagulating in an hour or two.

McCoy and Moore[51] electrolyzed a solution of tetramethyl ammonium chloride in absolute alcohol at a mercury cathode. The resulting amalgam decomposed violently when treated with water, giving highly dispersed, black colloidal mercury in the form of a hydrous precipitate.

PROPERTIES OF MERCURY SOLS

Composition and Stability.—Like copper, but unlike silver and gold, the particles in an unprotected mercury sol are usually positively charged. This is probably due to the presence on the particles of a film of oxide which adsorbs mercury and hydrogen ions sufficiently strongly that the inner portion of the double layer is positive. In the presence of the strongly adsorbed citrate ion, the particles are negatively charged. The charge on the protected colloids depends on the nature of the protecting agent. Thus the Lottermoser sol is negative since the protector is hydrous stannic oxide.

The oxide content of colloidal mercury preparations varies widely.

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[48] Svedberg: "Colloid Chemistry," 1st ed., 40 (1924); Egger: German Pat., 218,873 (1910).

[49] Kolloid-Z., **26**, 121 (1920); *cf.*, *also*, Zavrieff: Z. physik. Chem., **87**, 507 (1914).

[50] Schereschewsky: German Pat., 153,995 (1904).

[51] J. Am. Chem. Soc., **33**, 279 (1911).

In Bredig sols prepared by Laird,[52] an average of 37% of the mercury was found to be in the form of oxide. As already noted, the varying therapeutic action of colloidal mercury in its various forms is probably due largely to mercury ion derived from oxide in the sol.

Color.—Highly dispersed mercury sols are in general reddish brown, whereas those containing larger drops are gray. With decreasing particle size from 300 mμ to 80 mμ in diameter, Feick[53] observed the following color by transmitted light: gray, grayish blue, grayish violet, reddish brown, orange, and yellow; and by reflected light: very dark brown, sandstone red, Venetian red, loam-brown, field-gray, green, bluish green, greenish blue and petroleum-like blue, and indigo. The observed colors are in good agreement with what would be expected from Mie's theory (see page 78). This furnishes a good test of the applicability of the theory, since the liquid particles of mercury sols are probably more nearly spherical than are the solid particles in most sols.

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[52] J. Phys. Chem., **31**, 1034 (1927).

[53] Feick: Kolloid-Z., **37**, 257 (1925); Ann. Physik, (4) **77**, 673 (1925).

CHAPTER VI

COLLOIDAL NON-NOBLE METALS OF THE FIRST AND SECOND GROUPS

COLLOIDAL ALKALI METALS

The alkali metals have been obtained in the colloidal state in the form of organosols and of solid sols with the alkali halides as the dispersion medium.

ALKALI METAL ORGANOSOLS

Formation

Electrical Disintegration.—Sols of all the alkali metals in ethyl ether were first prepared by Svedberg[1] using an oscillating arc at a temperature of −100°. Sols of sodium and potassium were also obtained in liquid methane and in ligroin.

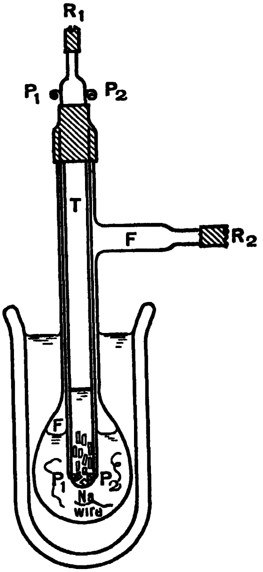

FIG. 23.—Svedberg's arrangements for the electrical pulverization of the alkali metals.

A diagram of the apparatus employed is shown in Fig. 23. Some fragments of the metal to be dispersed are introduced into the tube *T*, which is provided with two holes at the bottom and two platinum wire electrodes P_1 and P_2. The flask *F* contains the dispersion medium, *e.g.*, highly purified ether, in which is suspended some sodium wire to remove the last trace of moisture. Since the process is facilitated by low temperature, *F* is surrounded by a mixture of liquid air and absolute alcohol to give a temperature of approximately −100°. Hydrogen is conducted through *T* and *F* by the aid of the rubber tubes R_1 and R_2. The sparking and pulverization usually take place automatically when the current is closed, but to start the process it is sometimes necessary to tap the tube *T* gently.

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[1] Ber., 38, 3616 (1905); 39, 1705 (1906).

Condensation of Vapors.—Tomaschewsky[2] prepared a number of relatively stable alkali metal sols by the simultaneous condensation of the vapors of metal and dispersion medium on the tube cooled with liquid air. The apparatus, which is a simplified form of that shown in Fig. 1, consists of an outer vessel, with but two arms, into which is put a glass tube cooled with liquid air. In one of the arms is placed the liquid and in the other, the solid. The constituents are vaporized at a suitable rate by heating, the vapors condensing to a colloidal "ice" on the cold tube. On the removal of the liquid air the "ice" melts, giving an organosol. By this procedure, sols of sodium were prepared in ether, xylol, benzol, and hexane; of potassium, in ether and xylol; and of rubidium and cesium, in ether.

Properties

The color and stability of several organosols of the alkali metals have been summarized in Table XXIV. The nine preparations listed

TABLE XXIV

PROPERTIES OF ALKALI METAL ORGANOSOLS

Metal	Dispersion medium	Color	Stability at room temperature
Li	Ether	Brown	...
Na	Ether	Purple-violet to blue	6–7 hours
K	Ether	Blue to blue-green	Less than Na sol
Rb	Ether	Greenish blue to greenish	Less than K sol
Cs	Ether	Blue-green to greenish gray	Stable only at low temperatures
Na	Pentane	Reddish purple	....
K	Pentane	Blue to blue-green	.....
Na	Methane	Reddish	Exists only at low temperatures
Na	Methane	Bluish	Exists only at low temperatures
Na	Ether	Ruby red to violet-red	1 month
Na	Xylol	Ruby red to brown	12–20 hours
Na	Benzol	Dirty violet	3 days
Na	Hexane	Ruby red to violet-red	1 month
K	Ether	Ruby red	2 months
K	Xylol	Yellow-green to dirty blue	10 days
Rb	Ether	Clear blue	20 minutes
Cs	Ether	Dark blue	20 minutes

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[2] Kolloid-Z., **54**, 79 (1931).

in the upper part of the table were made by Svedberg; the last eight were prepared by Tomaschewsky. It will be noted that the sols formed by Tomaschewsky's method are much more stable than the Svedberg sols, and that the colors of the former are clearer and better defined. Svedberg pointed out that the colors of the vapors of the metals (purple for sodium, blue-green for potassium, and greenish blue for rubidium) correspond closely to the colors of his corresponding etherosols. This similarity does not hold in the case of Tomaschewsky's sols. Moreover, there is no obvious relationship between the color of the organosols and the color of the metallic fog formed by condensing the metallic vapors. Thus sodium fog scatters blue light and transmits, by resonance, the yellow which the particles absorb,[3] whereas the color of Svedberg's sodium organosol is purple by transmitted light and of Tomaschewsky's is ruby red by both transmitted and reflected light. The color of sol is not influenced greatly by the nature of the dispersion medium. Thus Tomaschewsky's freshly formed sodium sols in ether, xylol, and hexane are ruby red, and the benzosol is purple. As in other metallic sols, the color of a given preparation in influenced greatly by the size and shape of the dispersed particles.

ALKALI METALS IN SOLIDS

Solid sols of the alkali metals have been prepared as colored "ice" and as colored salts. The color of natural blue rock salt has been attributed to colloidal metallic sodium dispersed in the salt, but this is not necessarily the case.

Colored "Ice."—In Tomaschewsky's method for preparing organosols as above described, a colored "ice" is obtained as an intermediate stage in the process. The color of the dispersions of sodium in solid ether, xylol, benzol, and hexane is brown-violet; of potassium in solid ether, blue, and in solid xylol, greenish blue; of rubidium in ether, dark blue; and of cesium in ether, brownish green. The color of the "ice" varies somewhat from the color of the corresponding sol formed on melting, probably because the latter process results in some agglomeration of the dispersed particles.

Colored Salts.—The deep blue color of certain salt deposits attracted the attention of Sir Humphry Davy in 1818. The view that the blue salt is a colloidal dispersion of sodium in the crystals is supported by the fact that artificial preparations may be made, which

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[3] Wood: "Physical Optics," 639 (1911); *cf.* Bancroft: J. Phys. Chem., **23**, 569 (1919).

are quite similar in appearance to the natural salt, by methods which depend on dispersing the alkali metal in colorless salt crystals. This is readily accomplished with both sodium and potassium salts by heating the thoroughly dried crystals with the vapors of the metal at temperatures 50°–80° below the boiling point of the metal[4] or by exposing the colorless crystals to radiations[5] such as cathode rays, x-rays, ultraviolet light, or radium emanation, under the influence of which the salt is dissociated into free metal and halogen. The metallic vapors condense to ultramicroscopic crystals, imparting a blue color to the salt.

The color of the product formed by heating an alkali salt in contact with the vapor of the metal depends on the temperature. Crystals of sodium chloride containing sodium appear yellow or brown at first, but on heating they go through rose to blue-violet, and at still higher temperature, to the deep blue corresponding to the color of natural blue rock salt; at sufficiently high temperature the blue goes over to yellow, and finally the color disappears.

The cause of the coloration in the synthetic colored halides has been attributed to polymorphism, sub-halide formation, solid solution of metal in salt, and to a colloidal dispersion of metal in the halide.[6] The latter explanation is now generally accepted in the light of the ultramicroscopic observations of Siedentopf, who showed that, in the samples with which he worked, the gaseous metal had diffused into the irregular ultramicroscopic clefts of the crystal[7] and deposited there in ultramicroscopic needle- or plate-like, and in part pleochroic, sodium crystals. On dissolving in water, the color disappeared and the solution possessed a slight alkaline reaction.

Although this evidence seems quite conclusive, Przibram[8] has shown that rock salt can be colored by radiation, heat, and plastic deformation under such conditions that colloid formation is improbable. He is therefore led to conclude that the color may be due to what he terms color "centers" as well as to colloidal aggregates. A color center is regarded as a neutral atom with its immediate disturbed surroundings which influence its mobility and its absorption

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[4] Siedentopf: Physik. Z., **6**, 855 (1905); *cf.* Geisel: Ber., **30**, 156 (1897); Phipps and Brode: J. Phys. Chem., **30**, 507 (1926).

[5] Goldstein: Wied. Ann., **54**, 371 (1895); Wiedemann and Schmidt: **54**, 622 (1895); **64**, 78 (1898).

[6] Zsigmondy: "Zur Erkenntnis der Kolloide," 58 (1905).

[7] *Cf.* Rexer: Physik. Z., **32**, 215 (1931).

[8] For a summarizing article, *see* Sitzber. Akad. Wiss. Wien, 2A **138**, 483 (1929); Z. Physik, **68**, 403 (1931).

spectrum. Such a center may be produced by neutralization of a sodium atom by radiation, or by the introduction of sodium atoms as vapor, or by electrolysis. He recognizes three types of such centers distinguished by their specific color and by their stability toward heat and light. Colloidal metal as the source of color is distinguished from color centers by the pleochroism produced on compression.

By electrolysis of fused salts such as sodium chloride, Lorenz and Eitel[9] obtained colored liquids which were believed to be dispersions of metal in the molten salt and hence were termed pyrosols. Recent ultramicroscopic observations on a lead pyrosol at temperatures above 500° indicate that the lead is in molecular solution and not colloidally dispersed in the melt;[10] it is quite likely that the alkali metal pyrosols are also molecular solutions. The colored crystals formed on cooling down the pyrosols are probably colloidal dispersions, although, according to Przibram, the color may be due to neutral atoms forming color centers.

Natural Blue Rock Salt.—Because of the similarity in appearance, both superficial and ultramicroscopic, between the natural and artificial samples of blue rock salt[11] with which he worked, Siedentopf concluded that dispersed metallic sodium in the salt crystal is responsible for the color in both. Although this may be true in certain cases, evidence has accumulated which indicates that there are, as a rule, distinct differences between the natural blue salt specimens and the synthetic ones, especially those formed by heating the salt in contact with metal vapor. Thus it is pretty generally agreed that artificial preparations formed in contact with sodium vapor give an alkaline solution indicating the presence of an excess of the metal, whereas solutions of the natural blue salt are in general not alkaline,[12] although they may be in certain cases.[13] Siedentopf explains this by assuming that there is not enough excess sodium in the natural blue salt to given an alkaline solution. Even though this is true, it is not obvious, on the basis of the colloidal theory of the color, why so very much less sodium is effective in the natural product.

Another point of difference is that the artificial blue salt will undergo reversible changes in color on heating to around 400° whereas

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[9] "Pyrosole" (1926).

[10] Eitel and Lange: Z. anorg. Chem., **171**, 168 (1928); Heymann: **175**, 241 (1928); Kolloid-Z., **52**, 269 (1930).

[11] Other colors occur: Kreutz: Anz. Akad. Wiss. Krakau, 127 (1892); 112 (1896).

[12] Abegg: Z. Elektrochem., **4**, 118 (1897); Spezia: Centr. Mineral. Geol., 398 A (1909); Phipps and Brode: J. Phys. Chem., **30**, 507 (1926).

[13] Cornu: Neues Jahrb. Mineral. Geol., **1**, 22 (1908).

the natural salt remains colorless after heating to a much lower temperature.[14] A natural salt loses its color at 200°–300°; a salt colored with sodium vapors requires a temperature of 500° or more.[15] To account for the low temperature of discoloration of the natural salt, Siedentopf postulates the presence of suitable impurities to react with the dispersed sodium. As a matter of fact, the blue salt formed by radiations such as cathode rays is decolorized at a lower temperature than that prepared in contact with the vapor. This is attributed to a union of the metallic sodium with the chlorine gas present in approximately equivalent amounts in the irradiated crystals.[16]

Spectrophotometric data at room temperature, and over wide ranges of temperature, disclose that quantitatively there is a distinct difference between the color of natural blue halite from the Stassfurt deposits and synthetic blue preparations obtained by heating salt crystals with sodium vapor. To account for the difference, Phipps and Brode[17] assume that the Stassfurt blue is due chiefly to an abnormality in the constraint of the valence electron at various points in the halite lattice, the color resulting from the vibration of the electrons in their abnormal positions.[18] From this point of view a color center is a displaced electron rather than a sodium atom as suggested by Przibram.

A final point of difference between artificial and natural blue salt which may be mentioned, is the presence of strong pleochroism in the former and its absence in the latter. Siedentopf[19] showed, however, that the sample of natural halite with which he worked was dichroic under pressure. This is fairly conclusive evidence that he was dealing with a sample whose color was due at least in part to spherical metallic particles which were compressed into discs by pressure. From optical photoelectric observations Liermann and Rexer[20] concluded that sodium atoms are involved in the building up of coloring colloidal particles or centers in the natural blue salts.

From this survey, it would appear that the color of blue rock salt

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[14] Wöhler and Kasarnowski: Z. anorg. Chem., **47**, 353 (1905).

[15] Spezia: Centr. Mineral. Geol., 398 A (1909); Phipps and Brode: J. Phys. Chem., **30**, 507 (1926).

[16] Przibram and Bělăr: Sitzber. Akad. Wiss. Wein, 2A, **132**, 261 (1923); Przibram: **138**, 781 (1929); *cf., also,* Savostyanova: Z. Physik, **64**, 262 (1930).

[17] J. Phys. Chem., **30**, 507 (1926).

[18] *Cf.* Lind and Bardwell: J. Franklin Inst., **196**, 375 (1923).

[19] Ber. deut. physik. Ges., **9**, 621 (1907); **12**, 6 (1910).

[20] Naturwissenschaften, **20**, 561 (1932).

may be due to colloidal sodium but that it is more often the result of distortion in the normal lattice as a result of the formation of sodium atoms or of displaced electrons. Radium emanation combined with pressure probably accounts for the blue of many natural salt deposits.[21] In support of this, most of the natural blue rock salt has been found in Australia, a country rich in radium ore.

COLLOIDAL ALKALINE EARTH METALS

Colloidal dispersions of calcium, strontium, and barium in propyl alcohol and isobutyl alcohol were prepared by Svedberg, using an oscillating arc. Since the metals are rather hard to disperse it was necessary to use a high capacity in the discharge circuit in order to obtain sols of high purity. The sols were very stable and homogeneous, and they contained very small particles. The color of both the calcium and strontium isobutyl alcosol was black-brown in transmitted light and black in reflected light; the barium sol was red-brown in transmitted light and gray in reflected light.

COLLOIDAL MAGNESIUM, ZINC, AND CADMIUM

Colloidal Magnesium

Degen prepared a magnesium sol in ethyl alcohol by dispersion with the direct-current arc; but the preparation contained more carbon than magnesium. Svedberg allowed an oscillating current to arc between particles of the metal and obtained in this way sols in ether[22] and isobutyl alcohol. The ether sol was olive green in color, coagulating in a short time to give a greenish black, highly active mass. The isobutyl alcosol, which was brown in transmitted light and gray in reflected light, was stable indefinitely. Zavrieff[23] prepared a hydrosol stable for two days by dispersion with an oscillating current; but it is probable that the particles were largely oxide from the start.

Colloidal Zinc

Transient hydrosols of zinc were obtained by Bredig's method at ordinary temperatures,[24] but at 95°, a stable sol resulted in which only 12 to 25% of the dispersed solid was zinc, the remainder being zinc oxide.[25] Indeed, the reactivity of the zinc with water was so

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[21] Przibram: Z. Physik, **68**, 403 (1931).

[22] Svedberg: Ber., **38**, 3616 (1905); **39**, 1705 (1906).

[23] Z. physik. Chem., **87**, 507 (1914).

[24] Billitzer: Ber., **35**, 1929 (1902).

[25] Englehardt: Kolloid-Z., **41**, 234 (1927).

great that 50% of the dispersed zinc was converted into oxide in the course of 30 seconds. There seems no good reason for calling such preparations hydrosols of zinc.

With an oscillating arc between bits of the metal, Svedberg prepared ether and methyl alcohol sols which were quite stable, brown in color, and gave a black coagulum. A very stable isobutyl alcosol obtained in a similar way was brown-red in transmitted light and gray-black in reflected light.

Colloidal Cadmium

Cadmium Sols.—Since cadmium oxidizes somewhat less readily than zinc, a fairly stable, deep brown hydrosol may be prepared by the Bredig method out of contact with the air. But, as is true of all the less noble metals, the most satisfactory sols are prepared by electrical disintegration with an oscillating arc under organic media such as ethyl and isobutyl alcohol and ethyl ether.

As pointed out in Chapter I, there are always more or less coarse particles in addition to the colloidal particles formed during the electrical disintegration process. This varies with the nature of the arc employed. Kraemer and Svedberg[26] have investigated the effect of using various types of oscillatory arc on the extent of sol formation and of decomposition of the dispersion medium, in the preparation of an ethyl ether sol of cadmium. The results are summarized in Table XXV. In the first column, m is the loss in weight of the electrodes in milligrams per minute; v_0 is the number of cubic centimeters of gas produced per minute (at 0° and 760 mm), which serves

TABLE XXV

EFFICIENCY OF OSCILLATING ARCS IN THE PREPARATION OF CADMIUM ETHEROSOL

	Kind of Oscillating Arc		
	Damped arc with low-frequency transformer	Undamped arc	Damped arc with high-frequency transformer
Percentage sediment..	38.5	30.0	54.0
v_0/m..............	1.60	1.43	0.46
v_0/m_c..............	2.60	2.04	1.00

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[26] J. Am. Chem. Soc., 46, 1980 (1924).

as a measure of the decomposition of the dispersion medium; v_0/m is the decomposition per milligram of metal; and v_0/m_c is the decomposition per milligram of sol formed. It is apparent that the use of the high-frequency oscillating arc gives a much lower decomposition of the medium than the other arrangements. Moreover, it was found that the amount of pulverization is independent of the nature of the dispersion medium in the case of ethyl alcohol, ether, and water. The percentage sediment is somewhat greater in all cases with the high-frequency transformer, but this is relatively unimportant in the synthesis of sols since the large particles are readily removed by filtering or by sedimentation with the aid of a centrifuge.

Cadmium Jelly.—Börjeson[27] allowed 0.5% cadmium ethyl alcosols, prepared by the oscillatory arc, to stand undisturbed for a few days in contact with the air at constant temperature. In some cases the sol coagulated to give a jelly, the process being favored by the production of a small amount of oxide or carbonate on the surface of the cadmium particles. This remarkable metal jelly was very instable, separating out a flocculent precipitate when jarred or touched with a glass rod. An ultramicroscopic picture of such a jelly would undoubtedly show that the particles in coagulating formed a loose network which entrained all the liquid.[28]

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[27] Svedberg's "Colloid Chemistry," 2nd ed., 279 (1928).

[28] *Cf.* Weiser: Bogue's "Colloidal Behavior," 1, 389 (1924).

CHAPTER VII

COLLOIDAL METALS OF THE THIRD TO SEVENTH GROUPS

Because of the difficulty of preparing pure sols of the metals found in the third to the seventh groups of the periodic table and their limited applicability as sols or as highly dispersed solids, a chapter dealing with their colloidal behavior is necessarily brief, at this time. It is certain, however, that this will not be true at some future date. The case of colloidal lead furnishes a striking example of how a proposed use for a metal in the colloidal state will stimulate investigation of the methods of formation and properties of the dispersed substances. Accordingly colloidal lead will be considered first, after which the other metals of the several groups will be taken up collectively. Boron, silicon, and arsenic, which are usually classed with the non-metals, are included in this chapter.

COLLOIDAL LEAD

Prior to 1926, colloidal lead constituted just one more example of metallic sol. But in that year Blair Bell[1] announced that he had observed quite marked improvement in certain cases of cancer treated by intravenous injection of colloidal lead. Although experience has shown that this treatment alone or in conjunction with x-ray or radium therapy is of questionable value, investigations along this line resulted in developing methods for synthesizing sols that are suitable for injecting into the veins of the patient.

Formation and Properties of Lead Hydrosols

Electrical Dispersion Methods.—Relatively pure stable lead hydrosols have been obtained only by arcing between lead electrodes or granules under water. Bredig and Haber[2] employed the direct-current arc preferably in dilute potassium hydroxide solution containing a small amount of potassium chromate. Bell in his cancer work employed a Bredig sol prepared by the following procedure.[3] A

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[1] Lancet, 1, 537 (1926).

[2] Ber., 31, 2741 (1898).

[3] Lewis: J. Cancer Research, 11, 38 (1927).

solution containing 0.5% gelatin and 0.027% calcium chloride was poured onto a layer of granulated lead connected with the source of current by lead electrodes.[4] By arcing between the granules for 15 minutes, a black sol resulted which was centrifuged for 3 minutes at 1700 r.p.m. to remove the larger particles. After sterilization, salts were added to make the mixture slightly hypertonic. The final preparation contained 0.5% lead as metal and carbonate, 0.5% gelatin, 0.054% calcium chloride, 0.54% potassium chloride, and 1.10% sodium chloride. The preparation was regarded as safe to inject intravenously for 3 days but was not stable more than 4 days.

Telkes[5] showed that the presence of carbon dioxide cuts down enormously the stability of lead hydrosols by converting the lead to lead carbonate or basic carbonate which settles out. He dispersed the metal with an undamped oscillating arc (see page 13), using a current of 1 ampere at 500 volts with a condenser of 0.034 microfarad in parallel. Pure water saturated with hydrogen was employed, and the resulting black sol was sealed in an atmosphere of hydrogen or nitrogen. If the concentration was not over 0.2% lead, the sol remained stable for months. On opening to the air the black particles turned gray and precipitated out chiefly as lead carbonate. Bishoff and Blatherwick[6] likewise worked in an indifferent atmosphere using a high-frequency 10,000-volt arc in an ice-cooled solution containing 0.4% gelatin and 0.5% glucose adjusted with potassium hydroxide to a *p*H of 7.2 to 7.6. The centrifuged sol containing up to 0.78% lead remained stable for months when kept sealed up, and the toxity did not increase with age. Gelatin and glucose stabilized the sol, but a preparation formed with a 220-volt, 60-cycle, alternating-current arc, in dilute gelatin solution, precipitated in a week in the presence of air.[7] Sodium oleate is said to be a better protecting agent than gelatin.[8]

It was pointed out by Pennycuick and Scott that very pure samples of sol formed in an indifferent atmosphere are less effective in producing the results described by Bell than those prepared by the ordinary exposed method.[9] It is probable that lead hydroxide or carbonate is the effective agent because of the lead ions which they furnish. Unfortunately, it appears impracticable to administer enough lead

[4] *Cf.* Cofman: Rev. gén. colloides, **8**, 337 (1930).

[5] J. Am. Chem. Soc., **49**, 1382 (1927).

[6] J. Pharmacol., **31**, 27 (1927).

[7] Stenström and Reinhard: J. Biol. Chem., **69**, 607 (1926).

[8] Reinhard, Burchwald, and Tucker: J. Cancer Research, **2**, 160 (1928).

[9] Pennycuick and Scott: Australian J. Exptl. Biol. Med. Sci., **5**, 95 (1928).

ions to destroy cancer growth without at the same time producing disastrous effects on the liver and kidneys.

Woodard[10] used a direct-current arc of 1.4 to 7 amperes at 120 volts in dilute solutions of acids, bases, and salts. In general, a stronger sol results in an alkaline or neutral salt solution than in an acid or ammonium salt solution. For the positive lead sol, the cations have a greater effect than the anions in influencing sol formation; the reverse condition obtains in the formation of the negative silver sols (see page 117). The use of a small amount of sodium thiosulfate exerts a marked stabilizing effect on the sol especially in the presence of gelatin.[11] Under these conditions, lead sulfide forms on the surface of the particles, but the action affects only about one-fourth of the metal in a month and is not complete after 6 months. The trace of lead sulfide formed on aging is said not to be toxic and not to diminish the therapeutic activity. Cofman[4] says that the most satisfactory sol, from the standpoint of stability, is obtained by passing an arc between granular particles of lead in a solution of 0.05% potassium chloride[7] and 0.5% gelatin, and adding 0.5% sodium thiosulfate after the arcing.

Werner[12] reports that radioactive lead and bismuth in aqueous solution at extreme dilution do not exist as ions, but as aggregates formed by adsorption of the radioactive ions by solid impurities present accidentally.

Organosols of lead are obtained by methods to be described in the next section.

Electrolytic Methods.—Colloidal dispersions are obtained by electrolyzing a dilute solution of alkali with a high current density at cathodes of lead, tin, bismuth, thallium, arsenic,[13] and antimony. This is especially true of lead, which separates as black clouds that settle only very slowly.[14] The metal is very reactive, white lead being formed by the simultaneous action of carbon dioxide and air on the sol. A similar result obtains in acid solution with lead but not with tin.

As already indicated (*cf.* page 15), the mechanism of the dispersion process consists in the initial formation of an alloy of the metal

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[10] Ann. Surgery, **86**, 607 (1927); J. Am. Chem. Soc., **50**, 1835 (1928); J. Phys. Chem., **34**, 138 (1930).

[11] Ganassini: Arch. ist. biochim. ital., **1**, 3 (1929).

[12] Mikrochemie, (2) **4**, 360 (1931).

[13] Lecoq: Compt. rend., **150**, 700, 887 (1910).

[14] Reed: J. Franklin Inst., **140**, 68 (1895); Bredig and Haber: Ber., **31**, 2741 (1898); Haber: Trans. Am. Electrochem. Soc., **2**, 190 (1902); Falk: French Pat., 676,244 (1929).

with hydrogen or alkali metal and in the subsequent decomposition of the alloy by water, throwing out the metal in the finely divided form.

Because of the reactivity of highly dispersed metals such as lead, tin, bismuth, and cadmium, the dilute instable sols which form merely by shaking[15] with water or organic solvent are oxide or carbonate sols rather than metallic sols.[16] The same is probably true of the sols formed by the action of ultraviolet light on such metals as lead and tin covered with water or alcohol.

Properties of Hydrosols.—A pure lead hydrosol is black in thick layers and brown in thin layers. The gray appearance which it assumes gradually on exposure to the air is due to the transformation of the particles to oxide and carbonate. The pure sol is positively charged, but the gelatin-protected sol is negatively charged.[7] The positive charge on the pure sol is probably due to the adsorption of lead ions from lead hydroxide solution formed during the arcing process. The inner portion of the double layer is thus lead ions attached to a film of oxide or carbonate, and the contra ions are hydroxyl, which give the sol an alkaline reaction. Cofman[4] reports that shaking lead with pure water gives a solution having a pH value of 9. In such a solution, gelatin has a negative charge, which accounts for the negative charge on the particles in sols protected by an enveloping film of gelatin.

Lead sols are quite instable in the presence of electrolytes with multivalent anions. Clark and Pickett[17] report that x-rays have a slight stabilizing action on the sols. Since positive sols are in general coagulated by x-rays, the experiments should be repeated, and the explanation for the anomalous behavior, if it exists, should be sought.

Sols of Lead in Lead Chloride

If an optically empty crystal of lead chloride is exposed to light in the ultramicroscope, colloidal particles appear.[18] A similar system is obtained by adding metallic lead to molten lead chloride. The clouds caused by disintegration of the lead, color the liquid brown. After solidification, the ultramicroscope reveals the presence of numerous brown particles of lead dispersed in the halide crystals.

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[15] Gurwitch: Kolloid-Z., **33**, 321 (1923).

[16] *Cf.* Nordenson: Kolloid-Beihefte, **7**, 91 (1915).

[17] J. Am. Chem. Soc., **52**, 465 (1930).

[18] Lorenz and Eitel: Z. anorg. Chem., **91**, 46, 57, 61 (1915); Lorenz: Kolloid-Z., **18**, 177 (1916).

As already pointed out (see page 5), Lorenz's lead "pyrosol," formed by electrolyzing molten lead chloride, apparently contains the lead in a molecularly dissolved state; but when such solutions are cooled, solid sols of the metal in lead chloride are obtained.

MISCELLANEOUS COLLOIDAL METALS

Two general processes have been used more or less successfully in the synthesis of sols of the several elements under consideration in this chapter: electrical disintegration and mechanical-chemical peptization. But three of the metals, arsenic, antimony, and bismuth, are obtained in the colloidal state by chemical reduction methods. It seems advantageous to consider the elements collectively from the standpoint of the methods of colloid synthesis.

Organosols by Electrical Dispersion

All the metals considered in the last chapter and most of those to be taken up in this chapter are less noble than hydrogen. Bredig recognized thirty years ago that such metals do not as a rule form pure, stable hydrosols. Svedberg,[19] on the other hand, showed that all such metals form more or less stable organosols by electrical dispersion with an oscillating arc. In Table XXVI are listed the color and the approximate stability of the isobutyl alcosols of most of the metals still to be considered. In this table a stability of 20 hours means that the entire sol is precipitated in that time, leaving a clear supernatant solution. The stability varies widely even with different metals in the same family.

Svedberg also prepared, by means of the oscillating arc, sols of aluminum, arsenic, and bismuth in ethyl ether, and lead and tin in methyl alcohol. A deep black, very stable lead organosol is formed by dispersion with the oscillating arc in benzol containing 1% of caoutchouc as protecting colloid.[20] Burton[21] obtained methyl alcosols of copper, bismuth, lead, tin, and iron with the direct-current arc, but they were highly contaminated with carbon.

Hendrick and Burton[22] prepared a negatively charged arsenic hydrosol by Svedberg's method, using a small amount of gelatin as protecting colloid. This sol was employed in the treatment of bone sarcomata. It produced no toxic effect when injected intravenously

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[19] Ber., **39**, 1705 (1906); Bodforss and Frölich: Kolloid-Beihefte, **16**, 301 (1922)'

[20] Bayer: German Pat., 260,470 (1913).

[21] Phil. Mag., (6) **11**, 475 (1906).

[22] Can. Med. Assoc. J., **24**, 642 (1931).

TABLE XXVI

PROPERTIES OF SVEDBERG'S ISOBUTYL ALCOSOLS

Metal	Color of Sol in		Stable
	Transmitted light	Reflected light	
Al	Black	Gray-black	Indefinitely
Tl (in ether)	Brown	Black	......
La	Black (violet tinge)	Black	20 hours
Ce	Black (violet tinge)	Black	Indefinitely
Sn	Brown-red	Gray	Indefinitely
Pb	Brown	Black	Indefinitely
As	Red-brown	Brown-black	15 hours
Sb	Brown-red	Black	20 hours
Bi	Brown	Black	Indefinitely
V, Ta, Cr, Mn	Brown-black	Black	1–2 weeks
Mo, W	Brown-black	Black	Indefinitely
Ur	Brown-black	Black	12 hours
Fe (in acetone)	Brown-black	Black	Indefinitely
Co	Brown-black	Black	Indefinitely
Ni	Brown-black	Black	35 hours
Pd, Pt	Brown-black	Black	Indefinitely
Ir	Brown-black	Black	40 hours

for over a year; but in a number of cases, it apparently assisted calcification and ossification of the bone and, at the same time, retarded bone destruction by the tumor cells. The young undifferentiated and rapidly growing tumor cells were affected most easily.

Hydrosols by Mechanical-chemical Peptization

A general method which is said to give hydrosols of boron, silicon, thorium, titanium, zirconium, molybdenum, tungsten, uranium, vanadium, columbium, tantalum, chromium, manganese, platinum, iridium, and osmium is the peptization method of Kužel referred to in the first chapter (see page 16). In this process the metal is first brought into a very finely divided state either by prolonged grinding or by cathodic disintegration. It is then rendered colloidal by repeated alternate treatments for long periods with dilute acid solution and dilute alkaline or neutral solution under the influence of moderate heat and violent agitation. After each treatment the material is washed thoroughly.

Colloidal Tungsten.—As an illustration of Kužel's method of sol formation, the technical preparation of colloidal tungsten will be described. Ten kilograms of the finely powdered metal were heated for 1–2 days with 75 kg of 15% hydrochloric acid, well agitated, decanted, and washed with distilled water until some colloidal metal began to pass into the filtrate. The metal was then treated for a day with 75 kg of a 1% solution of potassium cyanide, washed with distilled water, and heated with 75 kg of a 1% solution of ferrous sulfate. After washing to remove iron salts, the residue was treated with a 2% alcoholic solution of monomethylamine or a 0.5% solution of sodium hydroxide. By repeating this process several times practically all of the metal was peptized in distilled water. Lottermoser and Rideal[23] obtained a similar sol by alternate treatment of the finely divided metal with hydrochloric acid and sodium hydroxide. A very dilute polydisperse chromium sol was formed by the same procedure.

Ultramicroscopic examination of the Kužel tungsten sol showed the particles to consist of aggregates much larger than those in typical gold and silver sols. The characteristic properties of the sol are probably due to a layer of hydrous tungsten oxide or acid on the surface of the metal. The positive charge results from preferential adsorption of tungstate ions. The plastic coagulum from the sol obtained in this way was once used as a starting point in preparing tungsten filaments for incandescent lights.

All the sols formed by Kužel's laborious procedures are relatively impure, and there is no way of knowing which reactant is the effective one. It is certain that many of the preparations, especially those of the less noble metals, are chiefly oxide or basic salt sols rather than metallic sols.

Some metals obtained in the colloidal state by Kužel can be dispersed by greatly simplified modifications of the method. Among these are zirconium, molybdenum, and thorium.

Colloidal Zirconium.—It was observed by Berzelius[24] more than a century ago that zirconium formed by reduction of K_2ZrF_6 with potassium ran through the filter on washing. Later, Wedekind[25] carried out this reduction in a vacuum apparatus in order to exclude air, and thoroughly washed the metal to free it from potassium salts. On digesting with dilute hydrochloric acid followed by washing on a

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[23] Kolloid-Z., 52, 133 (1930).

[24] Pogg. Ann., 4, 117 (1825).

[25] Kolloid-Z., 2, 289 (1908); Z. Electrochem., 9, 630 (1903).

filter paper, a portion was peptized as a stable sol, yellow-gray in transmitted light and an opalescent gray in reflected light. By repeating the treatment a number of times, most of the metal was peptized to the sol state. The preparation purified by dialysis was found to contain positively charged particles of at least two distinctly different sizes and mobilities. Since the sol particles contained a considerable amount of oxygen it is probable that they were surrounded by a film of oxide or oxychloride, $ZrOCl_2$, which gave to the sol its characteristic properties. Such a film would be expected to adsorb ZrO^{++} or hydrogen ions giving the particles a positive charge with chloride ions constituting the diffuse outer portion of the double layer.

The sol formed by reducing zirconia with magnesium, followed by digesting with hydrochloric acid and washing, is chiefly an oxide sol.

Colloidal Molybdenum.—Like zirconium, a molybdenum sol was obtained by the peptizing action of dilute hydrochloric acid on the metal formed by reduction of the oxide with zinc.[26] The dialyzed sol was light brown in transmitted light and gray in reflected light and was quite stable, remaining unchanged for a half-year in the absence of air. The sol was positively charged like the oxides of hexavalent or pentavalent molybdenum with which the particles were doubtless covered. Like the oxide sols also, the particles were agglomerated quite readily by alkaline or neutral electrolytes, but not so readily by acids.

Colloidal Thorium.—A thorium hydrosol[27] was prepared simply by grinding the finely divided metal in a mortar with cold dilute acetic acid and washing to remove the excess acid. The brown sol was sufficiently stable to be purified by dialysis. The particles, which were positively charged, were much smaller than in the zirconium sol described above. The gel coagulated by electrolytes or by freezing contained but 20.5% thorium and 1.5% water, the remaining 78% being thorium dioxide. It was therefore essentially an oxide sol with a positive charge stabilized by adsorption of hydrogen ions.

Colloidal Boron and Silicon.—Davy and Berzelius obtained colloidal boron, in the early part of the nineteenth century, by thorough washing of the product formed by reduction of boric oxide with potassium.[28] Ageno and Barzetti[29] prepared the sol by reduction of 3 parts of boric oxide with 1 part of powdered magnesium and

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[26] Wedekind and Jochem: Z. angew. Chem., 40, 434 (1927).

[27] Wedekind and Baumhauer: Kolloid-Z., 5, 191 (1909).

[28] *Cf.* Svedberg: "Herstellung kolloider Lösungen Stoffe," 395 (1909).

[29] Atti accad. Lincei, (5) 19 I, 381 (1910).

washing in turn with dilute hydrochloric acid, concentrated acid, and finally with water. The resulting sol, which was reddish brown in color, coagulated promptly on the addition of electrolytes but was fairly stable in the absence of electrolytes. By this same procedure, Gutbier[30] obtained reddish yellow sols with magnesium as the reducing agent; greenish, with potassium; and blue, with sodium. Elder and Green[31] showed that sols formed in this way were quite dilute. A more concentrated sol was prepared by reducing boric oxide with magnesium in the ratio of 3 to 1 and refluxing 0.5 to 1.0 g of the element in 100 to 250 cc of distilled water, followed by filtration. The addition to the reduction mixture of sodium sulfate in concentrations of 0.001 to 0.01% of the boric oxide, gave a product which was more readily peptized. The sols formed in this way were very stable toward heat and electrolytes, in marked contrast to the sols prepared by Gutbier's procedure. The reason for this difference is not obvious and should be investigated.

Colloidal silicon can be made in much the same way as colloidal boron. Astfalk and Gutbier[32] reduced silicon dioxide with magnesium and obtained a brown product which was ground and washed in turn with dilute and concentrated hydrochloric acid, then with water, and finally with dilute alkali. Sometimes a weak, instable sol was obtained, and at other times a more concentrated, fairly stable sol resulted. Since it was impossible to predict what would happen, a further study of the method would seem to be in order.

Hydrosols by Reduction Methods

In addition to the above general methods, arsenic antimony, and bismuth may be prepared by reduction processes.

Colloidal Arsenic.—A stable arsenic hydrosol is formed by reduction of a slightly acid solution of arsenic trioxide with $Na_2S_2O_4$ in the presence of the extract of certain plants such as Tubera salep.[33] A stable sol is also prepared by reduction of a dilute solution of sodium arsenite with alkaline pyrogallol in the presence of such protecting colloids as lysalbinic acid, egg white, and gelatin.[34] By reducing a slightly acidic, alcoholic solution of arsenic trioxide with H_3PO_2 at 0°, a yellowish precipitate of arsenic is formed that is

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[30] Kolloid-Z., **13**, 137 (1913).

[31] J. Phys. Chem., **36**, 3085 (1932).

[32] Kolloid-Z., **15**, 23 (1914).

[33] Gutbier and Kräutle: Kolloid-Z., **20**, 186 (1917).

[34] German Pat., 202,561 (1908); *cf., also,* Gerasimov: J. Russ. Phys.-Chem. Soc., **61**, 269 (1929).

peptized by dilute alkali to give a transparent brown sol.[35] This can be purified from alcohol by precipitating with a slight excess of alkali and washing, first with alkali too concentrated to cause peptization, and finally with water. A sol also results on bubbling a mixture of arsine and hydrogen through water in a quartz cylinder illuminated by a quartz vapor lamp.[36] After a few minutes, a yellow, negatively charged sol is obtained which changes to red, blue, and finally blue-violet in the course of an hour or so, as the concentration increases. The blue sols coagulate spontaneously within 24 hours; but the dilute yellow and red preparations remain stable for months.

Attention is again called to the hydrosol, formed by Svedberg's method, which has been suggested for use in the treatment of bone sarcomata (see page 162).

Colloidal Antimony.—Antimony sols prepared by reduction methods are instable except in the presence of protecting colloids. Gutbier and Kräutle[37] obtained the sol by mixing 200 cc of 0.1 *M* potassium antimonate solution slightly acidified with tartaric acid, and 100 cc of 1% extract of salep, followed by reducing with 50 cc of 1% $Na_2S_2O_4$ solution and the slow addition of 5 cc of normal hydrochloric acid. After the dark brown solution no longer changed in color, it was precipitated with 300 cc of absolute alcohol, washed by decantation, and finally on the filter paper with dilute alcohol. The mass was peptized in warm water, and the resulting dark brown sol was dialyzed carefully. It could be evaporated to dryness on the water bath to give a completely reversible residue. Like the protecting colloid, the protected sol was stable in the presence of acids and neutral salts but was coagulated by alkalies.

Colloidal antimony was also obtained by reducing a fine suspension of antimony oxychloride in water with a boiled solution of titanous chloride containing some colloidal titania. Hydrous titania was the protecting colloid; hence the preparation was an antimony-titania "purple." Antimony in the sol state oxidizes so readily that it must be kept sealed in an indifferent atmosphere.

Antimony hydrosol is said to have a curative action on leprosy ulcers when injected intramuscularly.[38]

Colloidal Bismuth.—Preparations of highly dispersed bismuth possess more than passing interest because of their suggested use in

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[35] Auger: Compt. rend., **145**, 718 (1907).

[36] Dede and Walther: Ber., **58**, 99 (1925).

[37] Kolloid-Z., **20**, 194 (1917).

[38] Cawston: Brit. Med. J., II, 855 (1920).

the treatment of syphilis.[39] Although there is little likelihood of colloidal bismuth and its compounds supplanting arsenicals in syphilis treatment, the very highly dispersed element[40] associated with mercury is reported to have certain advantages that may result in their wider application.[41]

Like antimony sols, the hydrosols of bismuth formed by reduction are usually quite instable except in the presence of protecting colloids. Moreover, the finely dispersed metal is so reactive that it must be sealed out of contact with the air to avoid rapid conversion to oxide unless the particles are coated over completely with a film of indifferent material.

The hydrosol was first obtained in the form of a bismuth "purple" by reduction of a solution of bismuth tartrate with stannous salt.[42] Lottermoser[43] obtained a very satisfactory preparation by mixing bismuth nitrate and stannous chloride to each of which was first added sufficient ammonium citrate to dissolve the initial precipitate, followed by neutralization with ammonia. On heating the mixture, a black gelatinous mass precipitated which was peptized to a stable sol by thorough washing with water.

A bismuth-titania "purple" can be made by the same method used in forming the above-mentioned antimony-titania preparation, if bismuth hydroxide is substituted for antimony oxychloride. The simultaneous presence of the hydrous oxide of tin or titania was avoided by Kuhn and Pirsch[44] by adding 25 cc of 0.1 N $Na_2S_2O_4$ solution to 300 cc of a very slightly alkaline solution of bismuth tartrate. The resulting sol of low bismuth concentration was stable for months out of contact with air. This preparation may be regarded as an unprotected sol.

The most frequently prepared bismuth hydrosols result from reduction in the presence of organic protecting colloids. For example, Gutbier[45] mixed 1 part of a 10% solution of bismuth nitrate in glycerin, 50 parts of water, 40 parts of 1% hemoglobin as a protecting colloid, and 10 parts of freshly prepared 0.1% $Na_2S_2O_4$. The resulting sol, deep black by reflected light and dark brown by transmitted light,

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[39] Sazerac and Levaditi: Compt. rend., **172**, 1391 (1921).

[40] *Cf.* Lacapere: Ann. mal vénérien, **18**, 285 (1923).

[41] Rangel: Bol. assoc. brasil. pharm., **11**, 3 (1930).

[42] Schneider: Pogg. Ann., **88**, 45 (1853); Vanino and Treubert: Ber., **32**, 1072 (1899).

[43] J. prakt. Chem., (2) **59**, 489 (1899).

[44] Kolloid-Beihefte, **21**, 78 (1925).

[45] Z. anorg. Chem., **151**, 153 (1926).

was quite stable in the absence of air. Other protecting colloids used with $Na_2S_2O_4$ as reducing agent were gelatin, salep extract, and gum arabic.[46] Alkaline formaldehyde may be substituted for $Na_2S_2O_4$ as reducing agent in the presence of protecting colloids.

As might be expected, the degradation products of albumin have been employed as protecting colloids in preparing sols of bismuth for therapeutic purposes. Paal and di Pol[47] reduced colloidal BiOOH, protected by sodium protalbinate and lysalbinate, with an excess of solution consisting of equal parts of 2 *N* sodium hydroxide and formaldehyde. After prolonged heating under a reflux condenser to effect complete reduction, the sol was cooled, precipitated with acetic acid, and dried over sulfuric acid in an atmosphere of carbon dioxide. The gelatinous mass was reversible when first prepared. Gerasimov[48] reduced a solution of bismuth chloride in hydrochloric acid containing Paal's lysalbinic acid, with 25% H_3PO_2 solution at 80°. A black precipitate was thrown down which was peptized to a stable sol with dilute alkali.

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[46] Gutbier and Kautter: Z. anorg. Chem., **146**, 166; Gutbier, Kautter, and Genter: **149**, 167 (1925).

[47] Ber., **59**, 874, 877 (1926).

[48] J. Russ. Phys.-Chem. Soc., **61**, 269 (1929).

CHAPTER VIII

COLLOIDAL METALS OF THE EIGHTH GROUP

Iron, nickel, and cobalt are prepared in the sol form much less frequently than the metals of the platinum family because of the instability of the dispersions of the former and the ease with which they oxidize in the presence of air. The colloidal metals of both the iron and platinum families find their widest use as contact catalysts. In this chapter the formation and properties of the sols will be taken up, and in the two following chapters the preparation and properties of the highly dispersed solids will be considered.

THE IRON FAMILY

Iron Sols.—The sol formed by arcing between iron electrodes under water is chiefly an iron oxide. Schmausz[1] carried out the process in water containing gelatin and obtained a yellow sol of ferric oxide in a shallow dish and a clear green sol of ferrous oxide in a tall, narrow tube. Svedberg prepared stable sols in ether and acetone, but not in isobutyl alcohol, by his oscillating-arc method.

Nickel Sols.—Both the hydrosols and organosols of nickel are relatively instable except in the presence of protecting colloids. Thus the isobutyl alcosol prepared by Svedberg's method coagulated in less than 2 days (see page 163). Traces of water are said to reduce the stability of nickel dispersed in acetone with a high-frequency arc;[2] but traces of mineral acids appear to exert a stabilizing action. Meta-hydroxybenzoic acid and -nitroaniline as well as other meta and ortho compounds have a stabilizing effect on the sol, but the corresponding para compounds do not. The reason for this behavior should be investigated.

The nickel benzosol formed by the thermal decomposition of nickel carbonyl[3] is likewise instable except in the presence of a suitable

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[1] Physik. Z., **6**, 506 (1905).

[2] Folley and Henry: Mem. Proc. Manchester Lit. Phil. Soc., **73**, 100 (1929).

[3] Ostwald: Kolloid-Z., **15**, 204 (1914); *see* page 5.

protecting colloid. Hatschek and Thorne[4] have shown that rubber is a satisfactory protecting colloid for the sol in both benzol and toluol. For some unknown reason, the most stable preparation results with a mixture of toluol and benzol in the presence of rubber. Thus by heating 750 cc of a toluol solution of nickel carbonyl containing 1 g of nickel with 150 cc of a 1% solution of rubber in benzol, a black sol resulted which was stable for more than 6 months. If the rubber was dissolved in toluol instead of benzol, the resulting sol was less stable and was greenish or greenish brown in color. Both positive and negatively charged particles were present in the black sol as indicated by the fact that electrophoresis for 1 hour with nickel electrodes 5 mm apart and a potential gradient of 400 volts/cm gave uniform brown films of nickel mixed with rubber, on both electrodes.[5] Ultramicroscopic examination of this anomalous behavior showed either an absence of drift or a curious drift in layers that was not uniform even near the electrodes. When the field was cut off the particles ceased drifting suddenly and resumed normal Brownian movement.

The most probable explanation of the existence of particles of different charge in the same sol is a difference in composition of the outer layer of the particles which is too small to detect analytically. In support of this, it was found that the colloidal particles, consisting of approximately 80% nickel, were negatively charged in sols formed by decomposition of nickel carbonyl in a hydrogen atmosphere and in the absence of protecting colloid. On the other hand, solutions of the carbonyl in toluol or benzol gave a pale green precipitate of a hydrous basic nickel carbonate which was dispersed in the presence of 0.17% caoutchouc to give a positively charged sol. Mutual discharge of the oppositely charged particles was prevented for a time by the protecting colloid, but Hatschek and Thorne reported the absence of cataphoresis in a sol that had stood for some hours.

Stable sols of nickel were obtained by reduction of a solution of nickel formate in glycerin in the presence of gelatin or gum arabic as protecting colloid; and with hydrogen, hydrazine hydrate, hydroxylamine, or formaldehyde as reducing agent.[6] For example, a solution of 1 g of nickel formate and 1.5 g gelatin in 100 g of pure glycerin was treated with a few drops of hydrazine hydrate and heated in the

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[4] Proc. Roy. Soc. (London) **103 A**, 276 (1923); Kolloid-Z., **33**, 1 (1923); **36**, 12 (1925).

[5] *Cf., also,* Humphry and Jane: Kolloid-Z., **15**, 293 (1927).

[6] Kelber: Ber., **50**, 1509 (1917).

oil bath to 200°. The resulting brown sol was miscible with alcohol, acetic acid, or dilute mineral acid but was precipitated by pure water. The brown-black gel washed with alcohol and dried was repeptized by dilute acids or by acidified glycerin or alcohol. Nickel acetate or a suspension of nickel hydroxide in glycerin may be substituted for the formate as a source of nickel.

Franck[7] prepared a reversible hydrosol of nickel by reduction of a nickel acetate solution containing 1% of gum arabic, by means of hydrazine hydrate in the presence of a small amount of nuclear solution of a noble metal. Sols of cobalt, iron, manganese, mercury, and copper were formed by the same procedure. The purity of such preparations depends on the extent to which gum arabic prevents oxidation of the dispersed particles.

A nickel hydrosol was obtained by Paal[8] by catalytic reduction of colloidal nickel hydroxide protected by sodium protalbinate. The reducing agent was hydrogen in the presence of colloidal palladium. The mixed sol was chestnut brown by transmitted light and black by reflected light.

Cobalt Sols.—Although cobalt sols are seldom prepared, it is probable that they could be formed by most of the methods above described for the formation of nickel sols. For example, Paal and Boeters[9] obtained stable cobalt sols by catalytic reduction of colloidal cobaltic hydroxide stabilized by sodium protalbinate and lysalbinate. The reduction was accomplished by hydrogen in the presence of colloidal palladium. During the first 3 days the process was carried out at room temperature and atmospheric pressure, after which the temperature was raised to 50° and the pressure to 100 mm of mercury. The reduction was complete in 8 to 14 days, but it is probable that rather rapid oxidation of the cobalt would take place in the air in spite of the protecting action of the protalbinate and lysalbinate on the particles.

THE PLATINUM FAMILY

Until comparatively recently, observations on the colloidal behavior of the platinum elements have been concerned primarily with their use as catalysts. Thanks, however, to the comprehensive investigation begun by Beans and Eastlick and continued by Pennycuick, quite as much is now known of the constitution and properties of platinum

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[7] German Pat., 412,167 (1925).

[8] Ber., **47**, 2202 (1914).

[9] Ber., **58**, 1542 (1925).

sol formed by the Bredig process as of any other metallic hydrosol. Accordingly, this chapter will deal primarily with colloidal platinum, with occasional reference to the other elements of the family: iridium, osmium, ruthenium, rhodium, and palladium.

FORMATION AND STABILITY OF SOLS OF THE PLATINUM FAMILY

Hydrosols by Reduction Methods

Unprotected Hydrosols.—Platinum hydrosol may be prepared like the gold hydrosol by reduction of a platinic chloride solution with formaldehyde. Lottermoser's[10] method is as follows: To 25 cc of a solution containing 0.6 g chlorplatinic acid per liter is added 4 cc of a 0.2 *N* sodium hydroxide solution, and the mixture is heated to boiling. After the flame is removed, 5 cc of a formaldehyde solution containing 1 cc of 40% commercial formaldehyde in 100 cc of water is added. The mixture is again heated, and while it is boiling briskly, 5 cc more of the dilute formaldehyde is added. The resulting dark brown sol is freed from electrolytes by dialysis. To obtain a stable sol, Lottermoser emphasized the importance of using pure reagents and vessels such as recommended by Zsigmondy for the preparation of gold hydrosol (see, however, page 24). The stability of the sol is increased by the presence of a small amount of sodium citrate.[11]

Lottermoser's method is also used for the preparation of hydrosols of palladium, iridium, and rhodium. It is probably the most satisfactory chemical method for preparing the platinum metals sols in the absence of protecting colloids; but as in the case of gold sol formation, a wide variety of other reducing agents may be employed. Among those that have been used more or less satisfactorily in preparing the several sols are: acetaldehyde (Pt); propyl aldehyde (Pt); salicyaldehyde (Pt); resorcinol[12] (Pt); acrolein[13] (Pt, Pd, Os); hydrazine hydrate[14] (Pt, Pd, Ir, Rh, Ru, Os); and NaH_2PO_2[15] (Pt).

Protected Hydrosols.—Because of the relatively low stability of pure platinum metal hydrosols formed by reduction, it is customary to use a reducing agent which possesses a protecting action or to add a protecting colloid to the reduction mixture. Among the reducing

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[10] "Anorganisch Kolloide," 33 (1901).

[11] Shigena: Repts. Imp. Ind. Research Inst., Osaka, Japan, **8**, No. 2 (1927).

[12] Garbowski: Ber., **36**, 1215 (1903).

[13] Castoro: Z. anorg. Chem., **41**, 126 (1904).

[14] Gutbier: Z. anorg. Chem., **32**, 352 (1902); Gutbier and Hofmeier: J. prakt. Chem., (2) **71**, 358, 452 (1905).

[15] Sieverts: Kolloid-Z., **12**, 263 (1913).

agents which exert a simultaneous protecting action are pyrogallol,[16] gallic acid, and tannin.[12] Thus, 0.2 to 0.5 cc of 0.001 *N* gallic acid added to 0.0001 *N* neutralized chlorplatinic acid solution gives a green sol relatively rapidly. The color becomes more intense with higher concentrations of reactants, a black opaque sol resulting with 0.001 *N* chlorplatinic acid and 0.01 *N* gallic acid. The sol is stable, and in very thin layers it is transparent and of a dark green color. Under similar conditions tannin gives a stable olive green sol.

Stable sols are formed with almost any reducing agent in the presence of suitable protecting colloids. Thus hydrazine hydrate has been employed as reducing agent in the presence of: sodium protalbinate and lysalbinate (Pt, Ir, Os, Ru, Rh, Pd)[17]; gum arabic[18] (Pt, Ir, Os, Rh); gelatin[19] (Pt); quince-seed extract[20] (Pt); and iceland moss[21] (Pd). An ether solution of phosphorus gives a red platinum sol in the presence of gelatin.[22] A similar red-colored sol results from the reduction of a solution of platinous chloride with stannous chloride.[22] This sol like the corresponding gold sol owes its stability to the simultaneously formed hydrous stannic oxide. On standing, it agglomerates, changing to a brown color, and gives a chocolate brown precipitate, a platinum "purple" resembling the gold purple of Cassius. Similarly, sols of rhodium[23] and palladium[24] stabilized by hydrous titania are obtained by reducing the respective halide solutions with titanium trichloride. In general, the sols formed in the presence of a suitable excess of protecting colloid can be evaporated to dryness and the powder repeptized by shaking with water.

An interesting method of preparation is the reduction of a dilute chlorplatinic acid solution containing gum arabic, with hydrogen in the presence of a small amount of colloidal platinum or palladium

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[16] Stoeckl and Vanino: Z. physik. Chem., **30**, 98 (1899).

[17] Paal and Amberger: Ber., **37**, 124 (1904); **40**, 1392 (1907); Gutbier and Hofmeier: J. prakt. Chem., (2) **71**, 358 (1905); Paal: Ber., **50**, 722 (1917); Zenghelis and Papaconstantinou: Compt. rend., **170**, 1058 (1920).

[18] Gutbier and Hofmeier: Z. prakt. Chem., (2) **71**, 359 (1905); Gutbier: Kolloid-Z., **5**, 46, 105 (1909).

[19] Gutbier and Emslander: Kolloid-Z., **31**, 33 (1922); Gutbier and Zweigle: **31**, 346 (1922).

[20] Gutbier and Wagner: Kolloid-Z., **19**, 298 (1916).

[21] Gutbier, Huber, and Kuhn: Kolloid-Z., **18**, 57 (1910).

[22] Wöhler and Spengel: Kolloid-Z., **7**, 243 (1910).

[23] Gutbier and Ottenstein: Z. anorg. Chem., **164**, 274: Gutbier and Luitheusser: 281 (1927).

[24] Gutbier and Weithase: Z. anorg. Chem., **169**, 264 (1928).

which catalyzes the reduction.[25] Colloidal iridium is likewise formed by reduction of protected colloidal iridium oxide with hydrogen.[26]

Hydrosols by Peptization

Sols of all of the platinum metals can be prepared by fine pulverization followed by alternate treatment with acid and alkali according to the method of Kužel (see page 163). It is probable that thorough washing of the precipitated metals from reduction processes would give sols with all the metals. An interesting case of this was observed by Benton.[27] During the preparation of platinum black for catalysis studies, he mixed 1500 cc of sodium chlorplatinate containing 27 g of platinum per liter with an equal volume of a boiling 5% solution of sodium formate. The gelatinous precipitate settled out and was washed by decantation with 600 cc portions of boiling water. This caused marked peptization, the second washing giving a highly concentrated platinum sol which set to a stable jelly on standing. The jelly contained 40 or 50 parts of water to 1 of platinum; it underwent slow syneresis like a silica jelly and was not reversible after drying. Unfortunately, Benton was unable to duplicate this preparation.

Hydrosols by Bredig's Method

The most important method of preparing relatively pure sols of platinum consists in passing an electric spark between electrodes of the metal. Unlike the results with gold, a stable hydrosol is formed by the arcing process without the previous addition of electrolyte to the water. Pennycuick[28] used water having a conductivity less than 0.6×10^{-6} mho. To prevent contamination by carbon dioxide, the water was placed in a short-necked borosilicate flask supplied with a stopper through which two platinum electrodes passed to a small ebonite frame above. One electrode was fixed; the other had a small range of vertical freedom which was used to adjust the spark gap. The cork was supplied also with an inlet and outlet tube which served the double purpose of conducting carbon dioxide-free air or nitrogen through the water during the arcing and of introducing water and removing the prepared sol. About 450 cc of sol was made at each operation, and during the arcing, the sample was kept close to 0° by means of a freezing mixture. A direct current of 5–6 amperes

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[25] Skita and Meyer: Ber., **45**, 3579 (1912).

[26] Paal: Ber., **50**, 722 (1917).

[27] J. Phys. Chem., **30**, 1415 (1926).

[28] Australian J. Exptl. Biol. Med. Sci., **4**, 99 (1927); J. Chem. Soc., 2600 (1927).

at 220 volts was employed, and the actual sparking time for preparing 450 cc of sol was 18–20 minutes.

Stable sols of rhodium are obtained by the Bredig process in conductivity water,[29] but a little alkali should be added to the water in preparing palladium and iridium sols. The use of a high-frequency arc is said to give smaller and more uniform particles than the Bredig method.[30]

Organosols by Svedberg's Method

Pure platinum organosols were prepared by Svedberg,[31] using the oscillatory arc, in certain organic dispersion media but not in others, as shown in Table XXVII. It is obvious that the dielectric constant is not the determining factor since stable sols result in amyl and ethyl acetates which have a low dielectric constant and not in ethyl and methyl alcohol in which the dielectric constant is 5–6 times as great. Apparently the dipole moment of the medium, as shown in

TABLE XXVII

ORGANOSOLS OF PLATINUM

Medium	Stability	Dielectric constant	Dipole moment $\mu \times 10^{18}$
Amyl acetate	Stable	4.78	1.8
Ethyl acetate	Stable	5.85–6.4	1.74
Amyl alcohol	Stable	16.0	1.83
Isoamyl alcohol	Stable	15.6	1.76
Isobutyl alcohol	Stable	20.0	1.72
Acetone	Stable	20.7	2.70
Propyl alcohol	Stable	22.2	>1.53
Water	Stable	81.1	1.70
Ethyl ether	Instable	4.3	1.22
Chloroform	Instable	5.2	1.10
Ethyl alcohol	Instable	25.8	1.43
Methyl alcohol	Instable	31.2	1.25

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[29] Lancien: Compt. rend., **153**, 1088 (1912); Thiroloix and Langden: Pharm. J., **89**, 74 (1912).

[30] Thorén: Svensk Kem. Tid., **42**, 134 (1930).

[31] Kolloid-Z., **1**, 161, 229, 257 (1906); **2**, 142 (1907); Ber., **39**, 1705 (1906).

the last column of the table, is the chief factor in determining the stability.[32]

Although it is impossible to prepare a stable sol in pure ethyl ether, this is readily accomplished if a little water is added to the ether.[33] Raising the temperature induces coagulation of such sols at a rather definite point. The coagulation temperature rises rapidly with increasing concentration of added water, and in the presence of a little more than 0.5%, the sol is stable at the boiling temperature. Curiously enough, the velocity of raising the temperature has an effect. Thus if a sol containing below 0.5% water is heated rapidly, it can be raised to a higher temperature without coagulation than if it is heated slowly. The phenomenon apparently occurs only with noble-metal sols and with media that do not affect the particles chemically. Thus it is observed with platinum and gold sols, but with silver sols the coagulation point is very indistinct. Svedberg suggests that a film of adsorbed water around the particles protects them against coagulation. From this point of view, rise in temperature would cause coagulation by cutting down the adsorption. Ostwald[32] thinks the dipole moment of the addition agent is the important thing since isobutyl and ethyl alcohol as well as water, which have high dipole moments, stabilize an ether sol, whereas chloroform, amyl ether, and pentane with low dipole moments have little stabilizing action.

Errera[34] prepared a stable ethyl alcosol by the Svedberg process. Since Svedberg was unable to prepare the pure sol, it is probable that Errera's sol contained a trace of water. Mixed organosols prepared by adding 3 cc of water or organic liquid to 1 cc of the alcosols were obtained with water, nitrobenzene, methyl and ethyl alcohol, acetone, and glycerin. These liquids have relatively high dielectric constants and dipole moments. Coagulation of the sol takes place on adding the following liquids of relatively low dielectric constant arranged in the order of increasing coagulation power: chlorbenzol > chloroform > ether > toluol > *o*-xylol > *m*-xylol > *p*-xylol > hexane > carbon tetrachloride. This is the approximate order of decreasing dielectric constant and of dipole moment.[35]

Isobutyl alcosols of palladium and iridium have also been prepared by Svedberg's method.

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[32] Ostwald: Kolloid-Z., **45**, 56, 114 (1928).

[33] Svedberg: Kolloid-Z., **2**, 142 (1907); Lindemann and Svedberg: **29**, 1 (1921).

[34] Kolloid-Z., **32**, 240 (1923).

[35] *Cf.* Ostwald: Kolloid-Z., **45**, 331 (1928).

COMPOSITION OF PLATINUM HYDROSOLS

Unlike gold, finely divided platinum is relatively easily oxidized.[36] Accordingly, when the metal is vaporized in the electric arc under water, it is not surprizing to find partial oxidation of the element by the oxygen formed by electrolytic decomposition of the water. Rocasolano[37] demonstrated that hydrogen gas, but not oxygen, is given off during the formation of a platinum sol by the Bredig process, indicating that the equivalent amount of oxygen has combined with the metal to give oxides or oxyacids. This was confirmed by Pennycuick,[38] who showed that air or oxygen dissolved in the water is not essential for the formation of a typical sol. Thus a similar sol is obtained by arcing in the presence of nitrogen and only such oxygen as results from electrolysis during the arcing. The sol formed in the presence of nitrogen is somewhat less stable than that formed in the presence of oxygen, probably because the surface of the particles of the former is not covered completely with a film of oxide. If oxygen is passed into a sample of the nitrogen sol sometime after preparation, it becomes comparable in every detail to the oxygen sol.

In addition to the oxide film on the particles, free electrolyte is formed during the arcing process. Thus Pennycuick[38] found that a sol containing 100–150 mg of platinum per liter has a specific conductivity of $6\text{–}8 \times 10^{-6}$ mho, which is increased by standing for a long time, or more rapidly by boiling, to 30×10^{-6} mho or more. Only an immeasurably small fraction of this is due to the colloid, the greater part resulting from electrolyte in the intermicellar solution. Conductivity titration[39] with strong bases gives a curve with a sharp minimum, showing the presence of titrable hydrogen ion. If it is assumed that this hydrogen ion is associated with a complex anion of low mobility, most of the conductivity should be due to the cation. That such is the case is indicated by the results in Table XXVIII, which gives the C_H values for several sols from titration and from conductivity, assuming that the total conductivity is due to hydrogen ion. This was verified by coagulating the sol by freezing and titrating the clear supernatant solution. Finally, *p*H values of 9 different pure sols determined directly with the quinhydrone electrode ranged from 4.6 to 4.28, corresponding to a C_H of 25×10^{-6} to 52×10^{-6}.[40]

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[36] Engler and Wöhler: Z. anorg. Chem., **29**, 1 (1901); Wöhler: 40, 423 (1904).

[37] Alexander's "Colloid Chemistry," **1**, 678 (1926).

[38] J. Am. Chem. Soc., **52**, 4621 (1930).

[39] Pennycuick: J. Chem. Soc., 2600 (1927).

[40] Pennycuick and Best: J. Chem. Soc., 551 (1928)

TABLE XXVIII

C_H OF PLATINUM SOLS FROM CONDUCTIVITY AND CONDUCTIVITY TITRATION

Sol No.	1	2	3	4	5	6	7
$\kappa \times 10^6$	6.57	7.00	12 76	15.03	15.35	21.46	41.2
$C_H \times 10^6$ from κ	19	20	36	43	44	64	120
$C_H \times 10^6$ from titration	17	16	37	44	45	65	140

Although the concentration of acid in the intermicellar solution is too low for quantitative identification, its behavior is such that Pennycuick[41] is almost certainly right in assuming that it is $H_2Pt(OH)_6$ or one of its dehydration products such as $H_2PtO(OH)_4$. In line with this, a saturated solution of $H_2Pt(OH)_6$ gave a conductivity titration curve very similar to that of the intermicellar solution obtained from the frozen sol. This complex platinum acid is the stabilizing electrolyte of the sol from which the platinum particles, probably surrounded by a film of oxide, adsorb the complex $[Pt(OH)_6]^{--}$ anion more strongly than hydrogen ion, the former therefore becoming the inside of a double layer on the surface of the particles, and the latter the diffuse outer layer. The colloidal particles become negatively charged thereby, and move to the anode under electrical stress.

Pennycuick, who uses the term adsorption quite reluctantly, objects to the assumption that the anion is adsorbed at the surface of the colloidal particles. Instead, he assumes that the anion is chemically combined with oxides on the surface. This raises the question as to how the surface film of oxide is bound to the surface or how the complex ion, formed by the alleged interaction between the surface oxide and $[Pt(OH)_6]^{--}$ ions, is attached to the crystal lattice of metallic platinum. One can put a thin film of water, zinc, or zinc oxide on an iron surface. This does not mean that a definite $Fe{-}H_2O$, Fe–Zn, or Fe–ZnO compound is formed. Similarly, a complex platinum anion on the surface of a platinum crystal does not give a definite chemical individual. The author subscribes to the point of view that unsatisfied forces on the surface of the platinum particles attract the anion, giving an indefinite adsorption complex. If one prefers to call $x\mathrm{Fe}\cdot y\mathrm{H_2O}$ and $x\mathrm{Fe}\cdot y\mathrm{ZnO}$ chemical compounds and to regard an indefinite complex anion such as $[x\mathrm{Pt}\cdot y\mathrm{PtO_2}\cdot z\mathrm{Pt(OH)_6}]^{2z-}$ as much a chemical individual as $Fe(CN)_6^{----}$, there is no objection,

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[41] J. Chem. Soc., 2108 (1928); Kolloid-Z., 49, 407 (1929).

provided everyone understands that the term chemical compound has been extended to include loose unions in indefinite proportions. The only difficulty is that some people are so old-fashioned that they cannot understand what is to be gained by attaching such a broad significance to a time-honored term. The author prefers to regard the loose indefinite union of the complex anion to the platinum as an adsorption complex. The implied difference in point of view as regards the constitution of the micelle might seem to be a mere matter of terminology. Although this is true in a measure, it is not the whole truth. One gets the impression that some investigators who formulate the composition of complexes by the use of x's and y's believe that they are dealing with definite chemical individuals of the Werner type, or the like. This feeling is not shared by those who attribute the loose union of chemical individuals at interfaces to adsorption.

When the freshly formed platinum sol is boiled, there is a gradual coalescence or agglomeration of the particles with a lessening of the specific surface together with a decrease in the adsorption of the platinic acid which enters the intermicellar solution in greater amount and raises the conductivity of the sol. Prolonged boiling finally causes coagulation of the sol.

Coagulation of Platinum Hydrosols by Electrolytes

The action of various acids, bases, and salts on the stability of Bredig platinum sols has been studied in considerable detail by Pennycuick, whose work furnishes the basis of this discussion.[42]

Change in Mobility

The change in the cataphoretic velocity of the platinum particles on adding various electrolytes to the sol is shown graphically in Fig. 24 as given by Pennycuick.[43] The electrokinetic potential corresponding to the mobilities, assuming that the particles are spherical (see page 72), and the zone of flocculation are also shown in the figure. The significance of the shape of the mobility-concentration curves will be considered in connection with the precipitating action of each of the several compounds.

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[42] *Cf., also,* Iwanitzkaja and Orlowa: Kolloid-Beihefte, **18**, 1 (1923).

[43] J. Chem. Soc., 1447 (1930).

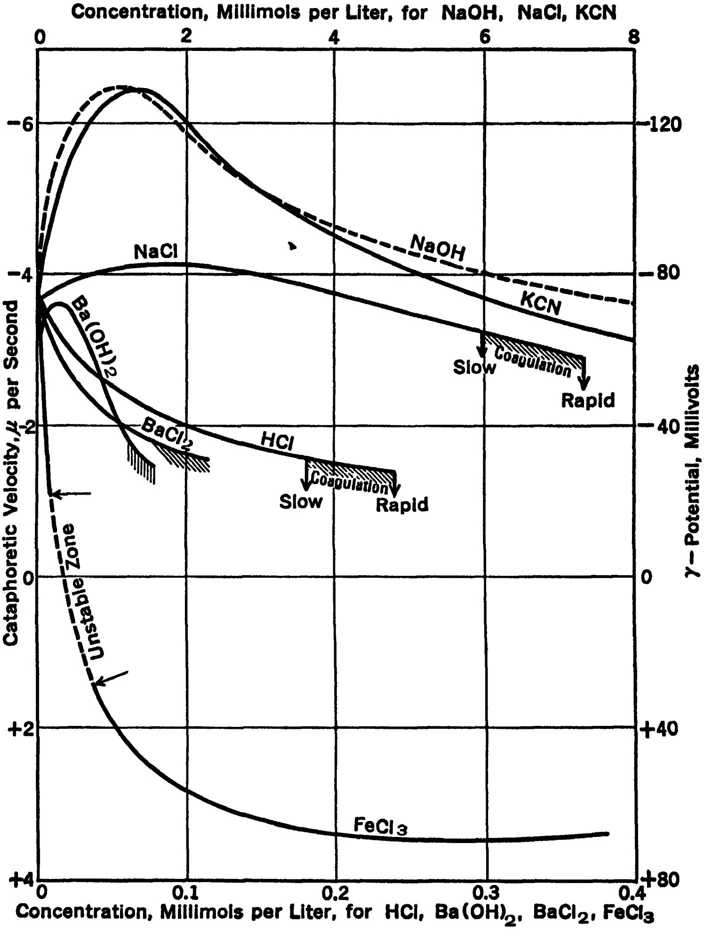

FIG. 24.—Effect of electrolytes on the cataphoretic velocity of the particles in platinum sols.

Coagulation by Acids

To determine the coagulation values, Pennycuick and Best[40] first found the approximate concentration and then prepared solutions of such concentration that they had comparable precipitating power, so that, at the coagulation point, the sol was diluted always to the same extent. Observations for complete coagulation with 8 different types of acids were made after 24 hours. The *p*H values of the supernatant solutions were determined with the quinhydrone electrode.

The results are given in Table XXIX. These observations led Pennycuick to conclude that coagulation occurs at an almost constant *p*H value and that no acid is removed during coagulation. Concerning the first of these conclusions, the significant thing is that although the *p*H values are similar they are not the same, varying from 3.69 ($C_H = 20 \times 10^{-5}$) in the case of hydrochloric acid and sulfuric acid to 3.44 ($C_H = 36 \times 10^{-5}$) in the case of citric. This variation would seem to be in the right direction. Thus with hydrochloric acid there is little or no adsorption of chloride ion, whereas with citric acid the relatively strongly adsorbed citrate ion tends to increase the charge on the particles so that the hydrogen ion concentration required for the latter acid to effect coagulation is almost twice as great as for the former.

TABLE XXIX

Coagulation of Platinum Hydrosol by Acids

Acid	Coagulation value, milligrams/l	*p*H	$C_H \times 10^5$		
			At coagulation	Of acid alone	Difference
Hydrochloric.........	0.196	3 69	20	18	2
Sulfuric..............	0 184	3 69	20	17	3
Nitric...	0 192	3.66	22	18	4
Benzoic..............	0 820	3 63	23	21	2
Tartaric.............	0.500	3.59	25	20	5
Salicylic..	0.205	3.57	26	24	2
Succinic.............	2.135	3.57	26	24	2
Citric...............	1 200	3.44	36	31	5

The conclusion that none of the added acid is carried down during coagulation is based on the observations that the C_H value of the sol is 3×10^{-5} and that the average value for the difference between the C_H value of the sol at coagulation and the C_H value of the equivalent concentration of acid alone, as given in column 6 of Table XXIX, is approximately 3. As a matter of fact, the data are scarcely accurate enough to say that none of the added acid whatsoever is carried down by the precipitate. Indeed, the data indicate that citric acid but not hydrochloric is adsorbed, which is what one would expect.

According to Pennycuick, the hypothesis that the lowering of charge on particles by the addition of electrolytes is due to adsorption of ions of opposite charge has outlived its usefulness and will have to be abandoned since it fails to explain even the simplest case, namely, the coagulation of so-called acidoid sols such as platinum by acids where none of the coagulating acid is adsorbed by the particles. This conclusion is obviously based on an erroneous idea of the adsorption mechanism of the charge reduction process. The effect on the double layer surrounding the platinum particles of adding an acid such as hydrochloric, the anion of which is adsorbed but little if at all, is shown diagrammatically in Fig. 25. In this figure, *a* represents a platinum particle with its inner double layer of $[Pt(OH)_6]^{--}$ ions and its diffuse outer layer of hydrogen ions. A part of these hydrogen ions have a relatively lower kinetic energy and are held so close to the inner layer that they would not influence a hydrogen electrode. These are represented inside the dotted circle. The addition of hydrochloric acid to the sol increases the concentration of the hydrogen ion atmosphere around the particle, thereby diminishing the thickness of the double layer and increasing the number of ions that would not be detected potentiometrically as shown within the dotted circle in Fig. 25*b*. In other words, the adsorption of hydrogen ion is increased with increasing concentration of this ion in the intermicellar solution. This reduces the charge to the critical value for agglomeration, and the particles settle out, carrying with them equivalent amounts of the adsorbed $[Pt(OH)_6]^{--}$ and hydrogen ions. This is the picture, in terms of the adsorption theory, of what Pennycuick prefers to call the decrease in activity of the colloid ion which leads to coagulation.

Contrary to the behavior of hydrochloric acid which lowers the ζ-potential from the start,[44] the addition of hydrocyanic acid to the sol[45] at first increases the ζ-potential and then decreases it to the critical value (see Fig. 24). Moreover, the conductivity of the sol is greater in the presence of the weakly dissociated acid than in its absence. The most probable explanation of this behavior is that the cyanide ions are much more strongly adsorbed than the platinate ions by the oxide-coated platinum particles. This adsorption not only serves to bring about an initial increase in charge but also the adsorbed hydrocyanic acid molecules eventually displace completely the inner layer of platinate ions from the surface and the latter carry with them the outer layer of hydrogen ions thereby increasing the conductivity of the sol.

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[44] *Cf., however,* Iwanitzkaja and Proskurnin: Kolloid-Z., **39**, 15 (1926).

[45] Pennycuick: J. Am. Chem. Soc., **52**, 4621 (1930).

Coagulation by Bases

Sodium Hydroxide.—Like the behavior of hydrocyanic acid, the stepwise addition of sodium hydroxide to the platinum sol causes at first a sharp rise in the ζ-potential followed by a slow decline to the critical coagulation value. The initial rise in particle charge following neutralization of the platinic acid in the intermicellar solution is due to strong adsorption of hydroxyl ion or of the anion of a complex platinic acid, possibly $Na_2PtO_2(OH)_2$, which may form by the action of sodium hydroxide with PtO_2 on the surface. In view of the large initial increase in particle charge, Pennycuick is probably justified in assuming the formation of a platinate, since one would, in general, expect stronger adsorption of a platinate ion than of hydroxyl ion by the platinum surface. On the other hand, the intermediate formation of a complex ion is not essential since in a Zsigmondy gold sol, which

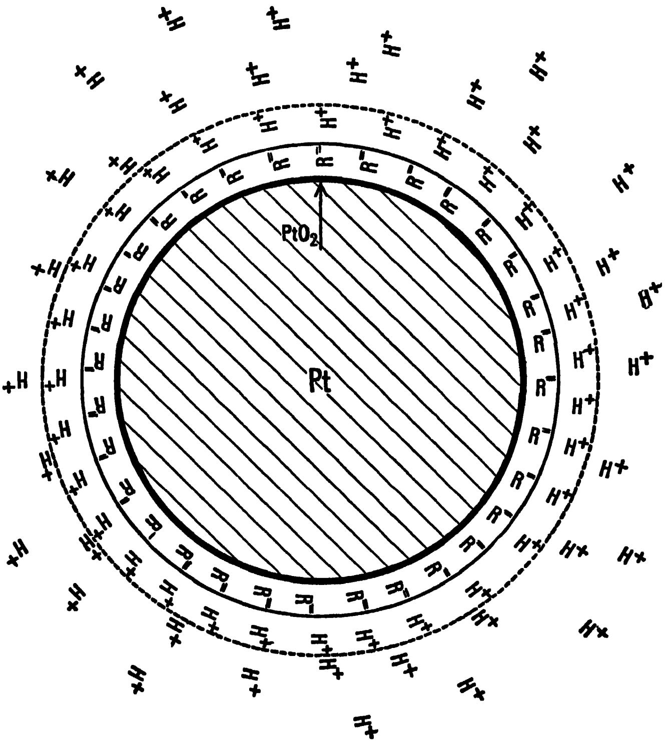

FIG. 25*a*.—Diagrammatic representation of the constitution of a colloidal platinum micelle before the addition of acid.

is free from surface oxide, the particle charge is increased by adding a small amount of sodium hydroxide (see page 51). Moreover, as we shall see, Pennycuick gives evidence to support the view that neutral salts such as the alkali halides undergo hydrolytic cleavage in the presence of colloidal platinum.[46] A definite acid platinum oxide may play a rôle in this process, but this is likewise not necessarily true since ash-free activated charcoal hydrolyzes sodium chloride, taking up hydrochloric acid and leaving the solution basic. In this case there is no experimental justification for postulating a basic oxide of carbon to account for the greater tendency of the carbon particles to adsorb hydrogen ions than hydroxyl ions. (For a full discussion of this phenomenon in the case of carbon, see Chapter XI, page 292.) Be that as it may, the stabilizing effect of the adsorbed

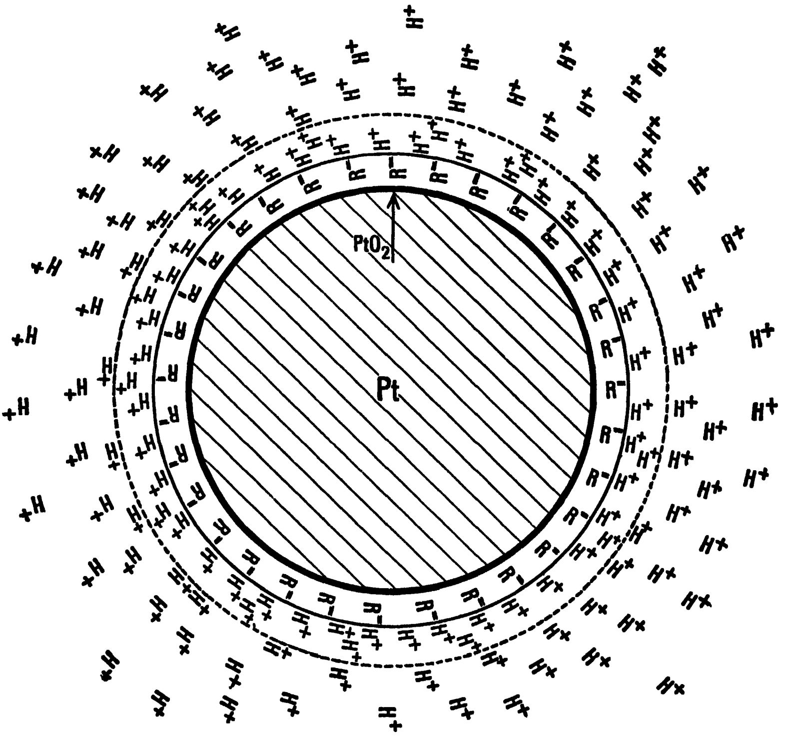

FIG. 25*b*.—Diagrammatic representation of the constitution of a colloidal platinum micelle after the addition of acid.

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[46] *Cf., also*, Frumkin and Obrutschewa: Z. anorg. Chem., **158**, 84 (1926).

hydroxyl ion, or possibly $PtO_2(OH)_2^{--}$ ion, causes the precipitation value for platinum sol of sodium hydroxide (0.02 mol/l) to be 7 times greater than that of sodium chloride (0.003 mol/l), which contains the relatively weakly adsorbed chloride ion.

Barium Hydroxide.—The initial increase in ζ-potential on adding barium hydroxide to platinum sol is very much less than that with sodium hydroxide and is confined to a narrower range since the peptizing action of the adsorbed hydroxyl or complex anion is opposed by the marked precipitating action of the strongly adsorbed barium ion. For this reason, barium hydroxide has only a very slight peptizing action on the coagulum obtained from the sol, whereas sodium hydroxide peptizes to a stable sol the coagulum thrown down by the precipitation concentration of sodium chloride. The precipitation value of barium hydroxide is about 0.1 milliequivalent/l, which is about 1/400 that of sodium hydroxide. But at the same concentration, the amount of barium carried down by the coagulum is 4 to 5 times as great as that of the weakly adsorbed sodium ion. Moreover, on the addition of a strong acid to the coagulum, the adsorbed barium ion is less readily displaced by hydrogen ion than adsorbed sodium ion.

To get some idea of the tenacity which which the ions are held, Pennycuick[47] carried out a conductivity titration of the coagulum with nitric acid. From these data, it was found in the case of barium that 26% is brought back into solution with 0.00001 *N* acid; 62% with 0.00002 *N*; 71% with 0.00004 *N*; and the last 25% is held very tenaciously. In the case of sodium the amount displaced is higher at all concentrations, and only the last 5% is quite difficult to displace. Since the titration shows that the added acid is neutralized to a certain extent, it is probable that a part of the barium is relatively loosely held in the coagulum as adsorbed barium hydroxide, or perhaps, in the specific case of platinum sol, as the barium salt of an acid sufficiently weak to be titrated with nitric acid. The remainder is more firmly adsorbed at certain points possessing a high surface attraction with the anion oriented toward the platinum and constituting the inner portion of a double layer. The outer ion is very difficult to replace with hydrogen if it is bivalent barium and more easily if it is a univalent alkali metal.

From the back titration experiments it is apparent that a platinum surface can retain an appreciable amount of base even in an acid solution. This relatively stronger attraction of the platinum particles for hydroxyl ion than for hydrogen ion would favor the hydrolytic cleavage of neutral salts added to the sol.

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[47] Z. physik. Chem., A148, 413 (1930); J. Chem. Soc., 618 (1929).

Coagulation by Salts

Barium Chloride.—The stepwise addition of barium chloride to the sol causes an immediate drop in the ζ-potential (see Fig. 24), and coagulation results at a concentration of approximately 0.1 millimol/l. As in all cases where the reduction of the charge on a colloidal particle results from strong adsorption of an ion of opposite charge, the more weakly adsorbed ion constituting the outer layer is displaced more or less completely. Pennycuick[48] showed that the platinum sol is no exception to the rule. In Fig. 26 is shown the hydrogen ion displaced on the addition of successive amounts of barium chloride. The decrease in ζ-potential, likewise shown in the figure, follows the same general course as the displacement of hydrogen ion, as would be expected. The author[49] observed a point of inflection at the coagulation point in the curve for chloride displacement on adding multivalent precipitating ions to hydrous oxide sols. The change in slope of the curve in the immediate region of the coagulation point is in the direction of relatively greater displacement of chloride accompanying the agglomeration and coalescence of particles. Since the amount of chloride displacement from the hydrous oxide sols is many times greater than that of hydrogen from the platinum particles,

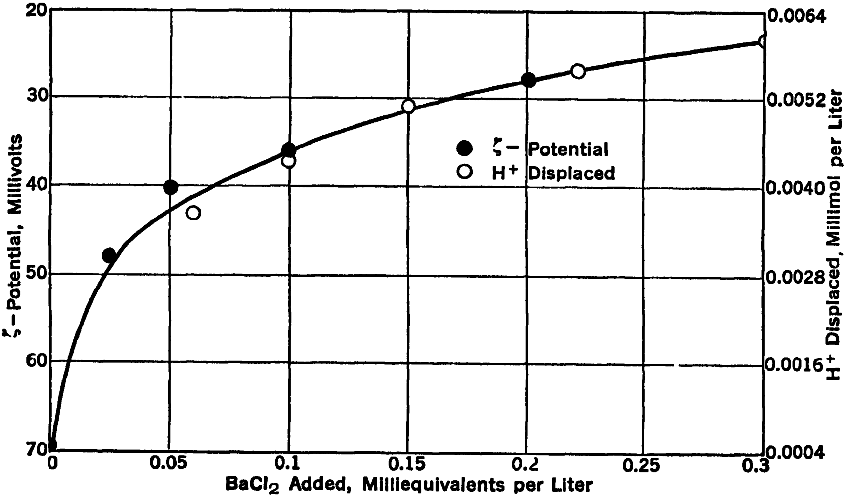

FIG. 26.—Displacement of hydrogen ion from platinum particles and the change in ζ-potential of the particles on adding $BaCl_2$ to the sol.

[48] Kolloid-Z., **54**, 21 (1931); J. Am. Chem. Soc., **52**, 4621 (1931).

[49] Weiser: J. Phys. Chem., **35**, 1, 1368 (1931); Weiser and Gray: **36**, 2178 (1932).

it is probable that in the latter case an increase in displacement in the coagulation zone is too small to be detected.[50]

The mechanism of the neutralization process is shown diagrammatically in Fig. 27. In Fig. 25*a* is represented the colloidal particle before the addition of barium ion. On adding a small amount of this ion, it is adsorbed so strongly relatively that it takes a position close to the inner layer and hydrogen ion is displaced, going into the intermicellar solution, represented beyond the dotted circle, where it can be detected potentiometrically (Fig. 27). The thickness of the double layer is reduced as a result of this exchange adsorption, thereby lowering the charge on the particle, ultimately causing coagulation. The hydrogen ion displaced, as measured by the increase in the

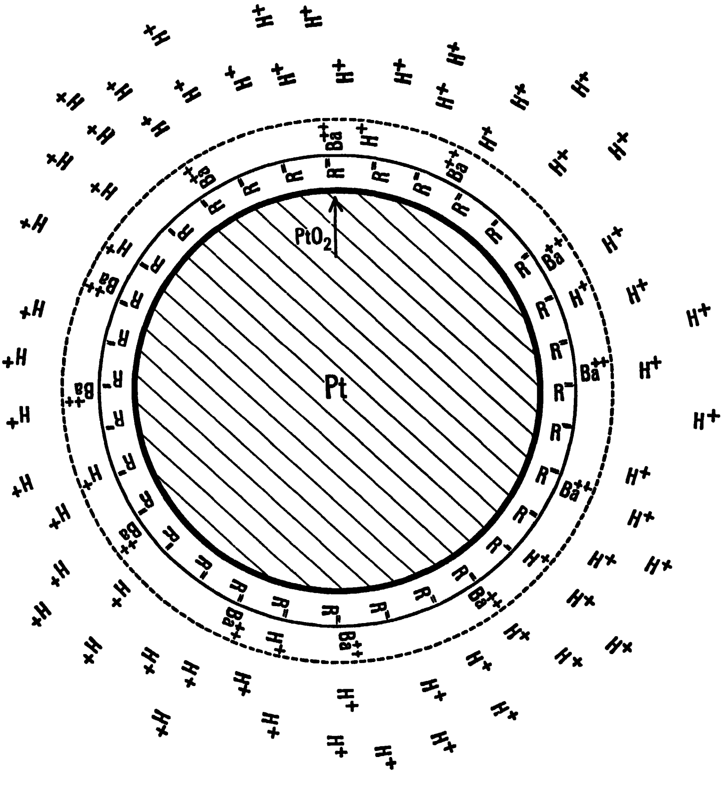

FIG. 27.—Diagrammatic representation of the constitution of a colloidal platinum micelle after the addition of $BaCl_2$. Compare with Fig. 25*a*.

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[50] *Cf.* Weiser and Gray: J. Phys. Chem., 36, 2796 (1932).

hydrogen ion concentration, is not equivalent to the barium ion adsorbed, since a considerable portion of the barium ion which enters the double layer corresponds to hydrogen ion measurable potentiometrically in the original sol.

Alkali Salts.—The mobility-concentration curve for the alkali halides on platinum sol shows a definite maximum (see Fig. 24), and the velocity is abnormally high at the coagulation concentration. This maximum in the curve with alkali salts was not observed by Briggs with Groll's gold sol (see Fig. 13, page 73) but was obtained by Thiessen and Heumann[51] with Zsigmondy's gold sol. A similar behavior was found by Briggs[52] with alkali salts on selenium and silver hydrosols; by Kruyt[53] with glass, arsenic trisulfide, and mercuric sulfide hydrosols; and by Powis[54] with oil drops. The explanation frequently given to account for this behavior is that the negative halide ion is adsorbed in low concentrations relatively more strongly than the alkali ion, thereby increasing the charge on the particles. Pennycuick[55] points out very properly that this explanation is unsatisfactory in the case under consideration since the adsorption of chloride ion by the platinum particles is negligibly small. As noted above, Pennycuick[56] makes the probable assumption that the affinity of the particle for hydroxyl is so much stronger than for hydrogen ion, that it causes hydrolytic cleavage of the salt. In this event the initial increase in charge is due to adsorption of hydroxyl ion or of complex platinate ion formed by the interaction of hydroxyl ion with the surface oxide. Because of the relatively weaker adsorption of the sodium ion than of barium ion, a much higher concentration of the former is necessary to bring about such a reduction in charge that coagulation results. Moreover, since the adsorption of sodium ion approaches more nearly that for hydrogen ion than does the much more strongly adsorbed barium, the displacement of hydrogen from the outer layer is much less with sodium than with barium at the respective precipitation values.[57]

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[51] Z. anorg. Chem., **181**, 379 (1929).

[52] J. Phys. Chem., **34**, 1326 (1930).

[53] Proc. akad. Wetensch., Amsterdam, **17**, 615 (1914); **19**, 1021 (1917); Kolloid-Z., **22**, 81 (1918); Kruyt and van der Willigen: Z. physik. Chem., **130**, 170 (1927); *cf.* Iwanitzkaja and Proskurnin: Kolloid-Z., **39**, 15 (1926).

[54] Z. physik. Chem., **89**, 91 (1915); Mukherjee and Raichoudhuri: Nature: **122**, 960 (1928).

[55] J. Chem. Soc., 1447 (1930).

[56] Nature, **124**, 987 (1929); J. Chem. Soc., 1447 (1930); Z. physik. Chem., **A148**, 413 (1930).

[57] *Cf.* Weiser: J. Phys. Chem., **35**, 1 (1931).

From the above considerations, it would follow that the stronger the adsorption of the anion of an alkali salt and the greater the normal tendency to hydrolyze, the higher will be the maximum in the ζ-potential concentration curve and the larger will be the precipitation value. This is illustrated by Pennycuick's observations given in Table XXX. It should be emphasized that hydrolytic cleavage is not alone responsible for the initial increase in ζ-potential and the variation in precipitation values with different salts. On the contrary, it probably plays a minor rôle in certain cases. Thus potassium acetate is relatively strongly hydrolyzed whereas potassium ferrocyanide is not, and the precipitation value and ζ-potential increase are much greater for the latter than for the former. Hydrolytic cleavage is probably an important factor in the action of the acetate, whereas the well-known strong adsorption of tetravalent ferrocyanide ion is probably the determining factor in producing the initial rise in ζ-potential with potassium ferrocyanide. In the light of the behavior of hydrocyanic acid referred to above, it is probable that with the highly hydrolyzed potassium cyanide, strong adsorption of cyanide ion is quite as important as adsorption of hydroxyl (or platinate) ion in causing the high initial rise in ζ-potential.

TABLE XXX

Action of Potassium Salts on Platinum Hydrosol

Potassium salt	Precipitation value, millimols/l	Maximum of the ζ-potential Initial value = −0.070 volt
Chloride	4.8	0.078
Formate	8.5	0.084
Acetate	10.0	0.084
Ferrocyanide	14.0	0.096
Cyanide	14.0	0.120
Hydroxide	20.0	0.120

Unlike the behavior of alkali halides, the strong adsorption of barium from barium chloride masks any direct indication of hydrolytic cleavage of the latter salt in contact with the platinum particles.

The ζ-potential at which the precipitation takes place is almost twice as high for the alkali halides as for salts with multivalent cations. It is not obvious why this should be. As we have seen (page 84), Kruyt attributed it to variation in the dielectric constant in the case of colloidal gold which requires a high concentration of alkali salt for precipitation; but with the low precipitation value of sodium chloride for platinum sol (0.004 *N*), this explanation seems inadequate.[58]

Like Zsigmondy's gold sol but unlike Bredig's gold sol, Bredig's platinum sol is sensitized toward the action of electrolytes by exposure to ultraviolet light.[59]

Ferric and Aluminum Chlorides.—Salts with the strongly adsorbed trivalent ions effect coagulation of platinum sol at extremely low concentrations, being 0.024 and 0.1 milliequivalent per liter for aluminum chloride and ferric chloride, respectively.[60] The ζ-potential concentration curve for ferric chloride reveals an initial sharp drop in ζ-potential to the coagulation point followed by a zone of instability and, ultimately, by charge reversal and the formation of a stable positive sol which coagulates only at a relatively high ferric chloride concentration.[61] Such an irregular series has already been considered in the case of colloidal gold with thorium nitrate (see page 88). In that connection, it was pointed out that charge reversal is usually attributed either to adsorption of the hydrous oxides formed by hydrolysis or to very strong adsorption of the multivalent cation. Kruyt ruled out the first of these possibilities in the case of colloidal gold and salts of trivalent and tetravalent cations, and reached the conclusion that cation adsorption is the determining factor. Pennycuick[58] showed that the reversal of platinum sol by ferric chloride was probably not due to adsorption of the colloidal hydrous oxide formed by hydrolysis since a solution one week old was not so effective as a freshly prepared solution in bringing about the reversal, although the former contained a much higher percentage of the hydrous oxide. This is not quite convincing, as pointed out earlier, since a freshly formed hydrous oxide doubtless contains more unsatisfied surface forces than an old oxide and so one would expect a greater attraction between oppositely charged particles with the former than with the latter. Pennycuick points out that adsorption of the cation is not the determining factor since aluminum chloride which causes precipitation in lower concentration than ferric chloride, because of stronger adsorption of aluminum ion than of ferric ion, does not effect charge reversal in any concentration.

The difference in behavior of aluminum chloride and ferric chloride

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[58] *Cf.* Pennycuick: Z. physik. Chem., **A148**, 413 (1930).

[59] Spear, Jones, Neave, and Shlager: J. Am. Chem. Soc., **43**, 1385 (1921).

[60] Pennycuick: J. Chem. Soc., 618 (1929).

[61] Buxton and Teague: Z. physik. Chem., **57**, 72, 79 (1904).

is apparently associated with the specific difference in the course of the hydrolysis in the two cases. Thus aluminum chloride hydrolyzes promptly to the equilibrium value, apparently giving hydrous aluminum oxide and hydrochloric acid.[62] The hydrolysis of ferric chloride, on the other hand, follows a slow abnormal course, the original product of the hydrolysis being basic salts which have an independent existence for a time before going over completely to ferric oxide and hydrochloric acid.[63] Adsorption of the cation of an intermediate basic salt, such as $Fe(OH)_2Cl$, probably with the hydroxyl portion of the complex cation oriented toward the particle surface, would impart a positive charge to the particles. In support of the view that an intermediate product is formed and kept from further hydrolysis, Pennycuick[58] showed that the conductivity rise, due to the formation of hydrochloric acid, is less rapid when a small amount of ferric chloride is added to the sol than when it is added to a sample of the intermicellar solution from the sol. The decrease in the tendency of an old solution to reverse the charge is due to the presence of relatively less basic salt and relatively more ferric oxide. Thorium nitrate follows a slow hydrolysis curve[64] like ferric chloride and gives a similar ζ-potential concentration curve with metallic sols.

Aluminum chloride can be made to give an irregular series like ferric chloride and thorium nitrate by the simple expedient of adding a small amount of sodium hydroxide which probably gives some basic salt such as $Al(OH)_2Cl$, the cation of which is adsorbed on the surface of the particles. It is unnecessary to assume that the cation forms a definite complex ion with the surface metal or oxide.

ADSORPTION FROM SOLUTION

Palmer[65] investigated the adsorption of benzol, ethyl alcohol, and acetic acid from gasoline solution on a plane surface of platinum and found Langmuir's equation (see page 199) to hold quite as satisfactorily as Langmuir[66] did for the adsorption of methane, nitrogen, and oxygen at −183°. The most marked adsorption was obtained with the polar molecules, the platinum surface remaining unsaturated with benzol molecules even in contact with relatively strong solutions.

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[62] Heymann: Kolloid-Z., **48**, 25 (1929).

[63] Tian: J. chim. phys., **19**, 190 (1921); Kolloid-Z., **31**, 165 (1922); Heymann: Z. anorg. Chem., **171**, 18 (1929); Kolloid-Z., **47**, 48; **48**, 25 (1929).

[64] Shukoff and Sokolova: Kolloid-Z., **48**, 71 (1929).

[65] Proc. Roy. Soc. (London) **122A**, 487 (1929).

[66] J. Am. Chem. Soc., **40**, 1361 (1918).

The adsorption of a number of organic acids—succinic, fumaric, maleic, itaconic, mesaconic, and citraconic—from aqueous solution by platinum black was studied by Platonov,[67] who showed that the amount of adsorption depends more on the structure of the molecule than on its solubility in water. The adsorption was greater if the molecule contained a double bond. A parallelism was noted between the amount of adsorption and the velocity of the catalytic hydrogenation in the sense that the most strongly adsorbed isomer hydrogenates the most readily. Cis-isomers are hydrogenated in the presence of platinum black faster than trans-isomers, and the former are adsorbed somewhat more strongly; however, the adsorption of cis-isomers is apparently accompanied by partial isomerization into the trans-form.

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[67] J. Russ. Phys.-Chem. Soc., **61**, 1055 (1929); Platonov, Borgman, and Salman: **62**, 1975 (1930).

CHAPTER IX

ADSORPTION OF GASES BY METALS

Investigations on the adsorption of gases by metals have been of so much value in throwing light on the nature of adsorption in general and of contact catalysis in particular that a chapter will be devoted to the more important aspects of this subject.

FORMATION OF METALLIC ADSORBENTS FOR USE AS CONTACT CATALYSTS

The metals most commonly employed as catalytic agents are copper and the eighth group elements. Favorable conditions for obtaining the several metals with a high adsorption capacity and catalytic activity will be outlined briefly.

Nickel.—The finely divided metal which is so important as a hydrogenation catalyst is prepared by reduction with hydrogen of the oxide formed by calcining the nitrate or an organic salt; or by precipitation from the solution of chloride or sulfate followed by thorough washing. The latter are the cheapest salts of nickel, but, if expense is not an item, the former are preferable, since halogen- or sulfur-containing compounds are catalytic poisons.

If the catalyst is to be supported on a finely divided support material such as kieselguhr, it is advisable to precipitate the oxide in the presence of the support in order to get a good distribution. If a coarser material such as pumice is to serve as the support, it is good practice to heat it above 100° and to immerse it while still hot in a hot concentrated solution of nickel nitrate. A concentration of 10% nickel in the final product gives a good supported catalyst, and this determines what the concentration of the nitrate solutions should be.[1] The temperature of calcination of the impregnated support or of the nickel salt alone is not so important as the subsequent reduction temperature; but Brown and Henke[2] suggest limiting the ignition temperature to 450° in order to avoid sintering.

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[1] Rideal and Taylor: "Catalysis in Theory and Practice," 241 (1926).

[2] J. Phys. Chem., **26**, 161, 272, 324, 631, 715 (1922); **27**, 52 (1923).

With reference to the reduction temperature, a general rule is that the lower the temperature employed the more active the catalyst but the longer the time consumed in the process. A satisfactory unsupported catalyst is obtained in a reasonable length of time at 300°. A supported catalyst is harder to reduce but is less sensitive to temperature than an unsupported one so that with the former a reduction temperature of 350° is permissible.[3]

In the preparation of metallic catalysts it should be borne in mind that, during use, a rise in temperature above the ignition temperature results in a loss in catalytic activity. Fortunately a promoted nickel catalyst is much less sensitive to overheating than one consisting of pure metal. Small amounts of ceria, thoria, and alumina are used as promoters (see page 236).

Copper.—Copper is obtained in a highly active condition by reduction of the oxide with hydrogen at as low a temperature as possible. Taylor[4] found that, by lowering the reduction temperature of a given sample of oxide from 200° to 150°, a fivefold increase in the adsorptive capacity of the resultant copper was achieved and a marked increase in catalytic activity was obtained. At a temperature of 150° the time for reduction of the oxide is too long for practical purposes, but a very satisfactory catalytic material may be prepared at 200°.[5] It is recommended that the reduction of the oxide be initiated at a temperature 50° higher than the chosen reduction temperature and subsequently lowered to the desired point after the process is started. This saves time because of the more rapid reduction rate at a copper-copper oxide interface.[6] The catalysts can be used satisfactorily only for reactions occurring below the reduction temperature. A catalyst formed by precipitation of copper oxide from the nitrate with sodium hydroxide followed by reduction is less sensitive to temperature rise than is a catalyst formed by reduction of the oxide obtained by ignition of the nitrate. The superiority of the former is attributed to the promoter action of traces of adsorbed alkali remaining in the catalyst.[7]

Iron.—Iron for use as a contact catalyst is usually prepared by reduction of the oxide with hydrogen. The temperature for complete reduction is above 600°, much higher than is necessary to reduce the oxides of copper and nickel. Unfortunately, when the reduction

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[3] Gauger and Taylor: J. Am. Chem. Soc., **45**, 920 (1923).

[4] Colloid Symposium Monograph, **1**, 97 (1923).

[5] *Cf.* Pease: J. Am. Chem. Soc., **45**, 1196 (1923).

[6] Pease and Taylor: J. Am. Chem. Soc., **43**, 2179 (1921).

[7] Rideal and Taylor: "Catalysis in Theory and Practice," 243 (1926).

temperature is too high, the metal tends to sinter, thereby materially reducing the active surface. The maximum reduction temperature for obtaining an active iron catalyst is not much above 400–450°. Under these conditions the reduction is rather slow and incomplete, but an active catalyst results, even in the presence of considerable amount of unreduced oxide. The activity of the catalyst for ammonia synthesis is materially augmented by preparing the oxide in the presence of alkali and alumina, which exert a marked promoter action.

Until recently the iron for ammonia synthesis was obtained by reducing the oxide precipitated in the presence of promoters. The Fixed Nitrogen Research Laboratory[8] discovered, however, that a more satisfactory catalyst results from reduction of the fused oxide formed by burning pure iron. For the best catalyst, the fused oxide is admixed with sufficient iron to give a composition corresponding to Fe_3O_4, and approximately 1% of Al_2O_3 and 0.25% of K_2O are added to the melt. Reduction is carried out at temperatures from 375–450° with a purified mixture of hydrogen and nitrogen at atmospheric pressure (see page 252).

Cobalt.—Cobalt catalyst is obtained preferably by reduction of the oxide formed by calcination of the nitrate. As with iron oxide, the reduction is complete only at relatively high temperatures, 600–700°, and, at such temperatures, the sintering is altogether too great to give an active catalyst. A calcination temperature for the nitrate of 400–450° and a reduction temperature of 400° is permissible especially in the presence of a catalyst support or a promoter. Under these conditions the catalyst is always admixed with considerable unreduced cobalt oxide, but this is preferable to raising the temperature to the point of complete reduction.

Platinum Metals.—The elements of the platinum family have been employed in adsorption and catalytic studies in the form of foil, "black," "sponge," and sol. The "black" is conveniently prepared by reduction of a solution of the salt of the metal with sodium formate.[9] Thus Benton[10] prepared platinum black by adding hot 6% chlorplatinic acid solution neutralized with sodium carbonate, to an equal volume of boiling 5% sodium formate solution, and washing by decantation with hot water until no further test could be obtained

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[8] Larsen and Brookes: Ind. Eng. Chem., **18**, 1305; Almquist and Crittenden: 1307 (1926).

[9] Loew: Ber., **23**, 289 (1900); Mond, Ramsay, and Shields: Phil. Trans., **186A**, 657 (1895).

[10] J. Am. Chem. Soc., **48**, 1859 (1926).

for chloride ion. The resulting product was dried on the water bath. If the metal is to be precipitated on a support such as asbestos or magnesia, the latter is impregnated with the metal salt solution and subsequently reduced.

The "sponge" form of the metal is prepared by partial sintering of the "black" by heating to 300–400° or preferably by ignition of the double chloride of the metal and ammonium.

THE ADSORPTION PROCESS

The phenomena involved in the adsorption process at metal-gas interfaces are conveniently classified under the headings: (1) adsorption isotherm, which gives the effect of pressure on the taking up of the gas at constant temperature; (2) adsorption isobar, which shows the effect of temperature on the taking up of a gas at constant pressure; (3) adsorption types; (4) activation energy of the adsorption process; and (5) heats of adsorption.

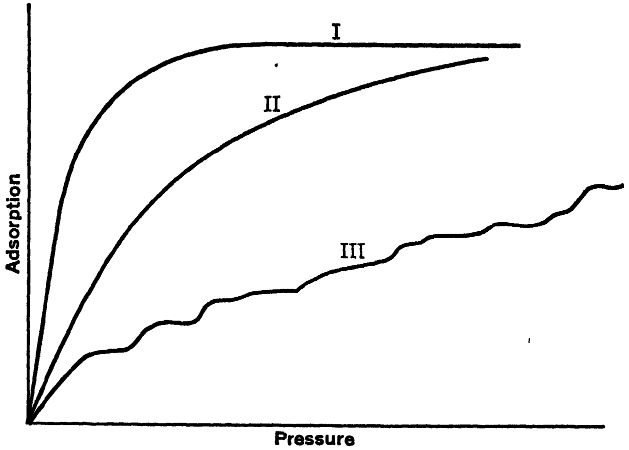

FIG. 28.—Types of adsorption curves.

The Adsorption Isotherm

Typical isotherms for the taking up of gases by solid adsorbents are represented diagrammatically in Fig. 28. The equations which have found widest use in formulating the relationship between pressure and amount adsorbed are due to Langmuir and Freundlich.

Langmuir's Equation.—Langmuir[11] has derived an equation on

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[11] J. Am. Chem. Soc., **38**, 1145, 2221 (1916).

kinetic grounds which is pretty generally applicable to adsorption of gases by metals especially if the surface is uniform. It is assumed that the adsorption on such a surface to form a more or less saturated monomolecular layer, results from the time lag between condensation of the gas molecules which strike the surface and their subsequent reevaporation. In the simplest case, the rate of condensation, S, is proportional to the gas pressure p, to the fraction of the surface which is not covered $(1 - A)$, and to f, the fraction of the collisions which are elastic. The value of f is frequently very close to unity. Hence, we have

$$S_1 = k_1 f p(1 - A)$$

Which for a given surface under constant conditions becomes:

$$S_1 = k_1 p(1 - A) \tag{1}$$

In the same way the rate of evaporation S_2 is proportional to the amount already adsorbed, that is, to the fraction of the surface covered, A. Hence,

$$S_2 = k_2 A \tag{2}$$

At equilbrium the rates are equal; hence,

$$k_1 p(1 - A) = k_2 A \quad \text{or} \quad A = \frac{k_1 p}{k_2 + k_1 p} \tag{3}$$

By making $k_1/k_2 = b$, Equation (3) becomes

$$A = \frac{bp}{1 + bp} \tag{4}$$

From this it is apparent that an adsorption isotherm at a given temperature will contain three parts which gradually merge into each other as shown diagrammatically in curve I of Fig. 28: (1) At very low values of p, $A \propto p$, or the extent of surface covered varies directly with the pressure; (2) at very high values of p where bp is large compared to unity, $A = 1$, that is, the surface covered is independent of the pressure; (3) between these extreme conditions there is an intermediate curved portion which is best represented by an expression:

$$A = kp^{1/n} \tag{5}$$

which is the well-known Freundlich equation.

In applying Equation (4) to actual adsorption data at uniform surfaces, it takes the form

$$A = \frac{\alpha\beta p}{1 + \alpha p} \quad \text{or} \quad \frac{p}{A} = \frac{1}{\alpha\beta} + \frac{p}{\beta} \tag{6}$$

in which α and β are constants obtained by plotting p/A as a function of p.

Freundlich's Equation.—When the extent of adsorption by non-uniform, non-specific adsorbents, such as carbon and silica, is plotted against the equilibrium pressure a curve like curve II of Fig. 28 is obtained. This is similar to the middle portion of curve I and so is best represented by an empirical expression of the form of Equation (5), $A = kp^{1/n}$, where A is the amount adsorbed at pressure p, and k and n are constants. This represents the facts fairly well in many cases even with highly dispersed metallic adsorbents especially in low-pressure regions, but agrees very poorly with experimental results at high pressures where the curve tends to become parallel to the x-axis.

Isotherms exhibiting discontinuities like those shown in curve III, Fig. 28, are frequently encountered in the adsorption of gases on metals. This phenomenon will be considered in the section dealing with adsorption by copper. The smooth curve following the general course of the discontinuous curve can usually be represented fairly well by the Freundlich equation.

The Adsorption Isobar

Since, in general, adsorption falls off with rising temperature, the variation in adsorption with change in temperature is represented by a smooth curve of the hyperbolic type. In certain cases, however, the rapid adsorption at low temperatures is followed by a slower adsorption, the rate of which increases for a time with rising temperature and then falls off. This behavior has been noted especially in the adsorption of certain gases by metallic and oxide catalysts. A typical adsorption isobar showing increase in adsorption with rising temperature over a certain range is the isobar for hydrogen at a manganous-chromic oxide surface, obtained by Taylor and Williamson[12] and reproduced in Fig. 29. It is apparent that the adsorption

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[12] J. Am. Chem. Soc., **53**, 813, 2168 (1931); Taylor: Nature, **128**, 636 (1931); *cf.*, *also*, Taylor and Sickman: J. Am. Chem. Soc., **54**, 602 (1932); Williamson: **54**, 3159 (1932); Benton and White: **52**, 2325 (1930); **54**, 1373 (1932); Garner and Kingman: Nature, **126**, 352 (1930); Kingman: Trans. Faraday Soc., **27**, 654 (1931).

at lower temperatures labeled "physical adsorption" passes through a transition range of "pseudo equilibrium" at intermediate temperatures, to the higher temperature adsorption labeled "activated adsorption." The significance of the form of the curve will be considered in the next section.

Types of Adsorption

The term adsorption as applied to the condensation of gases on the surface of solids has been found to involve two more or less distinct types of phenomena.[13] In the first type the surface condensation is due to physical, capillary phenomena more or less non-specific in character in that the adsorption parallels the physical character of the adsorbent. It has been referred to by different authors as "physical," "secondary," "reversible," or "van der Waals'" adsorption. Typical examples of this type are the taking up of carbon dioxide and sulfur dioxide by inert adsorbents such as charcoal and silica. The second type of adsorption which is due to primary valence forces is relatively strong

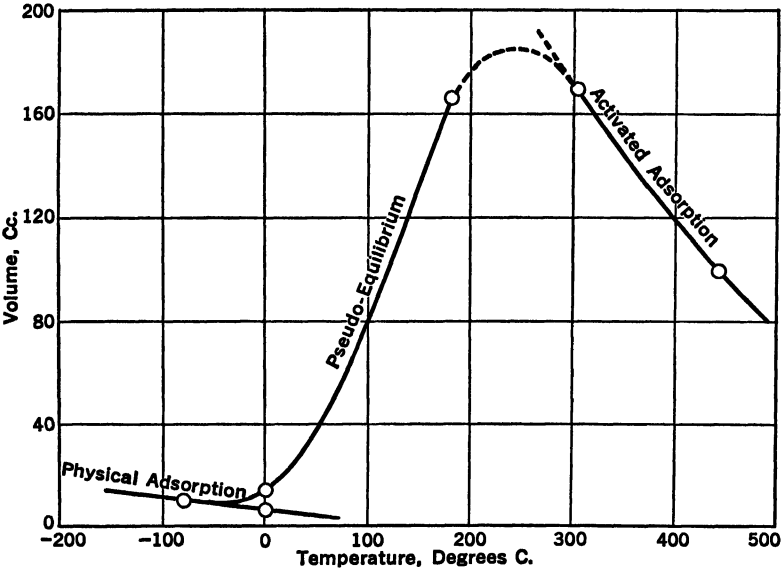

FIG. 29.—Adsorption isobars of hydrogen with manganous-chromic oxide catalyst at 165 mm.

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[13] *Cf.* Benton: J. Am. Chem. Soc., **45**, 887, 900 (1923); Trans. Faraday Soc., **28**, 202 (1932); Benton and White: **52**, 2325 (1930); *cf., however,* Hinshelwood: "Kinetics of Changes in Gaseous Systems," 193 (1929).

and specific in character, being independent of the physical character of the adsorbent; in other words, the adsorption is essentially of a chemical nature. This type is encountered at certain temperatures in the taking up of such gases as hydrogen and carbon monoxide by oxide and metallic catalysts. In contradistinction to the first adsorption type, the latter type has been termed at various times, "primary," "chemical," and, more recently, "activated"[14] adsorption.

Differentiation between Adsorption Types.—It is possible to differentiate more or less sharply between the two types of adsorption. Thus typical cases of secondary adsorption are accompanied by heat effects of the order of magnitude of the heat of liquefaction whereas in cases of primary adsorption the heat effects are much greater, corresponding in many instances more nearly to those of a chemical reaction (see page 206). It is also possible to differentiate the two types by observing the effect of temperature and pressure on the adsorption. Thus typical secondary adsorption decreases rapidly and continuously with increasing temperature, whereas primary adsorption increases at first and then falls off with rising temperature. In secondary adsorption the amount of a gas taken up increases gradually with increasing pressure, and complete saturation is not obtained until the pressures are relatively high. Primary adsorption, on the other hand, increases rapidly with increasing pressure at low pressures but soon reaches a saturation value constant for a given temperature beyond which further pressure increase does not alter the amount adsorbed. Langmuir[15] has differentiated the two types quite sharply in adsorption studies on mica, glass, and platinum. It is obvious, however, that under certain conditions primary and secondary adsorption will take place simultaneously and a sharp differentiation is impossible.

Some cases of pure secondary or van der Waals' adsorption have been established by London[16] in an investigation of the nature of molecular forces from the standpoint of the wave mechanics. Assuming that the adsorbed gas has the same equation of state as in the gas phase and that the forces of adsorption and van der Waals' forces are related, London deduced an equation by which he calculated the heat of adsorption of helium, nitrogen, argon, carbon monoxide, carbon dioxide, and methane on charcoal and found the results in good agreement with the observed values. This means that in these

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[14] Taylor: J. Am. Chem. Soc., **53**, 578 (1931).

[15] J. Am. Chem. Soc., **40**, 1361 (1918).

[16] Z. physik. Chem., **B11**, 222 (1930).

cases the adsorption is non-specific, the adsorbed gas is molecular, and the adsorption forces are van der Waals' molecular forces which are sharply distinguishable wave-mechanically from electrostatic or valence forces.[17]

As noted in the above section on the adsorption isobar, direct experimental evidence by Taylor and others indicates quite conclusively that certain gases can be adsorbed at certain surfaces in two different ways characterized by the extent of adsorption and its variation with the temperature. The low-temperature adsorption which falls off with rising temperature is usually very rapid and appears to be non-specific, consisting merely in a surface condensation of a large portion of the molecular collisions with the adsorbent. At higher temperatures, on the other hand, a slow specific adsorption is sometimes observed which may result in the taking up of more gas than that adsorbed at low temperature. The velocity with which the high-temperature type of adsorption occurs increases exponentially with the temperature. The adsorption of hydrogen by manganese-chromic oxide shown in Fig. 29 is a case in point. At −78° the adsorption is rapid and practically completely reversible by evacuation at the same temperature. This is a physical condensation of the van der Waals or secondary type. At 0° this type of adsorption is less than at −78° as would be expected, but above 0° there is a very slow increase in adsorption. At 100° and 132° there is little or no secondary adsorption and the primary or activated adsorption is increasing until at 184° and 305° it is 15 times as great as that obtained under similar pressures at −78°. At 440° it is distinctly less than at 304° but still several times greater than the secondary adsorption at −78°. Taylor observed a similar behavior with a zinc oxide adsorbent and Benton with copper, nickel, and iron adsorbents. The latter will be taken up in the section dealing with adsorption by typical metallic adsorbents.

Further evidence of a fundamental distinction between the low- and high-temperature types of adsorption is furnished by the heats of adsorption of the gas on the same surface in the two temperature regions. It is possible by means of the Clausius-Clapeyron equation to calculate the heat of adsorption from any two isotherms on which the equilibrium pressures for a given quantity of adsorbed gas have been determined. This equation in its integrated form is

$$\log p_1 - \log p_2 = \frac{\lambda}{4.58}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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[17] *Cf.* Taylor: Chem. Rev., 9, 1 (1931).

where p_1 and p_2 are the equilibrium pressure for a given adsorption at temperatures T_1 and T_2, respectively, and λ is the heat of adsorption. In the case of hydrogen adsorbed by a manganous-chromic oxide surface, λ comes out to be about 1900 calories in the low temperature range $-78°$ to $0°$; from the isotherms at 305° and 440°, a heat of adsorption greater than 19,000 calories is calculated. These data serve not only to distinguish two types of adsorption but also to account for the marked increase in the amount adsorbed at the higher temperature range.

Activation Energy of Adsorption Processes

Since the velocity with which the high-temperature type of adsorption takes place increases exponentially with the temperature, Taylor points out that one may speak of the activation energy of adsorption processes in the same way as one speaks of the activation energy of chemical reactions. The introduction of this concept leads to a modified theory of adsorption which differs from the classical theory in that the latter assumes the activation energy of adsorption to be zero and that of desorption to be λ, which is identical in magnitude with the usual heat of adsorption; the modified theory assumes an activation energy E for adsorption and, in consequence, an activation energy $E + \lambda$ for the desorption process. From this point of view the two types of adsorption which have been recognized differ in that one involves a low heat of adsorption and a low activation energy while the other involves a relatively high heat of adsorption and a high activation energy. This suggests the existence in certain cases of two adsorption isobars for the same gas at a given surface, that with the higher heat of adsorption and activation energy involving greater amounts of adsorbed gas at the same temperature and pressure. At sufficiently low temperatures, the adsorption involving low activation energy will prevail chiefly; at sufficiently high temperatures the process involving high activation energy will predominate.

Referring once more to Fig. 29, the lower adsorption isobar for hydrogen on manganous-chromic oxide is chiefly of the type involving low heat of adsorption and low activation energy, whereas in the higher isobar the process with higher activation energy predominates. Between the two a transition region of pseudo-equilibrium adsorption values is obtained which shows an increase in the amount of gas adsorbed with increasing temperature, the velocity of adsorption at a given temperature depending on the activation energy of the high-temperature adsorption.

The magnitude of the activation energies E can be calculated from the integrated Clausius-Clapeyron equation $d\ ln\ V/dT = E/RT^2$, which takes the form

$$\log v_2 - \log v_1 = \frac{E}{4.58}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where v_2 and v_1 are the velocities corresponding to the respective temperatures, T_2 and T_1. Some data obtained with a manganous oxide and a manganous-chromic oxide adsorbent are given in Table XXXI.

TABLE XXXI

Activation Energy of Adsorption of Hydrogen on Manganous Oxide

Adsorbent	H_2 adsorbed, cc	Time required in minutes at		E in cal/mol adsorbed
		218°	184°	
Manganous oxide	0–2	1.8	4.6	12,400
	2–3	2.7	11.7	19,400
	3–4	4.7	21.7	20,800
		132°	100°	
Manganous-Chromic oxide	0–10	3.2	6.0	5,920
	10–15	7.3	20.0	9,500
	15–20	15.9	48.0	10,400
	20–25	37.2	111.5	10,400

It is evident from these data that the activation energy is a function of the surface. Moreover, with increasing surface covered, the velocity of adsorption falls off and the activation energy rises.

From these and similar adsorption data, Taylor concludes that the only essential distinction between "secondary" and "primary" adsorption is that the former normally possesses small heats of adsorption and small activation energies while the latter may exhibit high heats of adsorption and moderate or large activation energies. The significance for contact catalysis of adsorption with high activation energies will be considered in the next chapter.

It should be mentioned that in the opinion of certain investigators the concept of activation energies in adsorption is all a delusion. While a relatively slow rate of adsorption and an increase of rate with temperature are important characteristics of the activated type of adsorption, rate alone does not distinguish the phenomenon from other slow processes. Thus Steacie[18] claims that the slow effects accompanying adsorption processes can be simply explained on the basis of existing data regarding the solubility of gases in solids. Ward,[19] on the other hand, believes that the slow process is a grain boundary diffusion involving activation energies rather than a lattice diffusion or solution (see page 212). A third possibility is that a slow displacement of strongly adsorbed gases by the adsorbate in question accounts for the increased adsorption at higher temperatures. Taylor contends, however, that solubility alone is inadequate to account for the quantitative amounts of adsorption involved at higher temperatures; that activated diffusion into the less accessible portions of the surface is indistinguishable experimentally from activated adsorption; and that the phenomena involved cannot be ascribed to displacement of adsorbed gases from the surface. It is nevertheless true that all these factors may and probably do contribute to the behavior of gases in contact with solid. To the extent that they do influence the rate of taking up of gas with temperature and are disregarded, the calculated activation energies are necessarily in error. Burrage[20] points out the difficulty of obtaining sufficiently clean surfaces to make significant measurements of rate of adsorption.

Heats of Adsorption on Metals

The heats of adsorption at 0° of several gases on some of the more common metals used in catalysis have been measured by Taylor and his pupils.[21] A few of the results compiled by Taylor[22] together with the heats of liquefaction of the several gases are shown in Table XXXII. It is significant that the heats of adsorption are greater in all cases than the corresponding heats of liquefaction and sometimes very much greater, corresponding more nearly to those of a chemical reaction. The very high heat of adsorption of oxygen on platinum is probably due in part at least to oxidation.[23] In any event, the adsorption is not reversible at practicable evacuation temperatures.

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[18] J. Phys. Chem., **35**, 2112 (1931); Trans. Faraday Soc., **28**, 617 (1932); *cf.* Taylor: **28**, 444 (1932).

[19] Proc. Roy. Soc. (London) **133A**, 506, 522 (1931); Trans. Faraday Soc., **28**, 399 (1932).

[20] Trans. Faraday Soc., **28**, 192 (1932).

[21] Beebe and Taylor: J. Am. Chem. Soc., **46**, 45 (1924); Beebe: J. Phys. Chem., **30**, 1538 (1926); Dew and Taylor: **31**, 277 (1927); Taylor, Kistiakowsky, and Perry: **34**, 799 (1930).

[22] Alexander's "Colloid Chemistry," **3**, 111 (1931).

[23] Engler and Wöhler: Z. anorg. Chem., **29**, 1 (1909).

TABLE XXXII

HEATS OF ADSORPTION AND LIQUEFACTION OF GASES ON CATALYSTS

Catalyst	Gas	Integral heat of adsorption, cal/mol	Pressure range, mm	Heat of liquefaction, cal/mol
Nickel	H_2	14,960	0–760	216 (−252.8°)
	NH_3	11,240	0–90	5100 (0°)
	O_2	98,000*	0	1640 (−182.9°)
Copper	H_2	9,600	0–760	
	O_2	82,000*	0	
	CO	30,000	0–1	1410 (−192°)
	CO_2	11,700	0–760	1350 (0°)
	NH_3	9,200	0–155	
	H_2	11,300†	0–0.01	
	C_2H_4	16,000†	0–0.01	
	C_2H_6	11,000	0–0 01	
Iron	NH_3	16,000	0–10	
Platinum	H_2	32,400	0–0 01	
	O_2	161,000	0–0.15	
	CO	34,600	0–0 005	
	SO_2	35,700	0–0.02	5900 (0°)

* Data of Russell and Bacon: J. Am. Chem. Soc., **54**, 54 (1932).

† See page 238.

In these cases the primary and secondary adsorption take place side by side; hence the above data give no indication as to what portion of the heat evolved is due to activated adsorption. In the adsorption of hydrogen and probably of oxygen, the observed heat effects are probably due chiefly to activated adsorption since this apparently occurs even at quite low temperatures on metallic surfaces.

ADSORPTION BY TYPICAL METALLIC ADSORBENTS

The principles and phenomena discussed in the preceding section are well illustrated from adsorption studies with metallic adsorbents. As typical examples the adsorption of gases by copper, nickel, platinum, and palladium will be considered in some detail.

Copper

A comprehensive study of the adsorption of nitrogen, hydrogen, and carbon monoxide by finely divided copper at temperatures ranging between −183° and 0° has been made by Benton and White.[24] Because of the scope of this work and its theoretical importance, it will be given special consideration.

Isotherms for Nitrogen.—In Fig. 30 are given the adsorption isotherms obtained by Benton and White at 0°, −78.5°, and −183° for nitrogen on a 51.5 g sample of copper prepared by reduction of the oxide as previously described (see page 195). The volumes of gas are given in cubic centimeters at 0° and 760 mm, and the pressure in millimeters of mercury at 0°. Curve I_a is the complete isotherm at −183° of which curve I is only the first part.

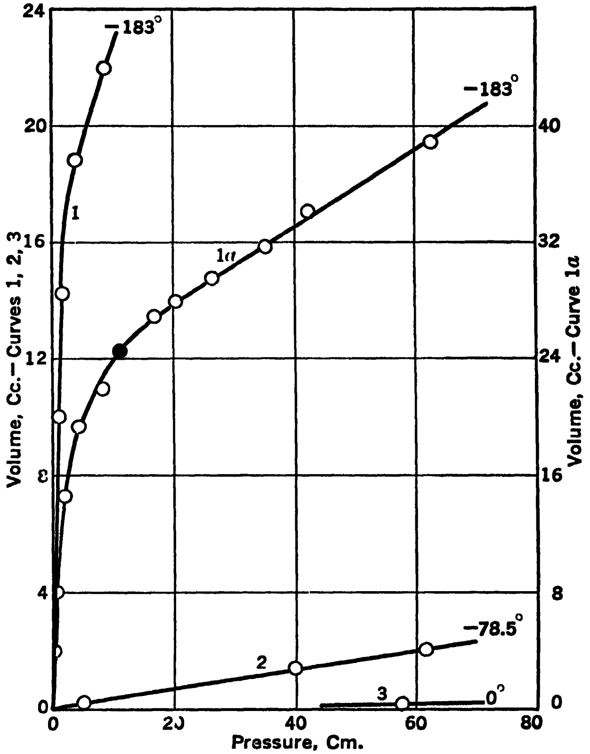

FIG. 30.—Adsorption isotherms for nitrogen with copper.

The form of the isotherms and the phenomena associated with the adsorption are typical of the physical, molecular, or van der Waals' type of adsorption. "Thus (1) equilibrium is reached from either side practically instantaneously (2) the isotherms do not appear to approach a saturation limit (3) there is no adsorption at 'zero'

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[24] J. Am. Chem. Soc., 54, 1373 (1932).

pressure (4) at temperatures far above the boiling point of nitrogen the adsorption is approximately proportional to the pressure (5) the adsorption at a given pressure decreases uniformly with rising temperature (6) the heat of adsorption is relatively small." The value of the heat of adsorption on different parts of the surface ranges from 4000 to 2000 calories per mol.

Isotherms for Hydrogen at Low Temperatures. Discontinuous Adsorption.—The isotherms for hydrogen at −183° and −195° are shown in Fig. 31 after Benton and White. The circles designate points obtained by proceeding from lower to higher pressures, and the dots indicate the reverse process. Disregarding for the moment the discontinuities in the isotherms, the curves and the phenomena associated with the adsorption are characteristic of the physical or van der Waals' type.

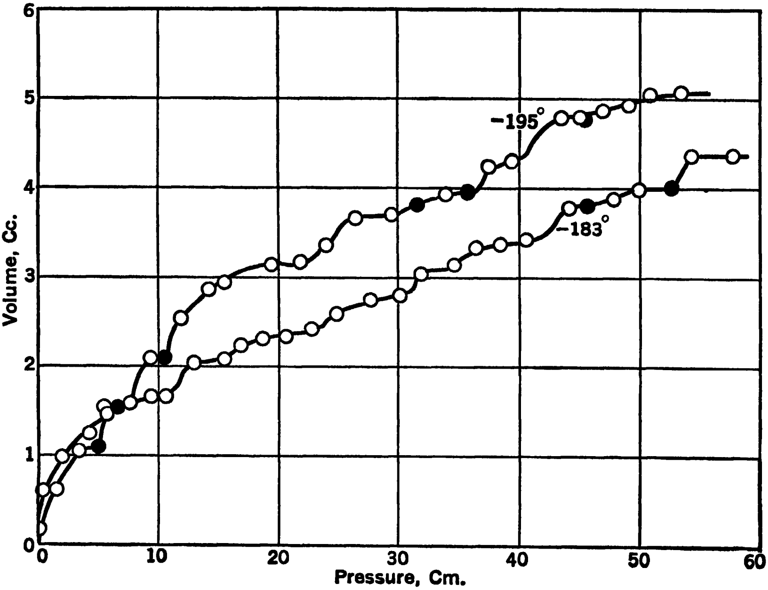

FIG. 31.—Adsorption isotherms for hydrogen with copper at low temperatures.

Discontinuities in adsorption isotherms like those shown in Fig. 31 are quite common with both metallic and non-metallic surfaces such as those of nickel, copper, iron,[25] and carbon.[26] This behavior cannot

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[25] Benton and White: J. Am. Chem. Soc., **52**, 2325 (1930); **53**, 3301 (1931).

[26] Allmand and Burrage: Proc. Roy. Soc. (London) **130A**, 610 (1931); J. Phys. Chem., **35**, 1692 (1931); J. Am. Chem. Soc., **53**, 4453 (1931).

be explained by assuming the successive formation of complete layers, since the metal surfaces were not completely covered by a unimolecular layer even after 10 or more steps had occurred. Thus the adsorption of hydrogen by copper at 0° and 1 atmosphere, which, being of the chemical or activated type, cannot exceed a unimolecular layer, is very much greater than the amount adsorbed at −183°, although, as noted in the figures, the latter process takes place in a number of steps. No evidence of steps in the activated type of adsorption has been observed.

To account for the steps in the isotherm, Benton and White assume that the physical type of adsorption consists in the formation of concentric rows of adsorbed molecules first at the edges of each crystal face and building up successively toward the center, thus giving a succession of steps. It is pointed out that the adsorption mechanism which involves the ordinary exchange of condensation and evaporation on a uniform surface does not preclude adsorption in steps if the probable assumptions are made (1) that neighboring adsorbed molecules evaporate from the surface less readily than isolated molecules and (2) that physically adsorbed molecules possess mobility in the plane of the surface.[27]

Isotherms for Hydrogen at Higher Temperatures.—The effect of varying pressures on the amount of hydrogen taken up at −78° and 0° is given in Fig. 32 after Benton and White. The observed phenomena at these temperatures differ markedly from those at liquid-air temperatures. One of the most striking differences is the relatively slow rate at which equilibrium is approached at the higher temperatures. The isotherms tend to flatten out and there is a large adsorption at "zero" pressure. Moreover, the amount of gas taken up is much greater than at the lower temperatures.

Illuminating experiments were carried out in which the adsorbent was saturated at a given temperature and pressure and the temperature changed rapidly. For example, a sample that took up 9 cc of gas at −78° was cooled rapidly to −183°. This did not cause a decrease to the ordinary value at that temperature, but instead there was an increase above the 9 cc which was almost as great as the entire adsorption obtained directly at the lower temperature. This again emphasizes the fundamental difference between the higher temperature adsorption and the physical adsorption at −183°, and shows the physical adsorption capacity of the copper to be altered but little by the large adsorption of the high-temperature type.

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[27] *Cf.* Volmer: Z. physik. Chem., 115, 253 (1925); Volmer and Adhikari: 119, 46 (1926).

Similar experiments carried out between −78° and 0° revealed another phenomenon. On warming the system in equilibrium at −78° rapidly to 0°, the gas adsorbed in the activated form at −78° was first given up, and this was followed by a slow solution. These results indicate that at −183° only physical adsorption occurs; at −78.5° activated adsorption predominates; and at 0° both activated

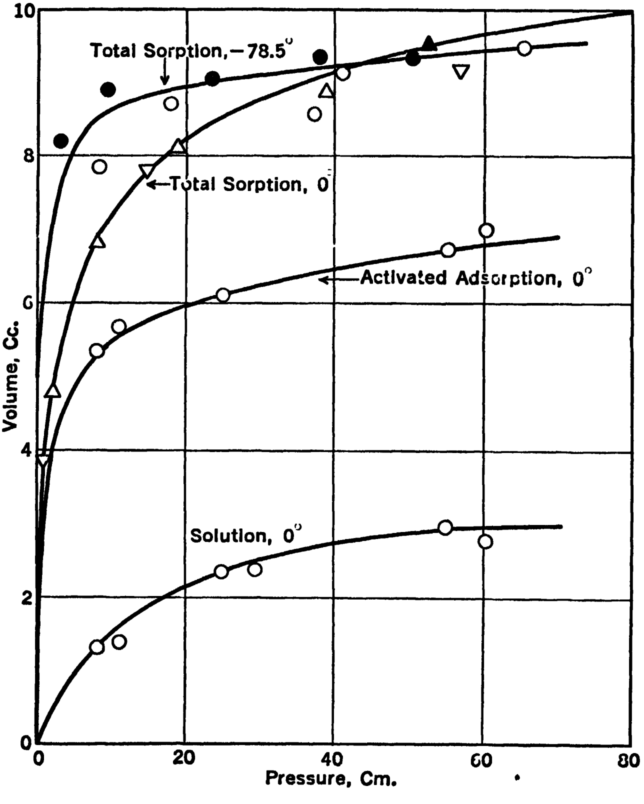

FIG. 32.—Isotherms for hydrogen with copper.

adsorption and solution take place, the former being almost twice as great as the latter as shown in the figure.

By procedures similar to those of Benton and White, Ward[28] obtained the adsorption isotherm for hydrogen on copper at 25° and 0.001–3 cm. The heats of adsorption and desorption, corrected for the gas dissolved and the heat of compression of the gas, were

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[28] Proc. Roy. Soc. (London) **133A**, 506 (1931).

found to be independent of the amount of gas adsorbed but decreased after each baking of the copper until a final value of 9000 cal/mol was reached. In accord with the usual behavior the isotherms were not affected by heating below 150°, the temperature of preparation of the adsorbent.

Isobars for Hydrogen.—The interrelationship between the two types of adsorption and solution is indicated clearly in the adsorption

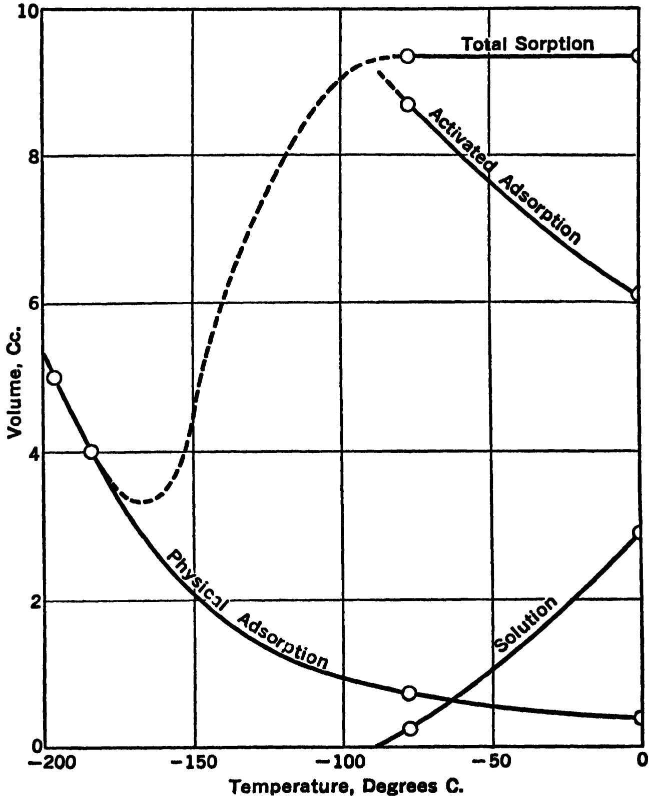

FIG. 33.—Isobars for hydrogen with copper at 500 mm.

isobars for hydrogen on copper adsorbent at 500 mm, as shown in Fig. 33 after Benton and White. The similarity between these curves and the isobars for manganous-chromic oxide, Fig. 29, is at once apparent. It is probable that experiments, at varying temperatures, similar to those carried out on copper, would reveal a solution process in certain temperature ranges with the oxide adsorbent also.

From a study of the rate of diffusion of hydrogen into copper at temperatures between 25° and 200°, Ward[29] found the rate at any temperature to be proportional to the amount of gas adsorbed on the surface and hence to be related to the gas pressure by the same form of equation as the adsorption process. Ward believes that grain boundary diffusion rather than lattice diffusion or solution takes place. From the variation in rate with temperature the activation energy of the diffusion process is calculated to be 14,000 g cal/mol. As already pointed out, Taylor contends that this activated diffusion to less accessible portions of the surface cannot be distinguished experimentally from activated adsorption. This is not the important thing from the standpoint of the catalytic action of surfaces; from this point of view, the important thing is whether the two activated processes are equally effective in rendering the molecules reactive. In this connection it should be pointed out that Taylor believes the activated adsorption of hydrogen to involve a resolution into atoms whereas Ward considers it altogether improbable that the diffusing molecules are split into atoms.

Nickel

Adsorption of Hydrogen.—The adsorption of hydrogen on nickel at various temperatures between 25° and 305° and pressures between 0 and 1 atmosphere was investigated by Gauger and Taylor,[30] who found that the adsorption reached a constant value at relatively low pressures and that this constant value decreased as the temperature was raised. Terwen[31] showed from Gauger and Taylor's data that at higher temperatures the amounts adsorbed approached asymptotically a value half that at lower temperatures and concluded that the adsorption occurs as atoms at the higher temperature and as molecules at the lower. Nikitin[32] measured the adsorption at −185°, 19°, and 336° and found less adsorbed at −185° than at 19°. Benton and White[33] confirmed and extended the observations in adsorption studies between −210° and 110°. It was found that at a given pressure the adsorption is relatively large at the lowest temperature, decreasing to a minimum at −200° to −175° depending on the pressure, then rising to a maximum in the neighborhood of −100°,

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[29] Proc. Roy. Soc. (London) **133A**, 506, 522 (1931); Trans. Faraday Soc., **28**, 399 (1932).

[30] J. Am. Chem. Soc., **45**, 920 (1923).

[31] Chem. Weekblad, **21**, 386 (1924).

[32] J. Russ. Phys.-Chem. Soc., **58**, 1081 (1926).

[33] J. Am. Chem. Soc., **52**, 2325 (1930).

and finally falling off once more at higher temperatures. This is well illustrated by the adsorption isobars at 200 mm, shown in Fig. 34. Here, again, along the low-temperature isobar the adsorption is chiefly of the van der Waals type; along the higher isobar, activated adsorption probably accompanied by more or less solution predominates; and between the two is a range of pseudo-equilibrium values. The isobars at 600 mm are similar except that between −110° and 0° the curve is flat, indicating the formation of a completely saturated single layer of adsorbed gas.

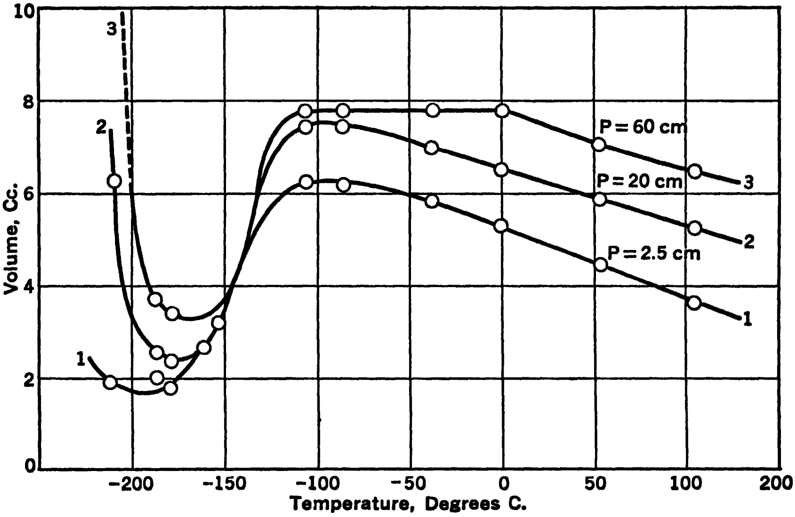

Fig. 34.—Isobars for hydrogen with nickel at 200 mm.

The isotherms in the region of liquid-air temperatures exhibit discontinuities similar to those observed with copper.

Platinum

The platinum metals have been used as adsorbents in the form of foil, "black," "sponge," and sol. In general, the amount of adsorption is determined by the extent of surface; hence the adsorption capacity of the several forms is in the order: sol > black > sponge > foil.

Adsorption by Platinum Foil.—Langmuir[34] showed that a plane surface of platinum takes up no hydrogen even at −180° until after the surface has been activated by heating to 300° in a mixture of

[34] J. Am. Chem. Soc., 40, 1361 (1918).

oxygen and hydrogen at low pressure. It will then adsorb the gas only in the small amounts corresponding to a monomolecular layer on the relatively small surface exposed. Carbon monoxide and oxygen are adsorbed very tenaciously, the maximum amount corresponding to a monomolecular layer. The oxygen is removed neither by heat nor by pumping, but a part of the carbon monoxide is removed by heating to 300°. The adsorption of carbon monoxide and oxygen is a typical case of primary adsorption accompanied by a very large heat effect. Water is reversibly adsorbed on a platinum surface giving a film many molecules thick.[35]

Schirmann[36] showed that metals are rendered porous and given a high adsorption capacity by repeated igniting and cooling of filaments, which loosen up the microcrystalline structure, and by removing adsorbed gases by evacuation or ion bombardment. Filaments of platinum, palladium, and gold treated in this way were found to adsorb 100 times the metal volume of each of the elements: argon, neon, helium, and nitrogen; and 1500 volumes of hydrogen. It is probable that the first four elements are held in the fine porous structure largely by adsorption on the surface, whereas the hydrogen is in part dissolved. Ordinarily, platinum foil dissolves less than 0.01 volume of hydrogen for 1 volume of platinum.[37]

Adsorption by Platinum Black and Sponge.—Unit volume of platinum sponge was found by Taylor and Burns[38] to adsorb 4.05 volumes hydrogen, 0.20 volume carbon monoxide, and 1.9 volumes oxygen as compared with 6.85 volumes hydrogen, 18.0 volumes carbon monoxide, and 26.5 volumes oxygen by platinum black. Using special precautions in the preparation of the black and in the manipulations, Benton[39] found that 36.7 volumes of hydrogen, 37.8 volumes of carbon monoxide, and 20.4 volumes of oxygen were adsorbed by 1 volume of the black at 0° and 1 atmosphere. Since the adsorption of hydrogen and carbon monoxide remains unchanged with higher temperatures and the oxygen value increases, it was assumed that at some temperature the adsorption of all three would be equal and would correspond to a monomolecular film over the very much

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[35] Ihmori: Ann. phys. chem., (2) **31**, 1006 (1887); McHaffie and Lenher: J. Chem. Soc., **127**, 1559 (1925); Stremberg: Chem. Abstracts, **24**, 4441 (1930).

[36] Physik. Z., **30**, 876 (1929).

[37] Sieverts and Jurisch: Ber., **45**, 221 (1912); Sieverts and Brüning: Z. anorg. Chem., **201**, 142 (1931).

[38] J. Am. Chem. Soc., **43**, 1273 (1921).

[39] J. Am. Chem. Soc., **48**, 1850 (1926).

extended surface. Pollard,[40] using a more active or more highly dispersed black supported on asbestos, observed an adsorption of 160 volumes of hydrogen and 300 volumes of carbon monoxide by 1 volume of platinum black at 0° and 760 mm.[41] The more strongly adsorbed carbon monoxide added in relatively small amounts displaced adsorbed hydrogen from the surface, a behavior which accounts for the poisoning action of carbon monoxide toward platinum in certain catalytic hydrogenations (see page 231).

Müller and Schwabe[42] found that 760 volumes of hydrogen were taken up by 1 volume of platinum formed by reducing the oxide with hydrogen at room temperature and absorbing the resulting water with phosphorus pentoxide. From 50 to 70% of the hydrogen was not given up on evacuation at 20°. Sieverts and Brüning[43] observed a similar behavior with platinum blacks formed by reduction with sodium formate and with finely divided magnesium. For example, with one adsorbent, 36.4% of the hydrogen adsorbed at 200° was not removed by evacuating over night at this temperature; 27.8% was retained at 140°; 35.8% at 80°; and 21.2% at 20°. The variation in the amount of loosely held hydrogen with pressure at temperatures ranging from −40° to 200° can be represented by the Freundlich equation, $A = x/m = kp^{1/n}$, in which the value of $1/n$ is 0.12. It is probable that the hydrogen which is not removed by evacuation is held chiefly by chemical or activated adsorption while the reversibly bound hydrogen is retained chiefly by physical or van der Waals' forces.

Shiels[44] showed that the adsorption of sulfur dioxide by platinum black between 0 and 40 mm pressure is a reversible process that can be represented by Langmuir's adsorption equation. Later[45] he found that as much as 84 volumes of sulfur dioxide under standard conditions was adsorbed per volume of platinum at 174 mm pressure, and the adsorption was not reversible. The difference in behavior with the two samples of black must be due to some variation in the heat treatment or purity of the preparations.

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[40] J. Phys. Chem., **27**, 356 (1923).

[41] *Cf.* Mond, Ramsay, and Shields: Phil. Trans., **186A**, 675 (1895); Gutbier and Maisch: Ber., **52**, 1368 (1919).

[42] Z. Elektrochem., **35**, 165 (1929); Z. physik. Chem., **A154**, 143 (1931).

[43] Z. anorg. Chem., **201**, 122 (1931).

[44] J. Phys. Chem., **33**, 1167 (1929).

[45] Shiels: J. Phys. Chem., **33**, 1175 (1929); *cf.* Pollard: **27**, 356 (1923); Mond, Ramsay, and Shields: Z. Physik. Chem., **25**, 667 (1898).

A platinum sol prepared by Paal's method was found to adsorb[46] nearly 750 volumes of hydrogen per unit volume of platinum. A portion of the adsorbed hydrogen was displaced by shaking with metallic mercury, giving a platinum-mercury-hydrogen hydrosol.

Palladium

Sorption by Foil.—Palladium takes up hydrogen much more strongly than platinum. Thus Graham[47] allowed heated palladium foil to cool in hydrogen and found that 500–900 volumes were taken up by unit volume of the metal. Tamman and Schneider[48] showed the importance of the preliminary thermal treatment on the rate of adsorption. This was most rapid if the metal was heated to 400°, the rate decreasing if a higher temperature was used. This behavior was correlated with the changes in crystal orientation on heating the foil. At temperatures up to 300°, the surface planes were all dodecahedral; at 400° there was apparently a maximum of icositetrahedron planes on the surface. Hence it was concluded that the maximum rate of adsorption occurred on the latter planes. A similar behavior was observed with iron foil.

Thoma[49] found that at room temperature a palladium wire took up but three times its volume of hydrogen, but the same wire sorbed[50] nearly 900 volumes of hydrogen when the wire was made the cathode at which the gas was liberated electrolytically. It is possible that the surface of the wire was "poisoned" by some adsorbed impurity which was removed by the electrolytic process. Thus Berliner[51] showed that a pure palladium foil sorbed 860 volumes of hydrogen, but if the foil was allowed to stand in a vacuum for an hour or in the air for 2 hours, it took up practically no hydrogen. The disturbing factor was possibly a trace of grease on the surface. Platinum foil behaved the same way. The power of the metals to take up hydrogen is diminished greatly by certain substances, notably hydrogen sulfide and lead salts.[52]

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[46] Paal and Auerswald: Ber., **60**, 1648 (1927).

[47] Proc. Roy. Soc. (London) **15**, 223 (1867); **16**, 422 (1868); **17**, 212, 500 (1869).

[48] Z. anorg. Chem., **172**, 43 (1928); Samson-Himmelstjerna: **186**, 337 (1930).

[49] Z. physik. Chem., **3**, 69 (1889).

[50] The term suggested by McBain to include both adsorption and absorption or solution.

[51] Wied. Ann., **35**, 803 (1888).

[52] Maxted: J. Chem. Soc., **115**, 1050 (1919); **117**, 1280, 1501 (1920); **119**, 1281 (1921).

Sorption by Black.—Mond, Ramsay, and Shields[53] showed that palladium black sorbs between 875 and 890 volumes of hydrogen and that palladium wire and sponge take up a similar amount. Sieverts[54] likewise claimed that the amount of hydrogen sorbed is independent of the superficial area of the metal and concluded that the phenomenon is simply a case of solution. This cannot be the whole truth, since colloidal palladium will take up almost 3000 volumes of hydrogen. Moreover, amorphous or submicroscopically crystalline palladium takes up more hydrogen than the ordinary crystalline variety, especially at low temperature.[55]

At constant temperature the amount of gas taken up is proportional to the square root of the pressure. With rising temperature the amount sorbed falls off rapidly to 600°, then slowly to 800° and above. Even at red heat the metal still sorbs large quantities of the gas if the pressure is raised sufficiently. Of the gas taken up, 92–98% is given up again in vacuum at room temperature.

To account for the large amount of hydrogen absorbed, Troost and Hautefeuille[56] claimed that a definite compound, Pd_2H, is formed. Pressure-composition diagrams obtained by Hoitsema[57] indicate, however, that the system is isothermally univariant throughout, and that, therefore, a compound Pd_2H is not formed. This conclusion was pretty generally accepted until Gillespie and Hall[58] showed that the isotherms of Hoitsema were not true equilibrium lines. It was found possible to bring the system to equilibrium by removing an excess of hydrogen from the gas phase producing a deficit; thereafter, heating the system a short time to about 360°; and finally, restoring the original pressure. Once the system was brought to equilibrium in this way it was possible to drive off the hydrogen by short heating to 360° and to return it once more to the solid reversibly, although it was not possible by isothermal operation to remove hydrogen and replace it with fresh hydrogen.

Using the above procedure the isotherms were determined at 0°,[59]

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[53] Phil. Trans., **186A**, 657 (1895); **190A**, 129 (1897); **191A**, 105 (1898).

[54] Z. physik. Chem., **88**, 451 (1914).

[55] Holt, Edgar, and Firth: Z. physik. Chem., **82**, 513 (1913); Andrew and Holt: Proc. Roy. Soc. (London) **89A**, 170 (1913); Holt: **90A**, 226 (1914); Firth: J. Chem. Soc., **117**, 171 (1920).

[56] Ann. chim. phys., (5) **2**, 279 (1874).

[57] Z. physik. Chem., **17**, 25 (1895); *cf.* Sieverts: **88**, 451 (1918).

[58] J. Am. Chem. Soc., **48**, 1207 (1926); Gillespie and Ambrose: J. Phys. Chem., **35**, 3105 (1931); *cf.* Ubbelohde: Trans. Faraday Soc., **28**, 275, 284 (1932).

[59] *Cf., also,* Gillespie and Perry: J. Phys. Chem., **25**, 3367 (1931).

30°, 80°, 160°, and 180°. The results are shown in Fig. 35. It will be noted that the curves consist of three parts, an ascending portion which passes fairly sharply into a horizontal portion which ends sharply and is succeeded by a rapidly ascending curve. The solid circles and the broken lines show the composition of the coexistent solid phases as functions of the pressure. These results show the presence of two solid solutions, the saturated solution richer in hydrogen having the composition Pd_2H at 80°, 160°, and 180°, but containing a progressively greater excess of hydrogen at lower temperatures.

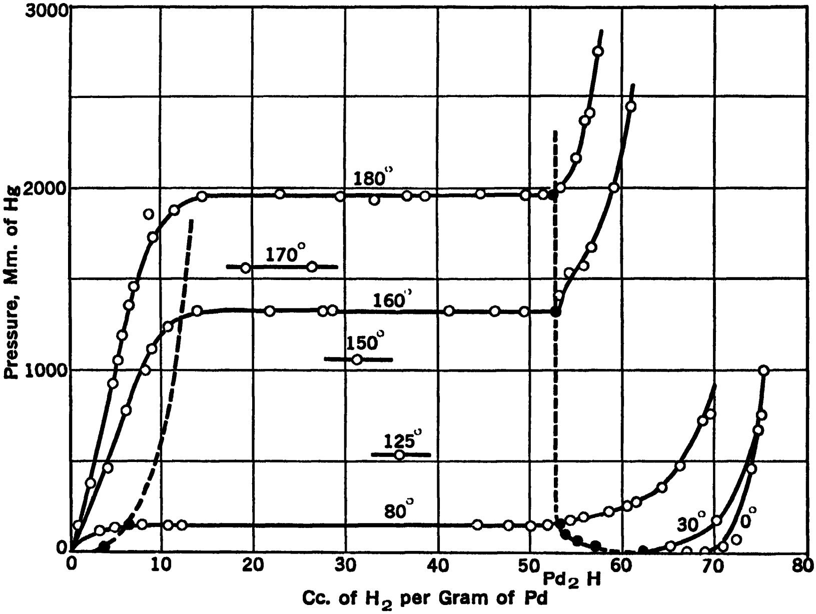

FIG. 35.—Isotherms for hydrogen with palladium. The solid circles and the broken lines represent compositions of the coexistent solid phases as functions of the pressure.

This has been confirmed by x-ray studies of Linde and Borelius[60] at 100°, 150°, and 200°.

Lambert and Gates[61] likewise obtained pressure-composition curves both on adding hydrogen to and withdrawing it from palladium. They found that the two curves are different, but that, in both cases, the most stable pressure corresponds to 0.5 atomic weight of hydrogen

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[60] Ann. Physik, **84**, 747 (1927).

[61] Proc. Roy. Soc. (London) **108A**, 456 (1925).

to 1 atomic weight of palladium, in other words to the compound Pd_2H. Tamman[62] insists, however, that no true compound of the atoms is formed since the heat of absorption is so great that if a compound were formed it would be stable instead of so instable that it decomposes in a vacuum at ordinary temperature. He prefers to regard the alleged compound as molecules of hydrogen held loosely to the metal atoms of the lattice. He therefore formulates the composition corresponding to Pd_2H as $Pd_4(H_2)$. Tamman discusses the similarities and differences between the taking up of hydrogen by palladium and that of nitrogen by chromium.

The specific gravity of palladium containing hydrogen is less than that of the metal, hence expansion takes place during the taking up of the gas. The electrical conductivity decreases with the amount of hydrogen absorbed up to 40 volumes, then asymptotically up to 600 volumes, and then proportionately once more. This break in the rate of decrease of conductivity indicates the formation of a compound, probably Pd_2H.[63]

From what is now known of the tendency of finely divided substances to adsorb gases, it is obvious that any mechanism of the taking up of hydrogen by palladium which leaves out the effect of adsorption forces cannot be complete. Indeed, the rate of sorption of the gas at a given temperature falls off in proportion to the amount of gas already held by the metal. This indicates that the process involves first an adsorption on the surface followed by slow diffusion from the adsorption layer into the mass of the metal.[64] The suggestion that the metal exists in two allotropic forms which take up the gas at different rates[65] has not been established experimentally.

Palladium is used in gas analysis to remove hydrogen from gas mixtures. It is usually heated to 100° because equilibrium is reached more rapidly at this temperature than at room temperature. Pure hydrogen may be obtained by liberating the gas electrolytically at a palladium cathode from which it is subsequently regained by gentle heating in vacuum.[66]

Like platinum, palladium adsorbs gases other than hydrogen, notably carbon dioxide[67] and monoxide.[68] Taylor and McKinney[69]

[62] Z. anorg. Chem., **188**, 396 (1930).

[63] Wolf: Z. physik. Chem., **87**, 575 (1914).

[64] Holt, Edgar, and Firth: Z. physik. Chem., **82**, 513 (1913).

[65] Andrew and Holt: Proc. Roy. Soc. (London) **89A**, 170 (1913).

[66] Hulubei: Compt. rend., **191**, 134 (1930).

[67] Holt: Proc. Roy. Soc. (London) **91A**, 148 (1915).

[68] Von Hemptinne: Z. physik. Chem., **27**, 429 (1898).

[69] J. Am. Chem. Soc., **53**, 3604 (1931).

have determined the adsorption isotherms for carbon monoxide at various temperatures between −187° and 280°. From these curves the isobaric adsorption at 150 mm was obtained as shown in Fig. 36. Once more, the results indicate the existence of a low- and a high-temperature type of adsorption. Since the latter cannot be separated from the rapid normal adsorption, it is not possible to calculate the activation energy of the high-temperature process from velocity data. In view of the rapidity of the activated adsorption between −78° and 0°, the energy of activation on the most active areas is probably of the order of a few thousand calories per mol. The heat of the activated adsorption on the less active portions of the surface was calculated to be 15,000 cal/mol.

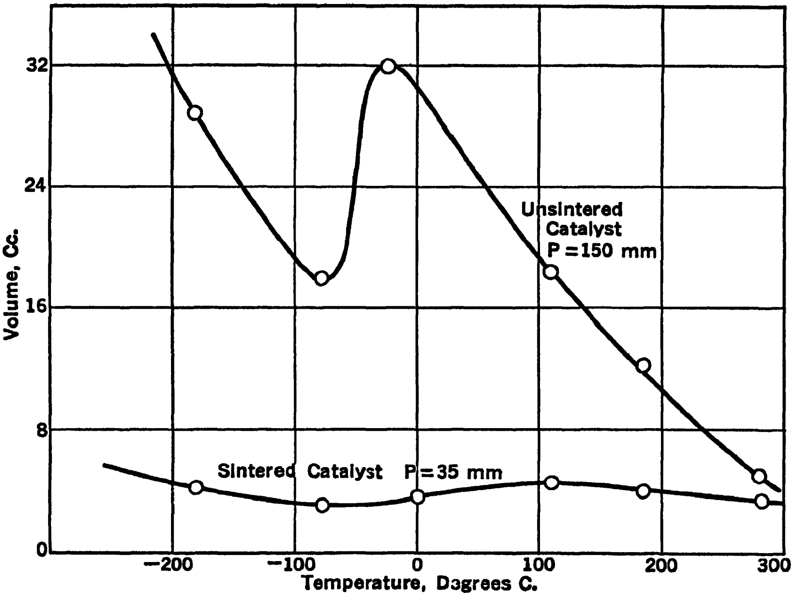

Fig. 36.—Isobars for carbon monoxide with palladium catalysts.

Ruthenium, Rhodium, Iridium, and Osmium

Of the other elements of the platinum family, iridium and rhodium take up certain gases quite strongly. Thus, if iridium foil is subjected to cathodic pulverization in a vacuum, the surface becomes dull and brittle, and it will take up 800 times its own volume of hydrogen at ordinary temperature. Colloidal rhodium will take up more than 2500 times its volume of hydrogen and 350 times its volume of carbon monoxide at ordinary temperatures and 1800 times at 60°.[70] None of the hydrogen adsorbed by rhodium, ruthenium, iridium, and osmium, formed by reduction of the respective oxides with hydrogen at room temperatures, is given up in vacuum; palladium formed under similar conditions will give up as much as 97.4% of the sorbed gas.[71]

Colloidal rhodium and palladium adsorb acetylene in large quantities, the process taking place with a steadily diminishing rate owing to the formation of condensation or polymerization products which envelop the metal particle. Colloidal solutions of iridium and osmium do not adsorb acetylene.[72]

[70] Zenghelis and Papaconstantinou: Compt rend., **170**, 1058 (1920).

[71] Müller and Schwabe: Z. physik. Chem., **A154**, 143 (1931).

[72] Paal and Hohenegger: Ber., **46**, 128 (1913); Paal and Schwarz: **48**, 1195 (1915).

CHAPTER X

COLLOIDAL METALS AS CONTACT CATALYSTS

Metals, especially those of the eighth group of the periodic table, are among the most important contact catalysts. Thus platinum is used in the Contact Sulfuric Acid Process, iron in the Haber Ammonia Process, platinum in the synthesis of nitric acid from ammonia, nickel and cobalt in hydrogenation processes such as the hydrogenation of liquid unsaturated fatty oils into solid fats, and copper and platinum in dehydrogenation processes such as the preparation of formaldehyde from methanol. In contact catalysis the reactions take place or are initiated at the surface of contact between the reactants and the catalytic agent. Accordingly in many cases it is essential or advantageous to use the catalyst in the colloidal state in which there is the maximum extent of surface for unit mass of catalyst. Thus platinum black is employed in the synthesis of sulfur trioxide from sulfur dioxide and oxygen, colloidal nickel reduced from the oxide in the hydrogenation of oils, and a roughened activated platinum gauze in the Ostwald Nitric Acid Process.

The first portion of this chapter will be concerned with the general theory of catalytic action especially as it is applicable to metallic surfaces, and the last portion with a consideration of a few applications of metal catalyst to processes that are especially important from a technical or theoretical standpoint.

THEORY OF CONTACT CATALYSIS

Specific Adsorption and Catalytic Activity

Most contact catalytic processes take place at a solid-fluid interface, and of these the larger proportion are at a solid-gas interface. In general, adsorption of one or more of the reactants is a necessary prerequisite for catalytic change. Langmuir[1] was the first to recognize clearly that catalytic activity results from primary or activated adsorption such as is frequently exhibited by active metallic adsor-

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[1] J. Am. Chem. Soc., 38, 1145, 2221 (1916).

bents, and not to secondary or van der Waals' adsorption (see page 201). The increased concentration of the reactants as a result of adsorption is relatively unimportant as a rule. It is known that a mixture of oxygen and hydrogen is quite stable even under a pressure of 2000 atmospheres, which indicates that the marked action of platinum in catalyzing the combination is not due primarily to increase in concentration resulting from adsorption. Moreover, oxygen and hydrogen are adsorbed strongly by both platinum and carbon, but the former is much more active than the latter in catalyzing the combination of the gases.

If catalytic activity results chiefly from primary adsorption, as seems probable, one would not, in general, expect to find a parallelism between the observed total adsorption values and the catalytic activity of the adsorbent. This is well illustrated by some observations of Benton[2] on the adsorption of carbon monoxide, carbon dioxide, and oxygen by a number of oxide catalysts. A large difference was noted between the ratios of adsorption of carbon monoxide to carbon dioxide and carbon monoxide to oxygen at 0° by the different catalysts. Assuming that in the case of silica the adsorption is wholly of the secondary type, the ratios furnish a means of distinguishing between the primary and secondary adsorptions. In Table XXXIII the several catalysts are arranged in the order of: I, total adsorption of carbon monoxide; II, secondary adsorption, calculated; III, primary adsorption; IV, observed catalytic activity in the combination of carbon monoxide and oxygen.[3] The tabulation

TABLE XXXIII

COMPARISON OF ADSORPTION AND CATALYTIC ACTIVITY

	Order of catalysts
I. Total adsorption of CO	Co_2O_3 > hopcalite > SiO_2 > MnO_2 > CuO > Fe_2O_3 > V_2O_5
II. Secondary adsorption of CO (calculated).. ..	SiO_2 > Fe_2O_3 > MnO_2 > Co_2O_3 > hopcalite > CuO > V_2O_5
III. Primary adsorption of CO........	Co_2O_3 > hopcalite > CuO > MnO_2 > Fe_2O_3 > V_2O_5 > SiO_2
IV. Catalytic activity......	Co_2O_3 > hopcalite > CuO > MnO_2 > Fe_2O_3 > V_2O_5 > SiO_2

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[2] J. Am. Chem. Soc., **45**, 887, 900 (1923).

[3] Rideal and Taylor: Analyst, **44**, 89 (1919); Rideal: J. Chem. Soc., **115**, 993 (1919); Lamb, Bray, and Frazer: Ind. Eng. Chem., **12**, 213 (1920); Merrill and Scalione: J. Am. Chem. Soc., **43**, 1982 (1921).

shows the absence of any parallelism between total or secondary adsorption and catalytic activity;[4] on the other hand, the order for the primary adsorption of carbon monoxide and the catalytic activity of the oxides is the same.

The specificity of adsorption by metallic catalysts is shown in a striking way by some observations of Taylor and Burns.[5] Thus the ratios of adsorption of CO to CO_2 at 25° for several hydrogenation catalysts are: Cu = 10.0; Co = 3.6; Fe = 2.8; Pd = 288; and Pt black = 10.6. Similarly, the ratios of adsorption of CO to H_2 are: Ni = 87 at 184°; Pt black = 3.3 at 100°; and Cu = 12. At oxide catalysts the adsorption ratios of CO to H_2 at −79° are: hopcalite = 33; MnO_2 = 100; CuO = 34; Co_2O_3 = 19; Fe_2O_3 = 35; V_2O_5 = 17; SiO_2 = 28. The much stronger adsorption of carbon monoxide than of hydrogen by the oxide catalysts accounts for the preferential catalytic combination at oxide catalysts of carbon monoxide and oxygen in the presence of a large excess of hydrogen. With metals, this preferential combination is less pronounced, the hydrogen being consumed with the carbon monoxide especially at the surface of nickel and platinum. With copper, on the other hand, the adsorption ratio of carbon monoxide to hydrogen is larger, and a fair preferential combustion of carbon monoxide may be attained.

Pease[6] investigated the combination of ethylene and hydrogen at the surface of a copper catalyst and found that high catalytic activity was paralleled by high adsorption capacity for both gases. Since the adsorption values measured both primary and secondary adsorption, there was no strict proportionality between the two. The sintering action of high temperatures reduced the catalytic activity proportionately more than the adsorption capacity. Taylor and Kistiakowsky[7] showed that two methanol catalysts, zinc oxide and zinc oxide-chromic oxide, exhibit an adsorption capacity for both hydrogen and carbon monoxide that is greater than that of metal catalysts. Moreover, the adsorptive capacity of the mixed oxides is greater than that of zinc oxide alone, and the catalytic activity of the former is the higher.

As intimated above, the method of preparation and subsequent heat treatment of a catalyst will influence its adsorption capacity and catalytic activity though not in direct proportion. Thus, 3 samples

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[4] *Cf.*, *also*, Sabalitschka and Moses: Ber., **60**, 786 (1927); Griffin: J. Am. Chem. Soc., **49**, 2136 (1927).

[5] J. Am. Chem. Soc., **43**, 1273 (1921).

[6] J. Am. Chem. Soc., **45**, 1196 (1923).

[7] J. Am. Chem. Soc., **49**, 2474 (1927).

of nickel oxide reduced at 300°, for varying periods from 12 hours to 2 days, adsorbed 47, 70, and 130 cc, respectively, of hydrogen per 100 g of nickel at 25° and 760 mm.[8]

Mechanism of Activation by Adsorption

Contact catalysis in heterogeneous systems results from activation of one or more of the reactants as a result of oriented adsorption[9] or, possibly, multiple adsorption.[10] Activation by oriented adsorption consists in an alteration of the configuration of the molecule or the opening up of primary valence bonds or secondary or residual valence bonds as a result of the primary valence forces on the surface of the catalyst. Since adsorption in this way does not usually lead to great molecular deformation, Burk and Balandin assume that activation results from suitable multiple adsorption, that is, the independent adsorption of the two ends of a molecule by active points on the catalytic surface. If these points are farther apart than the normal length of the molecule, sufficiently strong adsorption will cause stretching and distortion, which are assumed to increase molecular reactivity.

Activation of Hydrogen.—Since monatomic hydrogen produced in various ways will reduce the same substances that catalytically active hydrogen will reduce, it is assumed that activated adsorption of hydrogen results in the formation of electrically neutral hydrogen atoms. Taylor[11] is of the opinion that activation by adsorption of diatomic gases, generally, may consist in resolution into atoms and that the adsorbed atoms are the active ones.[12] Burk, on the other hand, thinks that hydrogen molecules stretched as a result of multiple adsorption may be more active than hydrogen atoms on the surface, since the bond catalyst-hydrogen atom would be stronger than the bond catalyst-H–H; hence, the former would require activation for the atomic hydrogen to become reactive. From Burk's point of view, an optimum degree of stretching of hydrogen would impart greater reactivity than complete resolution into atoms. Kistiakowsky[13] believed that he demonstrated the presence of atomic nitrogen at metallic surfaces, but Burk points out, very properly, that even

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[8] Taylor: Bogue's "Colloidal Behavior," **1**, 283 (1924).

[9] Langmuir: J. Am. Chem. Soc., **35**, 105 (1913); **38**, 2270 (1916).

[10] Burk: J. Phys. Chem., **30**, 1134 (1926); **32**, 1601 (1928); Balandin: Z. physik. Chem., **B2**, 289 (1929).

[11] Proc. Roy. Soc. (London) **113A**, 77 (1927); J. Am. Chem. Soc., **53**, 579 (1931).

[12] *Cf., however,* Herzfeld: J. Am. Chem. Soc., **51**, 2608 (1929).

[13] J. Phys. Chem., **30**, 1356 (1926).

if such were the case it would not follow that all the nitrogen on the surface is atomic or that the adsorbed atomic nitrogen is the more reactive. Be that as it may, there is no doubt that active hydrogen which is atomic is formed by passing hydrogen containing small amounts of oxygen over platinum at temperatures below 120°.[14] This active atomic hydrogen is instable but persists for a distance of 5 cm from the activating surface, reducing such substances as cupric oxide and the unsaturated group in olive oil. No such effect is obtained if the hydrogen is free from oxygen, indicating that the atomic hydrogen results from a reaction of hydrogen with oxygen at the platinum surface.

As already noted, oxygen is strongly and in part irreversibly adsorbed by platinum (see page 205). Assuming this to be held as atomic oxygen on the surface *S*, the following reactions yielding surface hydrogen atoms to the gas phase are suggested:[15]

$$S(\mathrm{O}) + \mathrm{H_2} \rightarrow S(\mathrm{OH}) + \mathrm{H}\uparrow$$

and

$$S(\mathrm{OH}) + \mathrm{H} \rightarrow S(\mathrm{OH_2}) + \mathrm{H}\uparrow$$

Since both these reactions are exothermic in the gas phase, the above mechanism is a plausible one not only for the formation of active hydrogen by surface action but also for the effect which surfaces may exert in initiating chains of reactions in oxygen-hydrogen mixtures.[15] On the other hand, oxygen must not be essential for the formation of hydrogen atoms on the surface of platinum at low temperatures, since, if such were the case, it is not obvious how the hydrogen electrode works.[16]

In considering the mechanism of activation of hydrogen, it is necessary to take into account the recently discovered fact that there are two isomeric modifications of molecular hydrogen, ortho and para,[17] which exist in ordinary hydrogen in the ratio of 3 : 1. The difference between the molecules is that in one the nuclei of the atoms are rotating in the same direction and in the other the nuclei are rotating in the opposite direction, thereby giving rise to marked difference in the spectrum, specific heat, thermal conductance, etc., of the two forms. Almost pure para hydrogen can be prepared by

[14] Mitchell and Marshall: J. Chem. Soc., **123**, 2448 (1923).

[15] Taylor: Chem. Rev., **9**, 1 (1931).

[16] *Cf.* Bancroft: "Applied Colloid Chemistry" (1932).

[17] Bonhoeffer and Harteck: Naturwissenschaften, **17**, 182, 321 (1929).

the adsorption on a charcoal catalyst at the temperature of liquid hydrogen. The equilibrium concentration of 50% para hydrogen can be obtained at liquid-air temperatures in contact with an active nickel catalyst as readily as with charcoal.[18] Mixtures containing an excess of para hydrogen above the 3 : 1 ratio are fairly stable under ordinary conditions, but the para is readily converted into the ortho in contact with certain metal and oxide catalysts. From the investigations of this para-ortho conversion by a number of authors,[19] it has been concluded that hydrogen becomes activated during its conversion from the para to the ortho form on metallic surfaces. Bonhoeffer and Farkas consider the activation at tungsten and platinum surfaces to consist in a surface dissociation into adsorbed hydrogen atoms.

The view entertained by some,[20] that the function of the catalyst is always to ionize the adsorbed gases, tacitly assumes that adsorption should necessarily lead to ionization and that ionization is a necessary preliminary state for chemical reactions in general. This point of view seems to be extreme. It is, of course, well known that the thermal emission of electrons and ions takes place at elevated temperatures, but these phenomena disappear at ordinary temperatures except when an enormous field is applied to the surface. There is no experimental justification for assuming that all catalytic reactions which take place at room temperature are preceded by ionization of the adsorbed molecules.

Specificity of Catalytic Action.—Bancroft[21] points out that, theoretically, oriented adsorption of ethyl acetate might lead to three different reactions depending on whether the ester is attached temporarily to the methyl group by one adsorbent, to the ethyl group by another, or to the carboxyl group by a third. Sabatier[22] claims that the action of alumina, titania, and thoria on ethyl acetate does give rise to three different sets of products. It is also known that ethyl

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[18] Taylor and Sherman: J. Am. Chem. Soc., **53**, 1614 (1931); Trans. Faraday Soc., **28**, 247 (1932).

[19] Bonhoeffer and Harteck: Z. physik. Chem., **B4**, 113; **B5**, 292 (1929); Farkas: **B10**, 419 (1930); **B14**, 371 (1931); Bonhoeffer and Farkas: **B12**, 231 (1931); Trans. Faraday Soc., **28**, 242 (1932); Taylor and Sherman: J. Am. Chem. Soc., **53**, 1614 (1931); Sherman and Eyring: **54**, 2661 (1932); Emmett and Harkness: **54**, 403 (1932).

[20] Bone: Proc. Roy. Soc. (London) **112A**, 477 (1926); Brewer: Phys. Rev., (2) **26**, 633 (1925); Proc. Nat. Acad. Sci., **12**, 560 (1926).

[21] "Applied Colloid Chemistry," 2nd ed., 46 (1926).

[22] Sabatier and Mailhe: Compt. rend., **152**, 669 (1911).

alcohol[23] decomposes in different ways at a nickel and an alumina catalyst:

$$C_2H_5OH \xrightarrow{Ni} CH_3CHO + H_2$$

$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O$$

A similar condition obtains with formic acid,[24] which undergoes catalytic decomposition in two different ways:

$$HCOOH \xrightarrow{Ni} H_2 + CO_2$$

$$HCOOH \xrightarrow{TiO_2} H_2O + CO$$

Adkins[25] showed that, in the case of oxide catalysts, the method of preparation is equally if not more important than the particular metallic element in the oxide. Thus, by changing the method of preparing alumina, Adkins and Nissen[26] changed the relative amounts of decomposition of formic acid into carbon dioxide and hydrogen, and carbon monoxide and water. The conclusion is reached that the spacing of the surface atoms[27] affects the reactivity of the adsorbed molecules, but Adkins is not clear as to why this should be. Burk[28] points out that there is nothing mysterious about this behavior in the light of a multiple adsorption mechanism of activation which would predict different degrees of activation with the probable formation of different products, as a result of variation in the number and spacing of the points of adsorption. Taylor,[29] on the other hand, considers a catalytic oxide to be a dual catalyst consisting of metal ion and oxygen ion each having its own specific catalytic activity. It is believed that hydrogenation and dehydrogenation processes take place chiefly on the metal ion, and hydration and dehydration

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[23] Sabatier-Reid: "Catalysis in Organic Chemistry," 252 (1922).

[24] Sabatier and Mailhe: Compt. rend., **152**, 1212 (1911).

[25] Adkins and Krause: J. Am. Chem. Soc., **44**, 385; Adkins: 2175 (1922); Adkins and Nissen: **45**, 809 (1923).

[26] J. Am. Chem. Soc., **45**, 809 (1923); **46**, 130 (1924); Adkins and Lazier: **46**, 2291 (1924).

[27] *Cf.* Langmuir: Trans. Faraday Soc., **17**, 610 (1922).

[28] J. Phys. Chem., **30**, 1134 (1926).

[29] Colloid Symposium Monograph, **4**, 25 (1926); Z. Elektrochem., **35**, 542 (1929); Williamson and Taylor: J. Am. Chem. Soc., **53**, 3270 (1931).

processes on the oxide ion. If such is the case, the extent of two alternative changes, such as those noted above, will be determined by (1) the extent of adsorption of the reactants on the two ions, (2) the relative frequency of the two ions in the surface, and (3) the specific catalytic activity of the individual ions. These three factors will be influenced in turn by the degree of saturation of the lattice ions and the extent to which they are already covered by poisons such as salts, water, etc. Another possibility is that the reactants may be oriented or attached in different ways on the two ionic types in the lattice and that this accounts for the different modes of decomposition. It should be emphasized that these are merely hypotheses for which little direct experimental evidence is available.

Taylor[30] has recently given a more definite explanation of specific surface action in the catalytic decompositiion of alcohol, as a result of his observation that a parallelism exists between the capacity of surfaces to induce dehydrogenation or dehydration and the efficiency of such surfaces in promoting the recombination either of hydrogen atoms or of hydrogen atoms and hydroxyl radicals.[31] The final stage in the dehydration or dehydrogenation of an alcohol must be a combination of the atoms or radicals at the surface and the subsequent evaporation of the resulting hydrogen or water. The reverse of this process would be the initial stage in the activation by adsorption of hydrogen or water, assuming that the activation involves dissociation. From this point of view, as Taylor points out, it should be possible to associate activity in dehydrogenation at a given temperature with an activated adsorption at a somewhat lower temperature, since desorption will occur more slowly than the adsorption and hence will require a higher temperature to attain a given velocity. It is known that activation of hydrogen by adsorption on metals and certain oxides occurs at temperatures which would permit the dehydrogenation reactions to take place fairly rapidly in the neighborhood of 200°. With alumina, which acts almost exclusively as a dehydration catalyst at 200°, there should be no activating adsorption of hydrogen gas if the above reasoning is correct. As a matter of fact, Taylor[32] found that a precipitated alumina ignited at 400° showed no measurable adsorption of hydrogen below 400°. A slow adsorption was observed at 440° and a more rapid adsorption at 525°. From the velocity data the activation energy of the adsorption was calculated

[30] Chem. Rev., 9, 36 (1931).

[31] Taylor and Lavin: J. Am. Chem. Soc., 52, 1910 (1930).

[32] Z. physik. Chem., Bodenstein Festband, 475 (1931).

to be 28,000 calories. The adsorption was reversible, and no water was formed by reduction of the oxide. The observations indicate rather conclusively that dehydrogenation does not occur on alumina surfaces at temperatures around 200° which are normal for such decomposition, because, at such surfaces at such temperatures, there is no adsorption activation of hydrogen molecules to form atomic hydrogen or the reverse process of recombination of hydrogen atoms to molecular hydrogen.

Intermediate Compounds.—In certain cases, contact catalysis is accompanied by the formation of definite intermediate compounds, and Sabatier,[33] who has been an active worker in this field for 35 years, believes that the formation of intermediate compounds is a sufficient explanation of catalysis. In many catalytic processes, however, it seems altogether unlikely that any orthodox compounds could form as intermediate products, and in other cases it is not obvious why intermediate compounds which are theoretically possible should be so reactive. Intermediate compounds appear to form, *e.g.*, in the catalytic decomposition of hydrogen peroxide at a mercury surface;[34] when acetic acid is passed over heated barium carbonate;[35] and when carbon monoxide is oxidized in the presence of the mixed oxides of cobalt and nickel.[36] In the latter case it is assumed that the oxygen carrier oxidizes the carbon monoxide and is in turn reoxidized by the oxygen of the air. This seems questionable, however, since the rate of oxidation of carbon monoxide by the higher oxides is relatively slow. Bray claims that it is impossible to decide whether a molecule of oxygen at the surface of the catalyst actually changes some of a lower oxide to a higher (and the reverse change with carbon monoxide), or whether the oxygen is merely held on the surface in an active state ready to combine with carbon monoxide.

Poisoning of Catalysts

The term "poison" in contact catalysis is applied to anything which cuts down the velocity of a given catalytic reaction. Since the reaction takes place at the surface of the catalyst, a poison is anything that decreases the rate at which the substances reach the catalytic surface[37] or which prevents them from reaching it.[38] In general, any substance that is adsorbed more strongly than the re-

[33] Ind. Eng. Chem., **18**, 1105 (1926).

[34] *Cf., however*, Hedges and Myers: J. Chem. Soc., **125**, 1288 (1924).

[35] Squibb: J. Am. Chem. Soc., **17**, 187 (1895).

[36] Lamb, Bray, and Frazer: Ind. Eng. Chem., **12**, 217 (1920).

[37] Taylor: Trans. Am. Electrochem. Soc., **36**, 149 (1919).

[38] Bancroft: J. Phys. Chem., **21**, 734 (1917).

actants will cut down the adsorption of the latter and thereby slow down the reaction. Thirty-five years ago, Harbeck and Lunge[39] showed that carbon monoxide reduces almost to zero the catalytic activity of platinum on a mixture of ethylene and hydrogen. Taylor and Burns[40] and Pollard[41] showed that this is due to the cutting down of the adsorption of hydrogen by platinum black. Even when the pressure of carbon monoxide is only a few millimeters, the active surface is covered so completely that acetylene and hydrogen do not reach the surface and so are not activated. Pease and Stewart[42] investigated this phenomenon quantitatively with a copper catalyst. The results are summarized in Fig. 37. It will be noted that but 0.05 cc of carbon monoxide will reduce by 88% the activity of a

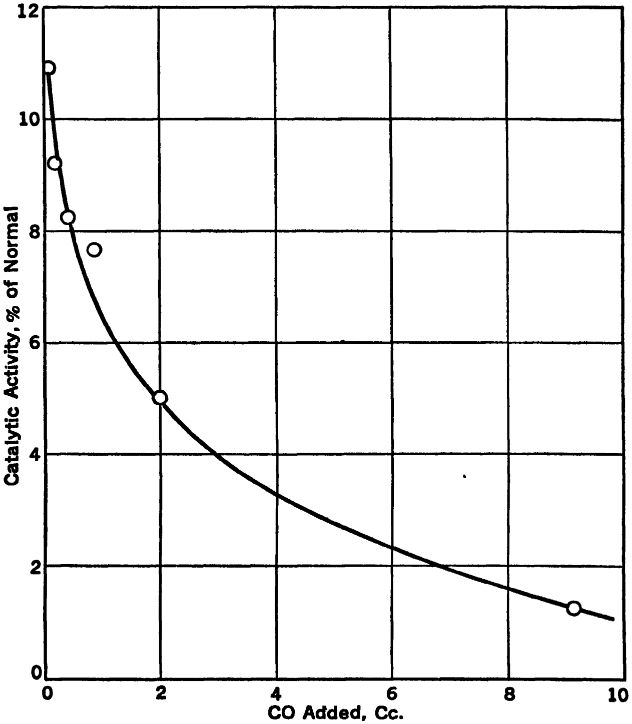

FIG. 37.—Effect of carbon monoxide on the catalytic activity of copper.

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[39] Z. anorg. Chem., 16, 50 (1898).

[40] J. Am. Chem. Soc., 43, 1285 (1921).

[41] J. Phys. Chem., 27, 356 (1923).

[42] J. Am. Chem. Soc., 47, 1235 (1925).

catalyst that adsorbs at less than 1 mm pressure, 1 cc of hydrogen, 2 cc of ethylene, and 5 cc of carbon monoxide. Pease[43] showed further that the vapor from 1 mm^3 of liquid mercury introduced into 100 g of reduced copper catalyst inhibits completely the reaction between ethylene and hydrogen at 0° and renders it very slow even at 100°. The mercury poisons by cutting down the adsorption of hydrogen rather than of ethylene. Measurements of the heat of adsorption of hydrogen on a copper surface poisoned by a small amount of oxygen indicate that the rôle of oxygen is to oxidize preferentially the most unsaturated surface atoms of the catalyst.[44]

The hydroxides of sulfur, selenium, tellurium, phosphorus, arsenic, and antimony were observed by Schönbein[45] to have a marked poisoning effect on the action of platinum with mixtures of air and hydrogen or ether. Ninety years ago it was not recognized that an adsorbed gas film could prevent the reactants from reaching the catalytic surface, and Schönbein assumed that the hydroxides decomposed and plated out a solid film on the catalyst. While this is not essential, Maxted[46] showed that, in the case of hydrogen sulfide, decomposition takes place with the evolution of hydrogen and the formation of a film of sulfur on the catalyst which prevents the adsorption of hydrogen. Within a certain concentration range, the adsorbing power and catalytic activity of the catalyst decreased linearly with increasing amounts of hydrogen sulfide.

Although the poisoning of catalysts is usually undesirable, Rosenmund and Zetsche[47] claim that partial poisoning may be utilized to advantage in increasing the yield of certain desired products. For example, practically no benzaldehyde is formed on treating a solution of benzoyl chloride in pure benzol with hydrogen in the presence of colloidal platinum; but a good yield of benzaldehyde is obtained from a solution in ordinary benzol containing thiophene. It is claimed that pure benzol poisons the platinum completely, but the presence of thiophene partially counteracts this poisoning action, giving a suitable surface for the benzaldehyde synthesis. The addition of other impurities to aromatic hydrocarbon solvents may likewise have a marked effect on reaction yields. Thus the addition of 1 mg

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[43] J. Am. Chem. Soc., **45**, 2299 (1924).

[44] Kistiakowsky: Proc. Nat. Acad. Sci., **13**, 1 (1927).

[45] J. prakt. Chem., (1) **29**, 238 (1843).

[46] J. Chem. Soc., **115**, 1050 (1919); **117**, 1501 (1920); **119**, 225, 1286 (1921); **121**, 1760 (1922); 2203 (1931).

[47] Ber., **54**, 425 (1921).

of thioquinanthrene to a solution of 2 g of benzoyl chloride in 10 cc of xylol, using 0.7 mg of palladium as catalyst, gives a 78% yield of benzaldehyde, and a like amount of sulfurized quinoline gives a 90% yield of benzaldehyde. The addition of pure quinolene, on the other hand, gives a zero yield of benzaldehyde since the reduction under these conditions continues to the benzyl alcohol stage.

In this connection, Adams[48] has shown that permanent poisons on the surface of catalysts may be employed to direct the catalysis.[49] For example, the addition of ferrous chloride to a platinum catalyst promotes (see page 236), the reduction of cinnamic acid to phenyl propyl alcohol. But if the platinum-iron catalyst is poisoned to a suitable degree with zinc salts, the product is cinnamyl alcohol. The efficiency of the latter process varies with the extent of poisoning by the zinc salts.

Autotoxic Catalysis.—If the reaction products are adsorbed so strongly on the active surface of the catalyst that the adsorption or rate of adsorption of the reactants is reduced, we have what is known as autotoxic catalysis. Thus the accumulation of sulfur trioxide on the platinum surface in the contact sulfuric acid process slows down the reaction by cutting down the adsorption of sulfur dioxide and oxygen by the catalyst.[50] Similarly, adsorbed water slows down the catalytic dehydration of ether[51] and of alcohol,[52] and adsorbed hydrogen the catalytic dehydrogenation of alcohol. Indeed, nickel and copper are essentially dehydration catalysts in the absence of hydrogen and hydrogenation catalysts in the presence of hydrogen. Hydrogen poisons a platinum wire for the catalytic decomposition of ammonia by the metal.[53]

The Nature of the Catalytic Surface

Non-uniformity of the Catalytic Surface.—A great deal of experimental data tend to show that the surface of a catalyst is not uniformly active. As Taylor[54] points out, this is indicated in the first instance by observations on adsorption. For example, Hurst and Rideal[55]

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[48] Carothers and Adams: J. Am. Chem. Soc., **45**, 1071 (1923); **46**, 1675 (1924); **47**, 1047 (1925); Tuley and Adams: **47**, 3061 (1925).

[49] *Cf.* Bancroft: "Applied Colloid Chemistry," 3rd ed., 54 (1932).

[50] Bodenstein and Fink: Z. physik. Chem., **60**, 1, 46 (1907).

[51] Ipatiew: Ber., **37**, 2996 (1904).

[52] Engelder: J. Phys. Chem., **21**, 676 (1917).

[53] Hinshelwood and Burk: J. Chem. Soc., **127**, 1105 (1923).

[54] "Fourth Rept. on Contact Catalysis," J. Phys. Chem., **30**, 145 (1926).

[55] J. Chem. Soc., **125**, 685, 694 (1924).

showed that the saturation capacity of a copper catalyst for carbon monoxide is 8.5 times as great as for hydrogen, and Maxted[56] found that mercury sols adsorb 3.5 times as many lead ions as mercury ions. If, at saturation, the surface is covered by a monomolecular layer of one substance, it is obvious that the surface is not covered by the second. One hypothesis is that the more strongly adsorbed substance is present in polymolecular layers, but it seems more reasonable to assume that the surface possesses variable adsorption capacity for different substances. This is indicated by the variation in the saturation ratio for adsorbed gases on different preparations of the same substances. Thus, as above noted, for the adsorption ratio of carbon monoxide to hydrogen on copper, Hurst and Rideal obtained the value 8.5 whereas Pease[57] got 2.86. Finally, the saturation ratio on the same preparation varies before and after heat treatment and before and after poisoning. Thus Pease showed that a copper catalyst poisoned with mercury changed the adsorption ratio of carbon monoxide to hydrogen from 2.86 to 19; heat treatment caused a change in the same direction.

Further indication of the non-uniform nature of the catalytic surface is furnished by a study of the action of poisons. Thus Pease and Stewart[42] found that adsorption of 0.03 cc of carbon monoxide, on a copper catalyst capable of adsorbing 1 cc of hydrogen at 1 mm pressure, reduces the rate of hydrogenation of ethylene by 90% and not by 3% as the extent of adsorption would indicate. Apparently all portions of the surface capable of adsorbing hydrogen are not equally effective in promoting catalytic hydrogenation; otherwise, the effect of the poison would be determined by the extent of surface it covers.

Although, in certain cases, only a part of the catalytic surface is active, in others practically the whole of the surface is active.[54] Since the former catalysts should be more sensitive to poisons than the latter, it follows that the activity of a catalyst may be suppressed in stages so that different reactions may be stopped successively by increasing amounts of a poison. An interesting illustration of this is given by Vavon and Husson.[58] They showed that the hydrogenation of propyl ketone by colloidal platinum was stopped by a limited amount of carbon bisulfide, but the poisoned catalyst would still catalyze the hydrogenation of piperonal and nitrobenzol. A further limited amount of carbon bisulfide suppressed the hydrogenation of

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[56] J. Chem. Soc., **127**, 73 (1925).

[57] J. Am. Chem. Soc., **44**, 2296 (1923).

[58] Compt. rend., **175**, 277 (1922).

piperonal but not of nitrobenzol; and finally, a large amount of the poison stopped the reaction with nitrobenzol. Also, Kubota and Yoshikawa[59] observed a similar phenomenon with nickel catalyst in the 3 reactions, hydrogenation of benzol, hydrogenation of ethylene, and reduction of nitro compounds. Progressive poisoning showed that only a very small fraction of the surface was active for the first reaction, a greater fraction for the second, and practically the whole of the surface for the third.

Theory of the Catalytic Surface.—From the above and other considerations, Taylor[54] proposed a theory of the catalytic surface that postulates the presence of active centers which are peaks of extra-lattice atoms of a relatively high degree of unsaturation. In a metal catalyst, "the surface of the granule may be regarded as composed of atoms in varied degree of saturation by neighboring atoms, varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint." This theory of varying lattice saturation of the different faces of the crystal and of the edges, corners,[60] and detached atoms of the particles accords well with the observation of adsorption and of the progressive changes in catalytic behavior under the influence of heat treatment and poisons.

Taylor's general concept of the nature of the catalytic surface has been a great stimulus to research in contact catalysis, and since its formulation it has been frequently adopted without question or has been modified to conform to the results of numerous investigations. To cite one example, Donnelly and Hinshelwood[61] find that the kinetics of the hydrogen-oxygen reaction on platinum, at atmospheric pressure, differs from Langmuir's results obtained at very low pressures. The differences are attributed to the presence of centers of varying activity on the catalytic surface. It is conceivable that at very low pressures most of the gas is adsorbed on the active centers which are relatively highly susceptible to poisons and may even be poisoned by too much of the reactant gas. At higher pressures, where the total adsorption is much greater, the larger proportion of the total reaction may be contributed by the less active centers because they are much more numerous and are less susceptible to poisoning.[62]

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[59] Sci. Papers Inst. Phys. Chem. Research (Tokyo) **3**, 223 (1925); Chem. Abstracts, **20**, 138 (1926).

[60] *Cf.* Schwab and Pietsch: Z. Elektrochem., **35**, 573 (1929); Z. physik. Chem., **B1**, 385; **B2**, 262 (1929); Smekal: Z. Elektrochem., **34**, 472 (1928); **35**, 567 (1929); Z. Physik, **55**, 289 (1929); Z. physik. Chem., **B5**, 60 (1929).

[61] J. Chem. Soc., **131**, 1727 (1929).

[62] *Cf.* Taylor: Alexander's "Colloid Chemistry," **3**, 115 (1931).

Although Taylor's concept of the catalytic surface has been useful, it should be remembered that it is only a theory and may not be in strict accord with the facts. Thus Burk[63] points out that the investigations on active centers do not necessarily lead to the conclusion that active centers are essential to catalytic activity[64] or that, when they exist, they are peaks of extra-lattice atoms, corners, edges, etc. Burk calls attention to the fact that the interface between minute crystals in a catalyst which must exist without assumption could and probably would serve just as well as the active centers assumed by Taylor. In this connection Bancroft[65] says: "Activation of charcoal by superheated steam would certainly take out the semi-detached atoms first and would not produce a good catalyst. Also, one does not see why a support should be so desirable for a catalyst if the active material is on a peak far from the support. The two essential features of Taylor's hypothesis are that only a small fraction of the catalytic surface is active and that the active atoms or molecules are the semi-detached ones. Either of these assumptions may be true without the other one being true."

Promoters.—A promoter is a substance which in itself may possess but slight catalytic activity but which materially increases the activity of the catalyst to which it is added in relatively small amounts. If the two substances are present in more or less equal quantities, the resulting product is called a mixed catalyst; if the non-catalytic material is in large excess, it is designated as a catalyst support.

Promoter action is a comparatively common phenomenon. Some examples of promoter action are the addition of: (1) molybdenum, tungsten, cerium, and more especially $K_2O—Al_2O_3$ or $Na_2O—Al_2O_3$ to active iron catalyst in the synthesis of ammonia; (2) bismuth, tungsten, or copper to active iron in the oxidation of ammonia; (3) copper or tellurium to nickel in the hydrogenation of ols; and (4) ceria to nickel in the hydrogenation of carbon monoxiide and carbon dioxide to give methane. The mechanism of promoter action is not known definitely, but there are several possibilities. Thus the presence of the promoter may increase or modify the surface of the catalyst. Wyckoff and Crittenden[66] showed that iron catalyst used in ammonia synthesis was made up of smaller crystal units when promoted with $K_2O—Al_2O_3$ than when pure, indicating that mere

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[63] J. Phys. Chem., 32, 1626 (1930); Balandin: Z. physik. Chem., B2, 289 (1929).

[64] *Cf.* Constable: Proc. Cambridge Phil. Soc., 23, 832 (1927).

[65] "Applied Colloid Chemistry," 56 (1932).

[66] J. Am. Chem. Soc., 47, 2866 (1926).

extension of surface may be one factor. It is probably not the important one, however, since Russell and Taylor[67] found in the synthesis of methane over nickel that a 20% increase in surface produced a tenfold increase in reaction velocity. This suggests that quality rather than quantity of surface is the important thing.

Since many reactions are known to take place chiefly at an interface between two solids,[68] it is possible that the promoter acts by furnishing an interface. The difficulty with this assumption is that the maximum effect of promoters frequently comes at low concentrations long before the interface is a maximum. Taylor[62] suggests that the promoter may act by increasing the number of active centers as a result of an increase in the number of crystal faces, edges, and corners on the catalytic surface. Other assumptions are that the promoter acts: by increasing the velocity of activated adsorption,[69] by changing the ratio of adsorption of the two reacting gases,[70] by activating one of the reacting substances which is not activated appreciably by the pure catalyst,[71] by decreasing the stability of an intermediate product,[72] and by decreasing the adsorption of one of the reaction products below the point at which it has a poisoning action.[73]

The mechanism of promoter action follows simply from a multiple-adsorption theory of activation. On the basis of this theory the incorporating of a suitable substance with a catalyst will provide other points of attachment of the molecules than those of the original substance, or the active points may be more advantageously spaced for stretching the molecules and therefore for weakening the relevant bond or bodily separating the atoms forming the bond. In support of the theory, Burk[74] predicted the effect of tungsten on the catalytic activity of platinum in the thermal decomposition of ammonia. The decomposition on platinum at 100 mm pressure is retarded by hydrogen but not by nitrogen; that on tungsten is not retarded by hydrogen.[75] It is probable, therefore, that tungsten attracts the nitrogen

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[67] J. Phys. Chem., **29**, 1325 (1925).

[68] *Cf.* Bancroft: J. Phys. Chem., **27**, 827 (1923); Bogue's "Colloidal Behavior," 1, 261 (1924).

[69] Taylor and Williamson: J. Am. Chem. Soc., **53**, 813 (1931).

[70] Rideal and Taylor: "Catalysis in Theory and Practice," 31 (1919); Hurst and Rideal: J. Chem. Soc., **125**, 685, 694 (1924).

[71] Taylor: J. Phys. Chem., **30**, 160 (1926).

[72] Larson and Smith: J. Am. Chem. Soc., **47**, 346 (1925).

[73] Carothers and Adams: J. Am. Chem. Soc., **45**, 1071 (1923).

[74] Proc. Nat. Acad. Sci., **14**, 601 (1928).

[75] Hinshelwood and Burk: J. Chem. Soc., **127**, 1105 (1923).

atoms of ammonia more strongly than the hydrogen atoms, and vice versa for platinum. From Burk's point of view, the decomposition of ammonia on a mottled surface of tungsten and platinum should be more rapid than on either alone. Although this proved to be the case, it does not follow necessarily that the mechanism involves multiple adsorption.

Activation Energy of Catalytic Reactions

It has been established that homogeneous reactions take place only as a result of collisions between molecules possessing a certain energy which has been designated the activation energy. The influence of a catalyst on the activation energy has been formulated and systematized by Langmuir,[76] Hinshelwood,[77] and Schwab.[78] For a monomolecular reaction where there are two reactant molecules, one strongly adsorbed and one weakly adsorbed but retarding the reaction velocity, the relation between the true activation energy E_t and the apparent activation energy E_a is given by the expression:

$$E_t = E_a + \lambda A - \lambda B$$

where λA and λB are the respective heats of adsorption of the strongly and weakly adsorbed molecules. This equation applies to the low-temperature catalysis of hydrogen and ethylene by copper which Pease[79] found to be proportional to the pressure of the hydrogen and to be retarded by ethylene. Substituting in the above equation the specially designated λA and λB for hydrogen and ethylene, as given in Table XXXII, and for E_a, Pease's values of 10,000 calories, we have:

$$E_t = 10{,}000 + 11{,}300 - 16{,}000 = 5300 \text{ calories}$$

On comparing this value with an activation energy of 35,000 calories for the homogeneous reaction which starts only around 400°, it is apparent that the catalyst reduces the activation energy to a value which is of the order of magnitude one might expect for a reaction which proceeds rapidly at low temperatures.[80]

If the activity of the copper catalyst is reduced by heat treatment,

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[76] J. Am. Chem. Soc., **35**, 105 (1913); **38**, 2270 (1916).

[77] "Kinetics of Chemical Change" (1926).

[78] Ergeb. Exakt. Naturwiss., **7**, 280, 291 (1928); *cf.* Taylor: "A Treatise on Physical Chemistry," 1072–85 (1931).

[79] J. Am. Chem. Soc., **45**, 1196 (1923).

[80] *Cf.* Burk: J. Phys. Chem., **30**, 1134 (1926).

both ethylene and hydrogen are weakly adsorbed so that the temperature must be raised to 200° before the reaction proceeds at a reasonable rate. Under these conditions the reaction becomes bimolecular, proportional to the product of the pressures of hydrogen and ethylene, respectively. Under these conditions,

$$E_t = E_a + \lambda A + \lambda B$$

That is, to get the true activation energy the heats of adsorption of both reactants must be added to the apparent activation energy. At the relatively inactive catalyst, the values of λA and λB are probably much less than at the active catalyst considered in the preceding paragraph, so that E_t will be less than 35,000 calories for the homogeneous gas reaction. Apparently, in this case also, the catalyst reduces the activation energy of the reaction. Taylor[81] points out that if these observations are general they lead to the following general conclusions: "Catalysts reduce the activation energy of chemical reactions, the more considerably the more active the catalyst."

It is apparent that equations of the above type will lead to correct conclusions only in case the observed heats of adsorption are heats of activated adsorption and not of mere surface condensation or a combination of the two. Moreover, as Taylor[82] points out, the equations relating true and apparent activation and heats of adsorption are applicable only when the adsorption processes involved are rapid as compared with the actual reaction process. They cannot hold rigorously when the rate of adsorption is relatively slow, as frequently happens in activated adsorption.

APPLICATIONS OF METALLIC CATALYSTS

Some typical catalytic actions at metallic surfaces that will be considered in order are: (1) the decomposition of hydrogen peroxide; (2) the synthesis of ammonia; (3) the oxidation of ammonia; and (4) the hydrogenation process.

Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide is catalyzed by a number of colloidal metals, more especially platinum, palladium, iridium, silver, and gold. The phenomenon has been studied so extensively

[81] Alexander's "Colloid Chemistry," **3**, 112 (1931).

[82] Chem. Rev., **9**, 41 (1931).

that an entire volume in Zsigmondy's "Kolloidforschung in Einzeldarstellungen" will be devoted to the subject. In the present brief survey, consideration will be given chiefly to the catalytic action of platinum which has been used most frequently in these studies.

Kinetics of the Catalytic Decomposition

The decomposition of hydrogen peroxide is increased by very low concentrations of colloidal metals. Thus an observable effect was noted with one gram atom of platinum in 70×10^6 liters; of palladium in 26×10^6 liters; and of gold in 1×10^6 liters.

Decomposition by Platinized Platinum.—The kinetics of the decomposition process has been studied by Bredig and his pupils[83] with platinum sol and with platinum black supported on platinum foil. In the latter case, Bredig[84] found that, over a considerable concentration range, the reaction was of the first order, determined by the diffusion[85] of hydrogen peroxide to the surface of the catalyst in accord with the equation

$$-\frac{dx}{dt} = \frac{DA}{\delta v}(a - x)$$

where a is the original amount of the peroxide in volume v; x is the amount transformed in time t; D is the diffusion coefficient; A, the area; and δ, the film thickness. This was true for the supported catalyst irrespective of whether the decomposition was in neutral, acid, or alkaline solution. The velocity constant was found to be proportional to the two-thirds power of the rate of stirring, to the first power of the area, and inversely proportional to the volume of liquid. The temperature coefficient was 1.28 for a 10° rise. These observations were extended by Smith and Rideal,[86] who showed that the reaction velocity rose to a well-defined maximum with the speed of rotation of a platinized platinum surface, and that the temperature coefficient for the maximum velocity was 1.28 above 25°, but was smaller below this temperature. These limiting velocities are not explainable on the diffusion hypothesis.

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[83] Bredig and Müller von Berneck: Z. physik. Chem., **31**, 258 (1899); Bredig and Ikeda: **37**, 1 (1901); Bredig and Reinders: **37**, 323 (1901); Bredig and Fortner: Ber., **37**, 798 (1904).

[84] Bredig, Teletow, and Antropow: Z. Elektrochem., **12**, 581 (1906); Sieverts and Brüning: Z. anorg. Chem., **204**, 291 (1932).

[85] Noyes and Whitney: Z. physik. Chem., **23**, 689 (1897); Nernst: **47**, 52 (1904); Brunner: **47**, 56 (1904).

[86] Rideal and Taylor: "Catalysis in Theory and Practice," 384 (1926).

Decomposition by Platinum Sol in Neutral Solution.—Observations on the catalytic action of platinum sol likewise render the diffusion hypothesis untenable. Thus the temperature coefficient was found to have the relatively high value of 1.7. Moreover, the evolution of oxygen and the Brownian movement of the particles in sols greatly modify the conditions assumed by Nernst for establishing a diffusion layer of appreciable thickness. As a matter of fact, if platinum in the form of sol is used as a catalyst in a neutral solution, the "constant" for a unimolecular reaction rises during the reaction. In the light of the adsorption theory of contact catalysis, one would expect the decomposition to be proportional to the amount adsorbed. Since adsorption is related to the bulk concentration, the velocity equation

$$-\frac{dx}{dt} = k(a - x) \tag{1}$$

becomes, by the Freundlich equation,

$$-\frac{dx}{dt} = k(a - x)^{1/n} \tag{2}$$

which on integration is,

$$k = \frac{n}{t(n - 1)}\left[a^{1-1/n} - (a - x)^{1-1/n}\right] \tag{3}$$

That this agrees well with the facts in the case under consideration is shown by the data of Bredig and Ikeda recalculated by MacInnes[87] using Equation (3) (see Table XXXIV). MacInnes showed further that the ratio of velocity constants calculated from Equation (3) when the same platinum sol was present in various dilutions was similar to the ratio of the platinum concentrations.[88]

Decomposition by Platinum Sol in Alkaline Solutions.—From the point of view of the adsorption mechanism, one would expect the active surface of the catalyst to be completely covered with a monomolecular film of hydrogen peroxide from sufficiently strong solutions. The reaction should therefore be of zero order over a range of concentrations from that just necessary for a complete layer up to very strong solutions. Bredig found this to be true in alkaline solutions above a certain strength. On this basis it is not obvious why the temperature coefficient should be 1.28 with a platinized platinum catalyst and

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[87] J. Am. Chem. Soc., **36**, 878 (1914).

[88] *Cf., however,* Bredig and Müller von Berneck: Z. physik. Chem., **31**, 258 (1899).

TABLE XXXIV

Velocity of Decomposition of Hydrogen Peroxide by Platinum Sol

(a = 0.0972 mol H_2O_2/l; sol contains 2 mg Pt/l)

t minutes	$a - x$	k from Equation (1)	k from Equation (3)
0	0.0972	. . .	. . .
6.03	0.0685	0.058	0.027
11.42	0.0475	0.063	0.028
15.85	0.0337	0.067	0.028
21.18	0.0219	0.071	0.028
26.70	0.0139	0.073	0.027
32.10	0.0079	0.076	0.027

have the relatively high value of 1.7 with the sol. It is probable that the latter value is not a true temperature coefficient, since other factors apparently come in.[89] For example, on small additions of alkali the velocity rises to a maximum as shown in Table XXXV at a concentration of about 30 millimols/l; at larger concentrations the

TABLE XXXV

Influence of Sodium Hydroxide Concentration on the Decomposition of Hydrogen Peroxide by Platinum Sol

(Pt content = 0.64 mg/l)

NaOH, mol/l	Half life of H_2O_2, minutes	Relative activity
0	255	9.0
0.00195	34	65.0
0.0039	28	79.0
0.0078	24	91.0
0.0156	25	90.0
0.03125	22	100.0
0.0625	34	65.0
0.1250	34	65.0
0.2500	70	31.5
0.5000	162	13.5
1.0000	520	4.2

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[89] *Cf.* observation of Galecki and Jerke: Roczniki Chem., 7, 1 (1927) on the catalytic action of colloidal gold on hydrogen peroxide.

velocity is lower than in the neutral solution. Moreover, with low concentrations of alkali the reaction is of zero order while with large amounts of alkali it lies between zero and first order. A similar behavior has been observed with colloidal gold,[90] silver,[91] and palladium,[92] but not with iridium.[93]

A plausible explanation of the effect of alkali on the reaction velocity is to be found, at least in part, in the peptizing and coagulating action of the electrolyte. Small concentrations doubtless peptize the colloidal aggregates into smaller units which increase the specific surface and hence the catalytic activity. Higher concentrations may reduce the rate of decomposition by coagulating the particles or by being adsorbed on the catalytic surface.[94] It will be recalled that the particles in the Bredig sol are coated at least in part with a film of oxide (see page 178). Rocasolano[95] believes that the catalytic action consists in the alternate oxidation of this oxide shell to a higher oxide, and subsequent reduction. If this be true, the alkali may have a decelerating action above a certain concentration by dissolving the oxide surface. In support of this, Euler claims that platinum black freed from oxygen has no catalytic effect on the decomposition of hydrogen peroxide. This is apparently not the case, however, since Spitalsky and Kagan[96] found that cathodic polarization, that is, the liberation of electrolytic hydrogen on the catalytic surface, enormously increases the catalytic activity of platinized platinum while anodic polarization with oxygen greatly checks it. Moreover, Roiter[97] showed that the activity of a platinum catalyst is increased by saturating it with hydrogen and is retarded by oxygen. A platinum foil saturated with hydrogen and hence free from oxygen remains under hydrogen peroxide for hours without losing its catalytic activity, probably because the liberated oxygen does not readily displace the adsorbed and dissolved hydrogen. Moderate removal of hydrogen, oxygen, or air by reduced pressure increases the catalytic activity, but excessive removal of the gases alters the surface and reduces the activity.

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[90] Bredig and Reinders: Z. physik. Chem., **37**, 323 (1901); Galecki and Krzeckovska: Bul. acad. polonaise, **93 A**, 111 (1925).

[91] McIntosh: J. Phys. Chem., **6**, 15 (1902).

[92] Bredig and Fortner: Ber., **37**, 798 (1904).

[93] Brossa: Z. physik. Chem., **66**, 162 (1909).

[94] *Cf.*, also, Wright and Rideal: Trans. Faraday Soc., **24**, 530 (1928); *see* page 230.

[95] "Nachr. Ges. Wiss. Göttingen," 177 (1924).

[96] Ber., **59**, 2900 (1926).

[97] Ber. Ukran. wiss. Forsch-inst. physik. Chem., **3**, 42 (1929).

The variation in the order of the reaction with varying amounts of alkali can be accounted for in the following way: Hydrogen peroxide combines with sodium hydroxide to give salts such as NaOOH.[98] At small alkali concentrations the relative amount bound by the excess alkali is appreciable. Thus, in a solution 1/80 *M* in sodium hydroxide and 1/40 *M* in hydrogen peroxide, the content of free sodium hydroxide is reduced 75%. If, therefore, the hydroxyl ion is reduced by combination with hydrogen peroxide to a point below that causing maximum reaction velocity, it approaches this value during decomposition and accelerates the process. If this acceleration is just as great as the falling off in the amount decomposed owing to the decrease in the amount of hydrogen peroxide, the rate will obviously be independent of the hydrogen peroxide concentration. Under these fortuitous circumstances the reaction is of the zero order.

Periodic Catalytic Decomposition.—That an oxide may form as an intermediate product in the catalytic decomposition of hydrogen peroxide by metals is indicated by the periodic course of the reaction at a mercury surface[99] which was observed to parallel the periodic formation and dissolution of a yellow oxide film.[100] Hedges and Myers,[101] on the other hand, are inclined to regard the film formation and disappearance as a result rather than a cause of the periodic decomposition, since they observed the film formation when the action was not periodic and failed to observe it in certain cases when the reaction was periodic. Moreover, the periodic effect manifested itself with a number of different catalysts such as (1) finely divided copper after vacuum heat treatment; (2) silver by reduction of ammoniacal silver nitrate; (3) copper-aluminum alloy and magnesium amalgam; (4) magnesium-copper, iron-zinc, silver-manganese, and copper-manganese couples; (5) freshly prepared cuprous oxide and barium oxide; (6) enzymes from sheep's liver and ox blood; and (7) freshly prepared sols of silver, gold, and platinum formed by reduction of chlorplatinic acid or by Bredig's method. The periodicity was not observed in a platinum sol 3 days old nor with platinum black.

Hedges and Myers do not commit themselves definitely as to the cause of the periodic behavior under certain conditions. In the

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[98] Calvert: Z. physik. Chem., 38, 527 (1901).

[99] Bredig and Weinmayr: Z. physik. Chem., 42, 601 (1903).

[100] Bredig and Antropow: Z. Electrochem. 12, 585 (1906); Antropow: Z. physik. Chem., 62, 513 (1908); Fredenhagen: Z. Elektrochem., 11, 859 (1907); Lemoine: Compt. rend., 162, 580 (1916).

[101] J. Chem. Soc., 125, 1282 (1924).

light of the observations of Spitalsky and of Roiter above referred to, it seems probable that the phenomenon is due to intermittent poisoning owing to the periodic piling up and diffusing away of oxygen from the active portions of the catalytic surface. Periodic decomposition by a fresh platinum sol and not by an aged one is probably connected with the relative ease of poisoning of the much more highly active fresh sol by the accumulation of oxygen.

Poisoning of Catalyst

Soluble Compounds.—Bredig in his investigation of the analogy between the action of enzymes and colloidal metals, or "inorganic ferments" as he termed them, showed that the catalytic activity of the latter could be cut down enormously by minute quantities of certain substances that greatly retard enzyme action. This is illustrated in a striking way by the results shown in Table XXXVI, which gives the data of Bredig on the poisoning of colloidal platinum and of

TABLE XXXVI

Poisoning of Catalysts for the Decomposition of Hydrogen Peroxide

Poison added	Concentration of poison required to decrease the decomposition 50% with	
	Colloidal Pt	Hemase
H_2S	*M*/300,000	*M*/1,000,000
HCN	*M*/20,000,000	*M*/1,000,000
$HgCl_2$	*M*/2,000,000	*M*/2,000,000
$HgBr_2$	....	*M*/300,000
$Hg(CN)_2$	*M*/200,000	*M*/300
I_2 in KI	*M*/5,000,000	*M*/50,000
NH_2OHHCl	*M*/25,000	*M*/80,000
$C_6H_5NHNH_2$	....	*M*/20,000
$C_6H_5NH_2$	*M*/5000	*M*/400
As_2O_3	*M*/50	No poisoning at *M*/2000
CO	Very poisonous	No poisoning
HCl	*M*/3000	*M*/100,000
NH_4Cl	*M*/200	*M*/1000
HNO_3	No poisoning	*M*/250,000
H_2SO_4	No poisoning	*M*/50,000
KNO_3	No poisoning	*M*/40,000
$KClO_3$	Slight poisoning	*M*/40,000

Senter[102] on the poisoning of hemase, the active enzyme of the red blood corpuscle, used in the catalytic decomposition of hydrogen peroxide. The similarity is apparent, but there are differences just as would be expected in view of the fact that the extent of adsorption of the substances which causes the poisoning will depend on the nature of the catalyst and the nature of the poison. It is particularly significant that such an extremely dilute solution of hydrocyanic acid, which is in general not strongly adsorbed, has such a marked poisoning action on colloidal platinum. The most obvious explanation of this behavior is that only a relatively small part of the surface is catalyticallly active.

Other substances that exert a poisoning or "narcotic" action on the decomposition of hydrogen peroxide in the presence of platinum are alcohols, ketones, and urethanes.[103] In these cases the action is reversible, the poison being removed by washing; the effect of concentration on the extent of poisoning follows an adsorption isotherm; and Traube's rule holds, the action increasing markedly from one member to another in an homologous series (see page 286).

Protecting Colloids.—The catalytic action of platinum sol is decreased in the presence of a protecting colloid such as gelatin.[104] Some data along this line by Rocasolano[105] are given in Table XXXVII. It will be noted that the rate of decomposition of hydrogen peroxide is reduced less than one-fourth by but 0.001% gelatin. In the presence of sodium lysalbinate, the rate passes through a minimum with rising concentration, increasing when the effect of the alkalinity begins to come in. There is no minimum with gum

TABLE XXXVII

EFFECT OF GELATIN ON THE CATALYTIC ACTIVITY OF Pt SOL

Per cent gelatin	Time for 50% decomposition of H_2O_2	Per cent gelatin	Time for 50% decomposition of H_2O_2
0.00	100	0.05	620
0.001	437	0.10	983
0 01	460		

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[102] Z. physik. Chem., **44**, 257 (1903); **51**, 673 (1905).

[103] Meyerhof: Pflügers Arch., **157**, 251, 307 (1914).

[104] Groh: Z. physik. Chem., **88**, 414 (1914).

[105] Compt. rend., **173**, 41, 234 (1921).

arabic, and its effect on the decomposition rate is much less than that of an equal weight of gelatin. Since the protecting effect of gum arabic on platinum sol is much less than that of gelatin, this observation confirms Iredale's finding that, the better a substance is as a protecting colloid, the more it inhibits the catalytic activity of platinum on hydrogen peroxide. In general, any increase in the stability of a sol by the use of a protecting colloid is accompanied by a loss in its catalytic activity.

Tartar and Schaffer[106] investigated the effect of different concentrations of acid and alkali on the decomposition of hydrogen peroxide by colloidal platinum in the presence of gelatin. In acid solution, the rate is apparently a function of both the *p*H value and of the nature and concentration of the anion; in alkaline solution, the rate of decomposition depends chiefly on the *p*H value, increasing as the latter increases. Until more information is available, all one can say is that both the gelatin and the catalysis itself are influenced by the *p*H value of the solution.

Other catalytic reactions which exhibit phenomena similar to those in the decomposition of hydrogen peroxide are the catalytic oxidation of chromous chloride to chromic chloride using platinized platinum[107] and platinum sol,[108] and the oxidation of tellurous sulfate to telluric sulfate in contact with platinized platinum.[109]

THE CONTACT SULFURIC ACID PROCESS

A century ago, Phillips obtained a patent for the use of spongy platinum as a catalyst for the oxidation of sulfur dioxide to trioxide. The process was not successful commercially because of the rapidity with which the catalytic material was poisoned. In 1875 Squire and Messel succeeded in making the process a technical success by using purified sulfur dioxide. Rapid development in the method did not come, however, until the opening years of the present century, when Knietsch[110] reported the results of his systematic investigations of the reaction velocities and the conditions of equilibrium in the reversible reaction $2SO_2 + O_2 \rightleftarrows 2SO_3 + 45{,}200$ calories. It was found that the most favorable temperature for the catalytic reaction with

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[106] J. Am. Chem. Soc., 50, 2604 (1928).

[107] Jablczynski: Z. physik. Chem., 64, 748 (1908).

[108] McBain: Dissertation, Heidleberg (1909).

[109] Denham: Dissertation, Heidelberg (1909).

[110] Ber., 34, 4069 (1901); *cf.* Taylor and Lenher: Z. physik. Chem., Bodenstein Festband, 30 (1931); Baur: A157, 315 (1931).

platinum is a little over 400°. Below this temperature the velocity drops off rapidly, and much above this temperature the equilibrium is displaced in the wrong direction since sulfur trioxide is decomposed to some extent at 500° and completely at 1000°. The results with platinum catalyst, under different conditions and with the less efficient burnt-pyrites and porcelain catalysts, are shown in Fig. 38. In these experiments, purified technical converter gas was employed of the following composition: SO_2 = 7%; O_2 = 10%; N_2 = 83%. Curve I was obtained by passing the mixture over platinized asbestos at varying temperatures with a flow rate of 300 cc per minute; curve II with a flow rate of 20,000 cc per minute; and curve III using burnt pyrites, Fe_2O_3 (CuO), as catalyst with a flow rate of 500 cc per minute. As the curves indicate, if the rate of flow is not too rapid the conversion at a platinum surface is almost 100% at a little above 400°. With pyrites, on the other hand, the reaction is too slow in the neighborhood of 400°; and at the higher temperature of 550°, the conversion is less than 50%. Curve IV shows the low efficiency with broken porcelain as the catalytic agent.

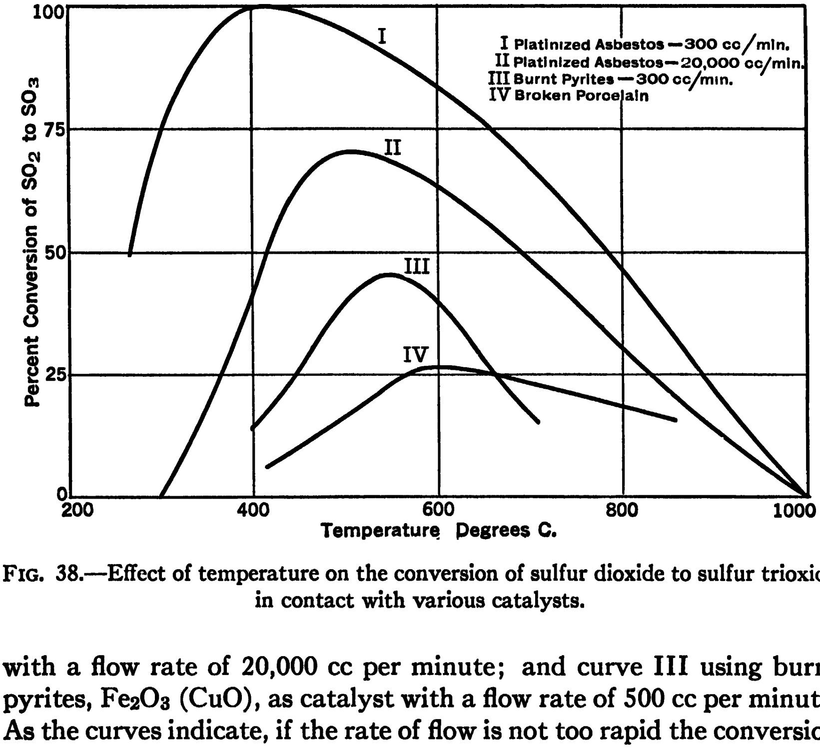

FIG. 38.—Effect of temperature on the conversion of sulfur dioxide to sulfur trioxide in contact with various catalysts.

An increase in the partial pressure of oxygen above the theoretical quantity necessary for complete conversion of sulfur dioxide to sulfur trioxide is desired, but there is a limit to the amount of air that may be admitted because of the diluting effect of the nitrogen. The optimum results are obtained when the quantity of excess air raises the oxygen content to the ratio $SO_2 : O_2 = 2 : 3$, or 3 times the theoretical amount.

Because of the expense of platinum, a great deal of attention has been paid to obtaining the maximum yield with the smallest amount of contact material. To this end the platinum black is precipitated on a support, usually asbestos,[111] silica gel,[112] or magnesium sulfate.[113] In general, the supporting material is impregnated with a platinum salt and then reduced. In the widely used magnesium sulfate support, the partially calcined compound is sprayed with a solution of platinum salt and then heated in the presence of sulfur dioxide, thereby reducing the salt to platinum which is deposited as a thin film on the porous dehydrated support. It is said that but 0.2 to 0.3% of platinum on the support gives an excellent contact material.[114]

Since the optimum conversion temperature at a platinum catalyst lies within a rather narrow range and the reaction is strongly exothermic (22,600 cal/mol of gaseous SO_3), the heat being liberated at the catalytic surface, the technical process requires an efficient temperature control. This is an engineering problem that has been met in a number of ways.[115]

One of the most serious problems in connection with the contact sulfuric acid process using a platinum catalyst, results from the ease with which the catalyst is poisoned. Compounds of arsenic and mercury exhibit the most marked poisoning action, but compounds of selenium, antimony, bismuth, lead, tellurium, and zinc should not be present in any appreciable quantities. An amount of arsenic equal to but 1 or 2% of the platinum will frequently destroy the catalytic activity completely. It is therefore essential for the success of the technical process that the sulfur dioxide be freed practically completely from any arsenic that may be present before it is brought in contact with the catalyst.

The most recent development in the preparation of sulfuric acid

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[111] Loew: Ber., **23**, 289 (1890).

[112] Reyerson and Thomas: Colloid Symposium Monograph, **3**, 99 (1925); Holmes, Ramsay, and Elder: Ind. Eng. Chem., **21**, 850 (1929).

[113] J. Soc. Chem. Ind., **22**, 348 (1903).

[114] Rideal and Taylor: "Catalysis in Theory and Practice," 167 (1926).

[115] Zeisberg: Trans. Am. Electrochem. Soc., **36**, 187 (1920); Chem. & Met. Eng., **30**, 829 (1924); Rideal and Taylor: "Catalysis in Theory and Practice," 168 (1926).

by the contact process consists in the use of vanadium compounds as a substitute for platinum black. It has been known since 1895[116] that vanadium compounds would catalyze the sulfur dioxide oxidation, but they have come into technical use only in recent years largely through the work of Jaeger[117] and his associates. The contact masses contain as their active ingredients non-siliceous base-exchange bodies in which vanadium is present in the non-exchangeable nucleus. The presence of certain other compounds is said to promote the catalytic activity of the vanadium mixture. A typical method of forming the catalyst consists in adding a solution of ferric chloride or ferric sulfate to a solution of potassium vanadate in such amounts that the so-called ferric vanadate is precipitated. This is then incorporated in a gel by mixing with a solution of alkali silicate which is subsequently precipitated. Holmes and Elder[118] recommend that the iron vanadium complex be peptized with excess ferric chloride before it is added to the water glass solution, thereby obtaining a single precipitate consisting of catalyst, promoter, and support.

It is claimed by Jaeger[119] that these catalysts, when used with the proper converter, exceed in efficiency the best platinum catalysts in technical use and possess the added advantage of cheapness, extraordinary resistance to high temperature, long life, and an almost complete indifference to gaseous poisons which destroy the activity of platinum.

The Synthetic Ammonia Process

This process is based on the direct union of nitrogen and hydrogen in accord with the equation:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + 24{,}200 \text{ calories}$$

This reaction results in an equilibrium mixture, the composition of which varies with the temperature and pressure as shown by the data in Table XXXVIII calculated from the experimental results obtained at the Fixed Nitrogen Research Laboratory.[120] It is

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[116] For bibliography, *see* Waeser: Metallbörse, **19**, 1349, 1406 (1929); Nickell: Chem. & Met. Eng., **35**, 153 (1928); Jaeger: Ind. Eng. Chem., **21**, 627 (1929).

[117] U. S. Pats., 1,657,754; 1,660,511; 1,675,308–9; 1,685,672; 1,694,123; 1,694,620; 1,696,546 (1928); 1,701,075 (1929).

[118] Ind. Eng. Chem., **22**, 471 (1930).

[119] Ind. Eng. Chem., **21**, 627 (1929); Spangler: **21**, 417 (1929).

[120] Larson: J. Am. Chem. Soc., **46**, 367 (1924); J. Chem. Ed., **3**, 284 (1926); *cf.* Haber and van Oordt: Z. anorg. Chem., **43**, 111 (1905); Haber and Le Rossignol: Ber., **40**, 2144 (1907); Z. Elektrochem., **14**, 181 (1908); Haber, *et al.*: **20**, 597 (1914); **21**, 89, 128, 191, 206, 228, 241 (1915); Nernst: **13**, 521 (1907); Jost: Z. anorg. Chem., **57**, 415 (1908).

TABLE XXXVIII

EQUILIBRIUM DATA FOR AMMONIA SYNTHESIS

Temperature, degrees	Percent NH_3 at equilibrium at the following pressures in atmospheres					
	1	10	50	100	300	1000
200	15.3	67.56	74.38	81.54	89.94	98.29
300	2.18	30.25	39 41	52.04	70.96	92.55
400	0.44	10.15	15.27	25 12	47.00	79.82
500	0.13	3 49	5 56	10.61	26 44	57.47
600	0.05	1 39	2.25	4.52	13 77	31.43
700	0 02	0 68	1 05	2 18	7.28	12.87

apparent that the yield of ammonia should be highest at low temperatures, but the rate of the synthesis is so slow under these conditions that the process is useless technically. If the mixture is heated to 400–500° so that the rate of synthesis is sufficiently great, the rate of decomposition of the resulting ammonia is so rapid that the equilibrium mixture contains less than 0.5% ammonia at 1 atmosphere pressure. Since the synthesis takes place with a decrease in pressure, raising the pressure increases the yield of ammonia.

The Haber Process.—The synthesis of ammonia was first realized technically by Haber,[121] who used a promoted iron catalyst at a temperature of 550° and a pressure of 200–250 atmospheres. The conversion efficiency under working conditions is in the neighborhood of 10%. This compels the adoption of a circulatory system in which the gases, after being freed from ammonia by absorption in water or by liquefaction, are returned to the incoming gases.

The first catalytic agents tried were nickel, manganese, iron, chromium, and later osmium and uranium carbide.[121] Osmium and uranium carbide proved the most satisfactory in the early laboratory experiments, but they are apparently not suited for technical use. The catalyst universally employed is iron in the presence of promoters. The most satisfactory contact material yet reported was developed by Larsen[122] and his associates in the Fixed Nitrogen Research Laboratory. The catalyst which gives approximately 14% conversion efficiency at 450° and 100 atmospheres consists of reduced iron with K_2O and Al_2O_3 as promoters. The efficiency of the catalyst was

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[121] J. Soc. Chem. Ind., **33**, 54 (1914).

[122] Larsen and Brooks: Ind. Eng. Chem., **18**, 1305 (1926); Almquist and Crittenden: **18**, 1307 (1926).

found to depend both on the state of oxidation of the fused oxide from which it is obtained and on the nature and amount of promoter employed. The most active catalyst results by reduction of a fused iron oxide in which the ferrous : ferric ratio is 1 : 2 as required for Fe_3O_4. The best promoter is K_2O mixed with a somewhat acidic oxide, preferably Al_2O_3. K_2O alone reduces the conversion efficiency of pure iron, and Al_2O_3 alone raises it. This is illustrated by the results given in Table XXXIX. The promoter probably acts both by retarding the sintering of the catalyst and by improving its quality.

TABLE XXXIX

ACTIVITY OF CATALYSTS FOR AMMONIA SYNTHESIS

Composition of oxides before reduction, per cent				Promoters, per cent		NH_3 at 450° and 5000 S. V.,* per cent	
Total Fe	Free Fe	Fe(ous)	$\frac{\text{Fe(ous)}}{\text{Fe(ic)}}$	Al_2O_3	K_2O	30 atmos.	100 atmos.
72.84	2.37	25.03	0.551	....	....	3.30	5.49
72.58	1.23	25.35	0.551	....	0.20	1.57	3.43
71.99	1.00	26.16	0.573	1.31	....	5.35	9.35
71 99	0.89	24.55	0.527	1.05	0.26	5.80	13.85

* "Space Velocity" is defined as the number of liters of gas, measured under standard conditions, flowing per liter of catalyst per hour.

The contact ammonia process is readily poisoned[123] by such substances as sulfur, selenium, tellurium, arsenic, boron, and their compounds; many organic compounds; lead, zinc, bismuth, tin; and oxygen, water vapor, and gaseous oxygen-containing materials, such as carbon monoxide and carbon dioxide. Almquist and Black[124] showed that a catalyst poisoned by water vapor could be brought back to its original activity by displacement with the pure reactant gases. Oxygen held irreversibly was shown to be present as oxide formed as a result of interaction of a trace of water vapor with the active iron atoms on the catalytic surface.

The nitrogen used in ammonia synthesis is usually obtained from producer gas, a mixture of nitrogen and carbon monoxide formed by passing air over hot coke; and the hydrogen from water gas, a mixture

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[123] Jöbling: "Catalysis and Its Industrial Applications," 44 (1916).

[124] J. Am. Chem. Soc., 48, 2814; Almquist: 48, 2820 (1926); Emmett and Brunauer: 52, 2682 (1930).

of hydrogen and carbon monoxide obtained by passing steam over heated coke. The producer gas and water gas are mixed with more steam and the whole passed over nickel or iron catalyst whereby the carbon monoxide is converted into carbon dioxide. The resulting mixture must be freed completely from carbon dioxide, carbon monoxide, water, and any other catalyst poisons.

The Claude Process.—The Claude process[125] developed in France differs from the German process in using temperatures of 600° and 900–1000 atmospheres' pressure. The maximum conversion claimed is 40%. No external heat need be applied after starting the process, and the bulk of the ammonia may be liquefied by cooling the gas, the residual ammonia with unchanged hydrogen being passed to a second catalytic unit where further conversion occurs. Thus, by placing a small number of catalytic units in series, an efficiency approaching 90% can be achieved without any circulatory plant.[126] Moreover, with the higher pressures, it is possible to use nitrogen-hydrogen mixtures of a somewhat lower order of purity. In spite of these advantages there are apparently a number of technical difficulties. The process was started in England but was discontinued.[127] On the other hand, the du Pont Ammonia Corporation is using high-pressure plants successfully at Belle, W. Va., and Seattle, Wash.[128]

Mechanism.—It is pretty generally believed that an iron nitride is formed as an intermediate product in the synthesis of ammonia at an iron catalyst. A study of the dissociation pressure of iron nitrides led Noyes and Smith[129] to conclude that the nitride of lowest nitrogen content formed on passing ammonia over iron possesses a dissociation pressure of 20,000 atmospheres at 460°. A recent phase-rule study of the iron-nitrogen system showed, however, that the iron nitride of lowest nitrogen content, Fe_4N, has a dissociation pressure at 460° of only 5300 atmospheres.[130] Even under these circumstances it would not be possible, at the pressures used in the technical processes, for ordinary metallic iron to react with nitrogen to give a stable nitride which could then react with hydrogen to form ammonia. Frankenburger[131] has calculated, however, that the

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[125] Bull. soc. chim., (4) **27**, 705 (1920); Compt. rend., **168**, 1001; **169**, 1039 (1919); **172**, 442; **173**, 655 (1921); **174**, 681 (1922).

[126] West: J. Soc. Chem. Ind., **40**, 420 R (1921).

[127] Harker: J. Soc. Chem. Ind., **41**, 388 R (1922).

[128] Ind. Eng. Chem., **22**, 433 (1930).

[129] J. Am. Chem. Soc., **43**, 475 (1921).

[130] Emmett, Hendricks, and Brunauer: J. Am. Chem. Soc., **52**, 1456 (1930).

[131] *Cf.* Emmett: J. Chem. Ed., **7**, 2571 (1930).

active iron atoms on the catalytic surface would be capable of reacting with nitrogen at pressures of 1 or 2 atmospheres.[132] In the light of the evidence, a possible mechanism consists "in the reaction of nitrogen molecules with highly active surface iron atoms forming some sort of surface nitride which when brought into contact either with gaseous hydrogen molecules or possibly with hydrogen molecules adsorbed or momentarily combined with adjacent active iron atoms, will result in the formation of a surface NH or NH_2 group intermediate to the completion of the ammonia molecule."[131]

THE OSTWALD NITRIC ACID PROCESS

It was observed by Kugelmann in 1839 that ammonia can be oxidized to nitric acid in the presence of platinum, but it was not until 1903 that Ostwald[133] put the process on a commercial basis. This process in connection with the Haber ammonia synthesis has given the world an inexhaustible source of nitric acid at a comparatively low price. These processes were the foundation of the chemical side of the German war program in 1914.

The reactions involved in the Ostwald process are as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The problem is complicated by the oxidation of some of the ammonia, probably in the following way:[134]

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (4)$$

Both reactions (1) and (4) are accelerated by platinum, but (1) takes place more rapidly than (4). The best results are obtained by keeping the reactants in contact with the catalyst as short a time as possible which, Bancroft[135] points out, indicates that reaction (4) is a secondary and not a simultaneous reaction. If (1) and (4) took place simultaneously, the ratio of the products formed should be independent of the rate of flow.

In the technical process,[136] ammonia containing approximately

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[132] *Cf.* Emmett and Brunauer: J. Am. Chem. Soc., **52**, 2682 (1930).

[133] Ostwald and Brauer: Chem.-Ztg., **27**, 100 (1903).

[134] Sabatier and Senderens: Compt. rend., **135**, 278 (1902).

[135] "Applied Colloid Chemistry," 63 (1926).

[136] *Cf.* Parsons: Ind. Eng. Chem., **19**, 789 (1927).

10 volumes of air heated to approximately 300° is passed through a converter consisting of cylinders made up of several layers of platinum gauze. For the best operation the actual temperature of the gas is 1025°. The du Pont Company[137] has developed a plant working at 7.8 atmospheres in which a platinum-rhodium alloy is used as the catalyst. Pressure operation is made possible by the use of chrome-iron, which is not attacked appreciably by nitric acid.

In operations at atmospheric pressure, yields better than 90% of the theory from ammonia to 50% nitric acid, can be obtained. Operation at 7.8 atmospheres gives equal or better yields of 60% acid. The increase in strength of the acid from 50 to 60% in the pressure synthesis halves the cost of concentration to 90% acid.[137]

Smooth platinum is not a good catalyst, but after being used for a time it becomes roughened and activated. When it is highly active, the period of contact with reactants need be no greater than 0.0006 second.[138] With platinum-rhodium catalyst, under operating conditions, the losses are said to be only one-half as great as with pure platinum.[137]

The catalyst is poisoned by such substances as phosphine, acetylene, and hydrogen sulfide. An amount of phosphine as low as 0.00002% of the reactants reduces the yield 20%;[138] but an amount of acetylene up to 0.4%, and of hydrogen sulfide up to 0.07%, exerts no injurious effect on the catalyst.[139] Indeed, a small amount of hydrogen sulfide up to 0.07% inhibits[140] the poisoning action of phosphine and actually increases the conversion efficiency.[141] Iron oxide, grease, oil, and tar have a marked poisoning action and must be avoided.

SABATIER'S HYDROGENATION PROCESS

Isolated cases of hydrogenation in the presence of a catalyst were observed prior to 1897, but this date is significant since it marks the beginning of the systematic study of the phenomenon by Sabatier,[142] who has developed it into a general hydrogenation process of wide applicability.[143] Sabatier's work started with the observation that

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[137] Taylor, Chilton, and Handforth: Ind. Eng. Chem., **23**, 860 (1931).

[138] Rideal and Taylor: "Catalysis in Theory and Practice," 176 (1926).

[139] Yee and Emmett: Ind. Eng. Chem., **23**, 1090 (1931).

[140] Decarrière: Compt. rend., **173**, 148 (1921); **174**, 460 (1922).

[141] Taylor and Capps: Ind. Eng. Chem., **10**, 457 (1918); Yee and Emmett: Ind. Eng. Chem., **23**, 1090 (1931).

[142] Sabatier and Senderens: Compt. rend., **124**, 1358 (1897).

[143] Sabatier-Reid: "Catalysis in Organic Chemistry," 125–216; 339–350 (1922); Jöbling: "Catalysis and Its Industrial Applications," 68 (1916).

acetylene and ethylene combine with hydrogen in the presence of reduced nickel. This simple synthesis has been extended to include a large number of direct hydrogenations not only in the gaseous phase but in the liquid state as well.

The method of procedure employed by Sabatier and his collaborators, Senderens, Mailhe, Ipatiew, and others, is characterized by its simplicity, rapidity, and high yields. A mixture of pure hydrogen with the vapors of the material under investigation is passed through a tube containing the specific metallic catalyst maintained at a temperature commonly between 150° and 200°, and the products are collected in a suitable apparatus on their emergence from the tube.

As in all catalytic processes, the catalyst is of particular importance. The metals arranged in the order of their efficiency for hydrogenation are: nickel > cobalt > copper > platinum > iron. Of these, nickel when properly prepared is by far the most important. The method of preparation consists in reduction of the suitably formed oxide by hydrogen as already described (see page 194).

The catalyst as well as the reactants must be pure. Traces of hydrogen sulfide, phosphine, arsine, and hydrogen chloride are active catalytic poisons. Electrolytic hydrogen freed from traces of oxygen and moisture is recommended. Under the most favorable circumstances, frequent renewal of the catalytic material is demanded because of gradual sintering or lowering of the catalytic activity due to poisons.

Sabatier classifies the hydrogenations in the presence of metallic catalysts under four headings, which are given in order, with specific examples in the form of equations:

I. Reduction without fixation of hydrogen.

$$C_6H_5OH + H_2 \rightarrow H_2O + C_6H_6 \qquad (1)$$

$$CS_2 + 2H_2 \rightarrow 2H_2S + C \qquad (2)$$

II. Reduction with simultaneous fixation of hydrogen.

$$2NO_2 + 7H_2 \rightarrow 2NH_3 + 4H_2O \qquad (3)$$

$$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O \qquad (4)$$

$$RCHO + H_2 \rightarrow R\cdot CH_2\cdot OH \qquad (5)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (6)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad (7)$$

III. Fixation of hydrogen with unsaturated compounds.

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{8}$$

$$CH_2{=}CHCH_2OH + H_2 \rightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot OH \tag{9}$$

$$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35} \cdot COOH \tag{10}$$

$$C_6H_5OH + 3H_2 \rightarrow C_6H_{11}OH \tag{11}$$

IV. Hydrogenation accompanied by decomposition of the molecule.

$$(C_2H_5)_2O + H_2 \rightarrow C_2H_6 + C_2H_5OH \tag{12}$$

$$C_6H_5OR + H_2 \rightarrow C_6H_6 + ROH \tag{13}$$

Among the above are several reactions that lie at the basis of technical processes. Thus (5) may be used in the synthesis of alcohol from acetaldehyde, which in turn is made by the catalytic hydrogenation of acetylene; (6) is of importance in the technical production of methane from water gas;[144] (7) in the synthesis of methyl alcohol, using zinc oxide promoted with Cr_2O_3 as catalyst;[145] (10) in the hydrogenation of liquid oils to solid fats;[146] and (11) in the preparation from phenol and *p*-cresol of cyclohexanol and *p*-methyl cyclohexanol, respectively, the starting point in the manufacture of isoprene and butadiene, the basis of synthetic rubber. For all of the above reactions and reaction types except (7), nickel is probably the most satisfactory catalyst.

In the organic laboratory, sols of platinum and palladium dispersed in various solvents such as water, alcohols, acetic acid, or hydrocarbons are now quite generally used in the saturation of unsaturated organic substances. In general, protected sols are employed because of their greater stability; but as already noted (see page 247), the gain in stability is accompanied by a corresponding loss in catalytic efficiency.[147]

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[144] Sabatier-Reid: "Catalysis in Organic Chemistry," 397 (1922).

[145] Chem. & Met. Eng., **30**, 881 (1924); Audibert and Raineau: Ind. Eng. Chem., **20**, 1105 (1928); Lewis and Frolich: **20**, 285 (1928); DeLong: J. Chem. Ed., **2**, 429 (1925).

[146] Sabatier-Reid: "Catalysis in Organic Chemistry," 339 (1922); Ellis: "The Hydrogenation of Oils," 2nd ed., 108 (1918); J. Soc. Chem. Ind., **31**, 1155 (1912); Shaw: **33**, 771 (1914).

[147] Groh: Z. physik. Chem., **88**, 414 (1914); Rideal: J. Am. Chem. Soc., **42**, 749 (1920); Jedale: J. Chem. Soc., **119**, 109 (1921); Rocasolano: Compt. rend., **173**, 41, 234 (1921).

PART II

THE NON-METALLIC ELEMENTS

CHAPTER XI

COLLOIDAL CARBON

The term colloidal carbon, strictly speaking, refers only to the carbon sols in which the element, in both the amorphous and crystalline forms, is dispersed in water or organic media. Adsorbent charcoal, the highly porous form of the element so widely used in purely scientific studies and in the industries, must, however, be considered in this category, since its extensive surface and its adsorption behavior are essentially colloidal in nature. The preparation, properties, and applications of the sol systems will be considered first.

CARBON SOLS

FORMATION AND STABILITY OF CARBON SOLS

Although the sols of carbon have received attention only in comparatively recent years, stable suspensions of the element were obtained more than fifty years ago by Bartoli and Papasgoli[1] during the study of the products resulting from the electrolysis of alkalies and acids with a carbon anode. They noted that the anode disintegrated in every case, and that with alkalies and ammonia a black liquid was formed which contained, among other things, carbon, mellogen, and mellitic and hydromellitic acids.

Four general methods of preparing carbon sols will be considered in order: electrical, partial solution, decomposition of organic compounds, and peptization.

Electrical Methods

Anodic Disintegration.—Sols by this method are best obtained in ammonia or alkali solutions. Thorne[2] carried out the ammonia electrolysis for 6 hours with a current density of 0.6 to 1.2 ampere/cm^2 and 220 volts. After the large particles were filtered off the ammonia

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[1] Gazz. chim. ital., **11**, 237, 468 (1881); **12**, 113, 125 (1882); **15**, 461 (1885); *cf.* Millot: Bull., (2) **33**, 262 (1880); **37**, 337 (1883).

[2] Kolloid-Z., **31**, 119 (1922).

content of the sol was 0.145 *N* and the amount of dispersed solid 0.034 g per 100 cc. The sol was deep black in layers more than 1 cm thick; thinner layers appeared brown. The residue after evaporation of the water was not taken up again in pure water, but a trace of ammonia repeptized it completely. Removal of the excess anion by boiling gave a sol which was more stable when subjected to dialysis than the unboiled sol. A boiled sol was still stable when the alkalinity was reducted to 0.005 *N*; an unboiled one coagulated if the alkalinity fell below 0.039 *N*. In both cases the dialysate was yellow, showing that some of the organic products of the electrolysis were dialyzable. It is probable that these organic products, mellitic acid and the like, were protective agents for the sol, supplementing the stabilizing action of hydroxyl ion. Since the boiled sol was stable in the presence of much less alkali than the unboiled one, it is probable that boiling polymerized the organic products to protecting colloids that did not dialyze out.

A sol with properties similar to the one described above was obtained by electrolysis of 0.1 *N* sodium hydroxide[3] at a current density of 3–4 amperes/cm². An analysis of the precipitate formed by coagulating the sol with barium chloride, washing with dilute hydrochloric acid, and drying, showed it to contain, in addition to carbon, hydrogen, and oxygen,[4] an incombustible residue of silica and iron derived from the electrodes. The hydrogen and oxygen were probably present chiefly as adsorbed water, but since the washings contained organic matter, it is certain that the precipitate retained some of this also.

Less stable sols were prepared by electrolysis of dilute sulfuric[5] and hydrochloric acids with amorphous carbon anodes; electrolysis of alkali solutions with graphite anodes gave only weak, relatively instable sols.

Definite indication that the sols formed by anodic disintegration are essentially carbon sols, rather than sols of complex carbon compounds,[6] was furnished by Podrouzek.[7] He electrolyzed a 10% solution of ammonium carbonate at a high current density using an anode prepared by molding very pure charcoal obtained by heating carbohydrates in a current of chlorine gas. Excessive heating was avoided during the electrolysis by passing water through a coil

[3] Thorne: J. Chem. Soc., **109**, 202 (1916).

[4] *Cf.* Söhngen: Chem. Weekblad, **11**, 593 (1914).

[5] Vanzetti: Kolloid-Z., **13**, 6 (1913).

[6] *Cf.* Coehn: Z. Elektrochem., **2**, 541 (1896); **3**, 424 (1897).

[7] Chimie et industrie, Special No. March, 291 (1930).

immersed in the bath. After the anode was consumed, the resulting sol was dialyzed for a month. The sol coagulated within the first few days, but the precipitate was kept in suspension by a mechanical stirrer. At the conclusion of the dialysis the precipitate was filtered off, washed, and finally dried in vacuum, yielding a fairly hard, black product containing 99.2% carbon. The mass was not repeptized by water or acids, but even dilute alkalies carried it completely into a colloidal solution in which the particles were around 25 mμ in diameter. The sol was coagulated by heat and by small amounts of salts with multivalent cations.

Disintegration in the Electric Arc.—Hydrosols of carbon are not formed by Bredig's method.[8] Stable organosols in ethyl alcohol, carbon tetrachloride, chloroform, benzol, etc., can be made by this method, but the carbon is derived for the most part from decomposition of the organic liquid rather than from the electrodes.[9] Svedberg[10] obtained an isobutyl alcosol of carbon with the oscillating arc which caused but little decomposition of the organic medium.

Partial Solution

The action of oxidizing agents, such as chlorates and hypochlorites, on charcoals, yields highly colored sols under suitable conditions.[11] The dispersed material may be in part elementary carbon, but prolonged action of the oxidizing agent probably gives chiefly colloidal complex oxidation products of carbon and of the hydrocarbons contained in the impure charcoals.[12]

Chirnoaga,[13] working in Donnan's laboratory, prepared a sol which he believed to be largely elementary carbon, by the action of sodium hypochlorite on a well-purified charcoal previously heated in vacuum to 900° and used in the adsorption of oxygen gas, whereby any adsorbed hydrogen was removed. The procedure was as follows: 0.3 g of charcoal was placed in a 100 cc flask and 5 cc portions of approximately $M/4$ sodium hypochlorite were added at intervals of 2–3 hours, the mixture being stirred rapidly in a thermostat at 25°. As sodium chloride is prejudicial to the stability of the sol, the opera-

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[8] Thomae: Kolloid-Z., **11**, 268 (1912).

[9] Tarczynski: Z. Elektrochem., **22**, 252 (1916).

[10] Ber., **39**, 1705 (1906).

[11] Berthelot: Ann. chim. phys., (4) **19**, 392 (1870); Dimroth and Kerkovius: Ann. **399**, 120 (1913); Hoffmann, Schumpelt, and Ritter: Ber., **46**, 2854 (1913); Hoffmann and Freyer: **53**, 2078 (1920).

[12] *Cf.* Bancroft: J. Phys. Chem., **24**, 342 (1920); Thorne: Kolloid-Z., **31**, 125 (1922).

[13] J. Chem. Soc., 298 (1928).

tion was stopped occasionally to dialyze out the excess salt before the addition of more hypochlorite. At the conclusion of the process the sol was well dialyzed to remove extraneous electrolytes. The preparation could be evaporated to dryness, giving a residue that was completely reversible on the addition of water. The solid residue obtained at 100° lost about 20% of its weight on heating to 300°. Chirnoaga attributed this loss largely to adsorbed water.

Ultramicroscopic examination of the sols containing 0.325 and 0.88 g of dry residue per liter gave 60 mμ and 68 mμ, respectively, for the average radius of the particles. There were, however, many smaller particles or other diffusible matter in the sol, since a double membrane of collodion and parchment paper did not prevent the diffusion of certain amounts of sol.

The mechanism of the sol-formation process was believed to be the gradual breaking down or etching of the surface of the charcoal whereby particles of colloidal dimensions were broken off. This is essentially the process of partial solution discussed in Chapter I.

The stability of the negative sol was attributed by Chirnoaga to the adsorption of chloride and hydroxyl ions derived from the hypochlorite solution. Although this may be true in part, the author is inclined to believe that the marked stability of the sol, and the reversibility of the residue resulting from evaporation, are due in large measure to the formation of some complex oxidation products of carbon which act as protecting colloids.

It is of interest that the brownish black liquid formed by evaporating the dilute sol can be used as an ink which is resistant to washing and to the action of chemical agents.

Decomposition of Organic Compounds

The action of sulfuric acid on carbohydrates, under suitable conditions, yields a sol mixture containing more or less carbon. Sabbatani[14] first prepared a sol in this way by adding 2 g of finely powdered sucrose to 20 cc of concentrated sulfuric acid, allowing the mixture to stand 24 hours, diluting to 80 cc, and dialyzing. Thorne emphasized the importance of adding the sugar very slowly to the acid, and Lachs and Gestel,[15] the necessity of keeping the temperature down during dilution of the acid mixture. The latter prepared

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[14] Kolloid-Z., **14**, 29 (1914).

[15] Z. physik. Chem., **A137**, 193 (1928); *cf.* Lachs: J. phys. radium, (6) **3**, 125 (1922); Goldberg: Kolloid-Z., **30**, 230 (1922); H. and Z. Beaszkowska: Ber. Ges. Wiss. Warschau, **9**, 261 (1916).

reproducible sols by adding 1.5 g of raw sugar to 20 cc of concentrated acid in a thoroughly dried vessel and, after 24 hours, allowing the mixture to drop so slowly into 80 cc of water that the temperature did not rise above 20°. The resulting sol, dialyzed for 8–10 days, was a perfectly clear brownish red.

Although the sols formed by the above process contain a considerable amount of colloidal carbon, it is certain that they are far from pure,[16] containing, among other things, undecomposed sugar and strongly dehydrated carbohydrates or their decomposition products. Lachs and Gestel report that their sols are very stable, remaining unchanged for more than six years. Fractional ultrafiltration experiments indicate that 75% of the particles have a diameter in the neighborhood of 140 mμ; 15% around 70 mμ; and the remainder around 4.4 mμ. The extraordinary stability of the sols with such large particles is attributed to their being agglomerates of highly hydrous units. The presence of a "water-soluble" protecting colloid that is strongly adsorbed by the carbon particles would have the same effect on the stability of the sol.

Gelatinous Carbon.—Sabbatani shook 2 g of sugar and 20 cc of concentrated sulfuric acid for 2 hours, stirred the mixture continuously for 3–4 days at room temperature, and placed it under a bell jar in a wide vessel alongside a vessel of water. The mixture took up water, and after 7–9 days the liquid set to a jelly which was removed from the vessel without losing its form. The jelly-like mass retained its shape on washing with repeated changes of water over a long period, but it shrank and disintegrated on drying in the air.

Peptization Methods

Peptization by Hydroxides.—Whitney and Straw[17] found that lampblack was peptized by dilute sodium hydroxide, the optimum concentration being 0.001 *N*, and Freundlich[18] obtained the most concentrated suspensions of fine wood charcoal in 0.01 *N* to 0.005 *N* alkali. Thorne[19] showed that the sols obtained in this way are very unsatisfactory at best. The presence of protecting colloids appears to be essential for the preparation of stable sols by this method.

Organosols of carbon in aniline, pyridine, and quinoline were

[16] Söhngen: Chem. Weekblad, 11, 593 (1914).

[17] J. Am. Chem. Soc., 29, 325 (1907).

[18] Z. physik. Chem., 57, 461 (1906).

[19] Kolloid-Z., 31, 119 (1922).

obtained by refluxing carbon with the liquids or by heating in sealed tubes at 200°.[20]

Aquadag and Oildag.—The terms aquadag and oildag are the technical terms for the colloidal dispersions of graphite in water and oil, respectively.[21] The "dag" portion of the name is compounded from the first letters of "deflocculated Acheson's graphite." Acheson's graphite is a synthetic product formed by heating amorphous carbon in the electric furnace in the presence of oxides such as silica, alumina, and ferric oxide which are capable of yielding carbides as an intermediate product. To prepare the hydrosol, the disintegrated graphite is treated with an aqueous sol of tannin containing 3–6% of the weight of graphite employed. The results are most satisfactory if a pasty mixture of graphite, tannin, and water is first prepared and masticated, say for a month, before dilution with water preferably containing a small amount of ammonia. The sol is quite stable and has an intense black color, and the particle size is much smaller than is possible of attainment by purely mechanical means. The tannin serves the combined rôle of peptizing agent and protecting colloid. The presence of a small amount of ferric oxide likewise has a stabilizing effect. The sol is negatively charged and is coagulated by a small amount of hydrochloric acid.

Oildag is prepared from aquadag by mixing the moist, well-masticated paste of graphite, tannin, and water with a light mineral oil, agitating the mixture thoroughly, and finally evaporating off the water.[22]

Colloidal Fuel.—The dispersion of pulverized carbon or coal in fuel oil is known as colloidal fuel. The processes for making the sols were worked out during the war by Bates[23] and others in the Eastman Kodak Laboratories under the direction of Sheppard.[24]

Two types of materials may be employed in preparing sufficiently stable sols of highly pulverized coal or carbon in fuel oil. These are the typical "oil-soluble" protecting colloids, and certain coal-tar distillates. The protecting colloids or fixatures that have been found most satisfactory are the alkaline earth soaps. A typical one is a variety of lime-rosin grease, specially prepared, in which lime, rosin, and water are incorporated into an oil carrier by the application of

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[20] Pertierra: Anales soc. españ. fis. quim., **29**, 663 (1931).

[21] Acheson: J. Franklin Inst., **164**, 375 (1908); Trans. Am. Electrochem. Soc., **12**, 29 (1907).

[22] Acheson: U. S. Pat., 1,030,372 (1912).

[23] Alexander's "Colloid Chemistry," **3**, 555 (1931).

[24] Ind. Eng. Chem., **13**, 37 (1921).

heat and stirring. The amount of fixature employed varies from 0.5 to 1.5%. The immediate effect of this is to increase the viscosity of the fuel oil and thereby to increase the stability of the suspension. This increased viscosity, though an important factor in stabilizing the preparation, is not the only one and may not be the most important one. The "oil-soluble" soaps doubtless exert a combined peptizing and stabilizing action similar to the action of tannin in the formation of stable graphite sols.

Bituminous coals and some other carbonaceous materials are peptized to a limited but sufficient extent by adding such coal-tar distillates as creosote and naphthalene-containing oils, and subjecting the mixture to a special heat treatment below the flash-point temperature. These and other measures can be combined so as to adapt the stabilizing treatment to the available materials. As an example, Bates reports that a very stable fuel consists of 30% coal, 10% coal-tar distillate, and 60% mineral oil containing an "oil-soluble" fixature.

PROPERTIES OF CARBON SOLS

Optical Properties.—The color of carbon sols varies from brown to deep black, depending on the method of preparation and the concentration. Ultramicroscopic observations[25] on a Sabbatani sol disclose the presence of very small, stationary, sparkling particles as well as submicrons showing rapid Brownian movement. The number of scintillating particles is proportionately much greater in the more concentrated sols. The scintillations are believed to be due to the plate-like or prismatic shape of the particles. The sol does not show streaming double refraction, and x-ray analysis indicates that all the particles are amorphous.

The Particle Charge.—The charge on the particles in impure carbon sols is usually negative, probably owing to the strong adsorption of hydroxyl ion and of negatively charged tannin so frequently used as a protecting colloid for the sols. Podrouzek[26] reports, however, that his almost pure carbon sol formed by peptizing the element with a weak base is electropositive. The addition of a "convenient" electrolyte reduces the charge to the isoelectric point, but with suitable amount of electrolyte the isoelectric point is passed and the sol is said to become electronegative. It would be difficult to account for this apparently anomalous behavior if it were not for the observations of

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[25] Lachs: J. phys. radium, (6) 3, 125 (1922).

[26] Chemie et industrie, Special No., March, 291 (1930).

Frumkin and Donde[27] that pure carbon containing adsorbed oxygen is positively charged and adsorbs acids but not bases, whereas pure carbon containing adsorbed hydrogen is negatively charged and adsorbs bases but not acids. (For the explanation of this, see page 292.) Under these conditions, one would expect the particles of pure charcoal to be positively charged when anodically dispersed, as Podrouzek found. Since the sols formed by anodic dispersion of impure charcoals are usually negative, one must conclude that in these cases the impurity in or on the charcoal is the important factor in determining the charge. In this connection, Kruyt and de Kadt[28] also found that ash-free adsorbent charcoal may exhibit either a negative or a positive charge. As a rule it is negatively charged when it is not heated too highly; but a purified Merck charcoal heated to 1000° in carbon dioxide or in vacuum was positively charged in water, was not easily wetted, and showed little tendency to adsorb sodium hydroxide. This positive carbon was readily changed to negative by heating at 400° in oxygen. In contrast to the positive preparation, the negative was readily wetted and adsorbed appreciable amounts of sodium hydroxide. The negative charge in water which the particles possess when heated in oxygen at low temperature was attributed to the formation, on the surface, of a carbon-oxygen complex[29] preliminary to the formation of mellitic acid in contact with water. The transformation to the opposite charge on heating to a high temperature was attributed to the destruction of the carbon-oxygen complex (see page 296).

Action of Electrolytes.—The stepwise addition to carbon sols of acids and alkalies, and probably of other electrolytes with univalent cations, causes at first an increase in the mobility of the particles followed by a decrease to the critical coagulation point.[30] Thorne[31] determined the precipitation values of several electrolytes for a dialyzed carbon sol prepared by anodic disintegration of carbon in dilute ammonia and for an Acheson's graphite sol. These data are collected together in Table XL. The amorphous carbon sol behaves toward electrolytes like a typical negative sol except in its high sensitivity toward alkalies and sodium chloride. The graphite sol is characterized by its abnormally high sensitivity toward acids, a

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[27] Ber., 60, 1816 (1917); Frumkin: Kolloid-Z., 51, 123 (1930).

[28] Kolloid-Z., 47, 44 (1929).

[29] *Cf.* Schilow, Schatunowskaja, and Tschmutow: Z. physik. Chem., A149, 211; 150, 31 (1930).

[30] Goldberg: Kolloid-Z., 30, 230 (1920); Iwantizkaja and Proskurnin: 39, 15 (1926).

[31] Kolloid-Z., 31, 119 (1922).

TABLE XL

PRECIPITATION OF CARBON SOLS

Electrolyte	Precipitation value in millimols/liter	
	Amorphous carbon sol	Graphite sol
HCl........	60.0	1.5
NaOH.....	290.0	580.0
NH_4OH....	>9000.0	>9000.0
NaCl.......	450 0	75.0
$BaCl_2$......	0.5	0.9
$AlCl_3$......	0.3	0.3

fact recognized by Acheson in his early experiments with this sol. The respective coagulation values in millimols per liter for a highly stable Sabbatani sol were found by Lachs and Gestel[32] to be as follows: LiCl = 1400; NaCl = 1350; KCl = 600; CsCl = 450; $BaCl_2$ = 30; $AlCl_3$ = 0.5; and $ThCl_4$ = 0.35.

APPLICATIONS OF CARBON SOLS

The most important applications of carbon sols are as inks and paints, lubricants, and fuel; some medicinal uses have also been suggested. These will be considered briefly in order.

Ink and Paints.—Inks were known as early as 2500 B.C. and then, as now, were used for writing. They were black, and like modern India ink and printer's ink derived their color from colloidally dispersed carbon.

The best grade of printer's ink consists of the highest quality carbon black dispersed in a pure linseed oil varnish made by heating the oil to 380–400°, taking precautions to avoid ignition. Cheaper printer's ink may be prepared by using lampblack of inferior quality and suspending it either in mineral oil containing resin and soap or in a mixture of these substances with linseed oil. According to Thorpe,[33] an average letter-press ink may be made by adding, to each gallon of the hot linseed oil varnish, 4 pounds of resin and 1 pound of soap. This is then thoroughly mixed with somewhat less than

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[32] Z. physik. Chem., A137, 193 (1928); Kolloid-Z., 59, 170 (1932).

[33] "Dictionary of Applied Chemistry," 3, 633 (1923).

one-third its weight of carbon black. The presence of soap is said to cause the ink to lift well, that is, to be completely transferred from the type to the paper. The soap and resin also have a protecting action on the sol.

India ink consists of a dispersion of carbon black or lampblack in a glue solution containing some preservative to prevent putrefaction of the glue. In modern drawing inks, gum arabic or shellac is used in place of glue, with borax as a preservative.

Carbon black is almost universally employed as the pigment in black paint and lacquers. The tinting effect of carbon black on rubber is of minor importance compared to its action in reinforcing the vulcanized material.[34]

Lubricants.—Acheson's oildag and aquadag have an important place in lubrication, since the colloidal graphite is adsorbed on the bearing surfaces and forms a protecting film against wear. The lubricating qualities of aquadag have resulted in its use in steam boilers and compressors and in drawing into wire of such elements as tungsten and molybdenum. Because of its inert qualities it is also employed as a parting compound in rubber molds and in die casting.

The addition of graphite to mineral oil produces a lowering in the interfacial tension between the oil and bearing metals and thereby lowers the coefficient of friction. Moreover, the National Physical Laboratory (England) reports "that a bearing lubricated with mineral oil to which oildag had been added would run with about one-third the minimum lubricant required with the same mineral oil without oildag. . . . This may be caused by the formation of a 'graphoid' surface on the journal and bush so that less oil will produce a film of sufficient thickness to carry the loads, or it may be caused by improved lubricating qualities due to the presence of graphite."[35]

In connection with the applications of colloidal graphite, mention may be made of the adsorption of the graphite from aquadag on the surface of non-conductors thereby imparting to the surface the capacity to conduct the current. For example, glass will adsorb graphite from aquadag and it can then be plated in the usual manner in the electrolytic bath.

Fuel.—The discoverers of colloidal fuel, prepared by the dispersion of carbon or coal in fuel oil in the manner described above, claim certain important advantages of the colloidal product over ordinary fuel oil.[36] In the first place, the fire hazard of colloidal fuel is less

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[34] *Cf.* Shepard: Alexander's "Colloid Chemistry," 4, 309 (1932).

[35] Acheson: Alexander's "Colloid Chemistry," 3, 547 (1931).

[36] Bates: Alexander's "Colloid Chemistry," 3, 555 (1931).

than that of oil fuel since the specific gravity of the former, containing over 15% of coal, is greater than unity. For this reason, if the colloidal fuel catches fire, it may be put out with water, and, in storage, fire may be prevented by a water seal. Moreover, the flash point of most colloidal fuels is higher than that of the fuel oil alone. Secondly, a good grade of colloidal fuel possesses more heat units per volume than either of its principal components, separately. This means that, where storage space in ships is of greater importance than weight, greater heating capacity and steaming radius may be obtained by the use of the colloid than by using oil alone, and much greater than by using coal. Thirdly, colloidal fuel may be prepared which possesses greater combustion efficiency than straight oil. The explanation is that in the combustion chamber the liquid film on the outside of the peptized particle gasifies first and that which penetrates the cavities of the coal gasifies next, thus exploding the particles. The areas exposed to oxidation are thereby made greater than that even of sprayed liquid droplets or of dry coal particles. Finally, colloidal fuel may be employed in the usual oil-burning installations without greatly modifying them.

Added to all the advantages claimed above is the important matter of the conservation of the liquid fuel supply of the world. If the fuel oil now available were converted into colloidal fuel, the liquid fuel supply would be increased by 50%. Under the circumstances it seems probable that colloidal fuel will be widely used in the not far distant future. In July, 1932, the Cunard Line's oil-burning liner *Scythia* made a round trip from Liverpool to New York using colloidal fuel, and the experiment was reported to be a complete success.

Pharmacology.—The suggested uses of carbon sols in pharmacology are based on the high adsorbing capacity of carbon. Thus the addition of the electrically formed sol to milk retards acidification, probably owing to adsorption of the lactic acid bacillus;[37] and its bactericidal action, generally, depends on its adsorptive power.[38] Sabbatani[39] suggests the intravenous injection of carbon in strychnine poisoning. This is likewise based on the tendency of carbon to adsorb strychnine. Poudrouzek[40] reports that animals anesthetized with chloroform awaken promptly after the intravenous injection of his pure carbon sol. By the same procedure he claims to have destroyed the action

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[37] Rénon, Richet, and Lepin: Compt. rend. soc. biol., 76, 64 (1914).

[38] Louros and Scheyer: Z. ges. exptl. Med., 55, 724 (1927).

[39] Biochem. Z., 59, 378 (1914).

[40] Chemie et industrie, Special No., March, 291 (1930).

of diphtheria toxin in 85% of the cases tried. These suggestions are interesting, but they have not developed to the practical state as yet.

ADSORBENT CARBON

Adsorbent charcoal has found such wide use in scientific laboratories and in the industries that a complete survey of the subject lies well beyond the scope of this volume. A volume on this subject has been written by Mantell,[41] and one is being prepared by Chaney for the American Chemical Society Monograph Series. In this section of the chapter, attention will be called to only a few of the more important characteristics of the adsorbent and to some of its outstanding scientific and technical applications.

The knowledge that vegetable carbon, obtained by heating wood in a closed vessel, will remove coloring matter from solutions seems to have been known in the fifteenth century. This phenomenon received slight attention, however, until 1785, when it was rediscovered by Löwitz, who was responsible for its use a few years later in the purification of raw sugar. Honig[42] points out that in 1808 a sugar refinery at Passy obtained with wood char a beet sugar free from the disagreeable taste of the beet roots, a fact which was of considerable importance in the early stages of the beet-sugar industry. With the discovery in 1811 of bone charcoal which possessed superior decolorizing qualities, vegetable charcoal received a setback from which it did not recover until comparatively recent years when methods were devised for increasing greatly the adsorbing power of carbons derived from various sources. The subsequent pages will be devoted chiefly to the preparation, properties, and applications of the modern activated carbons.

ACTIVATED CARBON

Methods of Activation

In the preparation of activated carbon, various raw materials have been employed such as the charcoals made from a wide variety of woods and nuts, and coke derived from coal, lignite, and peat, etc. Recent patent literature in various countries abounds with patents covering methods which have been more or less successful in increasing the adsorption capacity of the carbons derived from the several

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[41] "Industrial Carbon," Van Nostrand (1928).

[42] Kolloid-Beihefte, 22, 345 (1926).

sources. As an example of the methods of activation three of the most common procedures will be taken up in some detail.

Activation with Steam.—This process, which was developed during the war, consists, among other things, in the removal of adsorbed hydrocarbons from ordinary relatively inactive charcoal by a combination of oxidation and distillation with steam.[43] The charcoal to be activated is obtained by destructive distillation at relatively low temperatures, since carbon formed from the cracking of hydrocarbons at high temperature is not only relatively inactive but also difficult to activate. The so-called "primary carbon" from the low-temperature distillation contains adsorbed hydrocarbons which cut down its capacity to adsorb other substances. The adsorbed hydrocarbons could be removed by volatilization and cracking at high temperatures, but, as already stated, this would lead to the deposition of carbon more or less like ordinary graphite which is not only inert and non-adsorbent but also highly resistant to oxidation. Treatment with steam at a suitable temperature not only results in oxidation and volatilization of the adsorbed impurities but causes a partial oxidation of the "primary carbon." The latter process is doubtless advantageous up to a certain point, in enlarging the pores and rendering a greater surface more accessible; but it must not be carried to the point of uniting cavities, otherwise it decreases rather than increases the available adsorbing surface. The temperature at which the process is carried out must be chosen and regulated so as to oxidize the hydrocarbons rapidly and the carbon slowly. The optimum temperature for steam activation has been found to lie between 800 and 1000°. American gas-mask charcoal and "Norit" charcoal are technical adsorbents prepared by this general procedure.

Activation with Air and Other Gases.—Air, carbon dioxide, and chlorine may be used as oxidizing agent in the place of steam, the "primary carbon" being heated in a current of the gas at a suitable temperature. The optimum temperature for air activation of the charcoal used in American gas masks is between 350 and 450°.[43] Probably the chief advantage of the process lies in this conveniently low operating temperature. Unfortunately, it is open to the disadvantage that the oxidation of hydrocarbons, being an exothermic process, results in local heating and an excessive consumption of carbon before the hydrocarbons are removed. In steam activation, on the other hand, certain operating difficulties are increased by the higher temperature required, but since the reaction between steam

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[43] Lamb, Wilson, and Chaney: Ind. Eng. Chem., 11, 420 (1919).

and carbon is endothermic, local heating due to this cause is eliminated and a stable thermal equilibrium is possible. It is claimed that charcoal of the highest activity cannot be prepared by air activation alone; but E. J. Miller, in a private communication, states that he has repeatedly activated sugar charcoal in air so that its activity was higher than that of any charcoal on the market, irrespective of the method of activation.

Carbon dioxide with or without steam has been employed as an activating agent, the temperature being in the neighborhood of 1000°.

Activation with Zinc Chloride.—To prepare active carbon by the aid of zinc chloride, a mash is first prepared of wood or other uncarbonized material and concentrated zinc chloride solution, the ratio of salt to dry material varying between wide limits with the purpose for which the resulting charcoal is to be used. The mash is dried and calcined at a temperature between 400° and 800°, after which the charred mass is digested with water to remove the excess zinc chloride and finally thoroughly washed, ground to the desired degree of fineness, and dried.

Technical products prepared with zinc chloride and used as decolorizing agents or in the industrial adsorption of gases and vapors are sold under the trade names "carboraffin" and "radit" (from Czechoslovakia and Germany) and "antichromos" (from Italy). A carbon prepared in France using phosphoric acid in place of zinc chloride is known commercially as "diamond char."

Effect of Activation on the Properties of Charcoal

Adsorbing Power.—The effect of activation on the adsorbing power of various charcoals is well illustrated by some observations of Barker[44] on the adsorption of carbon tetrachloride from its saturated vapor at 24° as given in the second column of Table XLI. In the same table are given also the granular density and a statement of the physical character of the charcoal. It will be noted, for example, that activation increases the adsorption in milligrams of carbon tetrachloride per gram of charcoal, from 11 to 1480 for commercial wood charcoal and from 30 to 2715 for lignite semi-coke. At the same time the granular density decreases and the products change from a firm to a friable physical state.

True Density.—The density of powdered charcoal is determined in two ways. In the first procedure, the sample is heated and sub-

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[44] Ind. Eng. Chem., **22**, 926 (1930).

TABLE XLI

EFFECT OF ACTIVATION ON THE ADSORBING POWER OF CHARCOALS

Substance tested	Adsorption of CCl_4 per g substance, mg	Granular density	Physical character
Ironwood	22	0.96	Fibrous, hard
Primary ironwood charcoal	30	0.89	Hard
Activated ironwood charcoal	1160	0.72	Hard, friable, granular
Commercial wood charcoal	11	0.46	Firm, fibrous
Highest activated wood charcoal*	1480	0.30	Soft, friable
Cocoanut shells	18	1.20	Hard
Primary cocoanut charcoal	47	0.96	Hard
Activated cocoanut charcoal	630	0.84	Hard
Lignite semi-coke	30	1.09	Firm
Good activated lignite charcoal	640	0.89	Firm
Highest activated lignite charcoal*	2715	0 31	Friable, granular

* Further activation reduces the granule to a fine powder.

jected to a vacuum, then sealed in a tube, and the tube broken under water. The pores of the charcoal are filled more or less with the liquid, and the density is determined from the change in weight under the liquid.[45] In the second method, the sample is thoroughly outgassed, helium is admitted to the container from a measuring burette, and the volume of the charcoal substance is determined.[46] Some typical observations compiled by Barker are given in Table XLII. It will be noted that the method with helium gives higher values for the density than the method with liquids, probably because the helium can penetrate into fine pores that will not admit the liquids. The values with helium would seem to be the more nearly correct.

From the above data it is apparent that a marked increase in the density of charcoal takes place as a result of the activation process, the value for active charcoal being just below the true density of graphite. If the granular density given in Table XLI is considered in connection with the true density, it is seen that activation causes a marked increase in pore volume and that a large share of the increase is in the form of very minute pores or cracks.

[45] Cude and Hulett: J. Am. Chem. Soc., **42**, 391 (1920).

[46] Howard and Hulett: J. Phys. Chem., **28**, 1082 (1924); Stamm: **33**, 398 (1922).

TABLE XLII

True Densities of Wood and Charcoals

Substance	Density	Method	Observer
Wood	1.533	Helium	Stamm
Wood	1.536	Water	Stamm
Wood	1.479	Benzol	Stamm
Primary ironwood charcoal	1.46	Water	Barker
Primary willow charcoal	1.44	Helium	Howard and Hulett
Petroleum coke	1.43	Helium	Howard and Hulett
Activated ironwood charcoal	1.86	Water	Barker
Activated cocoanut charcoal	1.85	Water	Barker
Lignite coke (low temp.)	1.43	Water	Barker
Activated cocoanut charcoal	1.85	Water	Cude and Hulett
Activated cocoanut charcoal	2.15	Helium	Howard and Hulett
Activated cocoanut charcoal	1.65	Carbon tetrachloride	Cude and Hulett
Activated cocoanut charcoal	1.98	Carbon bisulfide	Cude and Hulett
Ceylon graphite	2.28	Helium	Howard and Hulett

X-ray Diffraction.—X-ray studies by Debye and Scherrer[47] indicate that active charcoal is made up of very minute graphite particles. From similar investigations, Ruff, Schmidt, and Olbrich[48] conclude, however, that active carbon is a true crystalline modification of the element which does not possess exactly the same lattice as graphite. It is apparently very difficult to decide definitely whether the positions of the diffuse lines in the x-ray diagram of activated charcoal are the same as those for graphite. In any event, Barker's x-ray and density studies lead him to conclude that, "primary charcoal substance having a true density of about 1.45 is partially converted to graphite or graphite-like carbon of crystalline structure having a true density of about 2.15." Until the matter can be settled definitely, the author prefers to regard the crystals in activated charcoal as graphite rather than as another graphite-like form of the element.[49] In this connection Barker reports that Alm[50] observed

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[47] Physik. Z., **18**, 291 (1917).

[48] Z. anorg. Chem., **148**, 313 (1925); *cf.*, *also*, Berl, Andress, Reinhardt, and Herbert: Z. physik. Chem., **A158**, 273 (1932).

[49] *Cf.* Hofmann, Groll, and Lemcke: Z. angew. Chem., **44**, 841 (1931); Hofmann and Wilm: Z. physik. Chem., **B18**, 401 (1932).

[50] Thesis, Mass. Inst. Technology (1927).

the ready formation of a graphite structure on heating or activating carbon blacks.

Mechanism of the Activation Processes

Activation with Steam and Air.—Chaney,[51] as a result of his pioneer investigations on the activation of charcoal by steam and air, came to the conclusion that elementary carbon (other than diamond and graphite) exists in two modifications, active and inactive; and that all primary amorphous carbon consists essentially of a stabilized complex of hydrocarbons adsorbed on a base of active carbon. From this point of view, activation by steam or air consists in the removal of the adsorbed film of hydrocarbons from the active carbon base by differential oxidation accompanied by an increase in porosity by partial oxidation of the carbon base. More recent observations show that this is by no means the whole story. In this connection E. J. Miller in a private communication points out that if activation consists merely in the removal of adsorbed hydrocarbons from a primary carbon, "simple distillation in high vacua at high temperatures in the absence of oxidizing gases should produce an active charcoal, but it does not. Furthermore, if hydrocarbons are placed on an activated charcoal they can be displaced by other highly adsorbed substances or they can be removed by simple heating or vacuum distillation leaving the activated charcoal in its original active condition." As noted above, during activation the density of the carbon is greatly increased, approaching that of graphite, and x-radiograms reveal the transformation from amorphous carbon to graphite. This increase in density produces an internal shrinkage of the charcoal which results in the formation of minute cracks and fissures in the granule.

In a good granular charcoal, the transformation to graphite is not complete, sufficient primary charcoal remaining to act as a binder. This is indicated by the slightly lower density of activated carbon and by the fact that an ultimate analysis of some of the best activated charcoals reveals the presence of considerable amounts of both hydrogen and oxygen. In this connection Langmuir[52] writes: "Truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibers of

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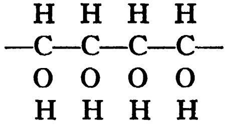
[51] Trans. Am. Electrochem. Soc., **36**, 91 (1919).

[52] J. Am. Chem. Soc., **38**, 2285 (1916).

cellulose from which charcoal is usually formed probably consist of practically endless groups of atoms



$$\begin{array}{c} \mathrm{H}\quad\mathrm{H}\quad\mathrm{H}\quad\mathrm{H} \\ -\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}- \\ \mathrm{O}\quad\mathrm{O}\quad\mathrm{O}\quad\mathrm{O} \\ \mathrm{H}\quad\mathrm{H}\quad\mathrm{H}\quad\mathrm{H} \end{array}$$

held together by primary valences in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat, the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. The porosity of the charcoal thus undoubtedly extends down to atomic dimensions. The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon."

The higher adsorbing power of the graphite formed during activation, as compared with that of ordinary graphite, is due to the extremely minute size of the crystals of the former and to their large surface energy resulting from loosely held electrons on the surface of the graphite lattice.[53] The inactive carbon formed by the decomposition of carbon-bearing materials at relatively high temperatures is probably a dense form of amorphous carbon of low porosity or is made up of relatively large graphite crystals of low specific surface. A graphite having an adsorbing capacity one-third to one-fourth that of the best adsorbent charcoal is obtained by oxidation of "graphitic acids."[54]

To summarize: the activation process (1) removes adsorbed hydrocarbons from charcoal by differential oxidation; (2) increases the interior surface area of the charcoal as a result of (*a*) the shrinkage accompanying an increase in density and (*b*) partial oxidation of the carbon itself; (3) produces a large volume of very small capillary spaces; and (4) changes the character of the surface from amorphous carbon to extremely minute graphite crystals possessing an enormous specific surface. Finally, it should be mentioned that it is by no means obvious why the minute graphite crystals which are formed during activation should possess a higher adsorbing power than an amorphous mass of disarranged carbon atoms. Nor is it clear why activation gives extremely small graphite crystals, since the high

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[53] *Cf.* Raman and Krishnamurti: Nature, **124**, 53 (1929).

[54] Lowry and Morgan: J. Phys. Chem., **29**, 1105 (1925).

temperatures that are necessary over a period of time would be expected to favor the growth of smaller crystals into larger ones.[55]

Zinc Chloride Activation.—The rôle of zinc chloride in the preparation of active charcoal appears not to be thoroughly understood. Honig's[56] suggestion that the salt acts as a dehydrating agent cannot hold under the conditions of charring. In view of the well-known peptizing action of zinc chloride on cellulose, the author is inclined to believe that the first action of the salt on wood pulp is to peptize it partially, thereby contributing to the formation of a gelatinous mass when the water is evaporated off. Ignition of this thoroughly impregnated mass yields charcoal deposited on a base of zinc chloride and probably some oxide or basic salt. The removal of the salt base with water and acid leaves a very highly porous framework of charcoal with high adsorbing power.

ADSORPTION BY CARBON

Adsorption phenomena on charcoal have received such detailed consideration in standard works on colloid chemistry that, even if space were available, little would be gained by going over the ground that has been covered so well by Freundlich,[57] Bancroft,[58] and others. In this section, it is proposed to deal more especially with a few recent observations on adsorption of gases and vapors and adsorption from solution, which throw light on the mechanism of adsorption processes.

Adsorption of Gases and Vapors

Adsorption by Wood Charcoal.—Some typical adsorption curves obtained with wood charcoal by Homfray[59] and by Titoff[60] are reproduced in Fig. 39.

It is frequently stated as a first approximation that a gas or vapor tends to be adsorbed more readily the higher its boiling point. The observations of Titoff in Fig. 39 support the rule, the adsorption increasing with increasing boiling point of the several gases in the order $NH_3 > CO_2 > N_2 > H_2$. No such regularity is to be found with the series of gases studied by Homfray. Thus the order of

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[55] *Cf.* Clark: Colloid Symposium Monograph, **4**, 155 (1926).

[56] Kolloid-Beihefte, **22**, 345 (1926).

[57] "Kapillarchemie," 4th ed., **1**, 125, *et seq.* (1930).

[58] "Applied Colloid Chemistry," 3rd ed., 3, *et seq.* (1932).

[59] Z. physik. Chem., **74**, 129 (1910).

[60] Z. physik. Chem., **74**, 641 (1910).

adsorption at 0° is: $C_2H_4 > CO_2 > CH_4 > CO > N_2 > Ar$; whereas the order of boiling points is: $CO_2 > C_2H_4 > CH_4 > Ar > CO > N_2$.

The effect of temperature on adsorption is well illustrated by Richardson's[61] data for carbon dioxide and ammonia on cocoanut charcoal, Fig. 40.

A glance at the several curves in Figs. 39 and 40 discloses that all of them are smooth and of the typical adsorption type, the data for which can be represented fairly well by the Freundlich equation (see page 199) especially in the lower pressure range. At higher pressures the adsorption falls off rapidly, indicating that at each temperature a maximum is reached which cannot be increased by raising the pressure. In this range of higher pressure where the curve parallels the pressure axis, the Freundlich equation cannot apply. Further examples of this type of adsorption will be given in the following paragraphs.

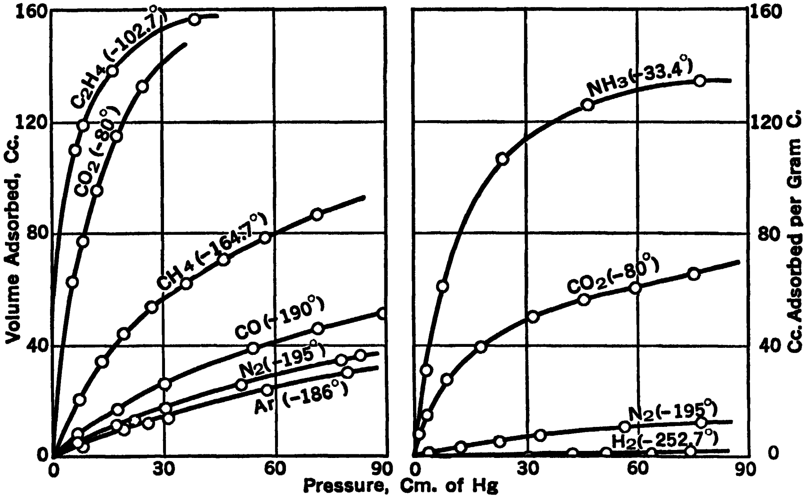

FIG. 39.—Adsorption isotherms at 0° for various gases on wood charcoals.

Adsorption by Activated Sugar Charcoal.—The adsorption of gases and vapors at pressures up to 60 atmospheres has been carried out by McBain and Britton[62] using pure sugar charcoals activated by both the steam and air processes. The experiments were carried out by the aid of a special microbalance, and special precautions were taken to remove all foreign gases by high evacuation of the charcoal and

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[61] J. Am. Chem. Soc., 39, 1828 (1917).

[62] J. Am. Chem. Soc., 52, 2198 (1930).

washing with the gases whose adsorption was to be measured. The results with nitrous oxide using steam-activated charcoal, and with nitrogen using both steam- and air-activated adsorbents, are shown

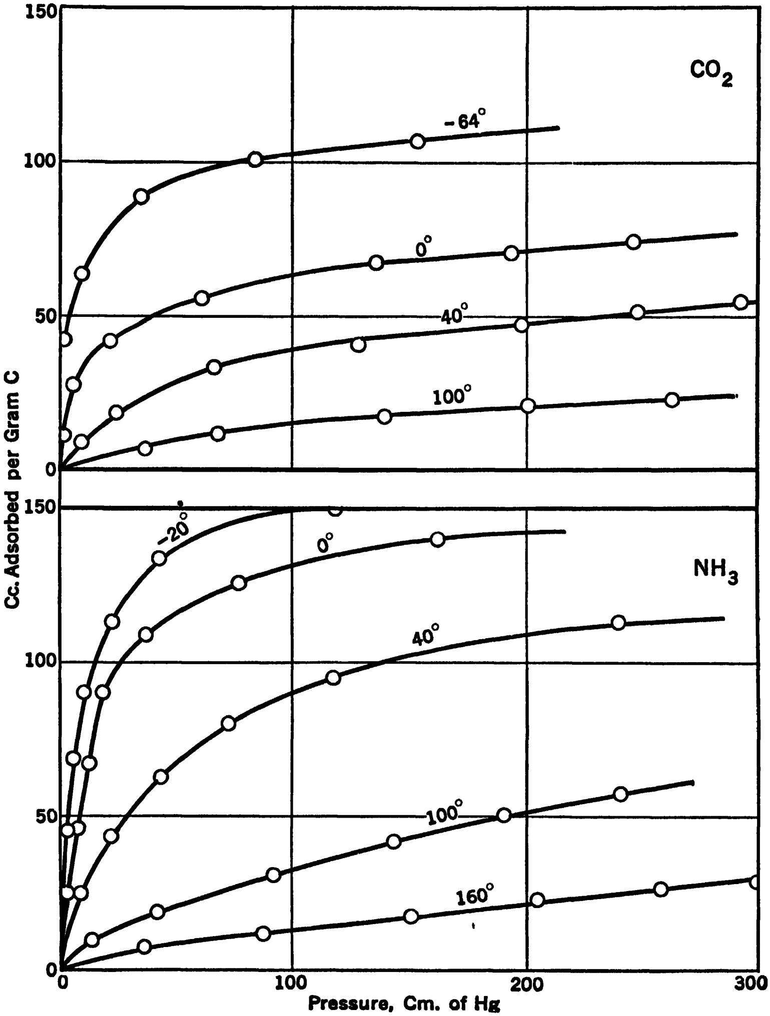

FIG. 40.—Effect of temperature on the adsorption of carbon dioxide and of ammonia by cocoanut charcoal.

graphically in Figs. 41 and 42, respectively. The adsorption values were calculated assuming the effective density of the charcoal to be 1.8.

It will be noted that the adsorption of nitrous oxide attains the

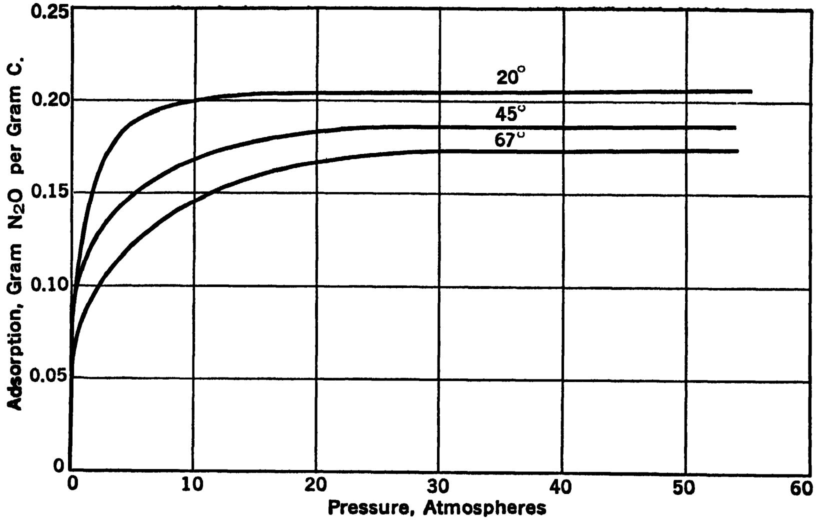

FIG. 41.—Adsorption of nitrous oxide at various temperatures by steam-activated sugar charcoal.

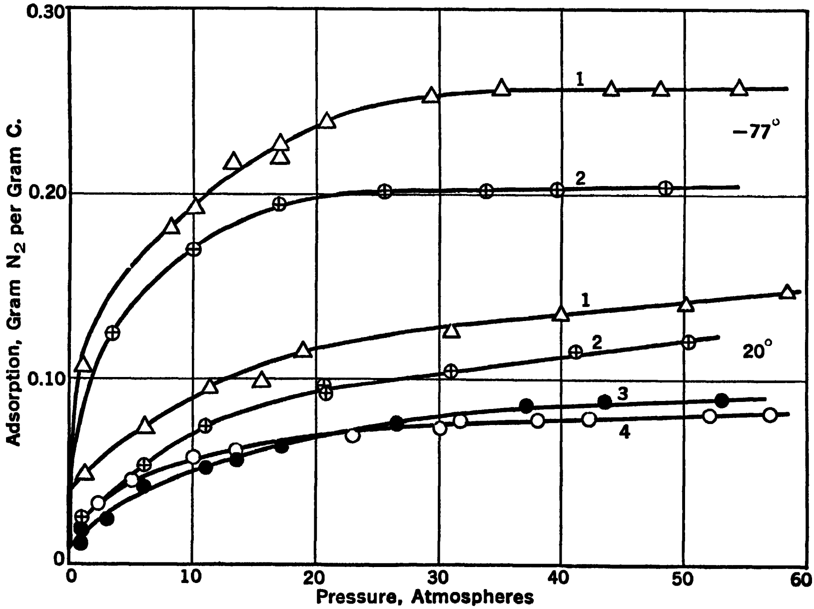

FIG. 42.—Adsorption of nitrogen by air-activated (curves 1 and 2) and steam-activated (curves 3 and 4) sugar charcoals at 20° and −77°.

saturation value at pressures in the neighborhood of 20 atmospheres at all temperatures investigated. Since the critical temperature of nitrous oxide is 36.5°, it is apparent that there is no special difference between the curves for gas and vapor.

For nitrogen at 20° a maximum is attained with the steam-activated charcoal but not with the air-activated adsorbent. This is not surprising in view of the fact that the adsorption value on the air-activated preparation at 20° and 60 atmospheres is only about one-half that of the saturation value at −77°.

The data on the adsorption of nitrogen appear to furnish a crucial test of the validity of the classical de Saussure[63] or Polanyi[64] theory that the adsorbed gas is in the form of a compressed fluid obeying an ordinary equation of state such as van der Waals', but under an excess compression due to the attractive force of the solid. Knowing the behavior of nitrogen under compression from Amagat's work,

TABLE XLIII

BEHAVIOR OF N_2 ON COMPRESSION

F atm.	Density at $1 + F$	Excess over density at 1 atm.	Density at $60 + F$	Excess over density at 60 atm.	Remarks
1000	0.5861	0.5849	0.5995	0.5279	Decrease *
100	0.1199	0.1187	0.1849	0.1133	Decrease
10	0.0130	0.01182	0.08353	0.01190	Very slight increase *
5	0.0071	0.00592	0.07759	0.00596	
1	0.0023	0.00112	0.0729	0.00127	

*** Experiment shows a many fold increase.**

McBain and Britton considered 1 cc of the adsorption space, that is, the region in which the attractive forces of the solid are operative, and calculated directly what the density of the nitrogen at 16° in 1 cc would be if the average pressure inside the adsorption space exceeds that of 1 atmosphere by any specified amount, F atmospheres. Similar calculations were made for 60 atmospheres, and the results compared, as given in Table XLIII. The density of nitrogen at 1 atmosphere was taken as 0.00118 and at 60 atmospheres as 0.07163. A com-

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[63] Gilbert's Ann., **47**, 113 (1814).

[64] Ber. deut. physik. Ges., **16**, 1012 (1914); **18**, 55 (1916); Z. Elektrochem., **26**, 370 (1920).

parison of the calculated data in Table XLIII with the observed adsorption values for nitrogen on charcoal as given in Table XLIV discloses that the latter are by no means in accord with the conception of an adsorption film differing from the surrounding atmosphere merely as a result of the compression caused by the attractive force of the adsorbent. Even if this compression is assumed to be only 1 atmosphere,[65] it is apparent that, of the nitrogen adsorbed, only a negligible proportion can be in the compressed state postulated by Polanyi. The remainder must be directly attached to the charcoal atoms as a monomolecular layer[66] or as a second layer attached to the first monomolecular film.[67] McBain's observations and calculations likewise render improbable Polanyi's[68] alternative hypothesis which attempts to conform the compressed film concept with monomolecular adsorption by assuming a sideways compression of the adsorbed layer such that it would be the equivalent of a two-dimensional gas or, at lower temperatures, form islands of liquid.

TABLE XLIV

ADSORPTION OF N_2 AT 1 ATMOSPHERE COMPARED WITH THE ADSORPTION AT A MUCH HIGHER PRESSURE

Tube No.	Pressure, atm.	Adsorption		Increase
		Uncorrected	Corrected	
I	1.0 61.0	0.002084 0.003636	0.00215 0.00784	3.5 fold
II	1.0 53.0	0.001063 0.004656	0.00113 0.00812	7.0 fold
III	1.0 50.6	0.002255 0 007692	0.00233 0.0114	5.0 fold
IV	1.0 58.5	0.004897 0.008918	0 00496 0.0125	2 5 fold

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[65] Advocates of the theory have estimated compressions as high as 37,000 atmospheres.

[66] Langmuir: J. Am. Chem. Soc., **38**, 2221 (1916); **39**, 1848 (1917); **40**, 1361 (1918).

[67] Lamb, Wilson, and Chaney: Ind. Eng. Chem., **11**, 424 (1919); Langmuir: Trans. Faraday Soc., **17**, 614 (1921).

[68] Z. physik. Chem., **A138**, 459 (1928).

Further support of Langmuir's theory of adsorption to the case at hand is furnished by the applicability of the Langmuir equation $A = \dfrac{\alpha\beta p}{1 + \alpha p}$, or $p/A = (1/\alpha\beta) + (p/\beta)$, throughout the whole range of pressures as evidenced by the straight lines obtained when p/A is plotted against p.

In the light of the above observations, McBain contends that adsorption and absorption are equally misnomers when applied to the taking up of gases by active charcoal. It is pointed out that the dissemination of the gaseous molecules and the carbon atoms is almost as intimate but is not so uniform as that of a true solid solution. But since the so-called pores are on an atomic or molecular scale, the concept of a surface disappears. The term "persorption" is suggested to describe such phenomena.[69]

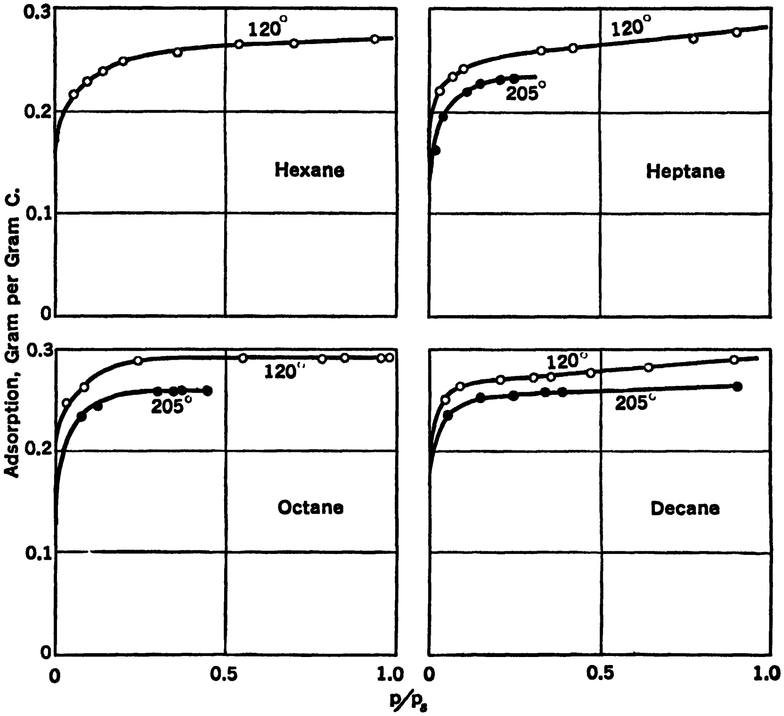

FIG. 43.—Adsorption of vapors by highly evacuated sugar charcoal.

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[69] McBain: Trans. Faraday Soc., **28**, 408 (1932); *cf.* Langmuir: J. Am. Chem. Soc., **38**, 2286 (1916).

In concluding this section, attention will be called to the form of the adsorption isotherms when vapors are adsorbed on activated and very highly evacuated sugar charcoal.[70] Some typical examples of such curves are given in Fig. 43, in which the $x/m = A$ value is plotted against the ratio of the pressure at which the adsorption is measured, to the vapor pressure at the temperature employed, p/p_s. It will be noted that practically all the adsorption occurs at very low pressures, little or no increase in adsorption being observed over the whole of the remaining higher pressures. This type of curve is approached more nearly the more drastic the preliminary purification of the carbon. It therefore represents the true characteristic behavior of a pure vapor when adsorbed on pure carbon. The curves of the more common type shown in Figs. 39 and 40 result when the charcoal employed contains more or less adsorbed impurities. The data for the type of curve given in Fig. 43 are represented adequately by Langmuir's equation. Freundlich's equation, on the other hand, applies only over the range of very low pressures.

The adsorption isotherms for gases and vapors on charcoal exhibit discontinuities[71] similar to those observed with metallic adsorbents (see page 208).

Adsorption from Solutions of Weak Electrolytes

In adsorption from solution by solids, two cases are possible: in the first, which is known as positive adsorption, relatively more of the solute is adsorbed than of the solvent; and in the second, which is termed negative adsorption, relatively more of the solvent is taken up than of the solute. A typical example of positive adsorption from solution is the taking up of the fatty acids from solution by blood charcoal. The results of some observations by Freundlich[72] are given in Fig. 44, in which A, in millimols adsorbed per gram of carbon, is plotted against the concentration c, in mols per liter. The data can be represented quite accurately by the Freundlich equation as evidenced by the fact that straight lines are obtained when the log of A is plotted against the log of c.

Traube's Rule.—Traube's well-known rule applies to the adsorp-

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[70] McBain, Lucas, and Chapman: J. Am. Chem. Soc., **52**, 2668 (1930); McBain, Jackman, Bakr, and Smith: J. Phys. Chem., **34**, 1439 (1930).

[71] Allmand and Burrage: Proc. Roy. Soc. (London) **130 A**, 610 (1931); J. Phys. Chem., **35**, 1692 (1931); Ubbelohde and Egerton: Proc. Roy. Soc. (London) **134 A**, 512 (1931); Allmand, Burrage, and Chaplin: Trans. Faraday Soc., **28**, 218 (1932).

[72] Z. physik. Chem., **57**, 385 (1907); *cf.* Roychoudhury: Kolloid-Z., **57**, 308 (1931).

tion data shown graphically in Fig. 44. This rule states that the adsorption of organic compounds from aqueous solution increases strongly and regularly as we ascend the homologous series. Some illustrative data taken from Fig. 44 are given in Table XLV. A similar behavior was observed by Freundlich in the adsorption of urethanes by blood charcoal. To account for the behavior of the fatty acids, it is reasonable to assume that the highly polar carboxyl end of the molecule is oriented toward the water and the non-polar

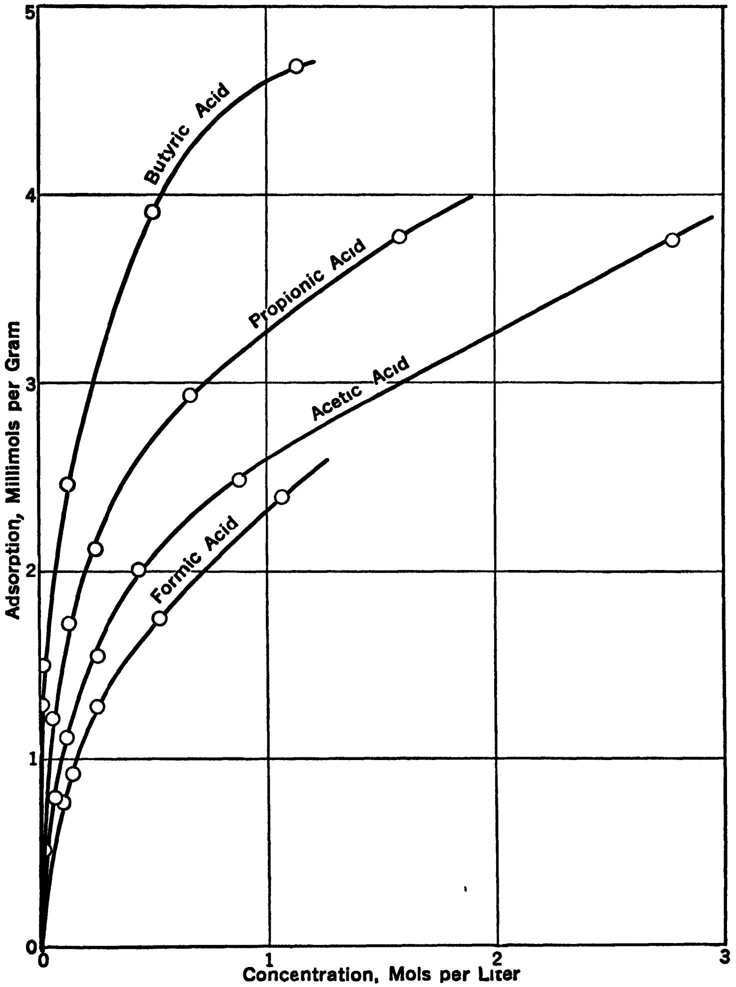

FIG. 44.—Adsorption of fatty acids from aqueous solution by purified blood charcoal.

TABLE XLV

TRAUBE'S RULE FOR THE ADSORPTION OF FATTY ACIDS BY BLOOD CHARCOAL

Adsorbed substance	c for $A = 1.26$	$\frac{c_n}{c_n + 1}$	A for $c = 0.1$	$\frac{A_n + 1}{A_n}$
Formic acid..........	0.251	. . .	0.79	....
Acetic acid..........	0.169	1.48	1.00	1.26
Propionic acid........	0.056	3.01	1.55	1.55
n-Butyric acid.......	0.016	3.48	2.43	1.56

alkyl group toward the non-polar solid adsorbent. Since the fatty acids of high molecular weight are less polar, they will be less strongly attracted by the water and more strongly adsorbed on the charcoal. From this point of view the adsorption of fatty acids from solution in a non-polar solvent like toluol by a polar adsorbent like silica should be the reverse of that observed with charcoal. Holmes and McKelvey[73] found this to be the case. On the other hand, this explanation appears to be inadequate to account for a reversal of Traube's rule of adsorption on activated sugar charcoals,[74] as observed by a number of investigators.[75] To account for this, Nekrassow assumed that the ash-free charcoal presents a surface that is more polar than water and hence adsorbs the higher homologs more strongly. Dubinin showed that Traube's rule held with a sugar charcoal activated in air at 550°, but an 800° activated charcoal gave a reversed series. Sabalitschka[76] was the first to suggest that the reversal of Traube's rule can be explained best on Herbst's[77] ultraporosity theory, namely, that active charcoal is an assembly of ultrapores such that the available adsorption area of the charcoal decreases for the increasing molecular size of ascending members of an homologous series.[78] This theory of ultraporosity has been accepted by

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[73] J. Phys. Chem., **32**, 1522 (1928); *cf.* Bartell and Fu: **33**, 676 (1929).

[74] A similar reversal was obtained in the adsorption from solution of fatty acids by powdered gold [Heymann and Boye: Kolloid-Z., **59**, 153 (1932)].

[75] Nekrassow: Z. physik. Chem., **A136**, 379 (1928); Dubinin: **140**, 81 (1929); **150**, 145 (1930); Il'in: **155**, 403 (1931); Landt and Knop: Z. Elektrochem., **37**, 645 (1931).

[76] Pharm. Ztg., **74**, 382 (1929).

[77] Biochem. Z., **115**, 204 (1921).

[78] *Cf.* Ockrent: J. Chem. Soc., 1864 (1932).

Dubinin and by Bruns[79] and is essentially the view held by Krczil[80] and Il'in.[81] At the same time, the activation of the charcoal doubtless renders it more polar as a result of the change from the amorphous to the crystalline state.

In addition to the above examples of the relationship between adsorbability and molecular weight, numerous other cases of constitutive influences in adsorption have been pointed out, especially by Freundlich[82] and by Miller.[83] Some observations of the latter on the effect of arrangement of polar and non-polar groups on the adsorption of organic acids and bases by purified blood charcoal are given in Table XLVI. From these data it is apparent that the position of the hydroxyl and amino groups in hydroxy- and aminobenzoic acids has a marked effect on their adsorption. The adsorp-

TABLE XLVI

ADSORPTION OF ORGANIC ACIDS AND BASES BY PURIFIED BLOOD CHARCOAL

(0.25 g charcoal; 100 cc solution)

Acid	0.01 *M* acid adsorbed, cc	Acid or base	0.01 *M* acid or base adsorbed, cc
Benzoic	73.00	Aminoacetic	0.00
o-Hydroxybenzoic	71.78	Butyric	35.39
m-Hydroxybenzoic	61.53	Isobutyric	27.42
p-Hydroxybenzoic	65.36	Valeric	49.39
o-Aminobenzoic	68.53	Isovaleric	44.12
m-Aminobenzoic	57.32	Caproic	62.13
p-Aminobenzoic	65.15	Isocaproic	59.67
Sulfosalicylic	56.10		
Acetic	15.68		
Chloracetic	27.45	Ammonium hydroxide	0.00
Dichloracetic	25.54	Tetramethylammonium hydroxide	1.20
Trichloracetic	17.78	Tetraethylammonium hydroxide	10.07

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[79] Kolloid-Z., 54, 33 (1931).

[80] Kolloid-Z., 58, 68 (1932).

[81] Z. physik. Chem., A155, 403 (1931).

[82] "Kapillarchemie," 4th ed., 1, 260 (1930).

[83] Colloid Symposium Monograph, 5, 69 (1928); Bartell and Miller: J. Am. Chem. Soc., 45, 1106 (1923).

tion values are greatest when these groups are in the ortho position, smallest in the meta position, and intermediate in the para position. This implies that the adsorption depends largely on the nature and arrangement of the atoms or groups in the molecule, certain groups favoring and others opposing the adsorption. Thus, chloro- and dichloroacetic acid are adsorbed much more strongly than acetic acid, and aminoacetic acid is not adsorbed at all. Isobutyric acid is adsorbed less than butyric acid, isovaleric acid less than valeric acid, and isocaproic acid less than caproic acid. Ammonium hydroxide is not adsorbed at all, but the opposing effect of the hydroxyl group is overcome by substituting methyl or ethyl groups for hydrogen in the base. Thus tetramethylammonium hydroxide is slightly adsorbed, and tetraethylammonium hydroxide is quite appreciably adsorbed. These facts indicate that molecular orientation is involved in the adsorption process. The statement that those substances which are least soluble are most strongly adsorbed is only a first approximation.[84]

Adsorption from Solutions of Strong Electrolytes

When non-electrolytes or very weak electrolytes are positively adsorbed, the solute molecule as a whole is necessarily attached to the adsorbent; but when salts are positively adsorbed, three possible cases arise. In the first case, both ions of the electrolyte are adsorbed in equal amounts, or the adsorption is molecular. In the second case, one ion is adsorbed but little, if at all, while the other enters into ionic exchange with an impurity in the adsorbent; this is termed exchange adsorption. In the third case, the specific adsorption either of hydroxyl or of hydrogen ion is so marked that the adsorption causes hydrolytic cleavage of the salt; this is known as hydrolytic adsorption. The several types of phenomena will be considered in this section.

The adsorption of electrolytes from solution by charcoal has been the subject of numerous investigations,[85] the results of which are frequently contradictory and discordant. This is especially true with reference to salt adsorption studies which were planned to demonstrate whether or not hydrolytic adsorption takes place. In the great majority of the earlier researches along this line, blood

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[84] Alexejewski: J. Russ. Phys.-Chem. Soc., 59, 1033 (1927); Roychoudhury: Kolloid-Z., 57, 308 (1931); *cf., however,* Lundelius: Kolloid-Z., 26, 145 (1920).

[85] *Cf.* Bancroft: J. Phys. Chem., 24, 342 (1920); "Applied Colloid Chemistry," 3rd ed., 112 (1932).

charcoal was employed since it possesses a relatively high adsorption capacity. The most commonly used material was Merck's blood charcoal, about which little or nothing was known except that it was purified by treatment with acids. In every case, however, it contained more or less inorganic material which remained as ash on burning off the combustible matter. In view of the marked effect which impurities may have on adsorption processes, it is not surprising that investigators were frequently unable to reproduce their own results, let alone those of other people.

Exchange Adsorption.—Freundlich and Losev[86] shook up a solution of the basic dye crystal violet with charcoal and found that the organic cation was taken up, but an equivalent amount of chloride remained in solution. Since the solution reacted acid it was at first assumed that the adsorption had hydrolyzed the dye salt. Later it was found[87] that the acid remaining in solution accounted for only a small fraction of the total chloride, the latter being present chiefly as salt. The explanation of this phenomenon is that the dye cation enters into ionic exchange with some cation, probably calcium, which is present as impurity in the charcoal. Similar investigations by Michaelis and Rona[88] with acid and basic dyes and with neutral salts led to the conclusion that the taking up of electrolytes by charcoal always involves exchange adsorption and that hydrolytic cleavage of a salt never occurs as the result of adsorption. The same conclusion was reached by Odén and Andersson.[89] They expressed the view that the acid or alkaline character of a solution, after adsorption of a neutral salt by charcoal, is due to displacement of impurities from the charcoal. In support of this, it was pointed out that those adsorbents which are said to adsorb base and set free acid are derived from acid solutions or have been treated with acids, whereas adsorbents which appear to adsorb acid and set free base are obtained from alkaline solution. The apparent change in reaction of neutral salt solutions following adsorption was accordingly attributed to the displacement of acids or bases which were present as impurities on the adsorbent. This raises the question as to the nature of the adsorption from neutral salt solutions by ash-free charcoal formed in the absence of both acids and bases. The results of the investigations with this type of adsorbent will be considered in the following paragraphs.

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[86] Z. physik. Chem., 59, 284 (1907).

[87] Freundlich and Neumann: Z. phyisk. Chem., 67, 538 (1909).

[88] Biochem. Z., 97, 57 (1919).

[89] J. Phys. Chem., 25, 311 (1921).

Hydrolytic Adsorption.—Bartell and Miller[90] prepared ash-free adsorbent charcoal by carbonizing pure recrystallized cane sugar and activating at a high temperature in the presence of a limited supply of air. Preliminary observations disclosed that the adsorption from salt solutions was hydrolytic, the pure charcoal adsorbing acids preferentially and setting free alkali to the solution. Proof of this behavior was furnished by the observation that the free alkali in the solution after adsorption was equivalent to the acid retained by the charcoal. The quantitative estimation of an adsorbed organic acid was made by shaking an aqueous suspension of the charcoal with an organic liquid such as benzol which displaced the adsorbed acid, and titrating it in the aqueous phase with a suitable indicator. The adsorbed inorganic acids were determined by boiling the charcoal several times with a given amount of standard alkali and titrating the alkali remaining in the filtrate and washings. This procedure was possible since it was found that air-activated sugar charcoal does not adsorb the inorganic bases. Some typical results obtained by Miller[91] are given in Table XLVII. In the light of these observations there can be no doubt that hydrolytic adsorption of the several salts has taken place. Moreover, since the chloride and sulfate extracted from the charcoal in the experiments with these salts is equivalent to the acid adsorbed, it is apparent that the adsorption in these cases is exclusively hydrolytic. This was confirmed with a number of potassium salts of inorganic acids and of less strongly adsorbed organic acids; but with salts of the more strongly adsorbed organic acids, such as benzoic and salicylic, the adsorption is partly hydrolytic and partly molecular. The concentration of potassium in solution after adsorption from solution of inorganic salts is greater than before adsorption, indicating that the base is negatively adsorbed by the charcoal. This was confirmed by independent observations of adsorption from potassium hydroxide solution. For some unexplained reason the extent of this negative adsorption decreases with time of contact of the solution with the adsorbent.[92]

Mechanism of the Hydrolytic Adsorption.—With the fact of hydrolytic adsorption established, the mechanism by which this takes place demands attention. Two theories have been proposed: the gas electrode theory of Frumkin and the oxide theory of Kruyt and

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[90] J. Am. Chem. Soc., **44**, 1866 (1922); **45**, 1106 (1923); Miller: **46**, 1150 (1924); **47**, 1270 (1925).

[91] J. Am. Chem. Soc., **46**, 1150 (1924); **47**, 1270 (1925); Colloid Symposium Monograph, **5**, 55 (1928).

[92] Miller: J. Phys. Chem., **36**, 2967 (1932).

TABLE XLVII

HYDROLYTIC ADSORPTION OF SALTS ON PURE CHARCOAL

Salt	0.01 *N* alkali set free during adsorption	0.01 *N* acid extracted from charcoal after adsorption
Sodium benzoate................	9.40	9.50
	29.00	28.16
Sodium salicylate................	7.84	7.90
	13.50	13.54
Potassium oxalate...............	3.90	3.76
	25.36	25.02
Sodium acetate..................	3.20	2.80
	1.64	1.78
Sodium chloride.................	11.36	11.33 *
	27.42	27.03 *
Potassium nitrate................	40.54	40.22
	25.18	24.67
Potassium sulfate....	30.58	30.76 †
	24.06	23 99 †
	26 60	26.91 †

* AgCl equivalent to 0.01 *N* HCl = 11.13 cc, and 27.33 cc, respectively.
† $BaSO_4$ equivalent to 0.01 *N* H_2SO_4 = 30.99 cc, 24.37 cc, and 27.14 cc, respectively.

Schilow and coworkers. Frumkin's theory, which seems to the author to be the more impressive, will be considered first.

According to Frumkin and his coworkers,[93] the observed adsorption of acids and not of bases by Miller's charcoal is due to the taking up of oxygen during the activation process. If the air-activated preparation is heated in a stream of hydrogen and then brought in contact with a solution of alkali, it adsorbs the alkali positively. Acids are not adsorbed by the oxygen-free charcoal and base is adsorbed and acid set free when the adsorbent is placed in a potassium chloride

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[93] Frumkin and Donde: Ber., **60**, 1816 (1927); Burstein and Frumkin: Z. physik. Chem., **A141**, 158, 219 (1929); Bruns and Frumkin: **A141**, 141 (1929); Frumkin: Kolloid-Z., **51**, 123 (1930); Frumkin, Burstein, and Lewin: Z. physik. Chem., **A157**, 442 (1931).

solution. A sugar charcoal prepared as nearly gas free as possible adsorbs neither acid nor base appreciably. Data illustrating this behavior are given in Table XLVIII. In the first three series of

TABLE XLVIII

EFFECT OF GAS ENVIRONMENT ON ADSORPTION BY CARBON

(Adsorption values in millimols per g C)

		C saturated with H_2	C in the presence of air
		KOH adsorbed	HCl adsorbed
I From *N* KCl	*a*	0.0215	0.025
	b	0.020	0.025
	c	0.0205	
II From 0.01 *N* HCl	*a*	0.0	0.14
	b	0.0	0.139
	c	0.0	
III From 0.01 *N* KOH	*a*	0.066	0.0
	b	0.0655	0.0
		C in vacuum	C in the presence of air
IV From 0.01 *N* HCl	*a*	0.0	0.140
	b	0.0	0.140
V From 0.01 *N* NaOH	*a*	0.0	0.0
	b	0.0	0.0

experiments, 10 cc of solution was brought in contact with 0.5 g of charcoal; and in the fourth and fifth series, 14 cc of solution was treated with 1 g of charcoal.

A platinum sponge electrode[94] behaves similarly to ash-free charcoal in the presence of electrolytes.[95] A gas-free electrode causes no

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[94] Frumkin and Obrutschewa: Z. anorg. Chem., **158**, 84 (1926).

[95] The importance of this in the determination of *p*H values by the hydrogen electrode has been studied by Kolthoff and Kameda: J. Am. Chem. Soc., **51**, 2888 (1929).

hydrolytic adsorption of sodium sulfate solution; but if the electrode is saturated with hydrogen in contact with the salt solution, the latter becomes distinctly acid. On the other hand, when the electrode is washed acid- and hydrogen-free in a current of air, the solution becomes distinctly alkaline.

Frumkin considers that, in analogy with the behavior of platinum in contact with hydrogen or oxygen, ash-free, activated charcoal acts as a gas electrode in accord with the following scheme: In the presence of oxygen, hydroxyl ions are formed at the expense of the adsorbed oxygen,

$$C_xO + H_2O \rightarrow C_x + 2\oplus + 2OH^-$$

the ions going into solution and the positive charge remaining on the surface of the charcoal. On the other hand, in the presence of hydrogen, hydrogen ions are sent into solution at the expense of the adsorbed gas,

$$C_x + H_2 \rightarrow C_x + 2\ominus + 2H^+$$

and the negative charge remains on the surface of the charcoal, which will now adsorb cations from solution.

In support of this proposed mechanism, Frumkin showed that the hydrochloric acid adsorbed by an oxygen-holding charcoal was equivalent to the oxygen adsorbed. The results of some observations are given in Table XLIX.

TABLE XLIX

ADSORPTION OF HCl BY CHARCOAL WITH ADSORBED O_2

Oxygen per gram C, milliequivalents	HCl adsorbed per gram C, milliequivalents
0.012	0.012
0.033	0.035
0.044	0.043
0.052	0.051

Although Frumkin's theory seems quite satisfactory so far as it goes, Schilow and his coworkers[96] pointed out that it has certain

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[96] Schilow and Tschmutow: Z. physik. Chem., **A143**, 41 (1929); **148**, 233 (1930); Schilow, Schatunowskaja, and Tschmutow: **149**, 211; **150**, 31 (1930); Bruns and Pyschow: **157**, 57 (1931); *cf.* Bretschneider: **159**, 436 (1932).

limitations which can be accounted for adequately only by the aid of a new theory with entirely different postulates. For example, Schilow claims that a completely degassed charcoal will adsorb small amounts of hydrochloric acid from dilute acid solutions. Moreover, contrary to Frumkin's observations, it was found that the curves for the adsorption of hydrochloric acid as affected by the oxygen pressure do not coincide with the adsorption isotherm for oxygen, but follow a stepwise course. At pressures up to 2 mm, the curves are horizontal, then there is a sharp break followed by another horizontal section. As a result of these and other data, such as Kruyt and de Kadt's discovery that charcoals heated at lower temperatures take up bases, Schilow formulated the theory that the adsorption of acids, bases, and salts by ash-free charcoal takes place through interaction with acidic or basic oxides of carbon on its surface.

In Fig. 45 are given the oxides postulated by Schilow. Oxide *A* is assumed to give a slightly basic carbon hydroxide with water; oxide *B*, a strongly basic hydroxide; and oxide *C*, an acidic oxide; *D* represents an inner salt of oxides *B* and *C*. To account for the results, it is assumed that (1) oxide *A* is stable at all temperatures and at oxygen pressures up to 2 mm, (2) oxide *B* is formed from *A* at 2 mm pressure, and (3) oxide *C* is formed from *B* by heating in oxygen at 300–700°.

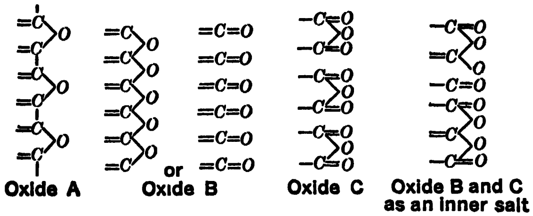
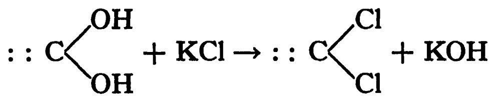


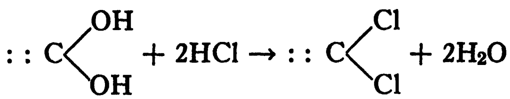
FIG. 45.—Schilow's oxides of carbon.

Schilow's explanation of the mechanism of hydrolytic adsorption of potassium chloride by oxide *B* can be represented by the following scheme:



$$::C\begin{cases}OH\\OH\end{cases} + KCl \rightarrow ::C\begin{cases}Cl\\Cl\end{cases} + KOH$$

The adsorption of HCl by oxide *B* can be considered as a reaction:



$$::C\begin{cases}OH\\OH\end{cases} + 2HCl \rightarrow ::C\begin{cases}Cl\\Cl\end{cases} + 2H_2O$$

Potassium hydroxide would not react at all with oxide *B* but it would with *C*.

In support of Schilow's theory, it seems probable that, in the presence of oxygen, a charcoal surface has an oxide or oxides of carbon on it as evidenced by the facts that, when oxygen is adsorbed on charcoal, it is not recoverable as adsorbed oxygen but as carbon dioxide at lower temperatures and carbon monoxide at higher temperatures, and the heat of adsorption of small amounts of oxygen is proportionately larger than that of larger amounts.[97] On the other hand, it is not possible at present to determine definitely the form in which the oxygen is bound. It is of course very easy to postulate oxides having the properties necessary to explain certain facts; but it is an entirely different thing to get independent proof of their existence. Kruyt's idea that the charcoal-oxygen complex is an intermediate product leading up to the formation of mellitic acid is supported by Miller's[98] observation that Kruyt's charcoal has properties in common with charcoal carrying strongly adsorbed complex organic acids. In this connection it should be recalled, however, that the evidence is against the view that mellitic acid is an oxidation product of pure carbon.[99]

The concept of basic oxides of carbon cannot be accepted without reservation, and, as Miller points out, it is difficult to understand why such a basic oxide as Schilow's hypothetical *B* should react with hydrochloric acid but not with benzoic or succinic acids when the fact is that the latter are much more strongly adsorbed by charcoal than is hydrochloric acid.

Frumkin questions certain conclusions of Schilow on the ground that the latter's charcoal was not heated at sufficiently high temperature for a long enough time to degas it completely. Frumkin admits, however, that electrolytes, especially if they are surface-active, may be adsorbed by completely degassed charcoal, and that the adsorption even of hydrochloric acid is not prevented by a hydrogen atmosphere, if the acid concentration is above 0.1 *N*. This behavior of capillary-active electrolytes in dilute solution, and of hydrochloric acid above 0.1 *N*, is attributed by Frumkin to molecular adsorption.

In a critical survey of the evidence for and against the two theories of adsorption of electrolytes by charcoal, Miller[98] points out that the field to which they apply is quite limited. Apparently, only those substances which are least adsorbed or not adsorbed at all in the

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[97] *Cf.*, *also*, Lowry and Hulett: J. Am. Chem. Soc., **42**, 1408 (1920); Miller: J. Phys. Chem., **36**, 2967 (1932).

[98] J. Phys. Chem., **36**, 2967 (1932).

[99] *Cf.* Bancroft: J. Phys. Chem., **24**, 342 (1916).

presence of air are influenced by the nature of the gas adsorbed on the charcoal, and these only in lower concentrations. Moreover, there are a number of facts which cannot be explained at present by either theory. For example, there is no apparent reason why sodium and potassium hydroxides are not adsorbed in the presence of air whereas the equally strongly dissociated organic base, tetraethylammonium hydroxide, is adsorbed, and, on the other hand, the weak base ammonium hydroxide is not adsorbed. It is also impossible to say why the adsorption of potassium chloride, which is exclusively hydrolytic, is affected by the gaseous atmosphere, whereas the greater hydrolytic adsorption of potassium benzoate is not affected. The effect of the introduction of polar groups on the adsorption (see page 289) is not explainable by either theory, nor is the negative adsorption of sodium and potassium hydroxide and its decrease with length of time of contact of solution and adsorbent.

In further experimental work which must be done along these lines, particular attention should be given to the experimental procedure. Miller calls attention to at least two errors inherent in recent experiments of Roychoudhury[100] which render his results of doubtful value.

Negative Adsorption

With but one exception, the examples of adsorption from solution so far considered have been cases of positive adsorption in which relatively more of the solute is adsorbed than of the solvent. Cases of negative adsorption, in which relatively more of the solvent is adsorbed than of the solute, are frequently encountered in nonaqueous binary systems.[101] Interesting examples of this phenomenon were obtained by Bartell and Sloan[102] in their study of adsorption by carbon from a number of non-aqueous binary systems over the entire concentration range. The change in concentration as a result of adsorption was measured by means of the interferometer, since the accuracy of measurement with this instrument is practically independent of concentration. In every case the adsorption curve was found to be S-shaped. Two typical examples are shown graphically in Fig. 46, in which ethyl alcohol is taken arbitrarily as the solvent, and benzol (curve I) and ethyl carbonate (curve II) as the respective

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[100] J. Indian Chem. Soc., **8**, 433 (1931); *cf.* Roychoudhury and Mukherjee: Z. physik. Chem., **A157**, 435 (1931); Kolloid-Z., **57**, 302 (1931).

[101] *See*, for example, Schmidt-Walter: Kolloid-Z., **14**, 242 (1914); Gustafson: Z. physik. Chem., **91**, 385 (1916).

[102] J. Am. Chem. Soc., **51**, 1637, 1643 (1929).

solutes. The concentrations are expressed in mol fractions instead of in mols. The adsorption is expressed in terms of change in concentration $H(x_0 - x)m$ or $H\Delta x/m$, in which H is the total number of millimols that make up the solution and x_0 and x are the mol fractions of solute present before and after adsorption, respectively.

Considering curve II, it is apparent that ethyl carbonate is positively adsorbed up to a value of $x = 0.55$, and negatively adsorbed above this concentration. Another way of stating it is that ethyl carbonate is preferentially adsorbed from solutions which are relatively dilute in ethyl carbonate, whereas ethyl alcohol is preferentially adsorbed from solutions relatively dilute in the alcohol. At a concentration of 0.55 mol fraction of ethyl carbonate, the solute and solvent are adsorbed equally and there is no change in concentration.

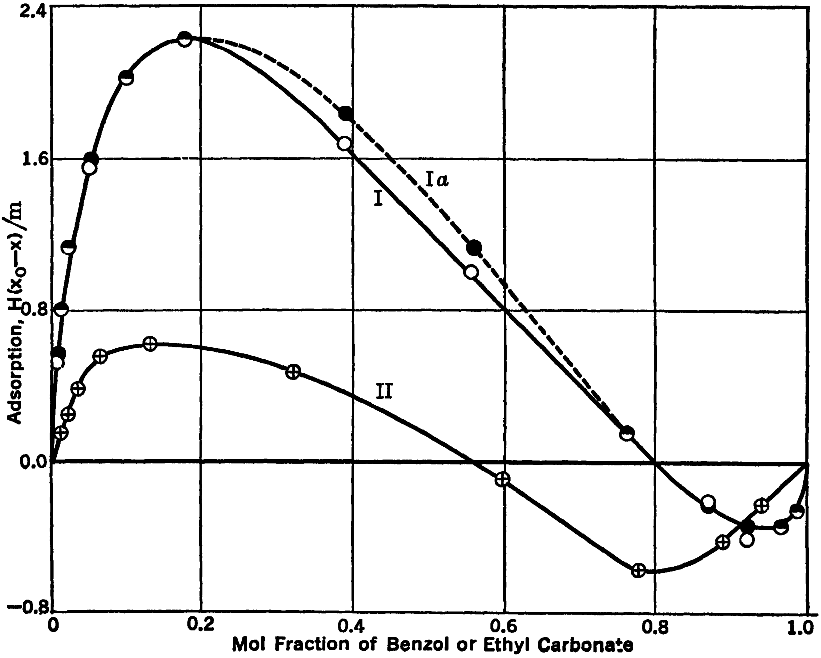

FIG. 46.—Adsorption from ethyl alcohol solution of benzol (curve I, observed; curve Ia, calculated) and of ethyl carbonate (curve II, observed) throughout the entire concentration range.

When adsorption is measured in terms of change in concentration the Freundlich adsorption equation takes the form

$$H\Delta x/m = kx^n(1 - x)$$

Since the apparent adsorption of each component can be represented by this equation, when that component is in low concentration, Bartell and Sloan have attempted to apply it over a greater concentration range. For example, if the change in concentration due to adsorption of benzol (curve I) is represented by the equation:

$$H\Delta x_1/m = \alpha x^n(1 - x)$$

and the change in concentration due to adsorption of ethyl alcohol by a similar equation:

$$H\Delta x_2/m = \beta(1 - x)^d x$$

then, the resultant change in concentration will be equal to the difference between these two terms. The decrease in mol fraction of benzol resulting from the simultaneous adsorption of the two components is, thus,[103]

$$H\Delta x/m = H(x_1 - x_2)/m = \alpha x^n(1 - x) - \beta(1 - x)^d x$$

On evaluating the constants by the method of successive approximations, the equation becomes, for the case under consideration,

$$H\Delta x/m = 9.76x^{0.532}(1 - x) - 6.26(1 - x)^{0.662}x$$

The dotted curve I*a* shows how closely the calculated adsorption values approach the observed values for the benzol-alcohol system.

APPLICATIONS OF ADSORBENT CARBON

A few of the more important scientific and technical applications of adsorbent carbon will be considered briefly.

Liquefaction of Gases.—Fifty years ago, Melsens[104] liquefied chlorine, sulfur dioxide, hydrogen sulfide, hydrobromic acid, and cyanogen by placing wood charcoal, saturated with the gas in question, into one arm of a sealed V-shaped tube, dipping this end of the tube into boiling water, and placing the other end in a freezing mixture. The heat cut down the adsorption of the gas by the charcoal, and the pressure developed by its release caused liquefaction in the cold end of the tube.

High Vacuum.—The well-established procedure of using adsorbent carbon to facilitate the securing of a high vacuum dates back to 1874 when Tait and Dewar[105] first used the method. A 300 cc bulb filled

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[103] *Cf.* Ostwald: Kolloid-Z., **30**, 279 (1922); **32**, 57 (1923); **36**, 289 (1925).

[104] Compt. rend., **77**, 781 (1873); J. Chem. Soc., **27**, 120 (1874).

[105] Proc. Roy. Soc., Edinburgh, **8**, 348, 628 (1874).

with air at a temperature of 15° and 1.7 mm pressure was connected with another bulb containing charcoal. By immersing the charcoal in liquid air, the air in the bulb was adsorbed so strongly that the pressure was reduced to 0.00005 mm, or 1/34,000 of the original pressure. Pressures as low as 2×10^{-7} mm have been obtained by this method[106] using activated charcoal.

Separation of Gas Mixtures.—In view of the difference in degree of adsorption of gases by charcoal, it is possible to separate mixtures to a certain extent. For example, Ramsay[107] was able to estimate the amount of neon, helium, and hydrogen in the air from adsorption studies with cocoanut charcoal. At 100° the charcoal adsorbs the oxygen, nitrogen, and argon, practically quantitatively, while the adsorption of neon and helium is slight. At the temperature of liquid air, practically all the neon is adsorbed and none of the helium. Ramsay's observations along this line indicate that the concentration of neon in the air at sea level is about 0.00123 volume per cent, that of helium about 0.00044 volume per cent, and that of hydrogen not over 1/500 of the combined volumes of neon and helium.

Krypton and xenon can be obtained[108] by passing air over charcoal at −183°, placing the charcoal tube in solid carbon dioxide at −78°, and allowing the gas which is evolved to escape. After the gas is removed from the charcoal by heating and exhaustion, it is purified from carbon compounds and oxygen, leaving a mixture of nitrogen, krypton, and xenon which is separated by condensation and fractionation. Another method consists in treating liquid-air residues with charcoal, allowing the oxygen to evaporate, and separating the gases remaining on the charcoal as above described.[109]

A recent important scientific application of adsorbent charcoal to which reference has already been made (see page 227) is the isolation of para-hydrogen in a practically pure state by adsorption at about the temperature of liquid hydrogen.[110] In this case the charcoal acts both as an adsorbent and a catalyst, which accelerates the rate at which equilibrium is reached.

The Gas Mask.—During the war, charcoal was found to be the

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[106] Woodrow: Phys. Rev., (2) **4**, 491 (1914).

[107] Proc. Roy. Soc. (London) **76A**, 111 (1905); **80A**, 599 (1908).

[108] Ramsay and Travers: Trans. Roy. Soc. (London) **197A**, 47 (1901); Moore: Proc. Roy. Soc. (London) **81A**, 195 (1908); Valentiner and Schmidt: Sitzber. preuss. Akad. Wiss., **38**, 806 (1905).

[109] *Cf.* Allen and Moore: J. Am. Chem. Soc., **53**, 2512 (1931).

[110] Bonhoeffer and Harteck: Naturwissenschaften, **17**, 182 (1929); Z. physik. Chem., **B5**, 292 (1929).

best all-around adsorbent for toxic gases and so was the basic material in most gas masks.[111] For this purpose the charcoal must possess a high adsorptive capacity, a high service time, and also a high velocity of adsorption, since the contaminated gas can remain in contact with the adsorbent for only a relatively short period. For effective use the adsorbent must reduce the concentration of the toxic gas from, say, 1000 p.p.m.[112] of chloropicrin in a rapidly moving current of air to less than 0.5 p.p.m. in less than the 0.3 second that the air takes to pass through the canister. The most satisfactory adsorbent for this purpose was found to be activated cocoanut charcoal. Not only did it possess the highest adsorption capacity, but in addition, because of its hardness, it withstood abrasion and powdering due to the rough treatment to which gas masks were subjected. To increase the protection against certain volatile gases such as phosgene and hydrocyanic acid, it was found necessary to use alkaline oxidizing agents in combination with the charcoal. The material actually employed in both British and American gas masks was granules of soda lime containing sodium permanganate.

Industrial Recovery of Vapors.—A number of types of industries use and frequently lose large quantities of valuable volatile solvents. Among these are such industries as dry cleaning and the manufacture of artificial silk, celluloid, cordite, rubber, and artificial leather cloth, where quick evaporation of the solvent is a prime necessity for the economical success of the operations. In many of these industries, charcoal may be used to advantage for the adsorption and recovery of the solvent vapors.

An important example of the industrial adsorption of vapors is the extraction of gasoline vapors from natural gas or refinery gases.[113] This process, which was a development of the world war, makes use of activated charcoal such as is used in gas masks. The technical operation consists essentially in passing gases containing gasoline vapors through a column containing the activated charcoal, distilling off the adsorbed vapors by means of steam, and subsequently condensing the vapors. Three adsorption units are used successively in the process, in one of which adsorption and in the second distillation is effected, while the third is kept in readiness for the adsorption process. If the charcoal shows signs of decreased activity it is reactivated by the treatment with superheated steam.

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[111] Lamb, Wilson, and Chaney: Ind. Eng. Chem., **19**, 420 (1919).

[112] Parts per million by volume.

[113] Oberfell, Shinkel, and Meserve: Ind. Eng. Chem., **11**, 197 (1919); Burrell: "The Recovery of Gasoline from Natural Gas," 286 (1925).

Decolorizing Agent.—Probably the most important technical application of adsorbent charcoal is its use as a clarifying agent in the sugar industry. As already stated, bone char was used exclusively in the refinery operations before the discovery of activated vegetable charcoals. Strachan,[114] with the Norit company in Holland, outlines at some length the advantages of vegetable over animal charcoal for the decolorizing process.

Charcoal is also used as a decolorizing agent in the synthetic organic chemistry laboratory and in the manufacture of such products as pharmaceutical glycerin; photographic salts; citric, tartaric, and gallic acids and their salts; alkaloids, etc. A suitable charcoal filter will render potable a highly colored and infected water, but its use is more expensive than other methods of water purification.[115]

Catalytic Action.—Although carbon is a good adsorbent for a large variety of compounds, it is not an active catalyst for many reactions. Among those which may be mentioned are certain oxidation processes. As already pointed out (see page 297), a portion of the oxygen taken up by charcoal is irreversibly adsorbed, probably by conversion into carbon oxides; but another portion is reversibly adsorbed under certain conditions. This reversibly adsorbed oxygen possesses catalytic properties, bringing about the low-temperature autoxidation of carbon and accelerating the oxidation of compounds such as the following: ethyl alcohol vapor and gaseous hydrocarbons;[116] solutions of sulfides, chromates, and iodides;[117] malonic,[118] oxalic, and certain amino acids;[119] glucose in the presence of phosphoric acid;[120] and phenylthio-carbamide.[121]

The autoxidation of carbon was found to be a reaction of the zero order. By selective poisoning, Rideal and Wright[118] showed that, with an active sugar charcoal of mean surface of 222 cm^2 per mg, only 0.38% of the surface was capable of autoxidation. The oxidation of acids, on the other hand, took place over a much greater area. Thus the fraction of a sugar charcoal catalytically active in causing the oxidation of oxalic acid was found to be 40.5%. Both acid and

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[114] J. Soc. Chem. Ind., **47**, 1211 (1928).

[115] *See* Gibbons: Ind. Eng. Chem., **24**, 977 (1932).

[116] Calvert: J. Chem. Soc., **20**, 293 (1867); Firth: Trans. Faraday Soc., **20**, 370 (1924).

[117] Feigel: Z. anorg. Chem., **119**, 305 (1921).

[118] Rideal and Wright: J. Chem. Soc., **127**, 1347 (1925).

[119] Warburg: Pflügers Arch., **155**, 547 (1914); Biochem. Z., **113**, 257 (1921); **145**, 461 (1924).

[120] Meyerhof: Biochem. Z., **135**, 558 (1923).

[121] Freundlich and Bjerke: Z. physiol. Chem., **91**, 31 (1916).

oxygen were adsorbed by the catalyst, the reaction velocity rising to a maximum and falling again as the acid concentration was increased. Optimum velocities were obtained with 0.0075 *M* oxalic acid and 0.050 *M* malonic acid.

Other reactions which may be catalyzed by charcoal are the saponification of ethyl acetate,[122] the removal of bromine from α, β-dibromopropionic acid by potassium iodide,[122] the union of chlorine with hydrogen and with carbon monoxide, and the chlorination of hexachlorethane at 350°. All the above reactions are accelerated by the presence of a suitable charcoal, except the saponification of ethyl acetate, which is retarded. Ash-free charcoal acts as a negative catalyst for the inversion of sucrose by acids owing to adsorption of the acids in such a state that they are unable to effect the inversion.[123] Since hydrogen ion is the effective agent in the inversion, the complete inhibition of the process cannot be accounted for as a result of oriented adsorption of sucrose or acid molecules. The most probable explanation, for the present, is that the adsorbed acid is held in the form of undissociated molecules. Apparently, in this case the adsorption of acid does not imply a high concentration of hydrogen ions around the adsorbent.

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[122] Kruyt and van Duin: Rec. trav. chim., **40**, 249 (1921).

[123] Miller and Bandemer: J. Am. Chem. Soc., **49**, 1686 (1927).

CHAPTER XII

COLLOIDAL SULFUR

The clouding of natural sulfur waters on exposure to the air has been known for a long time. This clouding is due to the formation of colloidal sulfur as a result of the oxidation of hydrogen sulfide by the oxygen of the air. The reaction was referred to by many writers in the latter part of the eighteenth and the early nineteenth centuries, among them being Scheele, Bergman, Le Veillard, Berthollet, Berzelius, and Dobereiner. Thus, in 1808, Berzelius says:[1] "It [H_2S] dissolves in water abundantly; . . . if the water contains atmospheric air, some part of the air is destroyed, the hydrogen being oxidized to water, and the sulfur set free, whereupon the water takes on a milky appearance."

FORMATION OF SULFUR SOLS

Oxidation Processes

Oxidation of Hydrogen Sulfide.—Near the middle of the last century, the milky liquid formed by passing hydrogen sulfide into an aqueous solution of sulfur dioxide was investigated in some detail by Wackenroder[2] and by Selmi.[3] At this time the term colloid had not been invented, but Selmi, who recognized quite clearly many of the differences between the milky dispersion and molecular solutions, called the system a pseudo solution.

The reaction between sulfur dioxide and hydrogen sulfide may be represented by the equation:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{1}$$

The reaction is more complicated than this, however, since it has been found that the so-called Wackenroder's solution contains, in addition to colloidal sulfur, all of the thionic acids from dithionic to

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[1] *Cf.* Svedberg: "The Formation of Colloids," 89 (1921).

[2] Arch. d. Pharm., **47**, 272; **48**, 140 (1846).

[3] Annali del Majochi, **15**, 88, 212, 235 (1844); Sobrero and Selmi: Ann. chim. phys. (3) **28**, 210 (1850); J. prakt. Chem., **49**, 417 (1850).

hexathionic[4] as well as some sulfuric acid. Thus pentathionic and hexathionic acids are formed in accord with the equations:

$$5H_2S + 10H_2SO_3 \rightarrow 3H_2S_5O_6 + 12H_2O \qquad (2)$$

$$3H_2S + 4H_2SO_3 \rightarrow H_2S_6O_6 + 6H_2O + S \qquad (3)$$

Odén[5] has shown that the amount of colloidal sulfur produced by the reaction and the degree of dispersity depend on the sulfur dioxide concentration, as shown in Table L. At the higher dilution, 0.225 *N*, the yield of sulfur approaches the value 17.3, which is the theoretical value for the simple reaction (1) above; but under these conditions the sulfur is chiefly non-colloidal. With higher concentrations of sulfur dioxide, less sulfur is formed but more of the precipitated particles are colloidal. Moreover, the higher the concentration, the greater the relative amount of amicroscopic particles formed in accord with von Weimarn's theory (see page 1). Another factor in determining the degree of dispersion of the particles is the amount of polythionic acids formed. At the higher concentrations where considerable pentathionic and hexathionic acids result[6] in accord with Equations (2) and (3), most of the sulfur is colloidal, whereas at low concentrations where Equation (1) takes place almost quantitatively, little or no colloidal sulfur is produced.

TABLE L

STATE OF SULFUR FORMED BY THE INTERACTION OF H_2S AND SO_2

SO_2 normality	Non-colloidal S in grams	Total	Colloidal S in grams		
			Amicroscopic particles	Nearly visible particles	Submicroscopic particles
1.8	0.01	8.33	0.91	4.22	3.20
1.44	0.29	9.89	0.16	2.10	7.63
0 9	0.40	13.02	0.05	0.21	12.76
0 45	14.91	1.94	Traces	1.94	
0 225	16.98	Traces	....	Traces	

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[4] Debus: J. Chem. Soc., **53**, 278 (1888).

[5] "Der kolloide Schwefel," 37 (1913).

[6] *Cf.* Freundlich and Scholz: Kolloid-Beihefte, **16**, 234 (1922); Bassett and Durrant: J. Chem. Soc., 2919 (1931).

The sol, which is frequently called Selmi's sol, may be purified by coagulating the particles with sodium chloride, centrifuging and discarding the supernatant solution, repeptizing in water, and dialyzing to remove the excess sodium chloride.

The reversibility of the sol is said to be increased by carrying out the reaction around 0° in the presence of protecting colloids.[7] A finely divided bluish sulfur results on allowing hydrogen sulfide and sulfur dioxide to react above the water in an aspirator bottle.[8]

Sols of sulfur in benzol, toluol, xylol, kerosene, acetone, and ethyl acetate can be prepared by conducting sulfur dioxide and hydrogen sulfide simultaneously into the respective liquids.[9] A benzol sol formed in this way and containing over 1.5% sulfur has a deep yellow color and is stable indefinitely. Neither electrolytes nor organic non-electrolytes which dissolve in benzol have an appreciable coagulating action. The cause of the marked stability should be investigated.

The sols in carbon bisulfide, benzol, and carbon tetrachloride are orange at first but turn yellow on standing and the sulfur settles out. If this precipitate is filtered and dried out of contact with air, it is repeptized by shaking with water, glycerin, and fats.[10]

Action of Acids on Sodium Thiosulfate.—Sulfur sols are conveniently formed by the action of hydrochloric acid (Engel[11]) or sulfuric acid (Raffo[12]) on sodium thiosulfate. Since sulfuric acid is most commonly employed the resulting sol is called Raffo's sol. The equations for a part of the reactions involved are as follows:

$$3Na_2S_2O_3 + 3H_2SO_4 \rightarrow 3H_2S_2O_3 + 3Na_2SO_4 \qquad (1)$$

$$H_2S_2O_3 \rightarrow S + SO_2 + H_2O \qquad (2)$$

$$2H_2S_2O_3 + 2H_2O \rightarrow 2H_2S + 2H_2SO_4 \qquad (3)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (4)$$

$$\overline{3Na_2S_2O_3 + H_2SO_4 \rightarrow 4S + 3Na_2SO_4 + H_2O}$$

To the extent that Equation (2) takes place, sulfur is formed by simple decomposition; but for the most part, it results from an oxida-

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[7] Vogel: Brit. Pats., 202,613; 210,363 (1923).

[8] Guareschi: Atti accad. sci. Torino., **53**, 589 (1918).

[9] Garard and Colt: J. Am. Chem. Soc., **49**, 630 (1927).

[10] Sarason: German Pat., 262,467 (1913).

[11] Compt. rend., **112**, 866 (1891).

[12] Kolloid-Z., **2**, 358 (1908).

tion process. In addition to sulfur, pentathionic acid[13] is formed in appreciable amounts in accord with the equation:

$$5H_2S_2O_3 \rightarrow 2H_2S_5O_6 + 3H_2O \qquad (5)$$

Odén[14] worked out the most favorable conditions for sol formation by Raffo's method and found the best results on adding concentrated sulfuric acid slowly to a cold concentrated solution of sodium thiosulfate. The impure dispersion must be coagulated with sodium chloride and repeptized repeatedly to remove the excess sulfuric acid, and finally dialyzed. The time of dialysis may be shortened appreciably by freezing the sol, which gives a reversible precipitate that is almost free from salt. This procedure may be used to advantage also with the Selmi sol.

The stability of sulfur sols is said to be increased to some extent if the sulfur comes out in the presence of protective agents such as gallic acids,[15] gelatin,[16] gluten,[17] and glycerin.[18] Odén showed, however, that gelatin possesses no such specific protective action on sulfur as it does on colloidal gold. Indeed, Ghosh and Dhar[19] found that very small amounts of gelatin sensitize sulfur sols toward electrolytes and larger amounts cause coagulation.

Sols with Particles of Uniform Size.—The sols prepared by the methods of both Selmi and Raffo contain particles of widely varying size. Since the coagulum formed on adding sodium chloride is completely reversible, Odén[20] worked out a method of fractional coagulation which makes it possible to divide the polydisperse sols into fractions containing particles of nearly uniform size. The method is based on the fact that the coarser the particles, the lower the concentration of sodium chloride required for coagulation. By adding gradually increasing concentrations of salt and centrifuging, a series of reversible precipitates, each containing particles of similar size, is obtained. The ultramicroscopic characteristics of a series of sols prepared in this way are given in Table LI.

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[13] Chancel and Diacon: Compt. rend., **56**, 710 (1863); Debus: J. Chem. Soc., **53**, 278 (1888).

[14] "Der kolloide Schwefel," 45 (1913).

[15] German Pat., 381,519 (1923).

[16] Lobry de Bruyn: Rec. trav. chim., **19**, 236 (1900).

[17] Kelber and Schwarz: German Pat., 245,621 (1912).

[18] Sarason: German Pats., 216,824–5 (1907); 262,467 (1913).

[19] Kolloid-Z., **44**, 218 (1928); Bhatia, Ghosh, and Dhar: J. Indian Chem. Soc., **6**, 129 (1929).

[20] "Der kolloide Schwefel," 55 (1913).

TABLE LI

CHARACTERISTICS OF MONODISPERSE SULFUR SOLS

NaCl in normality		Ultramicroscopic characteristics
Sol not coagulated	Sol coagulated	
0.25	∞	Faint amicroscopic light cone; no submicrons
0.20	0.25	Clear amicroscopic light cone; no submicrons
0.16	0.20	Strong amicroscopic light cone; no submicrons
0.13	0 16	Particles just visible (diameter about 25 mμ)
0.10	0.13	No amicroscopic light cone; diameter of particles 90 mμ
0.07	0.10	No amicroscopic light cone; diameter of particles 140 mμ
0.00	0.07	No amicroscopic light cone; diameter of particles 210 mμ

Hydrolysis

Sulfur monochloride is acted on by water to give sulfur and thiosulfuric acid. Since the latter yields pentathionic acid as previously shown, Freundlich and Scholz[21] write the gross equation for the reaction as follows:

$$5S_2Cl_2 + 6H_2O \rightarrow 5S + H_2S_5O_6 + 10HCl$$

These investigators prepared a sulfur sol similar in properties to Selmi's and Raffo's sols by vigorous shaking of 10 cc of sulfur monochloride with 70 cc of water at 35°. After a short time a strongly exothermic reaction takes place with the evolution of sulfur dioxide, and the vessel must be immersed in ice water to slow up the process. When the evolution of gas ceases, the resulting sol is purified by coagulating with sodium chloride, centrifuging, and repeptizing as in the case of Selmi's sol. The preparation will be referred to later as Freundlich's sol.

Replacement of Solvent

The general method of sol formation, which consists in pouring a solution of the element into a liquid in which the element is insoluble, may be used to advantage in preparing sulfur sols.

Sulfur in Hydrazine by Water.—If a solution of sulfur in hydrazine is poured into an excess of water, the sulfur comes out on standing in

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[21] Kolloid-Beihefte, **16**, 234 (1922).

a highly dispersed form, giving a very stable sol[22] which can be purified by dialysis. The stability of the sol is probably due to the presence of a small amount of some product formed by interaction of sulfur with hydrazine, which exerts a stabilizing action on the sol analogous to the polythionic acids in Selmi's sol and which is not removed by dialysis. In this connection, Ostwald and Egger[23] showed that a strong solution of sulfur in hydrazine hydrate, evaporated to dryness on the water bath, gives a sulfur residue which is peptized by hot water. The resulting sol is stable for several days, and the precipitate which settles out on standing is repeptized by shaking.

Sulfur in Alcohol by Water.—If a hot alcoholic solution of sulfur is poured into cold water, a milky bluish-white sol is formed which contains fairly large submicrons.[24] This preparation, frequently referred to as von Weimarn's sulfur sol, deposits an irreversible precipitate after a few days. A more stable preparation results on adding, drop by drop, a hot alcoholic solution of sulfur to an equal volume of a 1% gelatin solution and heating the mixture under reduced pressure until half the alcohol is evaporated.[25] Glycerin and erythretol solutions of sulfur likewise give hydrosols when poured into water.[26]

In this connection, mention may be made of the formation of organosols by cooling the solutions of sulfur and selenium in glycerin and erythretol to −80°. The lower solubility of the elements at the reduced temperature results in precipitation in the sol state.

Miscellaneous Methods

Condensation of Vapors.—Gutbier[27] obtained milky-white, opaque, polydisperse sols by condensing sulfur vapor in water. The sols are fairly stable, lasting from 2 to 6 weeks out of contact with air, probably owing to the presence of thionic acids formed by the action of the hot vapor with water. The stability is not appreciably increased by the presence of protecting colloids. Sols are also obtained by the

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[22] Lobry de Bruyn: Rec. trav. chim., **13**, 433 (1894); **15**, 174 (1896); **18**, 297 (1899); Ephraim and Piotrouski: Ber., **44**, 386 (1911); Meyer: **46**, 3089 (1913); Ostwald and Egger: Kolloid-Z., **43**, 353 (1927).

[23] Kolloid-Z., **43**, 353 (1927).

[24] Von Weimarn and Malyschew: Kolloid-Z., **8**, 216 (1911).

[25] Lora y Tamayo: Anales soc. españ. fis. quim., **27**, 110 (1929).

[26] Von Weimarn: J. Russ. Phys.-Chem. Soc., **45**, 1689 (1913).

[27] Z. anorg. Chem., **152**, 163 (1926).

simultaneous condensation of the vapors of water and sulfur at the liquid-air temperature by the method of Roginsky and Schalnikoff (see page 7).

A unique method of getting finely divided sulfur consists in spraying a carbon disulfide solution into a warm room, which vaporizes the solvent, giving an aerosol of sulfur.[28] The particles may be collected together by a modification of the Cottrell process[29] and shaken with water to give a hydrosol. The stability of the sol formed in this way is greatly increased by adding to the carbon bisulfide solution a small amount of a protecting agent such as a sulfurized naphthalenic acid which has a higher boiling point than the solvent. On vaporizing the latter, the sulfur particles are coated with a film of protecting colloid.

Electrical Methods.—A milky sol of sulfur is obtained by passing a 220-volt direct current through water, using a platinum cathode on which a little molten sulfur is deposited.[30] It is probable that hydrogen sulfide formed at the cathode is oxidized by oxygen from the anode to give colloidal sulfur.

An isobutyl alcosol was prepared by Svedberg, using an oscillating arc between aluminum electrodes surrounded by sulfur and covered with the alcohol.

Grinding.—By repeated grinding of rhombic crystals of sulfur with glucose and adding the mixture to water, von Weimarn and Utzino[31] obtained a dilute sulfur sol which began to separate out after one week but which was not completely precipitated in 8 months. Prolonged grinding with water containing a protecting colloid and a little sodium chloride is said to yield a sol of high concentration.[32]

Sols are also formed merely by extracting natural minerals such as markasite and magnetic pyrites that have been weathered for a long time.[33] Similar results are obtained with finely ground unweathered minerals by subjecting them to the action of water vapor and carbon dioxide.

Partial Solution.—An alcosol of sulfur, formed by cooling an alcoholic solution to a low temperature, may be made highly dispersed by partial solution at a higher temperature, as described on page 16.

[28] Sekera: Kolloid-Z., **31**, 148 (1927).

[29] *Cf.* German Pat., 438,221 (1926).

[30] Müller and Nowakowski: Ber., **38**, 3781 (1905).

[31] Alexander's "Colloid Chemistry," **1**, 659 (1926); Kolloid-Z., **36**, 265 (1925).

[32] German Pat., 470,837 (1922).

[33] Dittler: Kolloid-Z., **21**, 27 (1917).

Technical Protected Sols

Colloidal sulfur, in the form of dusting powders or sprays for use as insecticides and for controlling certain plant diseases, is usually prepared by the aid of protecting colloids. A few of these preparations will be described briefly.

Precipitation Methods.—Kelber and Schwarz[34] recommend the precipitation of sulfur by a suitable reaction such as the action of acetic acid on a polysulfide or sulfurous acid on sodium sulfide in the presence of albumin or one of its degradation products, *e.g.*, lysalbinic acid, as protecting colloid. After washing, the precipitate is peptized by dilute alkali, and the resulting sol may be purified by dialysis. On evaporation or precipitation with alcohol or acetone, a white residue results which is peptized to a milky sol by shaking with water. Sols with much finer particles are formed by the interaction of sulfur dioxide and hydrogen sulfide in the presence of gluten or its degradation products with organic acids.

The decomposition of ammonium sulfide by heating in the presence of protecting colloids yields sulfur in a finely divided form readily peptized by water. For example, if concentrated ammonium polysulfide solution is poured into a boiling 5% soap solution and heated until all ammonia and hydrogen sulfide are removed, a thick, yellowish white, sulfur milk results which gives with water a bluish sol containing particles 1 μ or less in diameter.

The firm of Heyden[35] used a modification of von Weimarn's method in preparing a technical sol. The procedure consists essentially in pouring an alcoholic solution of sulfur into a 0.1 to 0.2% solution of gelatin or of albumin or its degradation products. On the addition of acid the sulfur separates along with the protecting colloid. By washing, repeptizing in dilute alkali, and precipitating with alcohol, a reversible residue is obtained. Similarly, Winkler[36] shook 1 part of a saturated solution of sulfur in carbon bisulfide with 2–3 parts of a 35% solution of soap or turkey red oil. The resulting creamy liquid gave a stable sol from which the carbon disulfide was removed by warming and passing a current of air.

Important technical preparations are salves in which the sulfur is in the highly dispersed state. Sabbatani[37] makes such preparations by heating 100 g of a salve base with 2 g of precipitated sulfur at

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[34] German Pat., 245,621 (1912).

[35] German Pats., 164,664 (1905); 201,371 (1908).

[36] German Pat., 401,049 (1924).

[37] Kolloid-Z., 13, 249 (1913).

140–145° until the sulfur is completely melted, followed by rapid cooling. The sulfur comes down in fine particles from 0.5 to 6 μ in diameter, depending on the nature of the salve base. At the outset no particles are visible in a lanolin salve, the preparation exhibiting only a slight opalescence in thin layers; but in an hour, particles 0.2 to 0.5 μ in diameter appear. Cocoa butter, vaselin, lard, paraffin, and white wax salves are white and milky from the first.

Köhler[38] obtained highly dispersed, very reactive sulfur, for use in making salves and lotions, by the unique process of melting a mixture of equal parts of naphthalene and sulfur, cooling, and removing the naphthalene by a solvent or by gentle warming in a stream of air.

Mechanical Methods.—The Thomsen Chemical Company[39] prepared colloidal sulfur for use as an insecticide by grinding 50 parts of sulfur with 5 parts of glue or gum arabic in 50 parts of water until the emulsion had a creamy consistency, and diluting with water. Other protecting colloids which may be used are extract of soap bark, gum tragacanth, and Irish moss. Plauson[40] obtains similar preparations by the aid of the colloid mill. Thus, a milky emulsion is formed by grinding, for 1 to 3 minutes, 50 parts of sulfur in 50 to 100 parts of carbon bisulfide with 25 to 50 parts of ricinosulfonic acid in 150 parts of water. A solid sol results by grinding the above sol with 25 to 30 parts of gelatin or 10 to 15 parts of island moss, previously swollen in water.

COMPOSITION AND CONSTITUTION OF SULFUR SOLS

Hydrophilic and Hydrophobic Sols

The sol obtained by pouring a hot alcoholic solution of sulfur into water according to von Weimarn's method is distinctly different in many respects from the sols formed by the chemical processes of Selmi, Raffo, and Freundlich. The von Weimarn sol is a milky, bluish-white liquid the particles of which contain relatively little adsorbed water, and the behavior of the sol toward electrolytes is characteristic of hydrophobic colloids, coagulation taking place with relatively low concentrations to give an irreversible precipitate. In marked contrast, the sols formed by chemical reactions are relatively clear, yellow liquids, the particles are highly hydrous, and the rela-

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[38] German Pat., 192,815 (1907).

[39] German Pat., 273,761 (1914).

[40] German Pats., 388,022; 394,575 (1924).

tively high stability toward electrolytes puts them in the class of hydrophilic colloids.[41]

The Rôle of Polythionic Acids.—The reason one and the same substance should give a distinctly hydrophobic sol under one set of conditions and a hydrophilic sol under another, is not at once apparent. Some light has been thrown on this problem by a consideration of the properties of the different forms of sulfur.[42] As is well known, there are two well-defined forms of liquid sulfur: the straw-colored fluid S_λ which exists between 116° and about 160°, and the brown viscous S_μ which is formed above 160°. On slow cooling, S_μ is transformed into S_λ and subsequently into rhombic (or monoclinic) crystals which are freely soluble in organic solvents such as carbon bisulfide. But on rapid cooling in the presence of sulfur dioxide and acids, the S_μ solidifies to a tough amorphous solid (plastic sulfur) which dissolves much more slowly in organic solvents than S_λ. Smith considers plastic sulfur to be merely supercooled S_μ, but Freundlich[43] points out that this is inadequate to explain why sulfur dioxide and acids favor its formation, why it is not formed even on rapid cooling when the element is heated with ammonia, and why the amorphous mass obtained by sudden cooling changes to S_λ at ordinary temperatures in the presence of hydroxyl ions. Freundlich accounts for these phenomena by assuming that polythionic acids, especially pentathionic acid, $H_2S_5O_6$, are mixed with or adsorbed by the supercooled S_μ and that these in some unspecified way inhibit the transformation to S_λ at ordinary temperatures and influence the solubility in organic solvents. In line with this, it has been shown that pentathionic acid is obtained by heating sulfur in the presence of water and hence can be formed during the preparation of plastic sulfur. Moreover, this acid is stable in the presence of acids and instable in the presence of ammonia and alkalies, which suggests a probable connection between the conditions for forming plastic sulfur and the stability of the thionic acid.

Odén believes that the particles of von Weimarn's sol are S_λ, while those of the hydrophilic Selmi and Raffo sols are supercooled S_μ. Freundlich points out, very properly, that this characterization is insufficient in itself to account for the marked difference in the hydrous character of the sols, and attributes the hydrophilic

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[41] *Cf.* Bary: Compt. rend., **171**, 433 (1920).

[42] Smith and coworkers: Z. physik. Chem., **42**, 447 (1903); **52**, 602 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200, 209 (1908); **77**, 661 (1911).

[43] "Kapillarchemie," 4th ed., **2**, 382 (1931).

properties of the Selmi and Raffo sols to the presence of pentathionic acid in the micelles. Because of its high sulfur content this acid doubtless possesses an affinity for sulfur, and because of its high oxygen content, an affinity for water. It therefore serves as a connecting link between the particles and the water molecules. The von Weimarn sol is hydrophobic because of the absence of pentathionic acid in the micelles.

The probable presence of pentathionic acids in the Selmi and Raffo sols has been demonstrated by Freundlich and Scholz. The amounts have been determined by treating the sol with alkali which reacts with pentathionic acid to give thiosulfate that can be estimated iodometrically. One gram of sulfur in a Selmi sol was found to contain 0.13 to 0.15, and in a Raffo sol, 0.47 to 0.69 millimol of pentathionic acid.

The yellow color of Selmi and Raffo sols suggest that the sulfur is present as S_μ. The constitution of the micelles in the two different sols may be represented by the respective formulas:

$$[(S_\lambda \cdot zH_2O)_x OH]^-,$$

for the hydrophobic von Weimarn sol, and

$$[(S_\mu \cdot yH_2S_5O_6 \cdot z_1H_2O)_{x_1} S_5O_6]^{--}$$

for the hydrophilic sol formed by chemical methods. In these formulas, z_1 is much larger than z, and in general x is larger than x_1. Bassett and Durrant[44] believe the stabilizing ion to be hexathionate rather than pentathionate. It is altogether probable that both are present in varying amounts. In any event, the higher polythionates are stabilized and protected from hydrolysis by adsorption on the sulfur particles.

Further data bearing on the constitution of the sols will be brought out in the next section.

Composition from Membrane Equilibrium Studies

Donnan's Theory.—Donnan's theory of membrane equilibria[45] deals with the equilibria resulting when a membrane separates two electrolytes, one of which contains an ion that cannot diffuse. As a simple example, Donnan showed that, if one places HX on the inside and HCl on the outside of a membrane permeable to H^+ and Cl^- ions but not to X^- ions, when equilibrium is established the product of

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[44] Bassett and Durrant: J. Chem. Soc., 2919 (1931).

[45] Donnan: Z. Elektrochem., 17, 572 (1911); Chem. Rev., 1, 73 (1924).

the activities of the H^+ and Cl^- ions on the two sides of the membrane will be the same, as given by the equation:

$$\alpha H^+_{\text{I}} \cdot \alpha Cl^-_{\text{I}} = \alpha H^+_{\text{II}} \cdot \alpha Cl^-_{\text{II}}$$

where αH^+_{I} and αCl^-_{I} are the activities of the ions on the inside, and αH^+_{II} and αCl^-_{II} the corresponding values on the outside of the membrane.

In general, where there is but one diffusible electrolyte with two univalent ions, the equation of products at equilibrium is

$$\alpha_{1+} \cdot \alpha_{1-} = \alpha_{2+} \cdot \alpha_{2-} \tag{1}$$

where α_{1+} and α_{2+} are the activities of the cations inside and outside the membrane, and α_{1-} and α_{2-} are the corresponding values for the anions.

If, on the inside of the membrane, y represents the concentration and f_y the activity coefficient for the cation; w and f_w, the corresponding values for the anions; and z, the concentration of the non-diffusible X^- ions, then

$$\alpha_{1+} = f_y z; \quad \text{and} \quad \alpha_{1-} = f_w w \tag{2}$$

Since, at equilibrium, the liquid inside the membrane is neutral, it follows that

$$y = z + w \tag{3}$$

This means that so long as y has a finite value there are more diffusible cations than anions inside the membrane and more diffusible anions than cations outside the membrane.

From (3) and (2)

$$z = \frac{\alpha_{1+}}{f_y} - \frac{\alpha_{1-}}{f_w} \tag{4}$$

Substituting from Equation (1)

$$y = \frac{\alpha_{1+}}{f_w} - \frac{\alpha_{2+} \cdot \alpha_{2-}}{\alpha f_w \cdot \alpha_{1-}} \tag{5}$$

Unfortunately, the activity of the different ions is not known exactly, but in the case of hydrochloric acid as the diffusible electrolyte it is safe to assume that the activity of the two ions is approximately the same, that is,

$$\alpha_{2+} = \alpha_{2-} = \alpha_2$$

and Equation (5) simplifies to

$$z = \frac{\alpha_2}{f}\left(\frac{\alpha_{1+}}{\alpha_2} - \frac{\alpha_2}{\alpha_{1+}}\right) \tag{6}$$

If the non-diffusible ions are cations, Equation (6) becomes

$$z = \frac{\alpha_2}{f}\left(\frac{\alpha_2}{\alpha_{1-}} - \frac{\alpha_{1-}}{\alpha_2}\right) \tag{7}$$

Donnan has shown further that the unequal distribution of ions on the two sides of a membrane sets up a potential difference E across the membrane which is represented by the equation

$$E = \frac{RT}{F} \log \frac{\alpha_1}{\alpha_2}$$

in which R is the gas constant, T the absolute temperature, and F the faraday. Equation (7) can therefore be changed to the form

$$z = \frac{\alpha_2}{f}\left(e^{EF/RT} - e^{-EF/RT}\right) \tag{8}$$

Thus, from the membrane potential and the concentration of ions outside the membrane, it is possible to calculate the quantity of non-diffusible ions.

The membrane equilibrium theory has been tested and found applicable by Donnan, Loeb, Procter and Wilson, and others.[46] In these investigations an ion is assumed to be non-dialyzable only when its dimensions are so large that it cannot pass through a porous membrane. It is obvious, however, that an ion will become non-dialyzable by adsorption on a non-dialyzable colloidal particle. In this case, z in the above equations becomes the concentration of adsorbed ions.

Adsorption of Hydrogen by Colloidal Sulfur.—Rinde[47] prepared a Raffo sol and separated it into fractions with sodium chloride of varying concentrations according to Odén's method (see page 308). These fractions were coagulated repeatedly with hydrochloric acid to remove sodium ions, dialyzed, placed in collodion bags, and immersed in diluted acid. Equilibrium was established in 1 day, but the measurements of osmotic pressure, membrane potential, and hydrogen

[46] For bibliography, *see* Donnan: Chem. Rev., 1, 73 (1924).

[47] Phil. Mag., (7) 1, 32 (1926).

ion activity inside and outside the bag were made after 3 days. The membrane potential was obtained by placing saturated calomel electrodes on either side of the membrane. The hydrogen ion activity was determined with the quinhydrone electrode. At equilibrium the difference of the hydrogen potential inside and outside the bag must equal the membrane potential; this served to control the measurements. Fig. 47 shows the effect of the *p*H of the outer solution on the membrane potential. The latter has its highest value when the acidity of the sol is low, decreases as the acidity rises, and approaches zero. The osmotic-pressure curve is similar in form but approaches a certain positive value rather than zero, at lower *p*H values.

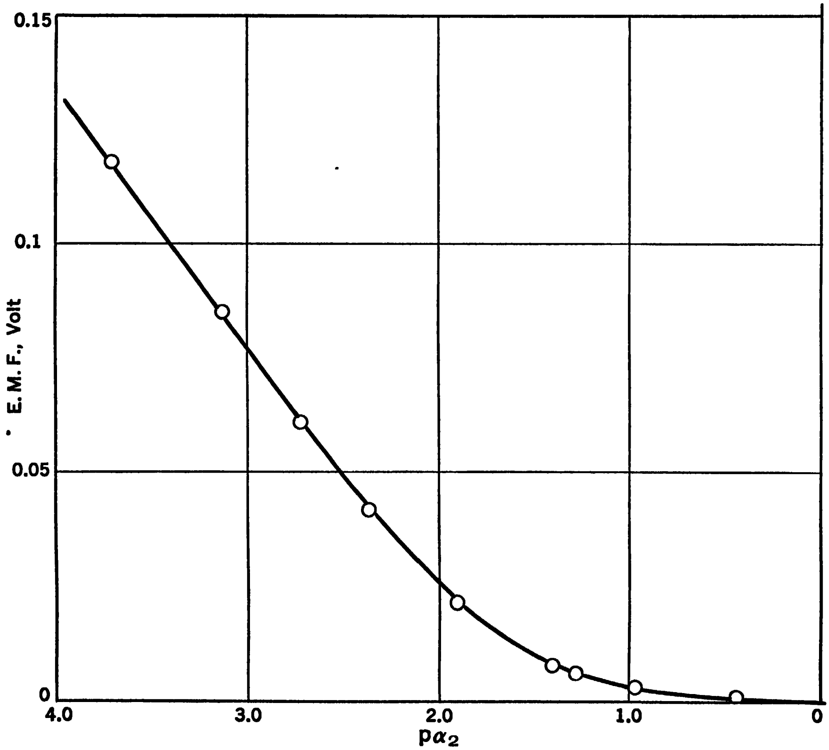

FIG. 47.—Effect of hydrogen ion on the membrane potential in a sulfur-acid system.

From the observed membrane potential and hydrogen ion activities, the adsorption of hydrogen, z, was calculated by Equation (8). In Fig. 48 the adsorption in millimols per gram of sulfur is plotted against the *p*H of the outer solution for the several fractions. As the figure shows, the quantity of adsorbed ions is fairly constant when the acidity outside the membrane is low and rises as the acidity increases. Since the sol was found to contain but few chloride ions, it is probable that the adsorbed ions are present chiefly as polythionic acid rather than hydrochloric acid. Some significant data are summarized in Table LII. The values for the amount of adsorbed hydrogen in the range of *p*H covered are of the same order of magnitude as the adsorption of pentathionic acid (0.47–0.69 millimol per gram sulfur) in a Raffo sol as determined by Freundlich and Scholz (see page 315).

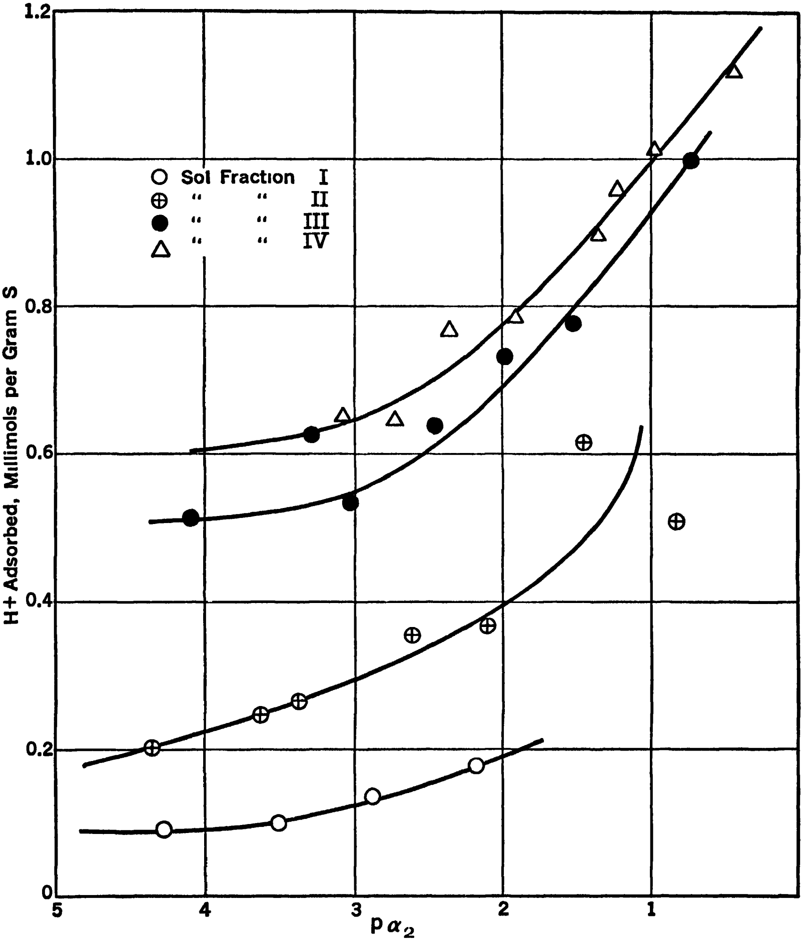

Fig. 48.—Adsorption of hydrogen ion by colloidal sulfurs of varying particle size.

TABLE LII

ADSORPTION OF HYDROGEN BY SULFUR SOL

Sol fraction	Normality of NaCl used in fractionation	S in sol g/l	z from Equation (8) millimols/g of S
I	0.1–0.2	14.75	0.09
II	0.2–0.3	7.99	0.2
III	0.3–0.4	29.17	0.5
IV	0.4–	34.21	0.6

Further evidence that the acid is adsorbed by the colloidal particles is furnished by the fact that the amount of hydrogen taken up at varying *p*H values can be represented by the Langmuir equation.

PROPERTIES OF SULFUR SOLS

Coagulation by Electrolytes

Titration of Sols with Electrolytes.—The coagulation which accompanies the stepwise addition of electrolytes follows a different course depending on whether the sol is polydisperse or monodisperse, that is, whether the dispersed particles vary in size or are approximately uniform in size. Some observations of Odén[48] on titrating both polydisperse and monodisperse sulfur sols with sodium chloride illustrate the difference in behavior in a striking way. With the polydisperse sols, there is a stepwise coagulation, the largest particles precipitating first followed by the smaller ones in order of decreasing size until the coagulation is complete. With an approximately monodisperse sol, on the other hand, the coagulation is almost complete within a rather narrow range of salt concentration. This is shown graphically in Fig. 49, in which the equilibrium concentration of sol is plotted against the total sodium chloride concentration, including that in the original sol. It is apparent that the polydisperse sol precipitates gradually over a wide range, whereas the monodisperse sol is largely coagulated within a narrow range, the greater part of the curve for the latter sol being almost perpendicular.

Comparison of Hydrophobic and Hydrophilic Sols.—Sulfur sols exhibit marked differences in behavior toward electrolytes depending on whether they are hydrophobic or hydrophilic. This is indicated

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[48] "Der kolloide Schwefel," 137 (1913).

by some observations of Freundlich and Scholz[49] on the precipitation values of electrolytes for the two types of sols as shown in Table LIII. Since the sols are polydisperse, the precipitation value is taken as that concentration of electrolyte which causes complete coagulation in 18 hours. Both types of sols are negatively charged, and it is the effect of the cation which predominates in the coagulation. The hydrophobic character of the von Weimarn sol is shown by the strong

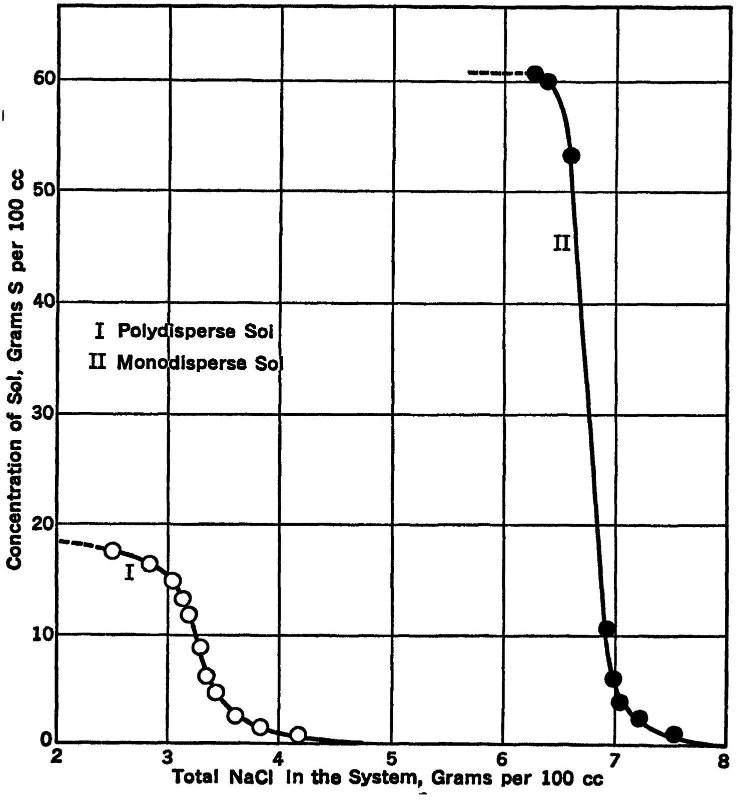

FIG. 49.—Course of the coagulation of sulfur sols titrated with sodium chloride.

influence of the valency and adsorbability of the cations and the more marked precipitating action of hydrogen ion than of other simple univalent cations. On the other hand, the Selmi, Raffo, and Freundlich sols all show the effect of their hydrophilic character. Thus the alkali salts have a coagulating power ten to twenty times weaker for the chemically prepared sols than for von Weimarn's sol. More-

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[49] Kolloid-Beihefte, 16, 234 (1922); *cf.* Odén: "Der kolloide Schwefel," 154 (1913).

TABLE LIII

PRECIPITATION VALUES OF ELECTROLYTES FOR DIFFERENT SULFUR SOLS

Electrolyte	Precipitation values in millimols per liter for			
	von Weimarn's sol 77 mg S/l	Raffo's sol 364 mg S/l	Selmi's sol 133 mg S/l	Freundlich's sol 133 mg S/l
LiCl	34.0	750.0	600.0	550.0
NaCl	33.0	190.0	145.0	140.0
KCl	32.0	85.0	85.0	90.0
RbCl	31.0	80.0	77.0	71.0
CsCl	30.0	95.0	100.0	95.0
$\frac{1}{2}H_2SO_4$	10.0	900.0	. .	
HCl	10.0	850.0	680.0	700.0
p-Chloraniline chloride	25.0	20.0	. ..	.....
Strychnine nitrate	1.0	2.1	.....	.....
$Be(NO_3)_2$	2.3	1.0	. .	.. .
$MgSO_4$	4.2	1.6	.....	.. ..
$MgCl_2$	3.7	1.5	1.1	1.1
$CaCl_2$	3.8	1.5	.	. .
$BaCl_2$	3.6	1.5	0.08	0.7
$AlCl_3$	.	0.05	0.03	0.04
$CeCl_3$	0.02	0.06	0.024	0.02

over, the lyotropic series of the alkali cations is well defined, the precipitating power increasing markedly from the highly hydrated lithium to the slightly hydrated cesium. Finally, acids have a much weaker coagulating action than the alkali salts, and alkalies change completely the properties of the sol.

Freundlich and Scholz attribute the marked difference in behavior of the two types of sols toward electrolytes to the presence of pentathionic acid in the micelles of the chemically formed sols and to its absence in the von Weimarn sol. The thionic acid is fairly stable in acid solution, and the content of this acid is believed to determine the stability and hydrous character of the particles. Since it is probable that a part of the pentathionate is present as sodium salt, the action of acids may be due to a transformation of the salt to the stabilizing pentathionic acid, thus raising the precipitation value for acids above that for the alkali salts. Alkalies, on the other hand, destroy pentathionic acid and probably for this reason destroy the stability and other properties of the hydrophilic sols. The process is not one of ordinary coagulation since the original yellowish sol becomes white and milky, the sulfur precipitating in the irreversible S_λ form which is soluble in organic solvents. Indeed, if the hydrophilic sol is sufficiently dilute it may be changed into a von Weimarn sol by adding an amount of alkali insufficient to cause coagulation. Hydrosulfuric acid, unlike other acids, changes the character of the hydrophilic sols by destroying pentathionic acid in accord with the equation:

$$H_2S_5O_6 + 5H_2S \rightarrow 10S + 6H_2O$$

Heat effects accompanying the coagulation of Raffo's sol are due to the heat of mixing of the coagulants with the thionic acids in the sol and the heat effects accompanying changes in ion adsorption, rather than to changes in dispersity of the sol during the coagulation.[50]

Ionic Antagonism in the Coagulation Process.—In the precipitation of Selmi and Raffo sols with mixtures of electrolytes, there is frequently an antagonistic action in the sense that more of one electrolyte must be used to effect coagulation than if the other were not added. This is especially true if one of the electrolytes is an acid. Fig. 50 gives the results of Odén's[51] observations on the precipitation of a Raffo sol with potassium chloride in the presence of varying

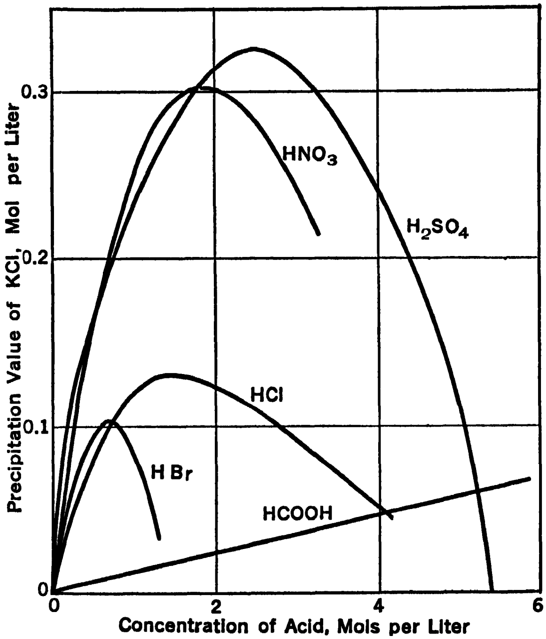

FIG. 50.—Precipitation values of potassium chloride for sulfur sol in the presence of varying amounts of several acids.

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[50] Browne: Colloid Symposium Monograph, 1, 7 (1923).

[51] "Der kolloide Schwefel," 118–154 (1913).

amounts of several acids. Freundlich and Scholz[52] have confirmed and extended Odén's observation with several mixtures of salts of univalent cations with those of bivalent and trivalent cations. Quite marked antagonistic effects were observed in certain cases. Thus, if 65% of the concentration of lithium sulfate necessary for coagulation were added to the sol, the concentration of cerium chloride required to complete the coagulation was 15,000% of the precipitation value in the lithium-free sol.

Odén attributed the above phenomena to the stabilizing action of the ions having the same charge as the sol,[53] for example, the sulfate ion in lithium sulfate. This view seems inadequate in itself to account for such an enormous stabilizing action of the sol toward cerium chloride. Since the antagonistic behavior is observed only with the hydrophilic sols and not with von Weimarn's sulfur sol or gold sol, Freundlich and Scholz conclude that the hydration of the particles and of the precipitating ions is of primary importance in producing ionic antagonism and so in determining whether the precipitating action of mixtures shall be additive or above the additive values. This leads to the conclusion that the behavior of colloids with mixtures of electrolytes is a suitable criterion for determining to what extent the stability of sols is influenced by their hydration. The general accuracy of this conclusion is rendered questionable by some observations on the precipitation of chromic oxide sol by mixtures[54] having widely different precipitating power, such as potassium chloride and sulfate. Although the sol is highly hydrous, the precipitation values of mixtures are less than additive by a quite appreciable amount, instead of being considerably above the additive values as would be predicted from the theory of Freundlich and Scholz. One may be reasonably certain, therefore, that hydration is not the only factor in bringing about the phenomenon of ionic antagonism and may be a relatively unimportant one in certain cases.

As a result of investigations on the anomalous behavior with arsenic trisulfide sol, hydrous oxide sols, and ferricyanide sol,[55] the author found that the precipitation values of mixtures of two electrolytes may be additive, may be greater than the additive values, or may be less than the additive values. Moreover, it would seem

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[52] Kolloid-Beihefte, **16**, 267 (1922); *cf.* Rossi and Marescotti: Ann. chim. applicata, **16**, 267 (1922).

[53] *Cf.* Dorfman: Kolloid-Z., **46**, 186 (1928); Dorfman and Scerbacewa: **52**, 289 (1930).

[54] Weiser: J. Phys. Chem., **28**, 232 (1924).

[55] Weiser: J. Phys. Chem., **30**, 20, 1527 (1926).

that three factors, at least, may influence the precipitation concentration of salt pairs: (1) the effect of each precipitating ion on the adsorption of the other, (2) the stabilizing action of ions having the same charge as the sol, and (3) the relatively greater adsorbability of ions at lower concentrations. In the case of sulfur sol the action of acids may raise the stability by converting pentathionate into pentathionic acid. The antagonistic action between precipitating ions of the same charge is important in raising the critical concentrations above the additive value only in case the ions show marked differences in adsorbability. Variation from the additive relationship with mixtures of salt pairs having a common precipitating ion results only when there is an appreciable difference in the adsorbability of the stabilizing ions, the magnitude of the variation from an additive relationship being determined by the differences in adsorbability. If the first and second factors referred to above are not too pronounced, the precipitation values of mixtures may fall below the additive value on account of the relatively greater adsorbability of precipitating ions at low concentration.

The view of Freundlich and Scholz that hydration influences are chiefly responsible for the antagonistic action with sulfur sol is probably correct, but it is not sufficiently definite to be helpful. So far as the adsorption of the ions is determined by their hydration[56] and that of the adsorbent, it is of course quite proper to say that cationic antagonism is determined by hydration influences. In this connection, Dorfman[57] showed that the coagulation values of lithium, ammonium, sodium, and potassium chlorides decrease with the addition of increasing amounts of alcohol. Moreover, the antagonism between mixtures of lithium chloride and the chlorides of sodium, magnesium, and aluminum decreases with about 30% of alcohol, and with 60% the effect of the ions is additive. Dorfman attributes this to the dehydrating action of the alcohol, but the details of the mechanism should be worked out.

Bassett and Durrant[58] attribute the antagonistic action of hydrogen and some other ions such as sodium to the high solubility of the complex sulfur-polythionic acid or salt. Since the system remains colloidally dispersed after the addition of a small amount of acid or alkali salt, Bassett and Durrant cannot be speaking of molecular

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[56] Lachs and Lachman: Z. physik. Chem., **123**, 303 (1926); Fajans and Beckerath: **97**, 478 (1921).

[57] Kolloid-Z., **52**, 66 (1930).

[58] J. Chem. Soc., 2919 (1931).

solubility. Moreover, the antagonistic action of salt pairs must be regarded as a mutual antagonistic action.[59] Thus the presence of lithium ion increases the precipitation value of magnesium for sulfur sol; but the presence of magnesium likewise increases the precipitation value of lithium. It does not explain anything to say that an ion like magnesium which forms a relatively insoluble salt (relatively low precipitation value) increases the "solubility" so that relatively more lithium must be added than if the magnesium were absent.

Adsorption of Precipitating Ions.—That cations are adsorbed during the precipitation of negatively charged sulfur sols was recognized by Odén during the course of his extended investigations on Selmi's sol. The adsorption studies were made on a quite highly dispersed sol containing particles of approximately the same size. The sol was coagulated with hydrochloric acid and repeptized a few times to remove sodium chloride and was then purified by dialysis. Six similar portions were placed in 200 cc centrifuge bottles and coagulated by the dropwise addition of the electrolytes, care being taken to avoid an excess. After centrifuging, the supernatant solution was poured off, the process being repeated a number of times. Finally, the coagula were pressed between filter paper, placed in a quartz dish, the sulfur burned off, and the residue weighed. The results are given in Table LIV. The adsorption values are very nearly equivalent, although the value for iron is less than for barium and for barium is somewhat less than the average for the univalent ions. Since it is impossible to remove all the supernatant solution from the precipitates by centrifuging, the data are not very accurate, and any deductions

TABLE LIV

ADSORPTION OF CATIONS DURING PRECIPITATION OF SULFUR SOL

Electrolyte	Analysis		Milliequivalents of cation per g of sulfur
	Sulfur, g	Salt chloride, g	
NaCl	0.1974	0.0216	1.9
KCl	0.2935	0.0410	1.9
RbCl	0.2745	0.0557	1.7
CsCl	0.2327	0.0823	2.1
$BaCl_2$	0.3153	0.0591	1.8
$FeCl_3$	0.2860	0.0105 (Fe_2O_3)	1.4

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[59] *Cf.* Weiser: J. Phys. Chem., **30**, 20 (1926).

therefrom may be open to question. It has been found, however, from adsorption studies[60] on hydrous oxide sols that the adsorption values of precipitating ions are not equivalent at the precipitation value, since less adsorption of the more strongly adsorbed multivalent ions will lower the charge on the particles to the critical value. It is probable, therefore, that the lower adsorption values for the multivalent iron and barium, at the respective precipitation concentrations for sulfur sol, are real and not the result of an inherent experimental error as Odén supposed. Bassett and Durrant[58] showed, however, that the coagulum from different sulfur sols always contains the precipitating cation in amounts equivalent to the polythionate in the micelles. This would mean that, for one and the same sol, the amounts of various cations adsorbed during coagulation will be equivalent, as Odén believed. If this should prove to be true, it would represent the ideal case that both Freundlich and the author failed to find among oxide, salt, and metallic sols.

Raffo and Rossi[61] found the conductivity and freezing-point lowering of dilute electrolytes to be decreased in the presence of colloidal sulfur owing to adsorption on the colloidal particles. After coagulation of sulfur sol by dyes such as new fuchsin and methylene blue, the sulfur flocks coalesce, causing a decrease in specific surface, and the adsorbed dye returns in part to the solution.[62]

Coagulation by Temperature Change

Varying the temperature of Selmi and Raffo sols brings about phenomena similar to those on varying the temperature of solutions. Thus, if a clear sol is cooled with ice, it is partially coagulated, and on warming it is repeptized. This process may be repeated as often as one desires. Svedberg[63] showed that a real temperature equilibrium exists between the concentration of colloidal sulfur in the liquid and in the coagulum, that is determined by the temperature and the nature and concentration of the electrolytes present. This means that the coagulated particles have a definite solubility or more correctly a peptizability, since the equilibrium values depend on the particle size in a different manner from true solubility. With a sol having particles of approximately the same size the sulfur content, S, of the sol may be calculated by the exponential equation $S = e^{k(t-t_0)}$

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[60] Weiser: J. Phys. Chem., **35**, 1, 1368 (1931).

[61] Gazz. chim. ital., **45** I, 119 (1915).

[62] Freundlich: Kolloid-Z., **17**, 153 (1915).

[63] Kolloid-Z., **4**, 49 (1909); *cf.* Raffo: **2**, 358 (1908); Debus: Ann., **244**, 76 (1888).

in which t is the temperature and k and t_0 are constants. The applicability of the equation to a monodisperse submicronic sol is shown in Table LV. The sodium chloride content of the sol was 0.101 N. The values of the constants obtained graphically were $k = 1.038$ and $t_0 = 14.5$.

TABLE LV

TEMPERATURE EQUILIBRIUM OF A MONODISPERSE SULFUR SOL

Temperature	Sulfur in g per 100 cc of sol	
	Found	Calculated
17.5	22.23	22.51
17.0	14.00	13.40
14.9	1.53	1.62
11.5	0.05	0.04
10.0	0.01	0.0

Odén[64] found that monodisperse sols of different particle size give different "solubility" curves. If curve X in Fig. 51*a* is for a fine-grained sol x, then curve Y will represent diagrammatically the equilibrium conditions for a coarser-grained sol y which is peptized to a lesser extent at the same temperature. The curves end at the upper portions at points which correspond to complete peptization, and they meet the axis of abscissas below at a temperature which corresponds to complete flocculation. If the sols x and y are mixed, both will be peptized along the line Z, and when the point p is reached, x is completely peptized and a part of y is peptized; above p the curve takes the forms of the pure sol y. If a sol contains a larger number of different-sized sulfur particles, the equilibrium curve will be like the one in Fig. 51*b*; if the number of particle sizes increases infinitely, the curve will approach a straight line as the limit. This serves as a means of distinguishing a polydisperse from a monodisperse sulfur sol. With the latter, a curve like X will be obtained, and with the former, a curve like D with many points or eventually a straight line will result.

An increase in the electrolyte content of the sol acts similarly to an increase in particle size, that is, with a greater electrolyte content a

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[64] "Der kolloide Schwefel," 162–170 (1913).

higher temperature is required to get a sol of the same concentration than with a sol of smaller salt content.

The behavior of colloidal sulfur with change in temperature shows conclusively that certain hydrophilic colloid systems can give "solubility" curves similar to those where true solubility prevails. The so-called solubility values of proteins, tannin, etc., doubtless represent only a colloid equilibrium such as obtains with sulfur sols.

Although heating through a limited temperature range will cause peptization of sulfur, boiling the sol may result in partial coagulation by cutting down the adsorption of stabilizing electrolyte at higher temperatures.[65]

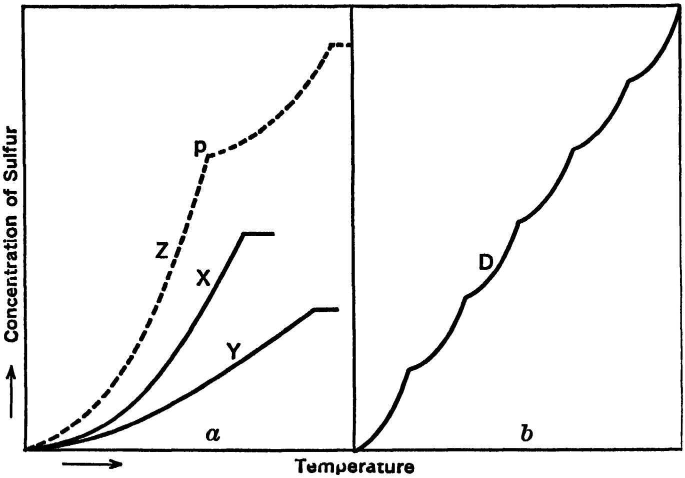

FIG. 51.—Diagrammatic representation of the temperature coagulation (*a*) of sulfur sols of different degrees of dispersity (*b*) of a mixed sulfur sol containing a number of different sized particles.

Sulfur and silver sols can be subjected to 9000 atmospheres' pressure without appreciable loss in stability, but rapid and complete coagulation of both sols takes place at 17,000 atmospheres' pressure.[66]

Color

Sulfur particles dispersed in a gas possess resonance colors which are determined by the particle size. The smallest particles appear blue, the color changing through green, green-yellow, yellow, to white-yellow as the particle size increases.[67] The suspended sulfur par-

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[65] Rossi: Rev. gén. colloides, 5, 581, 624 (1927).

[66] Wilson and Poulter: Proc. Iowa Acad. Sci., 36, 295 (1929).

[67] Parankiewicz: Physik. Z., 18, 567 (1917).

ticles are deflected away from a strong beam of light falling upon them. The velocity of this so-called photophoresis can be measured. It is very small with the smallest blue particles, but it increases as the particles increase in size from blue through green to yellow, reaching a maximum when the radius is 27.8×10^{-6} cm, and then falling off until it can be no longer detected with particles having a radius greater than 4×10^{-5} cm.

Sulfur hydrosols are yellow liquids if the dispersed particles are very small. With particles in the range of ultramicroscopic visibility, the sols have a reddish to reddish brown appearance; and with still larger particles, they have a purple to blue shade.[68] Coarsely dispersed sols are milky white.

Blue Sulfur.—Blue sulfur and blue sulfur sols have been obtained in a number of ways.[69] Earlier investigators observed them especially during the oxidation of hydrogen sulfide by ferric chloride[70] and during the precipitation of sulfur in the presence of cadmium and bismuth salts.[71] Odén is of the opinion that heavy metal impurities may determine the color in such cases. Although this is possible, there is no question that elementary sulfur may appear blue under certain conditions and that deep blue sulfur sols free from metallic impurities may be formed. Thus Liesegang[72] put a drop of 20% citric acid on a thin layer of gelatin jelly containing sodium thiosulfate and obtained a precipitate of sulfur which possessed a deep, lilac-blue color by transmitted light. The blue disappeared after a day, probably owing to a change from S_μ to S_λ accompanied by a marked increase in particle size.

Effect of Particle Size.—Sols exhibiting wide variations in color with change in particle size were prepared in one and the same dispersion medium by Ostwald and Auerbach.[73] In one set of experiments, 15 cc of *N*/20 sodium thiosulfate was mixed with 5 cc of phosphoric acid solution containing 0.1 cc of 90% H_3PO_4. As the sulfur separated and the particles increased in size, the color passed through the entire scale from clear yellow through green, red, and violet to blue, in the course of 20 minutes. Quite striking results of

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[68] Odén: Kolloid-Z., **8**, 186 (1911): Z. physik. Chem., **78**, 682 (1912).

[69] For a full bibliography, *see* Ostwald: Kolloid-Beihefte, **2**, 409 (1911); von Weimarn: **22**, 38 (1926); Mellor: "Inorganic and Theoretical Chemistry," **10**, 38 (1930).

[70] Wöhler: Ann., **86**, 373 (1853); Schiff: **115**, 68 (1860); Vogel: J. pharm., (3) **29**, 433 (1856).

[71] Orloff: J. Russ. Phys.-Chem. Soc., **33**, 397 (1901).

[72] Kolloid-Z., **7**, 307 (1910).

[73] Kolloid-Z., **27**, 223 (1920); Auerbach: **38**, 336 (1926).

a similar nature were also observed with the blue solution of sulfur in pyrosulfuric acid, $H_2S_2O_7$. Cryoscopic measurements disclosed that the sulfur in this acid with and without an excess of sulfur trioxide was molecularly dissolved as S_2. By diluting the blue solution with increasing portions of 1 : 1 sulfuric acid, which lowered the solubility of the sulfur, the original blue color changed successively to green, yellow, orange, red, violet, and, finally, to a second cloudy blue to green. With the appearance of the yellow color there was a weak opalescence showing the presence of colloidal particles, and the subsequent colors were accompanied by more and more clouding until yellow sulfur separated out. It thus appears that sulfur solutions with sufficiently wide variations in dispersion pass through the visible spectrum twice, analogously to the behavior observed by Piccard[74] on increasing molecular size by successive substitutions in certain organic compounds.

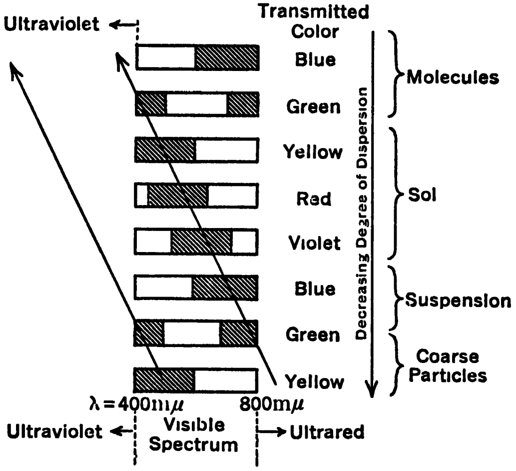

FIG. 52.—Diagrammatic representation of the variation in color of sulfur sols with the particle size.

The above observations support Ostwald's[75] view that the variation in color with particle size is due to a shifting of the absorption maximum toward the region of longer wave length, with decreasing degree of dispersion. This is represented diagrammatically, in the case of sulfur, in Fig. 52. Spectrophotographic observations on the blue molecular solutions show a band in the visible spectrum extending from 530 mμ to longer wave lengths, as well as two ultraviolet bands: one between 320 and 370 mμ, and the second beginning at 240 mμ and showing a maximum at about 230 mμ. The band in the visible portion begins sharply, indicating that the color due to it is quite definite and clear. On the contrary, no sharp line of demarcation exists between the two ultraviolet bands,

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[74] Ber., **46**, 1843 (1913); Rec. trav. chim., **41**, 581 (1922).

[75] Kolloid-Beihefte, **2**, 409 (1911).

indicating that the color produced by these bands is not clearly defined. This suggests the cause of the cloudy appearance of the color in coarsely dispersed systems in which the ultraviolet bands are chiefly concerned.

Pihlblad[76] failed to observe more than one absorption maximum in sulfur sols. He therefore questions Ostwald's explanation of the color variation in the sols and attributes the green, blue, and violet colors to the presence of an allotropic form of sulfur or to a sulfur compound.[71] There is no experimental justification for assuming that blue sulfur is a distinct allotropic form, and the blue color may result under conditions which render improbable the formation of a blue compound. It is more probable that the blue coloration appears when the element exists in a suitable state of dispersion. Since the molecular solution in pyrosulfuric acid contains S_2 molecules, Ostwald suggests that the blue solutions in hot glycerin, ethylene glycol, and in alkaline ethyl, propyl, isobutyl, and amyl alcohols, as observed by von Weimarn,[77] likewise hold the sulfur as diatomic molecules which are thus more highly dispersed than the octatomic molecules present in most organic solvents.

Von Weimarn recognizes four more or less distinct causes which may contribute to the formation of colored sulfur dispersions. First, a blue opalescence color observed only by reflected light; second, molecularly dispersed solutions of what von Weimarn terms "sulfurates," that is, very loose combinations of sulfur with other compounds; third, the blue color observed by transmitted light but due to the scattering of the light by relatively coarse colloidal particles; and, finally, the color which depends on the relation between the refraction coefficient of sulfur and the dispersed phase. It should be pointed out that there is no independent proof of the "sulfurate" anions postulated by von Weimarn in such solvents as pyrosulfuric acid, glycerin, ethylene glycol, and liquid ammonia. If the cryoscopic observations of Ostwald and Auerbach with solutions in pyrosulfuric acid are correct, it seems reasonable to assume, for the present, that the blue color of molecular solutions is due to the presence of sulfur as S_2.

Audubert[78] studied the aging of sulfur sols as indicated by their change in color. Chemically formed sols resulting from the action of acid on thiosulfate are red and clear at first but become blue and

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[76] Z. physik. Chem., 92, 471 (1917).

[77] Kolloid-Beihefte, 22, 38 (1926).

[78] Ann. phys., (9) 18, 5 (1922).

finally violet with time. Sols formed by adding a few drops of water to a solution of sulfur in acetone exhibit at first a white clouding which rapidly becomes blue to violet in transmitted light; and finally, the sulfur agglomerates and settles out. The aging in the latter case is much more rapid than with the chemically formed sol. If a little water is again added to the sol from which the sulfur has separated, the same color phenomena take place, but the rate of change is slower. After the process is repeated a number of times, a lasting blue sol results.

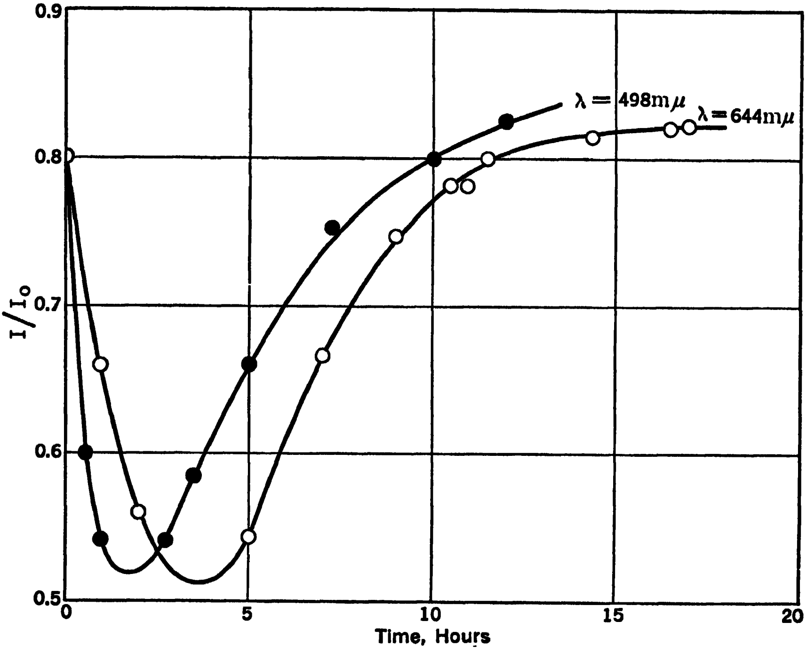

FIG. 53.—Effect of light of varying wave length on the aging of sulfur sols.

A quantitative study of the effect of light of varying wave lengths on the aging process discloses that light of short wave lengths hastens the aging and of long wave lengths retards it, while light with wave lengths between $\lambda = 580\text{–}600$ mμ is without effect. On plotting against time the ratio I/I_0, that is, the ratio of the intensity of the transmitted light to the intensity of the incident light, curves are obtained which exhibit a minimum as shown in Fig. 53. It is apparent that this minimum is reached most rapidly with light of shorter wave lengths; with yellow light, the minimum is reached in the same time as in the dark. From the form of the curves it is concluded that the initial decrease in the I/I_0 ratio is due to an increase in particle size by precipitation of molecularly dispersed sulfur on existing particles; and that the subsequent rise results from agglomeration of the particles with the accompanying decrease in surface, until the flocks settle out.

Ultramarine.—The common ultramarine pigments are alkali aluminum silicates containing sulfur, and may be blue, green, yellow, red, or violet in color. The exact constitution of the several preparations is not known, but the pure ultramarine blue of Guimet[79] can be represented approximately by the formula $Na_6Al_4Si_6O_{24}S_3$.[80] X-ray studies on the pigment show that the sulfur is not a part of the basic structure of the lattice[81] but is distributed statistically throughout the lattice either as a solid solution or a colloidal dispersion.[82] Ostwald and Auerbach[83] believe that the sulfur in clear blue and green ultramarine is in solid solution in the silicate. This is suggested by (*a*) the great purity of the colors which are similar to the clear blue and green molecular solutions of sulfur in pyrosulfuric acid, and (*b*) the ease with which ultramarines react with hydrogen ion giving hydrogen sulfide. Yellow and red ultramarines, on the other hand, are believed to owe their color to colloidally dispersed sulfur, both because the colors are not so clear as in the blue and green pigments, and because the rate of reaction of the former with acids to give hydrogen sulfide is much slower than with the latter. The color of violet ultramarine may be due either to a polydisperse mixture of S_2 and red coarsely dispersed sulfur or to violet colloidal sulfur.

Density, Viscosity, and Surface Tension

The density of sulfur sols varies linearly with the concentration and can be represented fairly well by the equation:

$$d_{\text{sol}} = d_{H_2O} + kC$$

where C is the sulfur concentration and k is a constant.[84]

In the absence of coagulation, the curve showing the effect of tem-

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[79] Pogg. Ann., **46**, 431 (1839).

[80] Jaeger and van Mille: Proc. Acad. Sci., Amsterdam, **30**, 479 (1927).

[81] Jaeger and van Mille: Proc. Acad. Sci., Amsterdam, **30**, 885 (1927).

[82] Knapp: J. prak. Chem., (2) **38**, 48 (1888); Rohland: Z. angew. Chem., **17**, 609 (1904); Hoffmann: **19**, 1089 (1906); Chem.-Ztg., **34**, 821 (1910); Kolloid-Z., **10**, 275 (1912); Ostwald: Kolloid-Beihefte, **2**, 451 (1911).

[83] Kolloid-Z., **38**, 336 (1926).

[84] Odén: "Der kolloide Schwefel," 79 (1913); Lifschitz and Brandt: Kolloid-Z., **22** 133 (1918).

perature on the viscosity of a Raffo sol is slightly concave toward the temperature axis, as in the case of pure water. On the other hand, if the temperature lowering induces partial coagulation (see page 328), a marked increase in viscosity takes place. The results of some observations of Odén[85] are shown in Fig. 54, in which the reciprocal of the viscosity, the fluidity $1/\eta$, of different sulfur sols is plotted

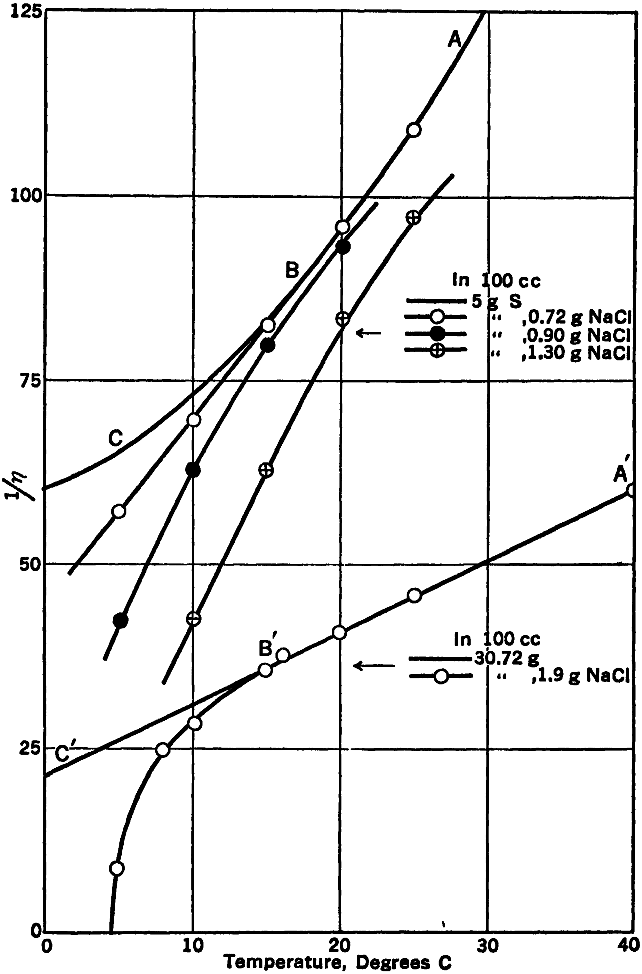

FIG. 54.—Effect of the addition of electrolytes on the fluidity of different sulfur sols at various temperatures.

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[85] "Der kolloide Schwefel," 89 (1913).

against the temperature. In the figure, *ABC* and *A'B'C'* represent the ideal curves for sols containing 5 and 30.7 g sulfur, assuming no coagulation. All the curves for the actual sols fall below the ideal curve, the extent of variation being greater the higher the sodium chloride content of the sol and hence the greater the coagulation at a given temperature. On standing, the viscosity of a sol gradually increases and the conductivity falls off.[86] The increase in viscosity is probably due to partial coagulation, owing to the spontaneous decomposition of pentathionic acid. The disappearance of the latter likewise accounts for the decrease in conductivity.

For the same sulfur concentration, the viscosity of a sol is greater the higher the degree of dispersion. This is not in accord with Einstein's[87] equation $\eta_1 = \eta(1 - kf)$, where η_1 is the viscosity of a suspension of rigid spheres in any liquid; η, the viscosity of the pure liquid; f, the ratio of the volume of the suspended matter to the total volume; and k is a constant equal to 2.5 for cases in which the suspended material occupies more than 40% of the total volume, and 4.5 for cases in which the suspended material occupies less than 40% of the total volume. Hatschek[88] attributed this anomalous behavior in the case of sulfur sol to the existence of an adsorption film of water around the sulfur particles, a factor which was not taken into account when the formula was derived. For particles having a diameter of 10 mμ, Hatschek deduced that the thickness of the film is 0.87 mμ, corresponding to an increase in volume of 62%.

The surface tension of a fresh surface of Raffo sulfur sol is approximately the same as that of water,[89] but it decreases with time.[90] The cause of this behavior is not obvious but it may be associated with the presence of pentathionic acid in the sol.

Chemical Properties

Raffo showed that the highly dispersed sulfur sol prepared by his method is an energetic reducing agent, converting silver sulfate into silver sulfide and liberating iodine from iodic acid. The reaction velocity of the reaction:

$$3Ag_2SO_4 + 4H_2O + 4S \rightarrow 4H_2SO_4 + 3Ag_2S$$

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[86] Dhar and Chakravarti: Z. anorg. Chem., **168**, 209 (1928).

[87] Ann. Physik, (4) **18**, 289 (1906); **34**, 591 (1911); Kolloid-Z., **27**, 137 (1922); Hatschek: **7**, 301 (1910); **27**, 163 (1920).

[88] Kolloid-Z., **11**, 280 (1912).

[89] Odén: "Der kolloide Schwefel," 79 (1913).

[90] Johlin: J. Phys. Chem., **29**, 1129 (1925).

was found to be of the first order, indicating that the reaction completes itself in the heterogeneous system.[91] The addition of sulfur sol to iodic acid solution sets free iodine immediately, as evidenced by the red coloration. After a time the sulfur-iodine mixture separates as a plastic mass.[92]

Freundlich and Nathansohn[93] observed that a mixture of either Raffo's or von Weimarn's sulfur sol with Carey Lea's silver sol exhibited color changes from brown through wine red, violet, steel blue, green-blue, green-brown, to yellow-brown. This phenomenon results from interaction between the micelles of the two sols. Negative arsenic trisulfide sol and Raffo's sulfur sol are rendered mutually instable by interaction between the stabilizing electrolytes of the two sols, hydrogen sulfide and pentathionic acid, respectively.

The transformation of maleic to fumaric acid is catalyzed by Raffo's sulfur sol.[94] The initial increase in velocity is followed by coagulation of the sol and, in consequence, a slowing down of the process. The initial stage is apparently an adsorption of maleic acid by the colloidal sulfur since the velocity of the reaction at the start can be represented satisfactorily by an equation (see page 241) of the form:

$$-\frac{dc}{dt} = kc^{1/n}$$

Moreover, for one and the same sol the velocity was found to be proportional to the sulfur content. The temperature coefficient of the reaction is given by the Arrhenius equation:

$$-lnk = -\frac{A}{T} + B \quad .$$

where k is the velocity constant, T, the absolute temperature, and A and B are constants which are somewhat larger than obtain in the case of most chemical reactions.

APPLICATIONS OF COLLOIDAL SULFUR

The use of colloidal sulfur as a spray in the control of insect pests has been referred to already (see page 312). The sol form is more toxic than the powder to such insects as red spider because of the

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[91] Raffo and Pieroni: Kolloid-Z., **7**, 158 (1910).

[92] Raffo and Rossi: Kolloid-Z., **10**, 278 (1912).

[93] Kolloid-Z., **28**, 258; **29**, 16 (1921).

[94] Freundlich and Schikorr: Kolloid-Beihefte, **22**, 1 (1926); Skraup: Monatshefte, **12**, 107 (1891).

greater rapidity of oxidation of the smaller particles in the sol.[95] The use of the sol is also recommended for certain fungus diseases of plants, especially mildew.[96]

In medicine, colloidal sulfur is used chiefly as a salve (see page 312) or ointment for eczematic conditions, acne, and suborrheic affections of the scalp. For this purpose the sulfur with or without other medicinal agents is dispersed in such media as benzoinated lard. An effective preparation for local application consists of fine talcum coated with colloidal sulfur.[97]

The intravenous injection of colloidal sulfur has been suggested for obscure disorders such as rheumatism and gout. In small injections it is said to increase the hemoglobin content of the blood, and to increase oxidation in the organism, augmenting the output of urea.[98] When injected in considerable amounts, it exerts both an anaphylactic and toxic effect. The portion of the sulfur in the colloidal state determines the anaphylactic type of shock, and the flocculated portion is reduced to hydrogen sulfide which exerts a toxic action.[99] Small injections daily over a period builds up immunity to anaphylactic shock.[100] The toxicity of sulfur sols is therefore determined by their method of preparation, age, concentration, and rate of injection. The toxic action as well as any therapeutic effect must be ascribed to the hydrogen sulfide derived from the sol.[101]

PHYSICAL CHARACTER OF PRECIPITATED SULFUR

The physical character of precipitated sulfur varies widely with the nature of the electrolyte in the solution from which it separates. Thus Stingl and Morawski[102] found that the element comes down plastic in the presence of potassium and barium salts and flocculent in the presence of calcium, magnesium, and sodium salts. Some observations of Weiser and Cunningham[103] on the form of pre-

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[95] deOng: J. Econ. Entomol., **17**, 533 (1924).

[96] Kuhl: Chem.-Ztg., **45**, 479 (1921).

[97] Kloeppel: Münch. med. Wochschr., **78**, 151 (1931).

[98] Montagnani: Physiol. Abstracts, **12**, 124 (1927).

[99] Rastelli and Casazza: Boll. soc. ital. biol. sper., **5**, 939 (1930).

[100] Montagnani: Physiol. Abstracts, **12**, 310 (1927).

[101] Sabbatini: Biochem. Z., **59**, 378 (1914); Messini: Arch. exptl. Path. Pharmakol., **127**, 368 (1928).

[102] J. prakt. Chem., (2) **20**, 76 (1879); *cf.* Odén: "Der kolloide Schwefel," 157 (1913).

[103] Colloid Symposium Monograph, **6**, 319 (1928); J. Phys. Chem., **33**, 301 (1928); *cf.* Bonvarlet: Rev. gén. colloides, **8**, 300 (1930).

cipitate obtained by coagulating a Selmi sol with various electrolytes are shown in Table LVI. Similar types of precipitates result on passing the sol-forming gases into dilute solutions of the respective salts.

TABLE LVI

COAGULATION OF SULFUR SOL BY ELECTROLYTES AND THE PHYSICAL CHARACTER OF THE COAGULUM

Electrolyte	Precipitation concentration, milliequivalents per cc	Physical character of the precipitate
HCl........	0.5	Slimy; reversible
LiCl.......	0.55	Gelatinous; reversible
NaCl......	0 25	Gelatinous reversible
KCl........	0 12	Plastic flocks; irreversible
CsCl.......	0.12	Plastic flocks; irreversible
$CuCl_2$.......	0 012	Gelatinous; reversible on repeated washing
$MgCl_2$......	0 015	Granular; reversible on repeated washing
$ZnCl_2$ ...	0.015	Granular; reversible on repeated washing
$CaCl_2$. . ..	0.008	Granular; partly reversible
$SrCl_2$..... .	0 006	Curdy; irreversible
$BaCl_2$......	0 0076	Plastic; irreversible
$FeCl_3$	0 00045	Curdy; almost entirely reversible
$AlCl_3$.......	0.00035	Curdy; almost entirely reversible
H_2S.........	(Saturated)	Only a small amount of slimy precipitate formed in 4 hours; almost entirely reversible
NaOH......	0.15	Curdy to plastic; slightly reversible

The above observations together with an extended microscopic and ultramicroscopic study of the phenomena have led to the following conclusions:

Sulfur precipitated in the presence of alkali cations varies from gelatinous to plastic on going down in the series from lithium to cesium; likewise, the precipitate formed in the presence of alkaline earth cations changes in the same way on going down in the series from magnesium to barium. In other words, precipitates formed in the presence of those ions which are generally recognized as the most highly hydrated are the most gelatinous, and the precipitation is reversed by washing; the precipitates thrown down in the presence of the less hydrated ions are dense and plastic, and the precipitation is not reversed by washing.

In the light of these observations it seems reasonable to conclude that, when the sulfur particles are partly neutralized by the adsorption of highly hydrated ions, the particles retain an envelope of water; hence the coagulated mass is an agglomerate of ultramicroscopic particles which have not coalesced. The film of adsorbed water, together with the water entrained during the agglomeration process, gives a flexible hydrous mass which is known as a gelatinous precipitate. The ultramicroscopic observations on gelatinous sulfur formed by coagulation of the sol with highly hydrated lithium, sodium, or magnesium ion give definite visual confirmation of the nature of a gelatinous precipitate deduced by Weiser[104] several years ago.

Since the highly hydrated ions that yield gelatinous precipitates are not adsorbed strongly, and since the ultramicrons retain their individuality in such precipitates, it follows that washing out the excess of precipitating ion should cause repeptization. This is very readily accomplished with the precipitates thrown down with the univalent lithium and sodium ions. Practically complete repeptization of precipitates formed in the presence of magnesium and zinc ions can also be effected, but the washing must be more thorough because of the stronger adsorption of the divalent ions.

Conditions are quite different if the neutralization of the particles below the critical value is accomplished by the adsorption of ions that are not sufficiently hydrated to maintain a film of water of sufficient thickness or rigidity to prevent coalescence of the individual ultramicrons. This condition is realized with potassium, cesium, and barium ions. After neutralization, the ultramicrons collide and coalesce, giving a more or less uniform mass of plastic sulfur which cannot be repeptized to give a sol no matter how thoroughly the precipitate is washed. If the individual particles are prevented from coming together by precipitating in the shallow Zeiss cardioid ultramicroscope cell, reversal can be accomplished by washing if the relatively weakly adsorbed potassium ion has been used to effect neutralization, whereas if the more strongly adsorbed bivalent barium ion is employed, it cannot be displaced by washing and reversal is impossible. With sodium hydroxide the precipitate is only partly reversible if thrown down in a test tube but is completely reversible if coalescence of particles is prevented in the cardioid cell. From these observations it appears that a reversible precipitate of any substance will be obtained when a sol is neutralized under such conditions as to prevent coalescence, either (*a*) by the intervention

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[104] Bogue's "Colloidal Behavior," 1, 387 (1924).

of a film of adsorbed solvent or (*b*) by preventing collisions of the neutralized particles. In either case it is essential that the adsorption of the neutralizing ion be sufficiently weak to permit its removal by washing.

In this connection it will be recalled that Freundlich and Scholz (see page 314) attribute the characteristic properties of Selmi and Raffo sols to the presence of pentathionic acid in the micelles. They are therefore led to the conclusion that the reversibility of precipitated sulfur depends on the formation of a stable pentathionate with the precipitating ion, that is, a pentathionate which does not decompose and thereby destroy the pentathionate ion. This view is not tenable, for in the case of potassium we have a precipitate which is reversible or irreversible depending on whether or not the particles are allowed to coalesce. Moreover, in the case of sodium hydroxide the reversibility of the precipitate formed in the cardioid cell cannot be due to the presence of pentathionate since pentathionic acid is destroyed by alkalies.

Ultramicroscopic observation of the change taking place when a highly hydrated cation is removed from a gelatinous sulfur clump, by displacing with a less hydrated, more strongly adsorbed cation, shows a very marked shrinkage as the result of the loss of adsorbed water and the coalescence of the particles. Ultramicroscopic convection currents in the surrounding liquid, due to the outflow of the adsorbed water, are visible during the change. The transformations are so distinct that motion pictures have been made of the phenomena accompanying the change in physical character of the clumps.

The formation of sulfur precipitates in quantity, either by neutralizing the sol by the addition of electrolytes or by carrying on the reaction between sulfur dioxide and hydrogen sulfide in the presence of electrolytes, can be visualized as follows: The first step following the formation of colloidal particles is their neutralization below the critical value necessary for agglomeration. When two or more such particles collide they either adhere or coalesce, the combination forming the nucleus for a larger clump. For the formation of a visible clump it is immaterial whether the particles actually coalesce or are held apart by a cushion of water. From the first collisions of discharged particles to form submicroscopic or microscopic nuclei, the general mechanism is the same: a larger clump enmeshes a smaller one and is in turn enmeshed by a clump larger than itself. The entire process resembles the accumulation of driftwood in a swollen stream. The growth of a clump, therefore, may be regarded as autocatalytic in nature. The shapes and sizes of the ultimate clumps depend upon the number and manner of chance collisions, except that the weakness of the binding forces in the gelatinous precipitates makes impossible the formation of very large clumps in the absence of packing. When the particles coalesce the size of the clumps is limited only by the quantity of material available. The fundamental nature of the clumps, that is, whether they are flexible, gelatinous, and readily repeptized or are hard or plastic and non-peptizable, depends on whether or not the conditions are favorable for the coalescence of the ultramicrons. This, in turn, depends on the nature and hydration of the adsorbed precipitating ion in the manner above described.

The action of 70 g of concentrated nitric acid on 150 g of finely powdered sodium thiosulfate gives sulfur in the form of a yellow gum.[105] It loses its elastic property by cooling to 0°, but the elasticity returns on placing in hot water; after 24 hours, crystallization sets in and the elasticity vanishes. A similar form of sulfur results on pouring a very fine stream of sulfur heated to 400° into liquid air.[106] After removal from the liquid air the fibers are very elastic, like rubber, and appear clear yellow in transmitted light without a trace of opalescence. After approximately one-half hour the fibers become cloudy and are plastic and viscous rather than elastic, and after 24 hours the plasticity disappears.

[105] Iredale: Kolloid-Z., **28**, 126 (1921).

[106] Von Weimarn: Kolloid-Z., **6**, 250 (1910).

CHAPTER XIII

COLLOIDAL SELENIUM AND TELLURIUM

COLLOIDAL SELENIUM

As would be expected, the colloid chemistry of selenium is similar to that of sulfur in many respects. In general, however, the hydrosols of selenium formed by chemical methods differ from the corresponding sols of sulfur in being less hydrophilic and consequently less stable. Accordingly, selenium sols are frequently prepared by methods involving the use of protecting colloids. When properly made, the varicolored unprotected sols are fairly stable, and in any given sol the particle size is quite uniform. For these reasons selenium sol has proved very satisfactory in the study of Brownian movement, the mechanism of the coagulation process, and the relationship between particle size and color in colloids.

FORMATION OF SELENIUM SOLS

Reduction Methods

Reduction with Sulfur Dioxide.—Schulze[1] first prepared a selenium hydrosol by treating a dilute solution of selenium dioxide with the calculated amount of sulfur dioxide, which reacts in accord with the following equation:

$$SeO_2 + 2SO_2 + 2H_2O \rightarrow Se + 2H_2SO_4$$

The resulting sol is red and opalescent by reflected light. If a concentrated solution of the dioxide is employed, a reversible precipitate is formed which is peptized on diluting with water. Doolan[2] recommends the following procedure: Into a solution of 0.5 g of pure selenium dioxide in a small amount of water, is conducted 0.58 g of sulfur dioxide at a temperature of 20°. The mixture is diluted to 1 liter, thereby peptizing the precipitate first formed to a ruby red sol.

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[1] J. prakt. Chem., (2) **32**, 390 (1885).

[2] J. Phys. Chem., **29**, 178 (1925).

The negatively charged sol is said to be coagulated by a parchment membrane, but dialysis may be carried out in collodion bags. At first some of the sol coagulates on the collodion, but thereafter the dialysis proceeds without difficulty. Cellophane should be a satisfactory dialysis membrane. If the dialysis is carried too far, the sol coagulates completely. Sols having a specific conductivity of 2.4×10^{-5} mho were quite stable for a month to 6 weeks. It is necessary to carry out the dialysis and to store the sols in the dark since they are quite sensitive to the action of light.

Sulfur dioxide is used as a reducing agent for sodium selenate in preparing sols in the presence of such protecting colloids as albumin, peptone, and sodium lysalbinate.[3]

If hydrogen sulfide is substituted for sulfur dioxide as a reducing agent, a mixed sol of selenium and sulfur is formed in accord with the equation:

$$SeO_2 + 2H_2S \rightarrow 2H_2O + Se + 2S$$

The sulfur may be extracted from the mixture with carbon bisulfide.[4]

Reduction with Hydrazine Hydrate. Unprotected Sols.—Probably the most satisfactory method for preparing stable unprotected selenium sols consists in the reduction of a solution of selenium dioxide with hydrazine hydrate. Gutbier,[5] who was the first to employ this method, dissolves 1 g of purified oxide in 500 cc of lukewarm water and adds a 1 : 2000 solution of hydrazine hydrate drop by drop with constant stirring. At the right temperature, a yellow coloration appears at once and becomes dark red, rapidly at the temperature of the water bath but slowly at room temperature. If concentrated solutions are employed, a gel is precipitated which is largely repeptized by dilution. The velocity of the reaction is directly proportional to the concentration of selenium dioxide and hydrazine and hence takes place in accord with the simple equation:

$$SeO_2 + N_2H_4 \cdot H_2O \rightarrow Se + N_2 + 3H_2O$$

The rate is approximately doubled for each rise of 10° in temperature.[6]

The sols purified by dialysis are red by transmitted light and an opalescent blue by reflected light. They may be filtered or boiled without coagulation, but the residue obtained by evaporation to

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[3] Heyden: German Pat., 164,664 (1904).

[4] Gutbier: Kolloid-Z., **5**, 46, 105 (1910).

[5] Z. anorg. Chem., **32**, 106, 349 (1902); Kolloid-Z., **4**, 260 (1909).

[6] Jablczynski and Kobryner: Roczynski Chem., **9**, 704 (1929); Bull. soc. chim., (4) **47**, 53 (1930).

dryness over sulfuric acid is only partly reversible. The use of hydroxylamine hydrochloride as a reducing agent gives a much less stable sol than hydrazine because of the presence of electrolytes in the reduction mixture. Sols formed with hydrosulfites as reducing agents are likewise instable.[7]

To obtain sols of quite uniform particle size, Kruyt and van Arkel[8] have modified Gutbier's method in the following way: 90 cc of water and 5 cc of 1.5 M hydrazine hydrate are heated to 100°, and 4 cc of 0.1 M selenium dioxide is added. After the mixture has become dark yellow, 1 cc more of the selenium solution is added. The heat is then removed, and after the mixture has stood for 10 minutes it is diluted to 400 cc with pure water. In this procedure the particles formed by the original reduction serve as nuclei and grow on the addition of a second portion of selenium dioxide without the formation of new particles. Sols containing $25\text{–}40 \times 10^9$ particles per cubic centimeter are entirely clear by transmitted light and are stable for a few months if kept in the dark.

Reduction with Hydrazine Hydrate. Protected Sols.—Highly stable sols are formed by reduction with hydrazine hydrate or hydroxylamine hydrochloride in the presence of Paal's lysalbinic and protalbinic acids or their sodium salts.[9] For example, to 3 g of protecting agent in 45 cc of water is added 1 to 3 g of selenium dioxide. The resulting precipitate is peptized with a little alkali, 2 g of concentrated hydrazine hydrate is added, and the solution is acidified with dilute hydrochloric acid. The mixture turns blood red, and, on warming, red flocks of a mixture of selenium and the protecting colloid separate. This precipitate is peptized by dilute alkali, giving a sol which when dialyzed and evaporated to dryness over sulfuric acid, leaves a residue completely repeptizable by water.

Gutbier and coworkers[10] obtained stable hydrosols by reduction of selenium dioxide with hydrazine hydrate in the presence of gum arabic, gelatin, saponin, etc. In every case, the reduction is accomplished by the dropwise addition of an amount of hydrazine hydrate insufficient for complete reduction. If the reduction is carried too far or not far enough, the clear red sols change to a cloudy blue from which irreversible flocks settle out in a short time. If the sols are evaporated to dryness, the residue is only partly reversible and the

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[7] Meyer: Z. anorg. Chem., **34**, 51 (1903).

[8] Kolloid-Z., **32**, 29 (1923); Rec. trav. chim., (4) **39**, 656 (1920); **40**, 169 (1921).

[9] Paal and Koch: Ber., **38**, 526 (1905).

[10] Kolloid-Z., **31**, 33 (1922); **32**, 255; **33**, 35 (1923).

resulting sols are relatively instable. Obviously the protecting colloids used by Gutbier are less effective than Paal's protalbinates and lysalbinates.

Reduction with Titanium Trichloride.—A very stable sol is formed by reduction of selenium dioxide with titanium trichloride.[11] The process takes place in accord with the equation,

$$SeO_2 + 4TiCl_3 + 6H_2O \rightarrow Se + 4TiO_2 + 12HCl,$$

the titania in the hydrous condition acting as a protecting agent. The resulting sol is in reality a selenium-titania "purple."

Reduction with Dextrose.—Gutbier[12] obtained selenium in the sol state by evaporating on the water bath, to a syrupy consistency, a solution containing 1 g each of selenium dioxide and dextrose, adding a drop of strong ammonia from time to time during the process. By this procedure a portion of the oxide is reduced, giving colloidal selenium and an oxidation product of dextrose which acts as a protecting agent. On dialyzing in a rotating rapid dialyzer,[13] the unreduced oxide passes through the membrane followed by a portion of the brown oxidation product, the sol at the same time changing from brown to a cinnabar red. The undialyzed sol is more stable than the dialyzed one, but the latter can be boiled for some time, using a reflux condenser, without depositing appreciable amounts of selenium. The residue formed by evaporation to dryness over sulfuric acid is almost completely reversible when first formed but loses this property gradually on standing.

Oxidation

The oxidation of hydrogen selenide by selenium dioxide gives a sol, the process being similar to Selmi's method of preparing sulfur sol.[14] The method is seldom used in preparing selenium sol probably because of the odor of hydrogen selenide and because simpler procedures are available. Sarason[15] obtained a coarsely dispersed sol by treating a saturated solution of hydrogen selenide in glycerin, with selenium dioxide.

Decomposition of Sodium Selenosulfate.—The decomposition of

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[11] Gutbier, Ottenstein, and Lossen: Z. anorg. Chem., **162**, 101 (1927).

[12] Gutbier and Fiechtl: Kolloid-Z., **33**, 334 (1923).

[13] Gutbier, Huber, and Schieber: Ber., **55**, 1518 (1923).

[14] Svedberg: "Formation of Colloids," 84 (1921).

[15] German Pat., 216,825 (1907).

sodium selenosulfate by hydrochloric or sulfuric acid takes place in accord with the following equations:

$$Na_2SeSO_3 + 2HCl \rightarrow 2NaCl + H_2SeSO_3$$

$$H_2SeSO_3 \rightarrow Se + H_2O + SO_2$$

If the reactions are carried out under suitable conditions, Meyer[16] showed that they lead to the formation of a stable sol. He dissolves in 5 cc of water an amount of sodium thiosulfate that will lie on the point of a knife, adds a like amount of selenium powder, boils for 30 seconds, and filters. One or more cubic centimeters of the solution is added to 1 liter of water together with 4 or 5 drops of dilute hydrochloric acid. The solution becomes orange-yellow to red, depending on the selenium concentration. The orange-yellow sols have the same color as a chromate solution and are quite clear; the red sols possess a slight opalescence in reflected light.

Sols formed in slightly acid solution as above described are in general more stable toward electrolytes than those formed by reduction with hydrazine or by diluting a solution of selenium in hydrazine hydrate with water (see page 348). Moreover, the acid sols are positively charged, whereas the alkaline sols are negatively charged. The former are coagulated at once by boiling; the latter are much less sensitive to heat.

Hydrolysis

Quite stable selenium hydrosols were obtained by Pochettino[17] by hydrolysis of 0.2% solutions of potassium selenide; with more concentrated solutions, red selenium deposited after a few hours. Gutbier and Engeroff[18] likewise prepared sols by a hydrolysis method starting with H_2SeBr_6 formed by the action of strong hydrobromic acid on selenium. The reaction takes place in accord with the following equation:

$$2H_2SeBr_6 + 5H_2O \rightarrow Se + H_2SeO_3 + 10HBr + 2HOBr$$

Because of the strong electrolytes in the reduction mixture, unprotected sols formed by this method are instable. Stable sols result by dropping the H_2SeBr_6 solution into a 1% solution of gum arabic. The yellow sol first formed changes gradually to a beautiful red which may be dialyzed to remove excess electrolytes.

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[16] Z. Elektrochem., **25**, 80 (1919).

[17] Atti accad. Lincei, **20** I, 428 (1911).

[18] Kolloid-Z., **15**, 198, 210 (1914).

Dilution of Solvent

Selenium in Hydrazine Hydrate by Water.—A saturated solution of selenium in hydrazine hydrate is prepared by shaking with the powdered element. On the addition of a few drops of the resulting viscous dark liquid to a quantity of distilled water, a stable, negatively charged, red selenium sol is formed which can be boiled without coagulating.[19] Similar results are obtained by starting with selenium dioxide in preparing the solution which gives a sol on dilution.[20] As would be expected, the sols are more highly dispersed and consequently more stable the higher the dilution. They cannot be freed completely from hydrazine hydrate by dialysis.

There is a difference of opinion as to the nature of the solution of selenium in hydrazine hydrate. Ephraim and Piotrowski[21] found no indication of chemical compound formation in the solution of sulfur in hydrazine, and Gutbier believes that selenium forms a molecular solution in the solvent. Meyer, on the other hand, suggests that the solvent action of hydrazine on sulfur and selenium is similar to that of alkalies on halogens. Thus, in the case of selenium, a hydrazine selenide and selenate may form in accord with the equation:

$$6NH_2NH_3OH + 3Se = 2(NH_2NH_3)_2Se + (NH_2NH_3)_2SeO_3 + 3H_2O$$

and polyselinides may also result. From this point of view, sol formation on diluting with water results both from a reaction between hydrazine selenide and selenate and by decomposition of polyselenides. Although these suggestions are interesting and may be in accord with the facts, there is no independent evidence to show that such is the case. According to Juna[22] no sol is obtained by this method in a nitrogen atmosphere free from both oxygen and carbon dioxide.

Organosols.—The method of dilution of solvent has been used successfully in preparing a number of organosols. Thus von Weimarn and Malyschew[23] saturated hot carbon bisulfide with selenium and poured 5 to 25 cc into cold ether while stirring vigorously. The resulting dilute sols had a beautiful rose color and under suitable conditions were stable for a few weeks. Similarly, sols were formed by pouring an aniline solution of selenium into water at various temperatures. The particle size in the several sols was found to

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[19] Meyer: Ber., **46**, 3089 (1913).

[20] Gutbier and Emslander: Kolloid-Z., **30**, 97 (1922); Ber., **54**, 1974 (1921).

[21] Ber., **44**, 386 (1911).

[22] Bull. Chem. Soc. Japan, **6**, 23 (1931).

[23] Kolloid-Z., **8**, 216 (1910).

decrease in every case with increasing percentage supersaturation, $(Q - L)/L$, irrespective of whether this increase is due to a decrease of the L value or to a rise in the Q value[24] (*cf.* page 27).

Sols in alcohol and glycerin are obtained by pouring the solution in hydrazine hydrate into the respective solvents.

Pochettino[25] melted selenium in a variety of solid solvents such as retene, fluorine, phenanthrene, anthracene, naphthalene, α-naphthol, α-naphthylamine, diphenylmethane, diphenylamine, triphenylamine, phenol, thymol, paraffin, etc., and allowed them to cool. The resulting solids were blue by transmitted light and red by reflected light, owing to the presence of dispersed selenium. When the solids were dissolved in organic solvents such as ether, benzol, chloroform, and alcohol, organosols were obtained of varying particle size and stability, depending on the nature of the two solvents. The alcohol and ether sols were most stable and the carbon bisulfide sols least stable. On standing, all deposited selenium, usually in the red form but in some cases in the black form.

In this connection it may be mentioned that boiling aniline and glycerin peptize selenium directly, but the resulting sols are instable, settling out in the black form within 24 hours.

Electrical Methods

Cathodic Pulverization.—Müller and Nowakowski[26] passed an electric current through water, using a platinum wire anode and a platinum sheet cathode coated with selenium by dipping into the molten element. Even at a low voltage a brownish red to light red coloration results at the point of contact of the selenium and platinum. At a voltage of 220, a sol forms rapidly, particularly if the hydrogen selenide which results simultaneously is washed away with a stream of hydrogen and if the anode is surrounded by a membrane to prevent the sol particles from coming in contact with the anode and coagulating. The resulting sol is very stable, only a little of the dispersed element settling out on standing several days.

Pochettino[27] showed that no sol is formed with a voltage lower than 1.8. At 48 volts and 0.007 ampere, the cathode loses 0.24 g in 5 hours. A part of the selenium is converted into H_2Se and H_2SeO_3; hence it is concluded that a part at least of the selenium in the sol

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[24] Von Weimarn: Alexander's "Colloid Chemistry," **1**, 84 (1926).

[25] Atti accad. Lincei, **20** I, 428 (1911).

[26] Ber., **38**, 3779 (1905); Z. Elektrochem., **11**, 931 (1905).

[27] Atti accad. Lincei, **18** II, 544 (1909).

state results from interaction between these compounds. Müller, on the other hand, attributes the formation of sol by this method to the intermediate formation either of Se^- ions which give Se and Se^{--} ions or of polyselenium ions such as Se_2^{--} which subsequently decompose into Se and Se^{--} ions, analogously to the behavior of tellurium under similar conditions (see page 359).

Electrochemical Reduction.—Colloidal selenium results from the electrolysis of a dilute aqueous solution of selenium dioxide.[28] Gutbier carried out the electrolysis at 220 volts without a diaphragm. At first there is a marked evolution of hydrogen without sol formation; but as the solution heats to boiling, it becomes yellow, yellow-red, red, blood red, and finally blue with the formation of more and more selenium. The element is not the primary product at the cathode but is formed as a result of the reducing action of the nascent hydrogen which increases greatly with rising temperature. The stability of the sol falls off with increasing selenium content and particle size. Thus the yellow sols containing some unchanged selenic acid are so stable that they can be filtered and dialyzed without coagulation; the yellow-red sols must be purified promptly by dialysis, otherwise they change in color to blue-red and finally coagulate; the red sols are still less stable and after dialysis must be diluted to avoid coagulation; and the blue-red and blue sols coagulate during dialysis.

Electrical Dispersion.—By passing a small, oscillating, high-tension arc between the best-conducting modification of selenium under isobutyl alcohol, Svedberg obtained a sol which was cinnabar red in transmitted light and bright red in reflected light. It was relatively instable, giving a red-brown coagulum within a day or two.

Miscellaneous Methods

Condensation of Vapors.—Selenium like sulfur gives a sol on conducting the vapors of the element into air-free water.[29] The rate of distillation must be such that the selenium condenses in the form of a red cloud. The rose-colored, cloudy sol formed under these conditions contains relatively coarse particles of widely varying size and is stable only a few days. If the condensation is carried out in the entire absence of air, yellow-red, highly dispersed sols are obtained which are more stable and can be dialyzed, although the dialysis decreases their stability.

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[28] Pochettino: Atti accad. Lincei, **18** II, 544 (1909); Gutbier and Weise: Ber., **52**, 1374 (1919).

[29] Gutbier: Z. anorg. Chem., **155**, 199 (1926).

Grinding.—Prolonged grinding of selenium with water does not give a sol,[30] but repeated grinding of the element with glucose[31] or lactose,[32] followed by adding the mixture to water, gives a stable sol. Thus, 0.1 g of selenium crystals is ground in an agate mortar for 1 hour with 0.9 g of anhydrous glucose, after which 0.1 g of the above mixture is ground with 0.9 g of glucose for 1 hour; and so on, the process being repeated four times. When the final mixture is poured into pure water an orange-yellow stable sol is obtained containing particles 28.8 mμ in diameter.

SOLID SOLS—SELENIUM GLASS

Attention has been called to selenium sols formed in solid organic media by melting the element and solid together and cooling. A much more interesting and important example of this type of sol is the case of selenium dispersed in glass.

Selenium in Borax Glass.—Hoffmann[33] added small amounts of selenium to molten borax and obtained melts that were rose colored to brown; on cooling, the solid was red-brown. Fenaroli[34] confirmed and extended these observations by adding selenium to a strongly heated borax-boric acid melt. On rapid cooling of such melts the selenium separates in the colloidal state and imparts a yellow color to the glass. On the other hand, if the glass is held in the molten state at as low a temperature as possible, the glass becomes redder and finally cloudy as the size of the particles increases. This color change is in accord with Ostwald's rule that the absorption maximum in the spectrum shifts toward shorter wave lengths with increase in the degree of dispersion (see page 331).

Selenium in Silicate Glass.—Fenaroli studied the coloration by selenium of a colorless glass formed by fusion of quartz, calcium carbonate, and sodium carbonate at 1400°. On adding 0.05 to 0.2 part of selenium per 100 parts of selenium dioxide, and cooling the melt slowly, a colorless, optically empty glass results. With increasing selenium content, the glass takes on an opalescent bluish appearance. Hydrofluoric acid liberates hydrogen selenide from the glass, but there is apparently no elementary selenium in the slowly cooled mixture. If 0.5 part of sugar charcoal per 100 parts selenium dioxide

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[30] Wegelin: Kolloid-Z., **14**, 65 (1914).

[31] Von Weimarn and Utzino: Alexander's "Colloid Chemistry," **1**, 659 (1926).

[32] Neugebauer: Kolloid-Z., **43**, 65 (1927).

[33] Z. angew. Chem., **19**, 1089 (1906).

[34] Kolloid-Z., **16**, 53 (1915).

is added along with the selenium, the slowly cooled melt assumes a red-brown color. The color is not caused by the charcoal and apparently is not due to colloidal selenium since the glass is optically empty except in the presence of a relatively large amount of the element when it assumes the bluish opalescence above mentioned. Unfortunately, the absorption spectra of selenium and polyselenides are so nearly the same that it cannot be determined definitely which of these substances is responsible for the red-brown color of the optically empty glass. The situation is more definite when the melt containing selenium and charcoal is cooled rapidly. Under these conditions the glass assumes a rose to wine red, or sometimes a purple to violet color, and exhibits a pale rose Tyndall cone. This is especially true if a part of the sodium of the glass is replaced by potassium.

To account for the above results, Fenaroli assumes the equilibrium represented by the following equation:

$$3Na_2O + (2n + 1)Se \rightleftarrows 2Na_2Se_n + Na_2SeO_3$$

In the hot, the equilibrium is shifted largely to the right and elementary selenium separates on rapid cooling; but on slow cooling, it shifts to the left, giving polyselenide. From this point of view, the optically empty, brown-red glass is colored by polyselenide, and the blue opalescence is due to some colloidal polyselenide which separates. The red opalescent color in the rapidly cooled melts is due to colloidal selenium, the particles of which are of the order of 40 $m\mu$ on the side, assuming them to be cubic.

Selenium is frequently added to glass, glazes, and enamels, imparting to them colors which vary from rose to ruby red, depending on the amount of the element used and the nature and composition of the vitreous substance.

PROPERTIES OF SELENIUM SOLS

Stability

Brownian Movement.—Selenium sols have been found quite satisfactory in the study of the Brownian movement and related phenomena. Westgren[35] used a sol prepared by adding 1 cc of 50% hydrazine hydrate to 100 cc of 0.001 *M* selenium dioxide, warming for 30 minutes on the water bath, and diluting tenfold. This was placed in a closed, flat microscope chamber and centrifuged until the particles were clumped together on one side of the chamber. Microscopic

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[35] Z. physik. Chem., 89, 63 (1914).

observations were then made of (1) the diffusion velocity, (2) the sedimentation equilibrium, and (3) the precipitation velocity after turning the chamber upside down. Calculations were made from these data as previously described (see page 67). The diameter of the particles was found to be 115 mμ, in good agreement with the value obtained by the counting procedure of Zsigmondy. The average value of the Avogadro number from sedimentation equilibrium and diffusion data was found to be 6.06×10^{23}, in agreement with Millikan's accepted value. These data furnish additional evidence of Einstein's view that, as with molecules, the average kinetic energy of the colloidal particles is independent of their mass. Since Stokes' law holds in this case within the limits of experimental error, it would appear that the particles are approximately spherical in shape. From 9000 determinations of the Avogadro number from sedimentation studies on selenium dispersed in gaseous media, a mean value of 5.94×10^{23} was obtained.[36] This likewise indicates that the particles are spherical.

Coagulation by Electrolytes.—A solution of selenium dioxide in water is usually the starting point in the preparation of selenium sols. This solution contains selenious acid which is dissociated to about the same extent as tartaric acid. The most stable unprotected sols are formed in the presence of a small excess of this acid or one of its salts. They are therefore negatively charged because of strong adsorption of the SeO_3^{--} ion which becomes the inner portion of the double layer surrounding the particles. The desensitizing action of light is probably due, at least in part, to reduction of the stabilizing selenious acid in contact with colloidal selenium. In dilute hydrochloric acid solution, hydrogen ion becomes the inner portion of the double layer and the particles possess a positive charge.

The precipitating action of electrolytes on negative selenium sol is similar to that on other typical hydrophobic sols. In Table LVII are given some observations of Doolan[37] on a sol formed by reduction of selenium dioxide by sulfur dioxide. For the purpose of comparison, the precipitating power of the electrolytes on hydrophobic tellurium sol and hydrophilic sulfur sol (Odén's data) is included. Although the data for selenium and tellurium sols are not strictly comparable with those for sulfur sol, it is apparent that the usual qualitative relationship between the valency of the cation and the precipitating power of the electrolytes holds for the hydrophobic selenium and

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[36] Schmid: Sitzber. Akad. Wiss. Wien, **129** IIa, 813 (1920).

[37] J. Phys. Chem., **29**, 178 (1925).

TABLE LVII

PRECIPITATING POWER OF ELECTROLYTES ON S, Se, AND Te

Electrolyte	Precipitating power (Reciprocal of precipitation value) for sols of		
	Selenium	Tellurium	Sulfur (Odén)
$NaCl$	2.5	2.5	6.1
NH_4Cl	2.5	1 25	2 3
KCl	10.0	3.8	47.5
KBr	4 0	3.8	.. ..
KF	1 66	2.0	.....
KI	1 25	1 66	.....
$ZnSO_4$	41.4	125.0	13.2
$MgSO_4$	33.3	32.0	107.5
$BaCl_2$	74 0	333.0	475.0
$Al_2(SO_4)_3$	1000.0	2500.0	227.0 ($AlCl_3$)

tellurium sols but does not hold for the hydrophilic sulfur sol. It is of interest to note that the precipitating power of potassium chloride is appreciably greater for selenium sol than for tellurium sol. In this respect only, selenium and hydrophilic sulfur sol are somewhat similar; but the reason for this is not obvious. The precipitating power of potassium is greater than that of zinc in the case of sulfur sol, but no such abnormality exists with selenium or tellurium sols.

Kinetics of the Coagulation by Electrolytes.—Observations of the change in cataphoretic velocity on the stepwise addition of electrolytes to selenium sol give results similar to those with colloidal gold.[38] A study of the kinetics of the coagulation process discloses that the Smoluchowski equation

$$\Sigma_v = \frac{v_0}{1 + t/T}$$

holds for the rapid coagulation at electrolyte concentrations appreciably above the precipitation value, but very definitely does not hold for the slow coagulation at or a little below the critical concentration. This is shown by data of Kruyt and van Arkel[39] reproduced in Table LVIII.

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[38] *Cf.* page 72; Briggs: J. Phys. Chem., **34**, 1326 (1930).

[39] Kolloid-Z., **32**, 29 (1923).

TABLE LVIII

VELOCITY OF COAGULATION OF SELENIUM SOL

"Rapid" coagulation with BaCl$_2$ (10 millimols/l)			"Slow" coagulation with KCl (59 millimols/l)		
t hours	Σ_v	*T* (calcd.) seconds	*t* hours	Σ_v	*T* (calcd.) hours
0.0	29.7 × 10^9	....	.....	29.7 × 10^9	....
32.4	10.5	17.7	0.66	20.9	1.5
64 4	5 5	14 7	4.25	19 1	7.6
140.0	3.2	16.9	19.0	14.4	18.0
217.0	1.8	14.0	43.0	10.7	24.0
302 0	1.45	15.7	73.0	7 7	25.0
600.0	0.6	13.0	167.0	6.45	46.0

In the rapid process, *T* is approximately constant; in the slow process *T* increases with time, showing that the coagulation gradually slows down. In other words, the probability of cohesion falls off as the size of the aggregates increases. To account for this, Kruyt[40] assumed that, with insufficient electrolyte for rapid coagulation, the surface of the particles is not uniformly discharged so that in some places the potential is above the critical value and at other places below it. Cohesion occurs at those points where the discharge has proceeded farthest, and as a result the parts with higher potential are on the outside; hence the larger the aggregates the smaller the probability of effective collisions among the particles.

Effect of Freezing.—A sol formed in the absence of protecting colloids, but in the presence of a small excess of selenious acid, can be frozen and thawed without coagulation, although the stability is reduced somewhat.[41] On continued dialysis which removes the stabilizing electrolyte, selenious acid, the sol becomes less stable and finally is completely coagulated by freezing. Sols formed by pouring a solution of selenium in hydrazine hydrate into water contain no excess selenious acid and so are coagulated at once by freezing. Sols formed by reduction with sulfur dioxide are more stable toward freezing than the hydrazine-reduced sols; but, as in the case of the latter, dialysis decreases the stability to the point where freezing causes

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[40] Proc. Acad. Sci. Amsterdam, **32**, 857 (1929).

[41] Gutbier and coworkers: Kolloid-Z., **29**, 161, 287 (1921); **30**, 97 (1922).

coagulation. The addition of a small amount of stabilizing electrolyte, such as 0.003 *N* hydrochloric acid or 0.013–0.052 *N* sodium carbonate, to the well-dialyzed sol renders it more stable toward freezing. Protecting agents such as dextrose and the sodium salts of protalbinic and lysalbinic acids prevent coagulation on freezing.

Color

If selenium is vaporized and the vapors condensed in an inert atmosphere such as nitrogen,[42] the particles appear first blue and green, then yellow and red, and finally as mixtures of orange and red. Determinations of the particle size by application of the Stokes-Cunningham law disclose that the smaller particles are blue and the larger ones red. The relationship between color and particle size, assuming the particles to be spheres, is given in Table LIX.

TABLE LIX

RELATIONSHIP BETWEEN COLOR AND SIZE OF Se PARTICLES DISPERSED IN N_2

Radius × 10^6	Color	Radius × 10^6	Color
Up to 8.2	Blue	9.7–11.5	Pure yellow
8.2–8.8	Blue-green	11.5–15.0	Gold-yellow to orange-red
8.8–9.0	Pure green	Above 15	Red
9.0–9.7	Green-yellow		

Suspended selenium particles like sulfur particles (*cf.* page 330) exhibit photophoresis in a strong beam of light. The phenomenon is more complex in the case of selenium since some of the particles are displaced toward the beam of light and some away from it.

Selenium sols exhibit colors varying from yellow to red, the red ones containing the larger particles. Auerbach[43] showed by freezing-point measurements that the green solution of selenium in pyrosulfuric acid contains the element molecularly dissolved as Se_2 molecules. On heating above 130°, the selenium is transformed into the metallic form and the yellow-red solution now contains monatomic selenium. By the gradual addition of water (in 1 : 1 sulfuric acid) to the green solution at room temperature, the selenium is reduced

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[42] Mattauch: Sitzber. Akad. Wiss. Wien, **129** IIa, 867 (1920); *cf.* Ehrenhaft: Ann. Physik, (4) **56**, 81 (1918); Parankiewicz: **57**, 504 (1918).

[43] Kolloid-Z., **38**, 343 (1926); Z. physik. Chem., **121**, 337 (1926).

in solubility and is precipitated in the colloidal state, the color changing to yellow, orange, red, violet, and blue with gradually increasing particle size. This behavior, which is similar to that observed with sulfur, lends further support to Ostwald's rule of the relationship between particle size and color. The color change of the yellow-red solution of the metallic form of the element on adding water above 130° is from red to violet to blue as the particle size increases. On the other hand, if water is added at room temperature to the yellow-red solution formed by heating above 130° and then cooling, the color changes to green, owing to the transformation from 2Se to Se_2. Thereafter, the color changes are the same as with the green solution. It should be pointed out that the second yellow-red color is different from the initial yellow-red in that the former is an opalescent sol whereas the latter is a clear molecular solution.

As in the case of colloidal sulfur, Pihlblad[44] observed only one maximum in the light-absorption curve for selenium sols, and this moved toward smaller wave lengths and increased in intensity with increasing degree of dispersion of the sol.

COLLODIAL TELLURIUM

The existence of tellurium in what is now known as the colloidal state has been recognized for a century. Thus in 1834 Berzelius[45] called attention to the blue liquid containing finely divided tellurium which results on exposing a very dilute solution of potassium telluride to the air. The colloid chemistry of tellurium parallels that of selenium in most respects except that stable tellurium sols are more difficult to prepare in the absence of protecting colloids.

FORMATION OF TELLURIUM SOLS

Reduction Methods

As in the case of selenium, a number of reducing agents have been employed in the preparation of tellurium sols, among them sulfur dioxide, sodium bisulfite, hypophosphorous acid, phenylhydrazine, and hydrazine hydrate. Of these, hydrazine hydrate is by far the most important in forming both unprotected and protected sols.

Reduction with Hydrazine Hydrate.—Gutbier[46] made unprotected

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[44] Svedberg and Pihlblad: Z. physik. Chem., **74**, 530 (1910).

[45] Pogg. Ann., **32**, 1 (1834).

[46] Z. anorg. Chem., **32**, 51, 349 (1902); Gutbier and Resencheck: **40**, 265; Gutbier: **42**, 177 (1904); Kolloid-Z., **4**, 184, 256 (1909).

tellurium sol by dissolving 2–3 g of telluric acid in 1 liter of distilled water, warming to 40–50°, and adding dropwise a solution of 1 part of 50% hydrazine hydrate in 2000 parts of water, short of the amount necessary for complete reduction. If the telluric acid is all reduced, the sol is so unstable that it coagulates on dialysis. Doolan[47] claims that the reduction does not start promptly as Gutbier says, but several cubic centimeters of reducing solution must be added before any color appears, and the resulting sol is unstable. Better results are obtained by dissolving 0.5 g of telluric acid in 50 cc of boiling water, adding the hydrazine hydrate drop by drop until turbidity almost occurs, and then adding cold water to a total volume of 250 cc. The bluish opalescent sol formed in the hot contains aggregates which are peptized by further addition of water, giving a quite stable, rich brown, negatively charged sol. Gutbier's procedure usually gives a more coarsely dispersed, gray-blue or steel blue sol.

Paal and Koch[48] prepared both brown and blue tellurium sols with a high degree of stability in the presence of sodium protalbinate and lysalbinate by procedures similar to those employed for selenium sols. Brown sols result by reduction at the temperature of the water bath with hydrazine hydrate; the coarser blue sols are obtained by long-continued boiling with hydroxylamine hydrochloride. Blue sols are likewise formed by reduction of a solution of tellurium dioxide in alkali in the presence of Paal's protective colloids. The reduction is accomplished at the boiling temperature by the gradual addition of hydrazine hydrate. The color changes from brown, through brown-violet and violet to blue, as the particle size increases.

Gutbier prepared a very satisfactory brown sol by the dropwise addition of dilute hydrazine hydrate to a mixture containing 2 g of telluric acid in 200 cc of water and 50 cc of 1% gum arabic solution previously heated for 3 hours at 95°. After dialysis, the resulting sol can be evaporated carefully to give a residue which is almost completely reversible. Other protecting colloids that have proved more or less satisfactory are gelatin[49] and the extracts from certain seeds.[50]

Reduction with Dextrose.—A solution of 1 g of telluric acid and 2.6 g of dextrose in 500 cc of water is evaporated to a syrupy consistency on the water bath, keeping the solution slightly alkaline

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[47] J. Phys. Chem., **29**, 178 (1925).

[48] Ber., **38**, 534 (1905).

[49] Lilienfeld: Brit. Pat., 173,507 (1921).

[50] Gutbier, Huber, and Eckert: Kolloid-Z., **32**, 255, 329 (1923).

by adding a drop of ammonia at intervals. On diluting the syrup to 100 cc and dialyzing, a very stable, negatively charged dark brown sol is obtained. The dextrose serves the simultaneous rôle of reducing and protecting agent.[51]

Electrical Methods

Cathodic Pulverization.—Müller and Lucas[52] passed a current through water or very dilute alkali, using a platinum wire anode and a piece of tellurium attached to a platinum wire as cathode. In analogy with the behavior with a selenium cathode (see page 350), a tellurium sol forms slowly even at 4 volts and quite rapidly at 220 volts. The dilute sols are reddish violet in color; the more concentrated ones, brown and opaque. The tellurium dissolves with an apparent valency of 1.2, which indicates that sol formation is not the result of purely mechanical pulverization. Moreover, the process is independent of the presence of oxygen in solution and so is not necessarily due to oxidation of hydrogen telluride. No hydrogen is evolved at the tellurium cathode. Müller suggests that the element goes into solution as Te^- ions which then pass into bivalent ions either by taking a second charge from the electrode or more likely by the reaction: $2Te^- \rightarrow Te + Te^{--}$. Polytelluride ions such as Te_2^{--} may also form, especially in dilute alkali solution, and these on breaking down will give colloidal tellurium and ordinary tellurium ions as follows: $Te_2^{--} \rightarrow Te + Te^{--}$.

Electrochemical Reduction.—Electrolysis of telluric acid solution with a current of 0.5 ampere in the presence of potassium cyanide gave a brown-violet tellurium sol, and in the presence of potassium oxalate, a steel blue sol. Continuing the electrolysis for too long a time caused flocculation. Dialysis of the incompletely reduced brown-violet solution gave a sol which was quite stable even after 6 months.[53]

Miscellaneous Methods

Dilution of Solvent.—Von Weimarn prepared a rather coarsely dispersed tellurium sol by dissolving 0.1 g of the element in 5 cc of boiling potassium hydroxide solution saturated at room temperature and pouring the solution into a liter of cold water, the mixture being stirred vigorously. The stability and degree of dispersion may be

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[51] Gutbier and Ottenstein: Z. anorg. Chem., **149**, 223 (1925); *cf.* Levaditi: French Pat., 626,506 (1927).

[52] Z. Elektrochem., **11**, 521; Müller and Nowakowski: 931 (1905).

[53] Gutbier and Resenscheck: Z. anorg. Chem., **40**, 264 (1904).

increased if protecting colloids such as gelatin are added to the water before the addition of the selenium solution.

Partial Solution.—The unique process of sol formation by exposing a dilute solution of potassium telluride to the air has been discussed in some detail in Chapter I (see page 16).

Grinding.—A red-brown, slightly opalescent, but very stable tellurium sol results by prolonged grinding of the element with dextrose in an agate mortar and adding the mixture to water. The procedure is similar in all essential respects to that described for preparing the corresponding selenium sol.

Tellurium in Glass

The presence of tellurium in a sodium-calcium glass, formed under reducing conditions, imparts to the mass a coral red or purple-red color. The colored glasses are not optically empty, but Fenaroli[54] believes that the red color is not due primarily to colloidal tellurium but to dissolved polytelluride, since the absorption spectrum of the glass is identical with that of potassium polytelluride solutions. With increasing concentrations of tellurium, the glass becomes brown to steel blue. These colors, which are similar to those of the hydrosol, are due to colloidal selenium in varying degrees of dispersion, the blue glass containing the larger particles.

PROPERTIES OF TELLURIUM SOLS

Tellurium sols are, in general, negatively charged, the unprotected sols owing their stability chiefly to strong adsorption of tellurate or tellurite ion. As already noted, the unprotected sols are less stable than the corresponding selenium sols, but unlike the latter they are not affected by light. Referring to Table LVII, it will be seen that the precipitating power of electrolytes on the unprotected sol is similar to that on typical hydrophobic sols. For some unknown reason the precipitating power of barium chloride is much higher for tellurium sol and hydrophilic sulfur sol than for selenium sol.

The color of the sols varies from brown through violet to blue with increasing particle size. Tellurium dissolves as monatomic molecules not only in pyrosulfuric acid, like selenium, but also in concentrated sulfuric acid, the solutions possessing a red color.[55] Diluting the sulfuric acid solution by the stepwise addition of water forms tellurium sols which change in color from brown through violet to blue as the particles increase in size.

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[54] Kolloid-Z., **16**, 53 (1915).

[55] Auerbach: Kolloid-Z., **38**, 343 (1926).

CHAPTER XIV

COLLOIDAL IODINE

Iodine is obtained in the colloidal state in the form of sol (1) as minute crystals dispersed in vapor or liquid and (2) as an emulsion consisting of fine droplets of liquid iodine dispersed in a saturated solution of the element. It is also obtained in a solid colloidal state that forms a hydrosol on shaking with water.

FORMATION AND PROPERTIES OF IODINE SOLS

Iodine in Air

If the vapors of iodine are allowed to condense, preferably on a smoke cloud in a glass bulb, an iodine fog results which persists for some time. Under the most favorable conditions, the fog has a distinct reddish color which is produced by selective scattering and not by absorption of iodine vapor.[1]

Organosols

As a result of the accidental observation that freshly prepared alcoholic solutions of iodine exhibit the Tyndall phenomenon, Amann[2] made ultramicroscopic observations of the formation of iodine solutions in a number of solvents such as carbon bisulfide, chloroform, carbon tetrachloride, benzol, toluol, xylol, and amyl alcohol. At the outset, the violet solutions were optically empty; but under the influence of light, particles appeared in lively Brownian movement in every case but especially in benzol, toluol, xylol, and alcohol solutions. The colloidal particles were quickly adsorbed by the surface of the vessel, forming brown drops which frequently had a minute crystal of iodine in the center. The phenomenon was accompanied by a change in color of the solution from violet to brown. On removal of the light the process was reversed, the particles dissolving and the original violet coloration returning. The mechanism of the precipitating action of light in these systems should be investigated.

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[1] Wood: "Physical Optics," 628 (1911).

[2] Kolloid-Z., 6, 235 (1910); Kolloid-Beihefte, 3, 337 (1912).

Holmes and Williams[3] showed that colloidal iodine in ether, amyl alcohol, and ethyl and amyl acetate acted as an emulsifying agent by concentrating at the interface of the organic liquid and water.

Hydrosols

Unprotected Sols.—Iodine can be thrown down in the sol state in a number of ways, for example by acidifying a dilute solution of a mixture of iodide and iodate or by adding rapidly a saturated solution of iodine in absolute alcohol or glacial acetic acid to cold water. As a rule the aqueous suspensions are brick red in color, but Harrison reports the formation of a transient blue sol by the interaction of iodic and hydriodic acids. The unprotected sols are extremely instable, changing almost instantly into a dark precipitate that settles out quickly. Bordier and Roy[4] obtained a fairly stable sol by adding a saturated alcoholic solution of iodine to a 0.4% solution of gelatin; and Chandler and Miller[5] prepared quite stable sols with gum arabic as protecting colloid. Because of the importance of the latter preparation for antiseptic purposes, its method of formation and properties will be discussed in some detail.

Chandler and Miller's Protected Sol.—The most satisfactory procedure for preparing a stable iodine sol consists in the rapid acidification with concentrated hydrochloric acid of a dilute solution of sodium iodohypoiodite in the presence of gum arabic at 0°. The iodohypoiodite for this purpose is obtained by treating a 2% solution of sodium hydroxide with iodine crystals until the straw-colored liquid, which forms immediately, just begins to turn red, and then pouring this solution from the remaining iodine crystals. On acidifying a solution of the iodohypoiodite, the iodine is precipitated in the colloidal state from a highly supersaturated solution in accord with the following equations:

$$Na_2I(OI) + 2HCl \rightarrow 2NaCl + HI + HOI$$

$$HI + HOI \rightarrow I_2 + H_2O$$

The amount of protecting colloid may be varied within rather wide limits. Four grams of gum arabic per 100 g of iodine gives a satisfactory product.[6] It is said that too much gum arabic in the final preparation

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[3] Colloid Symposium Monograph, **2**, 138 (1925).

[4] Compt. rend., **163**, 567 (1916).

[5] J. Phys. Chem., **31**, 1091 (1927); Chandler: Swiss Pat., 126,576 (1926).

[6] Private communication from E. J. Miller.

renders it undesirable for therapeutic use since it may hold the iodine in the tissue too long and cause some burning.

Sols formed in the presence of gum arabic may be brick red, light brown, or chocolate colored, depending on the conditions of precipitation and the concentration. When properly prepared, the sols show no appreciable settling in several weeks. After several months, the particles settle down somewhat, leaving a straw-colored supernatant liquid. During this slow settling, there is no apparent change in the degree of dispersion of the particles, and a uniform sol with the initial stability results on shaking.

A microscopic examination of the protected sol shows that the particles are, almost exclusively, minute globules in rapid Brownian movement. The largest particles possess a very uniform diameter of approximately 0.2 μ. Smaller particles, some probably of ultramicroscopic dimensions, are also present. The larger particles are unmistakably spherical in shape, and it is probable that the smaller ones are also spherical. This suggested that the sol is an emulsion of liquid iodine in a saturated aqueous solution of the element. Further indication that such is the case was furnished by microscopic observation of the sol formation process. Apparently the percentage supersaturation of the iodine is sufficiently high after acidifying the iodo-hypoiodite solution that the element is thrown out in the form of globules of liquid since there is not sufficient time for the molecular orientation necessary for crystal formation. In the absence of protecting colloid, crystals form promptly from the saturated solution in equilibrium with the droplets, which dissolve, the whole settling out in the crystalline state. On the other hand, in the presence of gum arabic, the globules are surrounded by a film of the protecting colloid and so are prevented from dissolving and reprecipitating as crystals. Further evidence in support of this view will be given in the next section.

SOLID COLLOIDAL IODINE

The Chandler and Miller hydrosol can be concentrated and even dried to a reversible solid by adding gum arabic, dextrose, sucrose, lactose, or dextrine to form a thick syrup, and evaporating.[7] The addition agents form a film or membrane on the surface of the liquid which prevents the escape of iodine molecules but not water molecules. Evaporating to a highly viscous liquid or a brittle solid causes no

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[7] Chandler: Brit. Pat., 267,558 (1926); Chandler and Miller: J. Phys. Chem., **31**, 1095 (1927).

coalescence of the iodine particles, which are readily redispersed when shaken with water. Powdering the brittle mass causes some iodine to be given off, probably because the protective coating of some of the particles is fractured, thus exposing the element. If the exposed iodine is driven off by gentle heat, the remainder is perfectly stable, as evidenced by the fact that the powder has little or no odor of iodine and can be kept in paper containers without staining the paper.

Further indication of the structure of the protected iodine system is obtained by observing the behavior on adding the concentrated syrup or powder to water or alcohol. When either one is put into water a saturated solution of iodine is formed almost at once, whereas days are required to saturate water with iodine crystals. The greater rate of solution of the colloidal particles is due to a higher solution pressure and lower surface tension than obtains for the same material in a coarser state. Since iodine is quite soluble in alcohol it might be expected that a strong alcoholic solution would result rapidly on shaking the colloid with the solvent. On the contrary, the rate of solution is much slower than in water, and the process is accompanied by flocculation and settling out of the gum arabic. The obvious reason for this behavior is that the protecting colloid, which is not peptized by alcohol, must be flocculated before the alcohol can come in contact with the iodine and dissolve it. In line with this, chloroform does not extract iodine from the powdered colloid. If, however, the powder is first wetted with water, the chloroform extracts the element from the aqueous solution, the process continuing until all the element has passed into the chloroform.

Cofman-Nicoresti[8] patented a process for obtaining a gel of colloidal iodine, which consists in converting the element into the colloidal state by dissolving it in oleic acid or a hydrocarbon oil and adding an alcohol, followed by the addition of a gelatinizing agent such as agar-agar, gelatin, pectins, gums, resins, tallow, etc.

USES OF COLLOIDAL IODINE

Colloidal iodine prepared by Chandler and Miller's method appears to have certain advantages over tincture of iodine as an antiseptic and disinfectant. For example, unlike alcoholic iodine solutions, the aqueous suspension of the element is practically non-irritating when applied to fresh wounds, and the injurious effect of alcohol on living tissue is avoided. The application of the colloid produces a stain

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[8] Brit. Pat., 320,719 (1928); French Pat., 686,154 (1929).

but does not blister unless the application is unnecessarily prolonged. Whatever the amount of colloid present, the solution in contact with the skin is only 0.034%, which is amply sufficient as a germicide but not enough to corrode the skin or tissues, as does tincture of iodine. Nyiri and Dubois[9] report that colloidal iodine is less than one-fourth as corrosive on mucous tissue as is the tincture. Furthermore, the iodine concentration is kept constant as long as any of the colloid is present. The stain from the colloid, unlike that produced by tincture of iodine, disappears completely within a few hours.

In view of the fact that water is the most convenient medium for bringing disinfectants in contact with microorganisms, the advantages of the colloidal solid are immediately apparent. It is only necessary to add the powder to water before application, or to dust it directly on the wound, since the water in the serum is sufficient to liberate the element from the powder. A very convenient method for using the colloidal iodine is in the form of applicators. These are made simply by dipping one end of a wooden stick or a glass or metal rod into the thick syrup above described, and drying.

Excellent results were reported by Chandler[10] in the treatment with colloidal iodine of certain types of dermatomycoses, such as ringworm and barber's itch. The penetrating power of the colloidal iodine appears to be much greater than that of the tincture. Thus Chandler[11] found that a colloid containing but 0.2% iodine penetrates coccidial oocysts and kills them within two minutes, whereas a tincture containing as much as 5% iodine does not penetrate them within a half-hour.

Intravenous injection of colloidal iodine has been recommended in the treatment of bubonic plague.[12]

[9] J. Am. Pharm. Assoc., **20**, 546 (1931).

[10] J. Mich. State Med. Soc., April (1927).

[11] Mich. Agr. Expt. Sta. Bull., 127 (1932).

[12] Grimes: Bull. soc. pathol. exot., **19**, 584 (1926).

INDEX OF AUTHORS

INDEX OF SUBJECTS