

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

EFFECT OF HYDROGEN-ION CONCENTRATION ON THE FLOCCULATION VALUES OF FERRIC OXIDE SOLS. I

BY FRED HAZEL AND C. H. SORUM

RECEIVED OCTOBER 2, 1930

PUBLISHED JANUARY 12, 1931

Preparatory to the investigation of an irregular series for colloidal iron oxide, using potassium ferrocyanide as the added electrolyte when working with sols of various H^+ -ion concentrations, it has been thought worth while to observe the behavior of these sols with a representative list of ions which do not produce the recharging phenomena. It is well known that colloidal iron oxide when freshly prepared by hydrolysis of ferric chloride contains, as the chief contaminants, hydrochloric acid and ferric chloride in relatively large quantities. Moreover, such sols show great stability toward added electrolytes. However, much of this stability is lost when the colloid is dialyzed and the impurities subsequently removed.

In the following study a large volume of a stock sample of the sol was prepared by hydrolysis of ferric chloride and dialyzed for a week or more at a temperature ranging between 80 and 90°. Later measurements showed the product to be quite free from hydrochloric acid, the P_H of the purified system being above 6. To obtain sols with a suitable range of hydrogen-ion concentrations the stock sample was diluted thus

Sol number	Diluted with
1	Equal volume of water
2	Equal volume of approximately $N/5000$ HCl
3	Equal volume of approximately $N/2000$ HCl
4	Equal volume of approximately $N/1000$ HCl
5	Equal volume of approximately $N/500$ HCl
6	Equal volume of approximately $N/200$ HCl

Concentration of sol (before dilution), 1.24 g. Fe/ liter

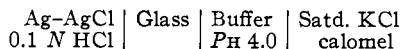
The H^+ -ion concentrations were determined with a glass electrode of the type described by MacInnes and Dole.¹ The membranes were from a glass recommended by them and were about 10 mm. in diameter. A vacuum tube potentiometer was selected for a "null" instrument. The apparatus is described by Partridge.² The circuit was modified, however, in that a wall galvanometer was used in place of the milliammeter and a student potentiometer in place of the voltmeter in his hook-up. The principle of operation is the same in both instances but the substitution of the galvanometer permits the use of a triode plate current which is much smaller (of the order of magnitude of 10^{-6} ampere) than that employed in the original device. P_H determinations on buffer solutions

¹ MacInnes and Dole, *THIS JOURNAL*, **52**, 29 (1930).

² Partridge, *ibid.*, **51**, 1 (1929).

made with this set-up using glass electrodes have been checked against values obtained with an ordinary, although accurate, hydrogen electrode circuit and have been found to agree within 0.03 of a P_H unit. Hydrogen-ion concentrations of the sols in this study were checked numerous times with as many as eight different glass electrodes, the results deviating by not more than ± 0.05 of a P_H unit from the value given. (P_H values have also been determined in other systems where repeated trials have given results dependable to 0.1 of a P_H unit.³ Among these systems may be mentioned Fe_2O_3 sol + H_2O_2 ; acid + H_2O_2 ; concentrated acid + SnCl_2 ; and methylene blue + hypochlorite.)

³ Standardization of the electrodes was accomplished by measuring the potential against buffer solutions the P_H of which had been previously determined by means of a hydrogen electrode. Thus if the e. m. f. of a cell



is 0.135 v., the constant of the circuit, which compensates for any current flowing through the cell at balance and also includes the asymmetry potential of the glass membrane, may be calculated by the equation

$$P_H = \frac{E_{\text{cell}} + C}{0.059} \text{ at } 25^\circ$$

Substituting the values of P_H and E , we have

$$4.0 = \frac{0.135 + C}{0.059} \text{ or } C = 0.101 \text{ v.}$$

Providing this particular electrode is sensitive to the right degree to changes in H^+ -ion concentration, it should show for a buffer of P_H 5.0 an e. m. f. equal to that calculated from the preceding formula

$$5.0 = \frac{E + 0.101}{0.059} \text{ or } E = 0.194 \text{ v.}$$

Similarly a buffer of P_H 6.0 should have an E value 0.059 v. higher than that for a solution of P_H 5.0. Of course this is true only if the constant of the circuit has undergone no change during the measurements; hence it is of advantage to check the constant before and after each determination using the standard buffer of P_H 4.0.

It has been found in the present work that newly prepared electrodes are rarely suitable for immediate use. Thus when a freshly blown electrode completes a cell containing a buffer of P_H 4.0 it may show a potential of greater than 0.6 v. It is impossible to work with such an electrode because the initial value of E is not constant. The high value of E indicates a large membrane potential. Moreover, such electrodes in the circuit seem to introduce capacity effects that make conditions such that measurements are not practical with the potentiometer described. However, upon aging these electrodes in an acid solution of more or less indifferent concentration, the value of E decreases until after several days it becomes practically constant. In other words, equilibrium is established in the membrane and the asymmetry potential is constant in so far that the constant, C , of the circuit does not vary over ± 0.005 v. during a day's run. Happily, also, capacity effects are absent at equilibrium and the electrode can be used for accurate measurements in a cell unprotected by shielding. It has also been found that when newly prepared electrodes show an initial value of E in the vicinity of zero, for the cell containing the standard buffer, they are sluggish in detecting changes in hydrogen-ion concentration even after weeks of aging.

Flocculation values were obtained by adding 2 cc. of sol to 3 cc. of electrolyte in 12.7-cm. pyrex test-tubes and permitting to stand for twenty-four hours. Those concentrations which were just sufficient to produce complete coagulation in the allotted time were taken as the limiting values, the so-called flocculation value being calculated in millimoles per liter from the latter in the usual manner. While this method has its recognized disadvantages, it was applicable in the present case where relative measurements were sought.

Table I includes representative data for some typical electrolytes. The P_H was determined after two volumes of the particular sols, whose flocculation values are given, were diluted with three volumes of distilled water.

TABLE I
REPRESENTATIVE DATA

Sol	1	2	3	4	5	6
P_H	5.9	5.4	4.6	3.9	3.4	2.9
	Flocculation values in millimoles/liter					
KCl	16	32	56	76	100	120
KBr	16	32	56	80	100	120
NH ₄ Cl	12	16	40	68	92	116
1/2 BaCl ₂	24	40	88	144	208	
1/3 FeCl ₃	252	252	252	252	252	252
1/3 AlCl ₃	360	360	360	360	360	360
K ₂ SO ₄	0.125	0.12	0.11	0.10	0.09	0.08
(NH ₄) ₂ SO ₄		.125	.115	.100	.090	.075
CaSO ₄	.15	.15	.14	.12	.11	.10
K ₂ CrO ₄	.05	.06	.08	.12	.16	.19
K ₂ Cr ₂ O ₇	.030	.04	.065	.080	.090	.100
K ₃ Fe(CN) ₆	.016	.020	.026	.026	.026	.026
KH ₂ PO ₄	.036	.048	.064	.072	.088	.104
K ₄ Fe(CN) ₆	.012	.016	.024	.028	.028	.028

The electrolytes in the table may be divided into groups: Group 1, which includes uni-univalent salts; Group 2, represented by barium chloride; Group 3, represented by ferric chloride and aluminum chloride; Group 4, including potassium sulfate, ammonium sulfate and calcium sulfate; Group 5, with potassium chromate and potassium dichromate; Group 6, which contains potassium ferricyanide and primary potassium phosphate; finally, Group 7, with potassium ferrocyanide.

With a positive sol, such as those used in the present work, the anion of the added electrolyte is the effective agent in producing coagulation. Hence we observe that the flocculation values for the monovalent anions are relatively higher than those for the bivalent ions and these in turn are higher than those for trivalent anions. The reason for the above grouping of electrolytes will become apparent with this and the following considerations. It can be noted that in groups one and two the flocculation

values of the sols increase strongly and regularly with increase in hydrogen ion concentration of the sols. On the other hand ferric chloride and aluminum chloride do not show any variation in this property of the colloid with changes in the initial P_H of the sol. The anomaly in the behavior of these two salts is explained by examination of the data in Table II, which gives the P_H of the sols after dilution of two volumes of the sol with three volumes of water. The P_H of the coagulated medium obtained by adding the critical concentration of certain of the electrolytes is also shown.

TABLE II
EXPERIMENTAL DATA

Sol.	1	2	3	4	5	6
After dil.	5.9	5.4	4.6	3.9	3.4	2.9
KCl	5.9	5.4	4.7	4.0	3.4	
NH ₄ Cl	6.0	5.5	4.7	3.9	3.4	2.9
FeCl ₃	1.7	1.7	1.7	1.7	1.6	1.7
AlCl ₃	3.5	3.5	3.5	3.5	3.5	3.5
K ₂ SO ₄	6.4	6.0	5.1	4.1	3.5	3.0
(NH ₄) ₂ SO ₄		6.3	5.5	4.2	3.5	3.0
K ₃ Fe(CN) ₆	6.3	6.0	4.9	4.1	3.5	3.0

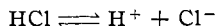
According to the data in this table, if the P_H of the coagulated system is determined after the addition of the flocculating concentration of either ferric chloride or aluminum chloride, the P_H values are constant regardless of the initial P_H of the sol. Both aluminum chloride and ferric chloride, being salts of a strong acid and weak bases, hydrolyze to a pronounced degree when dissolved in water to give hydrochloric acid as one of the products. We may then consider that when we use these salts as the coagulators we are adding not only the ions of the salts but also hydrogen ions. The amount of the latter derived by the introduction of the salt in any case will depend, among other things, upon the concentration of hydrochloric acid already present. For example, an aluminum chloride solution of a given concentration when added to sol number 1 with a H⁺-ion concentration corresponding to a P_H of 5.9 will hydrolyze to a greater extent and hence produce more hydrochloric acid than in the case of sol number 6 where the P_H is 2.9. In the simple case we may be dealing with the equilibria



or



and



so that a buffer action is maintained by the common ion effect and enables the one or the other reaction to be reversed, making the gross hydrogen ion concentration constant.

Freundlich⁴ states that small concentrations of hydroxyl ions raise the stability of negative sols but that the symmetrical effect of the H^+ ion with positive sols is less clearly visible since the latter are almost all hydroxide sols so that a chemical action takes place. (Incidentally, in the present work the concentration of acid used in charging the sols did not go above $N/200$ and the amount of ferric ion produced by the solvent action was only sufficient to give a very faint coloration with the ammonium sulfocyanate test.) Somewhat later, Freundlich and Lindau⁵ working with colloidal iron oxide have shown that the flocculation values for sodium chloride increase with increasing hydrogen-ion concentration of the sol. Their method was to alter the P_H of the system by adding different concentrations of sodium acetate-acetic acid buffers. Mukherjee and Sen,⁶ experimenting with an arsenious sulfide sol, account for the large flocculation value of salts with organic ions as being due to increased OH^- -ion concentration from hydrolysis, the hydroxyl ion serving to charge the colloidal particles more negatively.

In cases under Groups 1, 2 and 5, the charging property of the hydrogen ion on colloidal ferric oxide is shown clearly since the stability as measured by flocculation data increases as the acid concentration becomes greater. The same is true in Group 6, which includes the trivalent ferricyanide and phosphate ions. Here again we see that the flocculation value increases with increasing acidity. However, an anomaly is encountered when the electrolytes in Group 4 are considered. The flocculation values of potassium sulfate, ammonium sulfate and calcium sulfate decrease with increase in H^+ -ion concentration. The decrease in stability in this case is a well-defined, reproducible phenomenon. To avoid any possibility of error in observation of the peculiar conduct of these electrolytes, the experiment has been checked repeatedly using very pure reagents. The results have been the same. At present there is no available explanation for such an unexpected behavior. It may be mentioned, however, that other investigators have observed somewhat similar, if not related, abnormalities in the coagulation of colloids by ions with different valences. Mukherjee and Sen⁶ in studying the stabilizing effect of hydrogen sulfide on arsenious sulfide sols found that whereas it took higher concentrations of monovalent ions to coagulate such sols, they behaved in an anomalous manner when solutions of barium chloride, strontium chloride, magnesium sulfate, and thorium nitrate were used, the sols containing hydrogen sulfide becoming less stable. On the other hand, Ghosh and Dhar⁷ have found

⁴ Freundlich, "Colloid and Capillary Chemistry," Methuen and Co., London, 1922, p. 422.

⁵ Freundlich and Lindau, *Kolloid-Z.*, **44**, 198 (1928).

⁶ Mukherjee and Sen, *J. Chem. Soc.*, **115**, 461 (1919).

⁷ Ghosh and Dhar, *J. Phys. Chem.*, **30**, 830 (1926).

that "when a ferric hydroxide sol is coagulated by hydrochloric acid and potassium sulfate, appreciable stabilization takes place because of the adsorption of hydrogen ions. The precipitation value of potassium sulfate with ferric hydroxide sol is 0.10 millimoles per liter when no acid is present. In the presence of 0.1 cc. of *N*/500 hydrochloric acid the precipitation value becomes 0.15 mml. On further increasing the concentration of acid it is found that the precipitation value of potassium sulfate remains constant when 0.3, 0.4 or 0.5 cc. of *N*/500 hydrochloric acid is added." A comparison of their results, on a sol prepared by the Krecke method follows. Both sols had approximately the same concentration.

Ghosh and Dhar		Hazel and Sorum	
Concn. of HCl after dilution	F. V., mm./l.	Concn. of HCl after dilution	F. V., mm./l.
0	0.10	0	0.125
<i>N</i> /30000	.15	<i>N</i> /25000	.12
<i>N</i> /15000	.167	<i>N</i> /10000	.11
<i>N</i> /10000	.175	<i>N</i> /5000	.10
<i>N</i> /7500	.175	<i>N</i> /2500	.09
<i>N</i> /6000	.175	<i>N</i> /1000	.08

The agreement is not good and will have to be charged to the complex nature of the system with which we are working.

The potassium ferrocyanide data are for flocculation of a positive sol. Higher concentrations of this electrolyte recharge a positive ferric oxide sol to the negative form and it is thus possible to obtain an irregular series. A later paper will include the relation of the irregular series to H^+ -ion concentration of the sol.

Summary

1. The stability of colloidal iron oxide has been shown to be related to the H^+ -ion concentration of the sol.
2. The stability increases with increasing acidity for potassium chloride, potassium bromide, ammonium chloride, barium chloride, potassium chromate, potassium dihydrogen phosphate, potassium ferricyanide and potassium ferrocyanide.
3. Ferric chloride and aluminum chloride hydrolyze to such an extent that the initial P_H of the sol is altered to a constant value, the stability of the colloid being independent of the initial P_H but dependent on the constant value.
4. Sulfates are anomalous in that the sols with lower P_H values are less stable than those of higher P_H values.