was somewhat greater and where it was the only major change observed.

Summary

The Raman spectrum of a concentrated solution of silver perchlorate in toluene shows a band at 167 cm.$^{-1}$ which has no distinct counterpart in the spectrum of aqueous solutions of the same salt. Concentrated aqueous mercuric perchlorate also shows a band at this same position. It is suggested that this band may arise because of covalency between the metal atom and the perchlorate group.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

A Study of Bredig Platinum Sols

BY JOSEPH MINDEL AND CECIL V. KING

With the exception of the early work of Bredig,[1] Svedberg[2] and Benedicks,[3] studies of Bredig sols have emphasized composition and properties rather than mechanism of formation. Furthermore, the early investigators minimized the specific chemical reactions of the metals involved and correlated such physical properties as heats of fusion and heat conductivities of the metals, the characteristics of the electrical circuit, etc., with the distribution of particle size and the effectiveness of the arc in dispersing the metal.

The present work is a study of some of the processes involved in the formation of Bredig platinum sols. It is well known that stable platinum sols can be prepared by passing an arc under conductivity water. During arcing, the conductivity of the liquid increases.[4] The colloidal particles themselves carry only a small fraction of the current. Pennycuick[5] showed that the conductivity was due to the presence of hexahydroxyplatinic acid. He postulated,[6] on the basis of conductimetric titrations, that the colloidal micelle consisted of a platinum core, whose surface was covered with platinic oxide and hexahydroxyplatinic acid, while the intermicellar fluid was a solution of the acid. One of us[7] showed by direct analysis that the colloidal particles were not pure platinum. Pennycuick,[8] on the basis of a thorough analytical investigation, has proposed a formula for the micelle: 3.9 Pt, 1.16 PtO_2, 1.0 $H_2Pt(OH)_6$.

Experimental

The first phase of the present investigation was a study of the variation of the composition of the sol particles with changes in the nature of the dispersion medium and of the gas atmosphere.

The sols were prepared by arcing between platinum wires 2 mm. in diameter, using a source of direct current of 220 volts and 4 amperes. Water, hydrochloric acid (0.0001–0.0007 *N*) and nitric acid (0.0001–0.0004 *N*) were used as dispersion media, and air, oxygen and nitrogen as stirring gases. The arcing vessel was immersed in an ice-bath.

The sols were evaporated whole or coagulated by freezing to provide the dry residue for analysis. The evaporation was carried out at 50–60° and atmospheric pressure in tared beakers; freezing was accomplished by an ice–salt mixture and after thawing the coagulum was transferred to tared beakers and dried at 50–60°. The analysis was carried out in the beakers, platinum being determined as potassium chloroplatinate. Test analyses made on weighed samples of pure platinum agreed with the taken weights to within 1%.

Sols were allowed to stand for twenty-four hours before samples were taken for analysis. The coarse sludge that settled out in that time was separated and its platinum content determined.

The minimal concentrations of potassium chloride that coagulated the sols in twenty-four hours were determined to serve as rough estimates of stability. No attempt was made to study in detail the action of electrolytes.

Table I summarizes the results, the type of sol being denoted by the gas used for stirring and by the dispersion medium.

In any one series of analyses, the scattering of experimental values was greater than the systematic error of the method of determination, indicating a considerable degree of variation in the composition of each type of sol. It is evident that, despite the variation in the oxidative capacity of the gaseous atmosphere and of the dispersion medium in which the sols were prepared, the range of platinum content is relatively small.[9]

TABLE I

COMPOSITION AND STABILITY OF PLATINUM SOLS AS A FUNCTION OF GAS ATMOSPHERE AND DISPERSION MEDIUM

Type of sol	Per cent. of platinum in sol particles	Per cent. of platinum in sludge	Coagulation concn. of KCl (*M*)
Air–water	89.9 ± 2.4[10]	98.6 ± 0.6[10]	0.0054–0.0056
Oxygen–water	91.9 ± 2.6	98.8 ± 0.4	0.0034–0.0038
Nitrogen–water	89.5 ± 3.5	98.9 ± 0.9	0.0038–0.0042
Air–HCl	87.6 ± 3.0	98.5 ± 0.8	
Air–HNO_3	86.7 ± 6.5	97.1 ± 1.2	

In properties, too, the sols are similar. All are black, contain negatively charged particles, are stable for years

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[1] G. Bredig, *Z. angew. Chem.*, **11**, 951 (1898).

[2] T. Svedberg, "The Formation of Colloids" (Churchill, London, (1921)). This book contains references to previous papers.

[3] C. Benedicks, (a) *Kolloid-Beihefte*, **4**, 229 (1913); (b) *Kolloid-Z.*, **11**, 263 (1912).

[4] H. T. Beans and H. E. Eastlack, THIS JOURNAL, **37**, 2667 (1915).

[5] S. W. Pennycuick, (a) *J. Chem. Soc.*, 2108 (1928); (b) 2600 (1927).

[6] S. W. Pennycuick, (a) *Kolloid-Z.*, **49**, 407 (1929); (b) *J. Chem. Soc.*, 618 (1929).

[7] C. V. King, THIS JOURNAL, **60**, 144 (1938).

[8] S. W. Pennycuick, *ibid.*, **61**, 2234 (1939).

[9] The analysis of a few sols made by arcing in water in an atmosphere of hydrogen showed the particles to be 98.7 ± 0.9% platinum. These hydrogen–water sols were not noticeably less stable than the others. The nature of these sols is considered in the Discussion.

[10] Pennycuick's formula for the colloidal micelle corresponds to 89.3% platinum. He also found[8] that the sludge was practically pure platinum.

and coagulate only after prolonged boiling. The variation in stability to potassium chloride is small. The stability of sols made by arcing in acid was roughly inversely proportional to the original concentration of acid. For air-hydrochloric acid sols, the minimal concentration of potassium chloride that was needed to produce coagulation in twenty-four hours ranged from 0.0004 *M* in 0.0007 *M* hydrochloric acid to 0.0050 *M* in 0.0001 *M* hydrochloric acid. For nitric acid sols, the range was from 0.0004 *M* in 0.0004 *M* nitric acid to 0.0050 *M* in 0.0001 *M* nitric acid. Arcing in solutions of nitric acid more concentrated than 0.0004 *M* gave unstable dispersions that settled out in a few hours.

Analyses were made of the coagulum obtained by the addition of acid (hydrochloric acid in the case of oxygen- and nitrogen-water sols and nitric acid in the case of air-nitric acid sols), a molarity of a few ten-thousandths being sufficient to cause precipitation. The results are given in Table II; the compositions of the whole-sol particles are repeated for comparison.

TABLE II

COMPOSITION OF ACID-COAGULATED PLATINUM SOL PARTICLES

Type of sol	Per cent. of platinum Whole sol	Acid coagulum
Oxygen-water	91.9 ± 2.6	92.2 ± 2.5
Nitrogen-water	89.5 ± 3.5	89.7 ± 2.9
Air-nitric acid	86.7 ± 6.5	87.5 ± 2.9

The fact that the coagulum does not differ appreciably in composition from the whole sol is an indication that the nucleus of the micelle is not changed by coagulation.

Gas Phase Sols.—In the following series of experiments, the sols were prepared by passing an arc in a glass tube, so that the dispersion medium did not come in contact with the electrodes. A stream of gas (oxygen or nitrogen was used) blew the products of the arc into the water surrounding the glass tube which carried the platinum wires. This tube was wide enough (diameter 1 cm.) so that the heat of the arc caused no vaporization of the glass. The apparatus was similar to that used by Svedberg[11] in the preparation of organosols.

The same source of direct current was used. A slow-motion automatic making and breaking of the arc could be obtained by careful adjustment of the distance between electrodes. During the period when the arc passed, the wires heated greatly and expanded. When they made contact, the arc naturally stopped; as the electrodes cooled, they contracted, starting the arc once again.

The sols so produced[12] were much less concentrated than those obtained by arcing under water for the same length of time. The most concentrated contained 50 mg./liter of solid the average being 30–40 mg./liter while the liquid phase sols contained as high as 250 mg. of solid per liter.

The gas-sols were naturally less intensely colored than the liquid-sols. Nitrogen-sols (g. p.) were dull gray resembling very dilute air-water sols; oxygen-sols (g. p.) were brown. The migration of all sols toward the anode showed them to consist of negatively charged particles. Some gas phase sols coagulated after several days, but most of them were stable. One such sol is now more than a year old. Both types of gas phase sols were coagulated by concentrations of potassium chloride of 0.0045–0.0050 *M*.

Analyses were made of the sol particles (obtained by evaporation) and of the sludge that separated on standing. Most of the platinum disintegrated by the arc does not reach the water, but condenses on the inside of the arcing tube. This deposit was also analyzed. The results are given in Table III.

It is seen that nitrogen sols (g. p.) have approximately the same composition as air-water sols, while oxygen-sols (g. p.) contain more highly oxidized particles. In the former, the sludge formed on standing is pure platinum, whereas in the latter it is partly oxidized. Furthermore, in an atmosphere of oxygen, some oxidation of platinum takes place in the gas phase, but none, naturally, in the nitrogen atmosphere.

TABLE III

COMPOSITION OF GAS PHASE PLATINUM SOLS

Type of sol	Per cent. of platinum in sol particles	in sludge	in deposit in arcing tube
Oxygen	85.9 ± 6.7	95.0 ± 3.6	97.7 ± 0.8
Nitrogen	89.2 ± 5.3	100	100

Nitrogen sols (g. p.) are strikingly similar to normal air-water sols. Additional confirmation of this similarity comes from measurements of the catalytic effect of the sols on the hydrogen peroxide decomposition. The catalysis was measured in an apparatus like that described by Brønsted and Duus,[13] the reaction being followed by determining the pressure of the liberated oxygen.

The magnitude of the catalytic effect of colloidal platinum on the decomposition of hydrogen peroxide is a function of many factors, including acidity, the nature of the walls of the reaction vessel and the concentration of the sol. If the rate constant is calculated from the usual unimolecular reaction equation, it is found that the catalytic effect increases with increasing platinum content of the sol. The catalysis of air-water sols was measured to provide a standard to which the gas phase sols could be compared. The constant itself is therefore of minor importance.

Oxygen-sols (g. p.) had no catalytic effect that could be measured by the method used. This lack of activity suggests a saturated surface in accord with the higher degree of oxidation. Nitrogen-sols (g. p.) catalyzed the decomposition, and while the effect was smaller than that of air-water sols, the catalysis increased with concentration of the sol in the same way (Fig. 1).

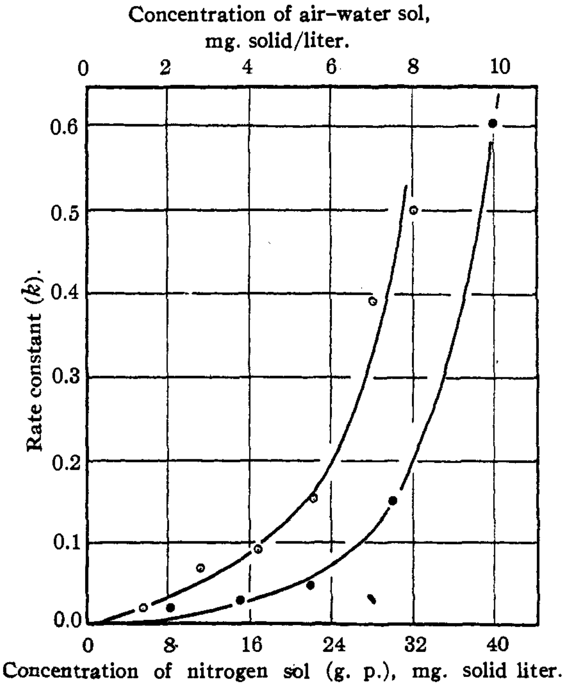

Fig. 1.—Catalysis of hydrogen peroxide decomposition: O, air-water sol; ●, nitrogen-sol (g. p.).

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(11) T. Svedberg, "Colloid Chemistry," 2nd ed., Chemical Catalog Co., N. Y., 1928, p. 41.

(12) For convenience, these sols may be called gas phase sols and designated (g. p.).

(13) J. N. Brønsted and H. C. Duus, *Z. physik. Chem.*, **117**, 299 (1925).

Discussion

In considering the constitution and properties of Bredig platinum sols, it is convenient to distinguish between the surface of the particle and the rest of the micelle. The extreme conditions of the arc lead to the formation of colloidal particles whose composition is little influenced by variations in the electrical circuit, in the nature of the dispersion medium and of the gaseous atmosphere. These factors do, however, affect the character of the surface of the particle, and these differences in micellar structure are responsible for differences in stability and in chemical and electrical behavior. The fact that the disparities are only skin deep is indicated by the similarity in platinum content between the whole sol and the acid-coagulated particles (Table II). It is confirmed by the absence of a sharp break in the cataphoresis curve at the moment of coagulation[14] and by the observation[7] that the catalytic effect of colloidal platinum on the decomposition of nitramide is not markedly different at the time of coagulation. The properties of the sol are determined by the nature of the particle surface, but the formation of a stable dispersion depends first of all on the synthesis of the micellar structure.

Both the colloidal particles and the intermicellar fluid contain oxidation products of platinum. The oxidation cannot be due to oxygen dissolved in the water, since arcing in oxygen-free water, stirred with nitrogen, yields stable sols of approximately the same composition as sols made in air atmosphere. Furthermore, Pennycuick[15] showed these sols to be similar in properties to air-water sols. Rocasolano[16] showed that hydrogen, but not oxygen, was evolved during arcing, so that water is the source of the necessary oxygen.

It has been assumed tacitly that this oxidation is due to electrolytic oxygen. A simple calculation shows that this source is insufficient to account for the oxidized platinum in sols. With a potential difference of 40 volts across the electrodes, taking the mean conductivity of the sol as 10^{-5} mho, 1.4 coulombs will pass in one hour of continuous arcing, releasing 2.4×10^{-4} g. of oxygen from water. The sol so produced would contain at least (probably more than) 150 mg. of solid per liter, giving a weight of oxygen combined with platinum, using Pennycuick's formula for the micelle, of 7.8×10^{-3} g., or more than thirty times the amount of oxygen available from electrolytic action.

The most probable mechanism is the oxidation of platinum by water. The preparation of stable sols by arcing in the gas phase is evidence for this view. When nitrogen was used, the deposit inside the arcing tube was pure platinum; but since the sol formed contained particles with only 89% platinum (Table III), oxidation must have taken place when the platinum came in contact with water. The sols so formed were similar in appearance, in stability to electrolytes, in composition, in charge and in catalytic effect to sols produced by arcing *under* water.

When oxygen was used, some oxidation took place in the gas atmosphere before the particles were blown out into the water. When the hot particles reached the water, further oxidation occurred, resulting in micelles with a lower percentage of platinum than in nitrogen-sols (g. p.) and with a less active catalytic surface.

It is only one step, therefore, to the conclusion that platinum sols, prepared by the usual Bredig method, are to a large degree gas phase sols, in the sense of the term employed in this paper. It is generally agreed that the high temperature of the arc creates around the electrodes a gaseous atmosphere containing water vapor, products of its thermal decomposition and atomic and polyatomic units of platinum. In this gas phase, platinum particles agglomerate to colloidal dimensions, subsequently to be dispersed in the medium. But condensation to the proper size will not alone yield stable sols; there are needed stabilizing ions or ionogens, which in this case must be oxidation products of platinum. It is proposed here that practically all of the oxidation takes place, not in the gas bubble around the electrodes, but when the platinum particles come in contact with the water in the surrounding dispersion medium.

There is an optimum size (or range of sizes) that results in the formation of stable particles. Larger agglomerates may be oxidized, but then the ratio of the number of surface ionogens to the mass of the particle is too small and the particle does not remain suspended. This is evidenced by the slight degree of oxidation of the sludge that separates after twenty-four hours (Table I). If, on the other hand, the particle is too small when it strikes the water, it may be completely oxidized to an oxide of platinum, which may hydrate yielding a hydroxo-acid. This is probably the major source of the acidity of Bredig platinum sols, although the dissociation of surface ionogens and the "dismutations" postulated by Pauli and his co-workers[17] undoubtedly play a part.

If this picture of the formation of colloidal platinum particles is correct, the presence during arcing of electrolytes in the dispersion medium should have little influence on the constitution of the micelle as a whole. This is borne out by the analyses. The surface ionogens may, however, be different, so that stability, cataphoretic velocity and other properties are affected. Yet the chloro-sols, prepared by Pauli and Schild[17a] by arcing in hydrochloric acid, are not greatly different from the usual hydroxo-sols.

Similarly, the gaseous atmosphere during arcing is of secondary importance in the formation of

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[14] S. W. Pennycuick, *J. Chem. Soc.*, 1447 (1930).

[15] S. W. Pennycuick, THIS JOURNAL, 52, 4621 (1930).

[16] Rocasolano, in Alexander, "Colloid Chemistry," Vol. I. Chemical Catalog Co., N. Y., 1926, p. 673.

[17] (a) W. Pauli and T. Schild, *Kolloid-Z.*, 72, 165 (1935); (b) W. Pauli and A. Baczewski, *Monatsh.*, 69, 204 (1936).

the micelle. Sols made in the presence of hydrogen appear to be exceptions; their platinum content was found to be 98.7%. But some data given by Bach and Balaschowa,[18] who studied the electrical properties of these sols, suggest that they are formed by the same mechanism as yields the other types. An arc was passed through water in a hydrogen atmosphere in a cell which permitted the measurement of conductivity. Periodically, the arcing was stopped and hydrogen was bubbled through the liquid. This resulted in a drop in conductivity. Subsequent arcing raised the conductivity, which again decreased when hydrogen was passed through. Since a decrease in conductivity must be associated with a lower concentration of oxidation products, it appears that the effect of hydrogen is to reduce oxides of platinum formed originally by the action of hot particles on water. Pennycuick[15] found that passing hydrogen through air–water sols caused them to lose their acidoid properties, which could be restored by passing oxygen.

If the preparation of stable metallic hydrosols in conductivity water by the Bredig method depends on the formation of small amounts of oxide by the action of hot particles on water, then the free energy of formation of the metallic oxide should be one of the determining factors in the process. Metals whose oxides have positive or small negative free energies of formation should not yield stable sols in pure water. (Such metals may give stable sols in water containing an electrolyte, for then the production of stabilizing compounds other than the oxide is involved.) Thus, gold and silver (Au_2O_3, $\Delta F = +18.7$ kcal./mole; Ag_2O, $\Delta F = -2.6$ kcal./mole) form stable Bredig sols only in acid, alkaline or salt solutions. Mercury (HgO, $\Delta F = -13.9$ kcal./mole) and copper (CuO, $\Delta F = -30.4$ kcal./mole) give permanent dispersions on arcing under water.[19] In fact, metals like zinc or cadmium, whose oxides have high free energies of formation, give sols consisting largely of the oxide.

Summary

1. Bredig platinum sols have been prepared in water, hydrochloric acid and nitric acid, in atmospheres of air, oxygen and nitrogen.
2. The composition and stability of these sols are only slightly affected by variations in the dispersion medium and in the gaseous atmosphere.
3. There is no change in the platinum content of the micelle on coagulation with acids.
4. Platinum sols prepared by arcing in the gas phase are similar to normal Bredig sols in color, charge, stability and catalytic effect.
5. A mechanism for the formation of Bredig platinum sols is proposed.

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[18] N. Bach and N. Balaschowa, *Acta Physicochim.*, U. S. S. R., 3, 79 (1935).

[19] Free energy data for the oxides of platinum are not available.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Crystal Structure of Boron Carbide

BY H. K. CLARK AND J. L. HOARD

Upon the basis of X-ray diffraction data, Zhdanov and Sevast'yanov[1] have recently proposed a most interesting and unusual structural type for crystalline boron carbide, B_4C. Although published during 1941, the journal describing their work has not reached our library, and the article was not abstracted until April, 1943. In the meantime we had been investigating the crystal structure of boron carbide as a part of a general program of study of boron[2] and its compounds being conducted in this Laboratory. We had succeeded in placing definitely nine of the fifteen atoms in the unit of structure when the abstract was published. Through the courtesy of Dr. E. J. Crane of *Chemical Abstracts* we were enabled to see the original article by Zhdanov and Sevast'yanov, and we have now confirmed the structure proposed by these investigators. Because of the curious coördination shown by boron and carbon, it seems desirable to publish a brief account of our work, emphasizing that part in which our methods of handling the X-ray data differed from those of Zhdanov and Sevast'yanov and elaborating on some of the unusual features of the structure which were not discussed in detail by these workers.

Earlier work[3,4] indicated that boron carbide belongs to one of the rhombohedral space-groups, D_{3d}^5, D_3^7, or C_{3v}^5, and contains three molecules of B_4C within the unit cell. We have confirmed these results with Laue, oscillation, and Weissenberg photographs, obtaining for the rhombohedral lattice constants, $a = 5.19$ Å., $\alpha = 65°18'$, and for the corresponding hexagonal lattice constants, $a = 5.60$ Å., $c = 12.12$ Å. These are in substantial agreement with previous values.

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[1] G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U. R. S. S.*, 32, 432–4 (1941) (in English).

[2] A. W. Laubengayer, A. E. Newkirk and R. L. Brandaur, *J. Chem. Ed.*, 19, 382–5 (1942); Laubengayer, Hurd, Newkirk and Hoard, THIS JOURNAL, 65, 1924 (1943).

[3] F. Laves, *Zachr. Ges. Wiss. Göttingen, Mathem-Physik Kl.*, Neue Folge 1, 57–58 (1934).

[4] N. G. Sevast'yanov, Zavodskaya Lab. 8, No. 12, 1317–18 (1939); *Khim. Reprat. Zhur.*, No. 5, 67–68 (1940).