RELATIVE DIFFUSION RATES.

	H_2/Air.	H_2/CO_2.	Air/CO_2.
Bottle 1	3.40	4.77	1.40
Bottle 2	3.24	4.78	1.48
Bottle 3	3.54	4.93	1.39
Mean	3.39	4.83	1.42

Further experiments on evaporation are being conducted in this laboratory, and the results of an investigation with a somewhat modified apparatus will be published at an early date.

Applications.—(1) The difference in the rates of evaporation of water into different gases may be used as a method of comparison between the molecular weights of gases. (2) The dependence of rate of evaporation upon the nature of the gas suggests that the feeling of warmth caused by carbon dioxide upon the nerves of the hand[1] may be due to retardation of the normal rate of perspiration. (3) The explanation of higher and more constant terrestrial temperatures in previous geologic eras notably in the carboniferous, may be connected with the slower evaporation of water into an atmosphere rich in carbon dioxide.[2]

SEATTLE, WASHINGTON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY. No. 256.]

THE ELECTRICAL SYNTHESIS OF COLLOIDS.

BY H. T. BEANS AND HERBERT E. EASTLACK.

Received September 27, 1915.

I. Previous Work.

Since the discovery by Bredig[3] of the electrical dispersion method of preparing metallic hydrosols and its modification by Svedberg[4] for the preparation of metallic organosols, very little conclusive experimental work has been brought forward with the object of a satisfactory explanation of the phenomenon.

Kutscherow,[5] from a study of the dispersion of bi-metal alloys in alcohol by Svedberg's method, found the amounts of the two metals in the highly dispersed colloidal condition to be proportional to their equivalent weights, and he concluded that the process was of an electrochemical nature, leading to an atomically dispersed condition, which was followed by condensation to the colloidal condition. The thermo-mechanical process

---

[1] Goldscheider, *Gesammelte Abhandlungen*, 1, 305 (1898).

[2] See Arrhenius, "Worlds in the Making."

[3] *Z. angew. Chem.*, 11, 951 (1898); *Z. Elektrochem.*, 4, 514 (1898).

[4] *Ber.*, 38, 3616 (1905); 39, 1703 (1906); also "Herstellung Kolloider Lösung Anorganische Stoffe," 1909, p. 423ff.

[5] *Z. Chem. Ind. Kolloide*, 11, 165 (1912).

which he assumed to *accompany* electrical colloid synthesis resulted only in the formation of a coarse dispersion which settled out rapidly.

Benedicks[1] criticised Kutscherow's inexact method of distinguishing between, and separating, the highly and the coarsely dispersed portions of the metal and his arbitrary choice of equivalent weights for metals of variable valence. From his own experimental results,[2] consisting of a careful study of the action of the arc on the electrode surfaces in the formation of "*Schmelzkratern*" and "*Schmelzkugeln*," and a comparison with the effects produced on other surfaces (asphalt, paraffin, etc.) by purely thermo-mechanical means, and also from a consideration of the total heat of fusion, thermal conductivity, and other properties of the metals in relation to their ease of dispersion, he concluded that electrical colloid synthesis was a purely thermo-mechanical process.

Quite recently an article has appeared by Mukhopadhyaya[3] in which an attempt has been made to add experimental evidence on the nature of the electrical synthesis of colloids. Although his opinions are in accord with those of Benedicks, there is nothing conclusive in the work.

II. Purpose of the Investigation.

Up to the present time the hypothesis that electrical colloid synthesis consists of a thermo-mechanical dispersion, as pictured by Benedicks and others,[4] has been sufficient, but, in view of new experimental facts, the former theory now becomes inadequate. The object of the present paper is to show that, in addition to a primary pulverization, the actual synthesis of the colloid is much more dependent upon a secondary process, which is of the nature of a chemical reaction between the metal and certain substances present, or formed in the dispersion medium during the preparation of the colloid. As the authors are of the opinion that this secondary process is of a similar nature to that assumed to be operative in the so-called "complex" theory of colloid formation, it will be necessary to consider some of the work that has been done in connection with the development of that theory.[5]

III. The Complex Theory of Colloids.

The idea that there is an intimate association with hydrosols of certain small amounts of electrolytes, which cannot be removed without impairing the stability of the sol, goes back to the time of Graham. Indeed, it has long been known that, to convert certain hydrogels into hydrosols, peptization by means of electrolytes is necessary.

---

[1] *Z. Chem. Ind. Kolloide*, **11**, 263 (1912).

[2] *Kolloidchem. Beih.*, **4**, 229 (1912).

[3] This Journal, **37**, 292 (1915).

[4] Cf. Freundlich, "Kapillarchemie," **1909**, p. 311; Von Weimarn, "Grundzüge der Dispersoid Chemie," **1911**, p. 83.

[5] For a more complete discussion and references see Cassuto, "Der Kolloide Zustand der Materie," **1913**, pp. 190–214.

Picton and Linder[1] have long regarded the hydrogen sulfide which they always found associated with metallic sulfide sols, and which could not be removed by indifferent gases, as an essential constituent of the sol.

Jordis and Kanter[2] showed that a small amount of acid, or alkali, increased the stability of silicic acid sol and the former[3] was unable to prepare a stable hydrosol free from electrolyte.

Lottermoser,[4] in a series of researches on hydrosols of difficultly soluble silver salts, found that a negative silver iodide hydrosol was formed by the addition of a dilute solution of silver nitrate to one of potassium iodide. The sol was stable so long as the potassium iodide was in excess. A positive sol was formed by the addition of the potassium iodide solution to an excess of the silver nitrate. When the solutions were brought together in equivalent amounts, the sol was unstable and precipitation occurred. His theory to explain these facts was that the hydrosols owed their existence to the formation of a complex between the colloid and that ion of the colloid which was present in excess.

Svedberg[5] found that the critical temperature (the temperature at which coagulation takes place) for electrically prepared platinum sols in commercial ether was higher than in carefully purified material, and was led to investigate the effect of the addition of small amounts of foreign substances to the pure medium. The nature of the curves obtained by plotting the critical temperature against the amount of substance added indicated that a stable sol in an absolutely pure medium would be impossible.

These observations are in accord with those of Duclaux.[6] He showed, for example, that the precipitate formed by the interaction of potassium ferrocyanide and copper chloride always contained potassium, no matter what excess of copper chloride was used. He considered that chemical complexes were formed and disputed the contention that the presence of the third ion was due to mechanical adsorption or occlusion. He investigated these sols in various stages of dialysis and found that the stability of the sol decreased as the purification continued. He therefore concluded that the stability of the sols depended upon the presence of certain amounts of electrolyte which he designated as the "active part" of the colloid.

Von Weimarn[7] considers that peptization is an important factor in the stabilization of sols and that it consists in the conversion of a practi-

[1] *J. Chem. Soc.*, 61, 114 (1892); 87, 1906 (1905).

[2] *Z. anorg. Chem.*, 35, 16 (1903).

[3] *Ibid.*, 44, 200 (1905).

[4] For a summary and earlier references see *Z. phys. Chem.*, 70, 239 (1910).

[5] *Kolloid Z.*, 2, 142 (1907).

[6] *J. chim. phys.*, 5, 29 (1907); 7, 405 (1909).

[7] "Grundzüge der Dispersoid Chemie," 1911, pp. 75–79 and 90.

cally insoluble substance into a compound whose solubility meets the requirements necessary (according to his theory) for the formation of a stable sol. He holds, however, that it is incorrect to assume that a sol cannot be obtained in an absolutely indifferent medium in the absence of a peptizing agent.

In general, therefore, it seems certain that the stability of hydrosols is vitally connected with the presence of small amounts of foreign substances usually related to, or derived from, the colloid itself, and it is upon this basis that the chemical or complex theory of colloids has been developed. The hypothesis, briefly stated, is that the particles of a hydrosol consist essentially of a complex between a substance of very low solubility and an ion of an electrolyte, the presence of which is necessary to the stability of the sol. A sol is stabilized only by certain ions and when these are removed or replaced coagulation occurs. The colloid owes its charge to the ion which stabilizes it.

IV. Are Sols of the Noble Metals Exceptions to the Complex Theory?

The sols of the noble metals, especially when prepared by electrical dispersion in "pure" water, have been considered exceptions to the complex theory.[1]

Bredig,[2] however, has recommended the use of 0.001 *N* alkali (NaOH) instead of pure water in the preparation of gold sols by his method. In referring to this point Whitney and Blake[3] state that "a more concentrated and more stable gold solution may be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a conductivity of 200×10^{-6}."

These two isolated instances of the stabilization of electrically prepared hydrosols by the addition of foreign substances, suggested that perhaps other electrolytes would be found to have a similar effect, and even suggested the possibility that these hydrosols were *not* exceptions to the complex theory of colloids. The fact that stable hydrosols have been prepared by electrical dispersion methods, without the addition of electrolyte, might then be explained either by the assumption that sufficient electrolyte was formed during the process of dispersion, or that the water used already contained the electrolyte necessary for the stabilization of the colloid in accordance with this theory.

In regard to the first of these assumptions, it is well known that when

---

[1] Cf. Freundlich, *Loc. cit.*, pp. 323–4 and 360; Cassuto, *Loc. cit.*, p. 213; Taylor, "The Chemistry of Colloids," **1915**, p. 110.

[2] "Anorganische Fermente," Dissertation, Leipzig, **1901**, p. 26.

[3] THIS JOURNAL, **26**, 1376 (1904), footnote. This statement was not discovered until after the present work including the preparation of red gold sols in 0.00005 to 0.002 *N* HCl had been completed. The conductivity 200×10^{-6} for hydrochloric acid corresponds to a concentration of about 0.0005 *N*, lying well within this range of concentration.

the more electropositive metals, *e. g.*, copper,[1] cadmium,[2] iron,[3] and lead,[4] are electrically dispersed in water the sols consist partially or entirely of the metallic hydroxide. McIntosh[5] observed that the conductivity of electrically prepared silver sol was 40 to 60 times that of the water used (2.2×10^{-6}). Blake[6] found the freshly prepared silver sol to be alkaline to phenolphthalein, and more recently the work of Kohlschütter[7] and of Rebière[8] has shown that a considerable portion (15 to 45%) of the total silver may be present as oxide or hydroxide. Indeed, even in the case of platinum, the work of Graeser[9] indicates that a certain amount of oxidation takes place when this metal is dispersed in the presence of air.

There are clearly two points open to experimental work which may throw some light on the nature of electrical colloid synthesis and possibly on the theory of colloids in general: (1) the relative extent to which oxidation of the metal (formation of ion) takes place during the preparation of gold and platinum sols, and (2) the nature and generality of the stabilizing effect of certain electrolytes in the preparation of gold sols as observed in the two cases noted above.

V. Oxidation in the Dispersion of Gold and Platinum.

The method employed in studying this point was to measure the increase in conductivity when gold and platinum sols are prepared in very pure water. While it is perfectly certain from the work of Kohlschütter[10] and of Rebière[10] that all of the electrolyte present in the sol does not contribute equally to its conductivity (probably on account of adsorption by the colloid) and quantitative results cannot therefore be expected, a qualitative idea of the relative amounts of electrolyte formed may be obtained from such measurements.

The Conductivity of the Colloid.

That any increase in conductivity is not due to the colloid itself[11] may

---

[1] Paine, *Kolloidchem. Beih.*, 4, 24 (1912).

[2] Bredig, *Z. physik. Chem.*, 32, 127 (1900).

[3] Schmauss, *Physik Z.*, 6, 506 (1905).

[4] Burton, *Phil. Mag.*, [6] 11, 425 (1906).

[5] *J. Phys. Chem.*, 6, 15 (1902).

[6] *Am. J. Sci.*, [4] 16, 431 (1903).

[7] *Z. Elektrochem.*, 14, 49 (1908).

[8] *Compt. rend.*, 148, 354 (1909); 154, 1540 (1912).

[9] *Dissertation*, Leipzig, 1903; cf. Freundlich, *Loc. cit.*, p. 324.

[10] *Loc. cit.*

[11] The prevailing confusion in regard to the conductivity of colloids arises more from an indefinite conception as to the constitution of a colloid than from experimental differences. It is generally admitted that the conductivity of a colloid is small compared to that of ordinary electrolytes—yet to just what extent the conductivity of a sol is due to the colloid proper seems to be a matter of considerable doubt. Cf. Stewart, "Recent Advances in Physical and Inorganic Chemistry," 1912, p. 93; Freundlich, *Loc. cit.*, p. 337; Cassuto, *Loc. cit.*, p. 45; and Taylor, *Loc. cit.*, pp. 62–5.

be reasoned from two viewpoints. First, the charge on the colloid is in all probability due to ions associated with it and any effect of removing ions already present in the medium or of decreasing their mobility would be to decrease the conductivity—as would also the adsorption of the molecular portion of the electrolyte. Second, the conductivity due to the colloid proper may readily be calculated from the mobility of the particles in an electric field and their number in a given volume. The necessary data are readily obtained from the literature.

The results of previous measurements of the migration velocities of gold and platinum particles are summarized in Table I.

TABLE I.

Sol.		Mobility.	Method.	Author.
Au	W. & B.	43.0×10^{-5} cm./sec.	moving boundary in verticle tube	Whitney and Blake[1]
Pt	Bredig	34.0×10^{-5} cm./sec.		Whitney and Blake[2]
Au	Bredig	21.6×10^{-5} cm./sec.	moving boundary in U-tube	Burton[3]
Au	Bredig	33.0×10^{-5} cm./sec.		Burton[4]
Pt	Bredig	20.3×10^{-5} cm./sec.		Burton[3]
Au	Bredig	26.0×10^{-5} cm./sec.	microscopic	Rolla[5]
Au	Zsigmondy	26.0×10^{-5} cm./sec.		Rolla
Pt	Bredig	24.0×10^{-5} cm./sec.		Rolla
Au	not given	6.7×10^{-5} cm./sec.		Coward[6]

Whitney and Blake do not claim any greater accuracy than to say that the migration velocities are of the same order of magnitude as those of the ions of neutral inorganic salts of monovalent elements. No refinements or great accuracy were attempted in Coward's work. Rolla's and Burton's values agree fairly well, but those of the former are more consistent among themselves and will be used for the purposes of calculation. As a matter of fact, the order of the results would not be affected by the use of either of the extreme values given above.

Zsigmondy[7] gives the following linear dimensions for the particles of various colored gold sols:

Color of sol.	Average size in μμ.			
Rose	6			
Deep red	10	15	18	32
Violet-red	23	32	35	75
Violet	35	95		
Blue-violet	54			
Dirty blue	30			
Purple-red	38			
Blue	130			

[1] *Loc. cit.*, p. 1365.

[2] Calculated from data given.

[3] *Phil. Mag.*, [6] **11**, 425 (1906).

[4] *Ibid.*, [6] **12**, 472 (1906).

[5] *Atti accad. Lincei*, [17] **2**, 650 (1908).

[6] *Trans. Faraday Soc.*, **9**, 149 (1913).

[7] "Zur Erkenntnis der Kolloide," **1905**, p. 104.

The average radius of colloidal gold particles evidently lies between the limits $3\mu\mu$ and $65\mu\mu$.

From the migration velocities and the radii, the charge on gold particles of various sizes[1] may be calculated with the aid of Stokes' Law, $e = 6\pi\eta rv/X$, where e is the charge, η the viscosity of the medium, r the radius of the particle, and v its velocity under a potential gradient X. Putting η for water at 20° = 0.01, $v = 26 \times 10^{-5}$ cm./sec. when X = 1 volt/cm. the charge e for various values of r is obtained. From the weight of gold contained in a known volume of the sol and the radii of the particles the number per cc. (N) is obtained. From the number of particles per cc., their charge, and mobility, the specific conductivity (k) due to the particles is readily calculated. Table II gives the values of e, N and k calculated for various values of r for a sol containing 100 mg. of gold per liter.

TABLE II.

r (cm.).	e (E. S. U.).	N (per cc.).	k (mhos).
10×10^{-7}	16×10^{-10}	124×10^{10}	1.7×10^{-10}
20×10^{-7}	32×10^{-10}	15×10^{10}	0.4×10^{-10}
30×10^{-7}	48×10^{-10}	5×10^{10}	0.2×10^{-10}
40×10^{-7}	64×10^{-10}	2×10^{10}	0.1×10^{-10}
50×10^{-7}	80×10^{-10}	1×10^{10}	0.07×10^{-10}

The conductivity of platinum sols would be of the same order of magnitude.

It is clear that the conductivity due to the colloid itself is negligible compared to those measured. Any increase in the conductivity must therefore be due to the introduction of electrolyte into the sol from one or more of several sources: (1) oxidation of the electrode, (2) impurities present in the electrode materials, (3) combination of foreign substances dissolved in the water, *e. g.*, nitrogen and oxygen, and (4) accidental introduction from outside sources during the preparation. Since the first of these is of primary importance in the present investigation, the others were eliminated, as far as possible, by the use of very pure materials, and the exercise of extreme care in the preparation of the colloid to avoid the accidental introduction of foreign substances.

Materials and Apparatus.

The water used in all the work presented in this paper was freshly distilled from alkaline permanganate, using a block tin condenser, and was collected hot in thoroughly steamed "non-sol" bottles. Its specific conductivity at 25° varied from 0.6 to 1.2×10^{-6} mhos.

The gold and platinum wire used was the purest obtainable from a

---

[1] According to the theories of Lamb (*Brit. Assn. Report*, 1887, 502) and Smoluchowski (*Bull. Acad. Sci. de Cracovie*, 1903, 182) the rate of migration should be independent of the size and shape of the particles. The experiments of Whitney and Blake, as well as those of Burton, support this view.

reliable firm. The electrodes were made by soldering about 5 cm. of the gold or platinum wire (No. 14, B. & S.) onto copper wires of the same diameter, using silver solder. The electrodes were carefully cleaned, polished with filter paper, and finally rinsed with conductivity water before each experiment. Only the gold or platinum portions of the electrodes came in contact with the water during the preparation of the colloid.

A conductivity cell and electrode adjustment were so designed (Fig. 1) that the colloid could be prepared in the cell itself and thus avoid the necessity of pouring the sol from one vessel to another. The cell was patterned after the Freas type and had a capacity of about 60 cc. The electrodes were concentric platinum cylinders 13 and 15 mm. in diameter and 25 mm. in height. They were fixed at a distance of about 1 mm. apart by three glass pinions near the top and three near the bottom. The surfaces were sandblasted, but not platinized. The constant of the cell (0.0092) was determined by comparison with a cell whose constant (0.3002) had been accurately determined against known solutions of both sodium and potassium chlorides. No great accuracy was attempted in the determination of the former constant, as all measurements were to be relative. In spite of the extremely low value of this constant, heating effects with solutions of conductivity approaching that of water were negligible. A Leeds and Northrup bridge with a wire about 7 meters in length and connections for reversing the ends was used. The resistances were checked among themselves, but an absolute standardization was unnecessary. All conductivity measurements were made in a thermostat at a temperature of 25° ± 0.01°.

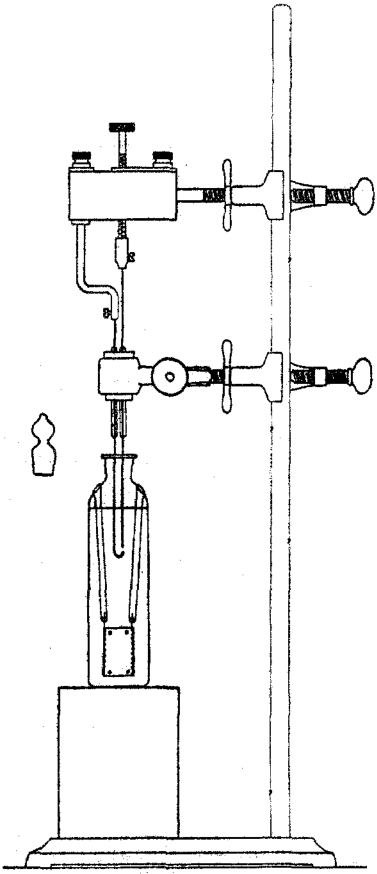

Fig. 1.—$^1/_4$ actual size.

The current for the preparation of the colloid was obtained from the 120 volt, D. C., lighting circuit. In addition to a variable resistance, an inductance coil was made by winding several layers of No. 22 (B. & S.) asbestos-covered wire around an iron pipe 2 cm. in diameter and 75 cm. in length. The coil was surrounded by an iron jacket and was employed as a principal resistance.[1] It allowed a current of about 5 amperes to pass from the 120 volt circuit and because of its large self induction a good arc could be obtained with a current of 3 to 4 amperes—the strength used throughout this work.

Results of Conductivity Measurements.

A number of experiments were carried out to determine the relative increase in conductivity in the preparation of gold and platinum sols. The arcing was continued for about one minute in each case, or until sols of approximately the same depth of color were obtained. Of a number of results those given in Table III are typical.

TABLE III.

Gold.			Platinum.		
$k_{H_2O} \times 10^6$.	$k_{sol} \times 10^6$.	$\Delta k \times 10^6$.	$k_{H_2O} \times 10^6$.	$k_{sol} \times 10^6$.	$\Delta k \times 10^6$.
1.03	1.62	0.59	0.89	4.28	3.39
1.10	1.14	0.04	0.73	3.49	2.76
0.99	1.14	0.15	0.78	3.81	3.03
0.96	1.24	0.28	0.88	4.11	3.23
1.12	1.62	0.50			
0.94	1.55	0.59			
0.58	0.75	0.17			
0.90	1.67	0.77			
0.83	1.18	0.35			

Average $\Delta k = 0.4 \times 10^{-6}$ mhos.

Average $\Delta k = 3.1 \times 10^{-6}$ mhos.

The average increase in conductivity is seen to be nearly 8 times greater for platinum than for gold. Since equal precautions were taken in the preparation of the two sols, the difference must for the most part be due to a greater oxidation in the case of the platinum. The important observation was made that *the platinum sols were invariably more stable than the gold.* All the gold sols were blue or bluish purple and usually precipitated in from 2 to 24 hours. The platinum sols on the other hand remained apparently unchanged on standing several weeks.

Thus, earlier evidence in regard to the relationship between the stability of these sols and the presence of small amounts of certain electrolytes is confirmed. The question as to the amount and nature of the electrolyte necessary for this stabilization still remains.

VI. The Stabilization of Gold Sols by the Addition of Electrolytes.

The average increase in conductivity in the preparation of the platinum sols was found to be 3.1×10^{-6} mhos, which would correspond to the presence of 0.0001 to 0.0003 *N* concentration of free electrolyte, depending upon the mobilities of the ions. The concentrations of alkali and hydrochloric acid, mentioned above in connection with the stabilization

---

[1] We are indebted to Professor Thos. B. Freas for assistance in the designing and construction of this coil.

of gold sols, are much greater than this, but, as will be seen from the following experiments, the addition of these, as well as of certain other electrolytes in concentrations of this order, to the water in which gold is dispersed effects a very marked stabilization of the sol.

In order to study the effect of electrolytes in the preparation of gold hydrosols, these sols were formed by striking an arc between pure gold electrodes immersed in solutions of the substances under investigation. The apparatus for this procedure was the same as that previously described, except that the conductivity cell was replaced by a thoroughly steamed flask of about 40 cc. capacity. The salts used were recrystallized from conductivity water and then either dried at 115° or fused in a platinum dish. From the salts, thus purified, stock solutions of 0.01 *N* concentration were made by weighing out the salt and making up to definite volume at 25°, using conductivity water. The solutions of lower concentration were made by diluting the stock solutions with conductivity water.

The results of these experiments are given in Tables IV–XII. The uniform manner in which the color of the sol varied from one concentration of electrolyte to another, made confirmation of the results by duplication of the experiments unnecessary. In some cases this confirmation was made, but the results are not given. The variation in color was so gradual that no sharp definition of the limiting values of the concentrations of electrolyte in which red, stable sols were obtained, could be made. The ease and certainty with which the results could be duplicated, however, is illustrated by the data given in Table XIII.

TABLE IV.—SODIUM HYDROXIDE.

Conc. NaOH.	Color of sol.	Remarks.
0.00005 *N*	purple	unchanged in 18 hrs.
0.0001	purple	
0.0002 to 0.0005	tinge of blue red, decreasing amount of blue	pure red after 18 hrs.
0.0007	pure red	
0.001		
0.002		
0.003		
0.004		
0.005		deep bluish purple after 18 hrs.
0.01	reddish purple	
0.02	bluish purple	pptd. in 18 hrs.
0.03	blue	pptd. in 2 hrs.

TABLE V.—HYDROGEN CHLORIDE.

Conc. HCl.	Color of sol.	Remarks.
0.00005 N	pure red	all pract. the same color remaining unchanged for weeks sharp change between 0.002 and 0.003 N
0.0001		
0.0003		
0.0005		
0.0007		
0.001		
0.002		
0.003	bluish purple	precipitated in 3 days
0.004	bluish purple	precipitated in 2 days

TABLE VI.—SODIUM CHLORIDE.

Conc. NaCl.	Color of sol.	Remarks.
0.0001 N	reddish purple	The red sols were united, evaporated on a water bath to a 0.002 N conc. of NaCl, filtered, and set aside for two months, at the end of which time the sol was apparently unchanged
0.0002 to 0.004	pure red	
0.005 to 0.009	tinge of blue red, increasing amount of blue	
0.01	bluish purple	

TABLE VII.—AMMONIUM CHLORIDE.

Conc. NH_4Cl.	Color of sol.	Remarks.
0.00005 N	red, faint tinge of blue	pure red after 2 days
0.0001 to 0.002	pure red	
0.003	red, trace of blue	reddish purple after 2 days
0.005	purple	precipitated in 2 days

TABLE VIII.—POTASSIUM CHLORIDE.

Conc. KCl.	Color of sol.	Remarks.
0.00001 N	purple	
0.00002	reddish purple	
0.00005 to 0.0002	faint tinge of blue red, decreasing amount of blue	The color was little changed in any of these sols after standing 24 hrs.
0.0003 to 0.003	pure red	
0.004	red, faint tinge of blue	
0.005	red, with more blue	
0.0075	purple	
0.01	purple	

TABLE IX.—POTASSIUM BROMIDE.

Conc. KBr.	Color of sol.	Remarks.
0.0001 *N* to 0.0004	purple red, tinge of blue	None of these sols had precipitated appreciably after standing 4 days
0.0005 to 0.001	pure red	
0.002 to 0.005	red, tinge of blue with increasing of blue, to deep purple	

TABLE X.—POTASSIUM IODIDE.

Conc. KI.	Color of sol.	Remarks.
0.0001 *N* to 0.0007	violet-purple with increasing amount of red	On standing overnight all of these sols had changed to about the same color—reddish violet to transmitted light and a golden red to reflected light. (See remarks below on these sols)
0.001 to 0.003	red, tinge of blue	
0.004 to 0.006	tinge of blue red, purple	

TABLE XI.—BARIUM CHLORIDE.

Conc. $BaCl_2$.	Color of sol.	Remarks.
0.00002 *N* to 0.00004	reddish purple, decreasing amount of blue	practically unchanged after 2 days
0.00005 to 0.0001	pure red	
0.00015	red, tinge of blue	
0.0002	reddish purple	
0.0003	bluish purple	partially pptd. in 2 days
0.0005	blue, trace of red	completely pptd. in 1 day
0.0007	blue	completely pptd. in 3 hrs.
0.001	blue	completely pptd. in 3 hrs.

TABLE XII.—SODIUM CARBONATE.[1]

Conc. Na_2CO_3	Color of sol.	Remarks.
0.0001 *N*	bluish purple	
0.0002	reddish purple	
0.0003	red, tinge of blue	
0.0005 to 0.003	red, all with faint tinge of blue	After 3 days the blue tinge had entirely disappeared.
0.005	reddish purple	
0.01	purple	

---

[1] Extrapolation from the curve obtained by plotting log V_m (molar volume) against log α (percentage of hydrolysis) indicates that at concentrations below 0.0007

Potassium fluoride,[1] nitrate, sulfate, chlorate, and sulfuric acid were tried in the same manner over similar ranges of concentration. Without exception the sols obtained were dirty blue in color and coagulated completely on standing for a few hours.

It is seen that hydroxide, chloride, bromide, and iodide ions, when present within certain limits of concentration in the water in which gold is electrically dispersed, exert a marked stabilizing action on the sol formed. The effect is *not* obtained by dispersion in pure water and subsequent addition of the electrolyte.

The upper limit of concentration seems to depend somewhat on the precipitating power of the cation present. Thus the upper limit for barium chloride, where the bivalent cation has a high precipitating power, is much less than for the chlorides of sodium, potassium, and ammonium. The relation does not seem to hold among the latter ions themselves and other factors undoubtedly aid in the determination of the upper limit of concentration.

The lower limit of concentration is seen to correspond closely in several cases with the concentration of electrolyte produced in the preparation of platinum sols in pure water. The amount of electrolyte formed in the latter case is then sufficient to account for the fact that the stability of that sol is greater than that of gold sol in pure water. It was thought possible that the lower limit of concentration might depend upon the amount of colloid formed, *i. e.*, with smaller amounts of colloid formed, red sols might be obtained in lower concentrations of electrolyte. Sols were therefore next prepared by arcing the gold for different periods of time in the same concentration of electrolyte. The sols were then diluted in Nessler tubes until the same density of color was obtained and the colors compared.

Table XIII.

0.00001 N KCl.		0.0001 N KCl.	
Time of arcing.	Color of sol.	Time of arcing.	Color of sol.
5, 10, 15, 20 and 25 sec.	purple	10, 20, 30, 45 and 60 sec.	red, tinge of blue

No difference in the colors of the sols of either series was apparent and there seems to be no relation between the color and the concentration of the colloid near the lower limit of electrolyte concentration.

Fluoride, nitrate, sulfate, and chlorate ions do not stabilize the gold sols. In fact, the sols prepared in solutions containing these ions are

---

N sodium carbonate would be completely hydrolyzed (cf. Morgan, "Elements of Physical Chemistry," 1914, p. 367). The above red sols in sodium carbonate solutions can be attributed to the concentration of hydroxide ion present rather than to any specific action of the carbonate ion.

[1] The C. P. salt was recrystallized from conductivity water in platinum vessels and fused in a platinum dish. The 0.01 N solution was practically neutral to litmus, although more concentrated solutions were preceptibly alkaline.

much less stable than those prepared in conductivity water. It is to be noted that these ions do not form stable compounds with gold, while chloride, bromide, iodide, and hydroxide, mentioned above as stabilizing the sols, form its most stable compounds. This point is of especial interest in the exceptional behavior of fluorine as compared with the action of the other halogens. From its great chemical activity it would be expected that gold fluoride would be among the most stable compounds of gold, yet fluorine appears to have little, if any, affinity for this metal. Lenher[1] has shown that "gold fluoride is incapable of existence, not only in the presence of water, but under ordinary laboratory conditions." That this unusual behavior should be duplicated in the behavior of fluoride ion toward gold hydrosol points strongly to *a relation between the stabilizing effect and the ability of the ion to form a stable compound with gold.* This indication is born out by the behavior of the other ions which do not readily form stable compounds with gold and likewise do not stabilize the hydrosol.

Compounds, if formed, should be present to the greatest extent in the red chloride sols. An examination of the filtrates obtained after coagulation of several of these sols with hydrochloric acid was made to determine the presence of any soluble gold compounds. So far all results have been negative. Apparently the amount of gold compound necessary to stabilize the sol is either extremely minute or is so firmly attached to the colloidal particles that it is not removed from the coagulum by washing with hydrochloric acid.

The red sols obtained in chloride, bromide, and hydroxide solutions are very similar in color and stability. The iodide sols, however, are quite different in color and much less stable. This suggests that an examination of the absorption spectra and a quantitative investigation of the stability of the other sols would show differences there also. Work along these lines is being undertaken. The iodide sols present an appearance which suggests the presence of free iodine. Treatment with carbon disulfide or starch fails, however, to show any trace of the free element.

On standing, any of these sols gradually deposits gold in the form of a fine, yellow powder which, upon examination under the microscope, appears to be made up of spherical particles ranging in diameter from 5μ down and very similar to the "*schmelzkugeln*" described and photographed by Benedicks. The rate at which the gold settles out decreases as the sol stands, as shown by the fact that a sol in 0.0001 N hydrochloric acid, which contained 100 mg. of gold per liter when first prepared, analyzed 84 and 73 mg. per liter after standing 10 and 50 days, respectively.

It was of interest, especially in the case of the hydrochloric acid sols,

---

[1] THIS JOURNAL, 25, 1136 (1903).

on account of the reversal of the charge on many negative colloids by hydrogen ion,[1] to examine the direction of migration of the particles in an electric field. A cell for the observation of electrophoresis was designed, which, on account of its ease of construction and manipulation, warrants description. A 25 × 75 mm. object glass, 2 mm. in thickness, was ground to the form shown in Fig. 2 and cemented to a similar unground glass. A narrow strip cut from a cover glass closed the front of the trough. Binding posts for the platinum electrodes were cemented into place as shown. A potential of from 4 to 6 volts with the electrodes about 2 cm. apart gave a sufficiently rapid motion to the particles to be readily observed. The advantage of this type of cell over those previously described[2] is that it combines ease of cleaning and filling with the use of small amount of the liquid. The volume is, however, sufficient to avoid the interference of the "reverse movement" near the walls[3] with the observations. Disturbing effects due to liberation of gases at the electrodes are also small.

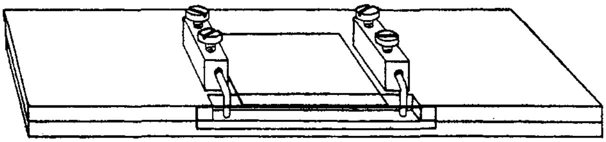

Fig. 2.—Actual size.

The cell was set up on the stage of a Siedentopf-Zsigmondy ultramicroscope and gold sols in sodium, potassium, and hydrogen chlorides, sodium hydroxide, and potassium iodide were examined. In each case the colloid migrated toward the anode and is therefore negatively charged. The hydrogen ion does not, therefore, have the effect of reversing the direction of migration of the gold particles in these sols.

VII. Conclusions Concerning the Nature of the Electrical Synthesis of Colloids.

From a consideration of the experimental evidence brought out in this investigation it seems that electrical colloid synthesis must be considered as being essentially more than a thermo-mechanical dispersion. It may be pictured as taking place in two distinct steps, the second of which is dependent upon the conditions produced by the first:

(1) a thermo-mechanical action by which the metal is dispersed in a molten or vaporized state as supported by the experiments of Benedicks, and

---

[1] Cf. Perrin, *J. chim. phys.*, 2, 601 (1904).

[2] Cotton and Mouton, *Ibid.*, 4, 365 (1906); Ellis, *Z. physik. Chem.*, 78, 321 (1911); and Coward, *Loc. cit.*

[3] Cotton and Mouton, *Loc. cit.*

(2) the formation of a colloidal complex between the highly dispersed metal, at a high temperature produced by the arc, and certain ions present in the medium.

The data are too meager to enable one to decide definitely as to the nature of this complex, the formation of which takes place simultaneously with the condensation of the dispersed metal in the liquid or vaporized state to the solid. It might be conceived to depend upon the action of certain ions as condensation centers, similar to the condensation of supersaturated water vapor upon dust particles or ions in a gas. The condensation of water vapor might be supposed to take place more readily on dust particles of calcium chloride than on particles of a chemically indifferent substance. By analogy, since a greater chemical potential exists between the atoms or ions of chlorine and of gold, for example, than between those of fluorine and gold, the former would very probably furnish points of condensation more readily than the latter. The initial stage of such a condensation would be chemical reaction in the ordinary sense. Subsequent growth of the particles would depend upon certain physical conditions, *e. g.*, increased radiation with the growth of the particle tending to increase its ability to serve as a point of condensation. In a pure medium, or one which contains no stabilizing ion, the dispersion takes place, but, owing to the lack of condensation centers, the condensation occurs at fewer points and the particles are consequently larger. The dispersion then behaves as an ordinary suspension and settles out rapidly. This would account for the great instability of gold sols in conductivity water and of Svedberg's metal organosols in pure media. The increased stability of the sols obtained in the presence of stabilizing ions is not alone, however, to be considered as dependent upon the increased dispersion obtained. The presence of these ions in the particles of the colloid constitutes in itself a stabilizing factor. It does not seem likely that the whole of the particle consists of a single chemical substance, and there can be little doubt that these sols, as well as those of metallic sols in general, regardless of their method of preparation, consist of essentially more than a dispersion of metallic particles in an indifferent medium.

VIII. Summary.

It has been shown that:

1. The specific conductivity due to the colloid proper of metallic hydrosols of average concentrations is, by calculation from reliable data, of an order of 10^{-10} mhos or about 0.0001 of that of conductivity water.

2. The oxidation of metal, *i. e.*, the formation of ion, which takes place during the electrical dispersion of platinum in water is considerably greater than in the case of gold.

3. Electrically prepared platinum sols in water of conductivity less than 1.2×10^{-6} mhos are much more stable than similar gold sols.

4. The free electrolyte formed in the above platinum sols (as distinguished from that which may be adsorbed and takes relatively little part in the conductivity) corresponds to an electrolyte concentration of 0.0001 to 0.0003 N.

5. The presence of chloride, bromide, iodide, or hydroxide ion in concentrations ranging from 0.00005 to 0.005 N (approximately) has a marked stabilizing effect on gold sols, and furnishes a quick and reliable method of preparing these sols.

6. The stabilizing effect is not produced by dispersion of the gold in pure water and subsequent addition of the electrolyte.

7. The upper limit of electrolyte concentration for a particular anion seems to be governed somewhat by the precipitating power of the cation.

8. The lower limit of electrolyte concentration required to produce a red sol is, within a wide range, independent of the concentration of colloid formed.

9. The particles in all of these red sols have been shown by electrophoresis to be negatively charged.

10. The stabilizing effect is not observed on the addition of fluoride, nitrate, sulfate, or chlorate ion in similar concentrations.

11. The stabilizing effect seems to be closely related to the ability of the ion to form stable compounds with gold. No gold, however, could be detected in the filtrate obtained after coagulation of the sol. The amount of gold compound necessary to stabilize the colloid is probably extremely minute.

12. Electrical synthesis of colloids is considered to consist of a thermomechanical dispersion of the metal which is followed by the formation of a colloidal complex between the dispersed metal and certain ions present in the medium.

In conclusion we desire to express our appreciation of generous assistance and advice from members of this department and of the Department of Physics.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY FOR GAS INVESTIGATIONS, U. S. BUREAU OF MINES.]

THE CRITICAL CONSTANTS OF NORMAL BUTANE, ISO-BUTANE AND PROPYLENE AND THEIR VAPOR PRESSURES AT TEMPERATURES BETWEEN 0° C. AND 120° C.

BY F. M. SEIBERT AND G. A. BURRELL.[1]

Received September 27, 1915.

In this report, one of a series dealing with the vapor pressures of gases, are shown the critical constants of N-butane, isobutane and propylene

---

[1] Published by permission of the Director of the Bureau of Mines.