Summary

The general behavior of colloidal platinum as a typical acidoid sol is discussed from the point of view of more recent work.

Experiments are quoted which show that the whole of the colloid surface appears to be coated with a layer of oxidized platinum. On passing hydrogen the oxide layer is reduced and the acidoid properties disappear. On repassing oxygen or air the acidoid properties are recovered.

The $H_2Pt(OH)_6$ combines with part of the surface oxide to form Werner compounds, which act as the stabilizing surface ionogens.

The rest of the oxidized surface remains uncombined, but exhibits the properties of an acid oxide.

All the reactions of colloidal platinum are intimately connected with the acidic nature of the surface. They may be divided into three classes: ionic replacement, complex or salt formation and hydrolytic cleavage.

The general action of acids, bases and salts is interpreted in terms of these three reactions.

It is shown that hydrocyanic acid increases the charge carried by the colloid particle, and at the same time appears to displace the surface hexahydroxyplatinic acid.

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THE DENSITY OF WATER ADSORBED ON SILICA GEL[1]

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It is well known that water adsorbed on a surface of a solid has undergone a thermodynamic change in state and that it is held to the surface by a force of great magnitude which may be expressed in terms of pressure, compressibility, etc. Among the early investigators to advance this idea were Rose,[2] Jungh[3] and Parks.[4] That silica gel holds adsorbed water as if under a high pressure is also more recently confirmed by data on the heat of adsorption of water by Lamb and Coolidge,[5] and Patrick and Grimm.[6] The object of this investigation was to measure by a direct method the volume of water adsorbed on silica gel and to determine its density when present in small amounts.

[1] This paper represents the thesis submitted by Charles H. Spurway to the Graduate School of the Michigan State College, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Rose, *Ann. Phys.*, 73, 1 (1849).

[3] Jungh, *Ann. Phys. Chem.*, 125, 292 (1865).

[4] Parks, *Phil. Mag.*, 4, 220 (1902); 5, 517 (1903).

[5] Lamb and Coolidge, THIS JOURNAL, 42, 1146 (1920).

[6] Patrick and Grimm, *ibid.*, 43, 2144 (1921).

Ikerman[7] and one of us have measured the adsorption of helium on an active silica gel and it was found that no appreciable quantity was adsorbed until the temperature was lowered to near that of liquid oxygen. It seemed advisable, therefore, to use this gas as a medium for determining the various volumes necessary in this investigation.

Experimental Procedure

Apparatus.—The design of the apparatus is similar to that heretofore used for adsorption experiments. All glass parts are of py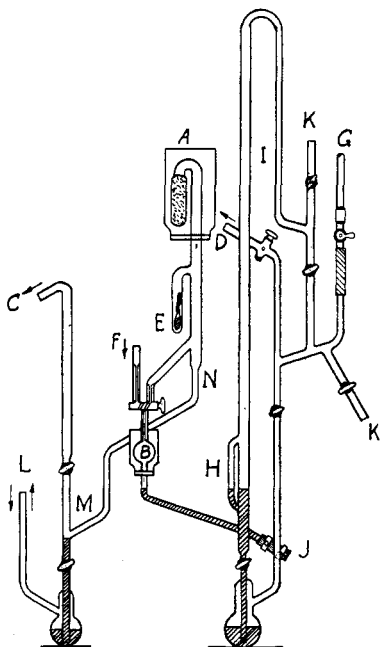rex glass. The form of the gel bulb A (Fig. 1) permits heating the gel by means of a cylindrical, electrical heating unit placed on from the top, and which could be replaced by a constant temperature bath as outlined in the illustration. B is a calibrated gas pipet used for measuring and admitting known volumes of helium to the gel bulb. Air pressure at G and suction at D permit rough adjustment of mercury levels in the apparatus for the several operations. Fine adjustments of mercury levels for the cathetometer readings were obtained by means of the short rubber tubing at J operated by means of a pinchcock. For more accurate readings, the calibration marks on the stem of the gas pipet and the gel bulb are vertical scratches, read from the lower points, instead of the ordinary cross-etchings. The water was admitted to the gel by means of the side tube E, which is shown as containing a glass capsule of water and a soft iron rod enclosed in glass.

Purification of the Helium.—The helium used in this work was furnished by the United States Bureau of Mines. As the experimental operations were conducted under conditions requiring adsorbable gases to be absent from the helium, it was necessary to purify the helium by removing these gases. The apparatus shown in Fig. 2 was designed for this purpose. A discussion of the operations performed in purifying the helium will also describe the uses of the different parts of the apparatus. After the apparatus was made ready for use, the "norite" charcoal bulbs O and P were heated to 500° by means of electrical heating units surrounding the bulbs, and the apparatus was evacuated through Q to activate the charcoal. The heating and evacuating occupied three periods of time of six hours each. After the minimum pressure was held for several hours, tube Q was sealed off, charcoal bulb O was surrounded with liquid air in a Dewar flask and when the temperature equilibrium was thought to have been attained, helium gas was allowed to flow slowly from the tank R through O to atmospheric pressure as was shown by the barometric gage S. Tube T was then sealed off, the liquid air was transferred to P and the helium was passed back and forth slowly through P seven times. The helium was finally stored in flask U and tube V sealed off. During all these operations mercury stood in tube F to the upper bend.

Fig. 1.—Adsorption apparatus.

[7] Ikerman, Master of Science Thesis, Michigan State College, 1927.

Preparation of the Gel.—A sample of commercial Patrick's gel was passed over a 2-mm. round-hole screen and the particles held on the screen were carefully sorted, saving only the clear, uncontaminated particles. The dark-colored, opalescent and chalky particles were discarded. After sorting the gel, it was carefully dusted by rolling it on a piece of black velvet cloth.

Filling the Water Capsule.—Especially purified water was used from which the air and other gases had been removed by heating and evacuating. A piece of glass tubing of suitable size was drawn to a capillary in the middle section and weighed. The capsule end was then filled nearly full with the water and evacuated for several minutes to the vapor pressure of water at the operating temperature. Maintaining the pressure, the top was sealed off at the capillary, the whole reweighed and the weight of the water determined.

Temperature Control of Constant Temperature Bath.—This temperature control was effected by means of a 25-watt electric light bulb, operating against a stream of cool air bubbled through the water of the bath to obtain circulation of the water, and connected through a relay to a thermo-regulator set to maintain a temperature of 25.020 ± 0.004° as measured by a Beckmann thermometer.

Barometer.—The atmospheric pressure readings were obtained from a barometer made from heat-treated evacuated pyrex tubing and filled with purified and evacuated mercury. Filling the tube with mercury was accomplished by breaking off the lower end of the evacuated tube under the mercury. After continuing the evacuation for some time to the lowest pressure obtainable and with further heat treatment of the upper end of the tube, the barometer was sealed off from the apparatus and attached to the apparatus rack near the manometer.

Pressure Readings.—All of the pressure readings were made with a cathetometer calibrated to read to 0.05 mm. The mercury column of the manometer was always forced upward to the mark, and the mercury columns of both the manometer and barometer were carefully equilibrated before reading them.

Fig. 2.—Apparatus for purification of helium.

Operation of Apparatus.—The minimum pressure obtained in the cool apparatus, and for all of the determinations requiring low pressure, was of the order 1 by 10^{-5} mm.

The silica gel, prepared as previously described, was admitted to the gel bulb through the bulb stem before sealing to the apparatus. After sealing the gel bulb containing the gel to the apparatus, the gel was heated to 250° and evacuated for several hours, the water tube E not being attached to the apparatus. When a satisfactory low pressure was obtained, the mercury trap M was closed and the mercury raised to N. Helium was then drawn from the storage flask into the gas pipet B and the volume measured in cc. at 25.02° and 760 mm. The helium was then admitted to the gel bulb, pressure readings were taken on it at certain intervals of time, and the volume not occupied by dry gel was determined under equilibrium conditions after several days. This volume subtracted from the volume of the gel bulb, determined by helium in the same manner, gives the volume of the dry gel. In the next step the mercury was drawn out of the manometer, and the water tube E, containing a known weight of water, was at-
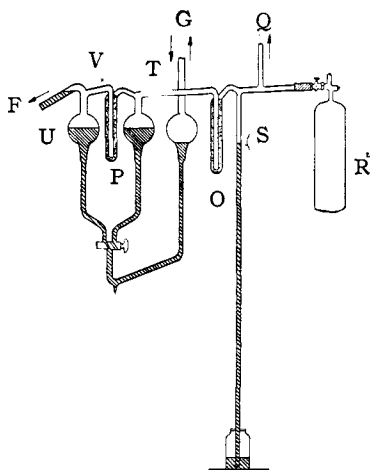
tached to the gel bulb stem below the calibration mark. Heat was again applied to the gel (250°), the gel evacuated to low pressure to remove the helium previously used, and the mercury elevated to fill the manometer up to the water tube inlet. The water capsule was then broken by raising the iron weight by means of an electromagnet and releasing it to fall on the capillary end of the water capsule. On breaking the water capsule, the water vapor was drawn rapidly into the gel, requiring about two hours for the largest quantity of water used (2.5667 g.) to disappear from the water tube, but the gel was allowed to stand for one day before further operations, in order to attain better equilibrium conditions. After sealing off the water tube close to the gel bulb stem, another volume of helium was then admitted to the gel bulb and the volume not occupied by gel and water was determined. From these results the volume and density of water adsorbed on the gel were calculated. The weight of the dry, evacuated gel was determined by sealing off the gel bulb under low pressure and making the requisite weighings.

TABLE I

PRESSURE READINGS OF HELIUM IN THE GEL BULB

Time, days	Press. on helium in gel bulb alone, mm.	Press. on helium in gel bulb with dry gel, mm.		
		1	2	3
1		501.35		511.55
2	750.15		502.95	511.10
3	749.70		502.85	510.70
4			502.75	510.80
5	749.40			
6		500.25	502.70	510.70
7	749.40	500.30		
8	749.35			

Time, days	Press. on helium in gel bulb with gel and different amounts of adsorbed water, mm.				
	2.5667 g.	2.1095 g.	1.6867 g.	0.6357 g.	0.4017 g.
1		524.70	532.60	513.10	
2	543.90		532.55		516.55
3	544.00	524.10	532.70	512.55	516.35
4	543.90	524.00	532.65	512.30	
5	543.85			512.15	
6	543.55			512.05	
7				512.10	
8					
9	543.00				
10	543.05				
11	543.00				516.30
13					516.25

TABLE II

VOLUME OF GEL BULB AND VOLUME OF DRY GEL

All volumes calculated in cc. at 25.02° and 760 mm.

Vol. of He taken, cc.	Equil. press., mm.	Vol. of gel bulb, cc.	Vol. of He in gel bulb, cc.	Vol. of dry gel, cc.
68.850	749.35	69.826		
a 34.325	500.25		52.147	17.679
b 34.498	502.70		52.154	17.672
c 35.044	510.70		52.150	17.676

Average vol. of dry gel   17.676 cc.

Wt. of dry gel *in vacuo*   38.6495 g.

Density of dry gel   2.1866 ± 0.0006

TABLE III

MEAN DENSITIES OF ADSORBED WATER

Wt. of ads. water, g.	Vol. of He taken, cc.	Equil. press., mm.	Vol. of He in gel bulb, cc.	Vol. of gel and water, cc.	Vol. of ads. water, cc.	Density of ads. water
2.5667	33.869	543.00	47.404	22.422	4.746	0.5408
2.1095	34.205	524.00	49.610	20.216	2.540	.8305
1.6867	35.401	532.55	50.510	19.316	1.640	1.0285
0.6357	34.719	512.05	51.531	18.295	0.619	1.0270
.4017	35.157	516.25	51.756	18.070	.394	1.0195

Discussion

The accuracy of the results depends on the correlation of equilibrium conditions of the several pressure determinations. In order to meet these conditions as nearly as possible, the pressure readings were taken until the daily change in pressure was small, in most cases 0.05 mm.

An interesting phenomenon was observed when the largest quantity of water was admitted to the gel. Immediately on breaking the water capsule, the water vapor was drawn into the gel with sufficient force to raise the iron weight (9.245 g.) and hold it against the top of the water tube until the water was nearly all in the gel. In some cases the water froze in the water tube. On adsorbing the first quantity of water vapor, the gel became warm at the top and the heat, passing downward through the gel, could be traced with the hand. Only a few minutes were required for the heat to become distributed throughout the gel. From this heat effect it is concluded that the water vapor was evenly distributed over the gel surface.

There is a close correlation between the density values for the 1.6867 g. and 0.6357 g. of adsorbed water, indicating one phase of water on the gel. The density value for the smallest quantity of water used is somewhat lower, probably because of the greater experimental error due to the small volume. The mean density values for the two larger quantities of adsorbed water are less than the density of liquid water at the operating temperature, indicating the presence of three water phases: compressed water, liquid water and water vapor. This water vapor, however, exerts only a low vapor pressure; hence, all three forms of water are held on the gel under pressure. A sudden break occurs in the mean density curve (Fig. 3) at a point near the value for 1.6867 g. of adsorbed water.

No measurable vapor pressure was shown on the manometer by the three smallest quantities of adsorbed water, but the two larger quantities gave a vapor pressure of 4 mm. each. The calculated volume of water vapor in the gel bulb corresponding to this pressure, however, was not significant in these determinations. These vapor pressure measurements show that the vapor pressure of the adsorbed water is very low.

By a calculation based upon the volume of the adsorbed water in the runs where the silica gel contained 1.6867 g. or 0.6357 g. of water, and a

correlation of Bridgman's compressibility data ("International Critical Tables," Vol. III, p. 40), it is shown that in these cases the pressure on the adsorbed water is of the magnitude of 750 atmospheres.

TABLE IV

ERRORS

Mean density	0.5408	0.8305	1.0285	1.0270	(1.0195)
Exptl. errors	± .0005	± .0017	±0.0031	±0.0083	±0.0129
He ads. errors	− .0027	− .0065	− .0099	− .0099	− .0102

The greatest probable error in these determinations was in reading the barometer and manometer and was calculated to be ±0.025 mm. on each reading or ±0.05 mm. on both in case the error was positive on one reading and negative on the other. Applying this error to the data, the values
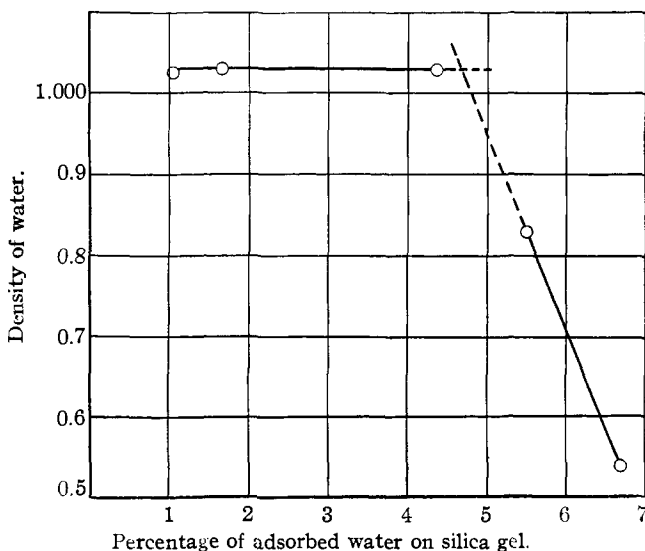

Fig. 3.—Mean density curve.

given as experimental errors in Table IV were obtained. The possible error due to the absorption of helium in the water was calculated from the data of Lannung[8] assuming that the water adsorbed on the silica gel absorbed helium to the same extent as does liquid water. This assumption is improbable, however, especially where the water is held under great pressure.

A noticeable drift occurs in the pressure readings with time (Table I), varying from 0.05 mm. with 1.6867 g. of water on the gel to 1.05 mm. both with dry gel and 0.6357 g. of adsorbed water. As this drift also occurs with helium only in the gel bulb, it must be due chiefly to adsorption of helium on the inner walls of the gel bulb or absorption of helium in the

[8] Lannung, THIS JOURNAL, 52, 68–80 (1930).

mercury exposed to the helium. Provided this drift was caused by adsorption of helium on the gel bulb only, it should be nearly the same in all cases as the gel bulb was heated and evacuated each time before admitting the helium. The differences in this drift may be caused partly by mercury surfaces in the manometer containing more or less absorbed helium when exposed to the helium in the gel bulb. In the three determinations of volume of dry gel made before the admissions of 1.6867 g., 0.6357 g. and 0.4017 g. of water, the variations from the mean were only +3 and −4 parts in 17,676, although the drifts in the pressure readings were were 1.05 mm., 0.25 mm. and 0.85 mm., respectively. The computations were made, therefore, on the basis of the volumes determined directly with helium, using the lowest pressure readings, and considering that a stable pressure equilibrium was reached in each case.

Summary

Values were obtained for the density of water adsorbed on silica gel by volume measurements using a gas dilatometer with helium as the inactive gas. For small quantities of water up to 4.36% these measurements showed that the density of water adsorbed on silica gel at 25.02° is greater than the density of liquid water at the same temperature.

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THE THERMODYNAMIC PROPERTIES OF MOLTEN SOLUTIONS OF LEAD CHLORIDE IN LEAD BROMIDE

BY E. J. SALSTROM AND J. H. HILDEBRAND

The investigation described in this paper represents a continuation of the plan begun several years ago in this Laboratory by Hildebrand and Ruhle[1] of studying the thermodynamic properties of fused salt solutions. There were two disturbing factors involved in that investigation, first, the system studied, solutions of lead chloride with potassium chloride, was somewhat complex, as indicated by the existence of several solid compounds; second, the chlorine electrode was produced by polarization, a procedure that did not guarantee its reversibility. In the present investigation a system has been selected, lead bromide with lead chloride, which, according to Monkmeyer,[2] shows no evidence of compound formation in the solid state. The freezing point varies linearly with the composition, indicating a continuous series of solid solutions. The second complication mentioned above has been avoided by our success in constructing a reversible bromine electrode suitable for use under these conditions.

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[1] Hildebrand and Ruhle, THIS JOURNAL, 49, 722 (1927).

[2] K. Monkmeyer, Neues Jahrbuch, 22, 1 (1906).