Table II

Experimental Results

m $HClO_4$	m $Mn(ClO_4)_2$	E_c, mv.	E_0
0.0940	0.050	1.2360 ± 0.1	1.238
.0992	.010	1.2525 ± 0.6	1.238
.0978	.005	1.2580 ± 0.4	1.237
.0983	.002	1.2663 ± 0.4	1.236
.0983	.001	1.2726 ± 0.4	1.234
		Average	1.237

Based on these results the value +1.236 for the normal potential of the electrode $MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$ is probably correct within 2 mv.

II. The Manganous–Permanganate Electrode.—Using the value +1.586 determined by Brown and Tefft[3] for the potential of the manganese dioxide–permanganate electrode and the value as determined above, the calculated value for the manganous–permanganate electrode in the presence of an acid at unit activity is +1.446 volts.

Summary

A value of +1.236 volts was obtained for the oxidation potential of the reaction $MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$ in perchloric acid solution.

For the oxidation potential of the reaction $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$, the value +1.446 volts was calculated.

Lincoln, Nebraska

[Contribution from the Laboratory of General Chemistry, University of Wisconsin]

CHLORIDE-FREE FERRIC OXIDE HYDROSOLS AND THE BURTON–BISHOP RULE

By R. C. Judd and C. H. Sorum

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Introduction

Although the general validity of the Burton–Bishop rule[1] relative to the effect of concentration of colloid on the flocculation values of electrolytes seems to be quite well established in the case of the widely studied arsenic trisulfide sols, it is quite as definitely discredited by the behavior of ferric oxide hydrosols. Kruyt and van der Spek[2] have shown that for colloidal hydrous ferric oxide the precipitation values of all electrolytes, monovalent as well as di- and trivalent, decrease with dilution of

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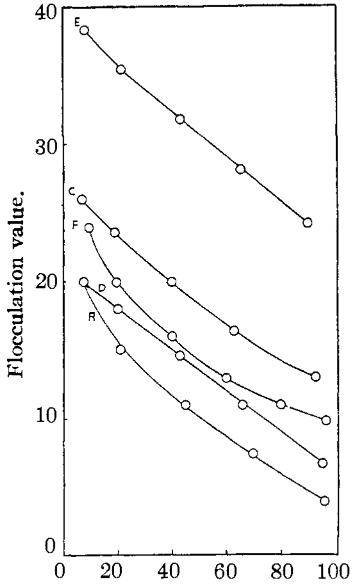
[1] Burton and Bishop, *J. Phys. Chem.*, **24**, 701 (1920).

[2] Kruyt and van der Spek, *Z. Kolloidchemie*, **25**, 3 (1919).

the sol. These results have been further verified by Weiser and Nicholas[3] and Boutaric and Perrean.[4]

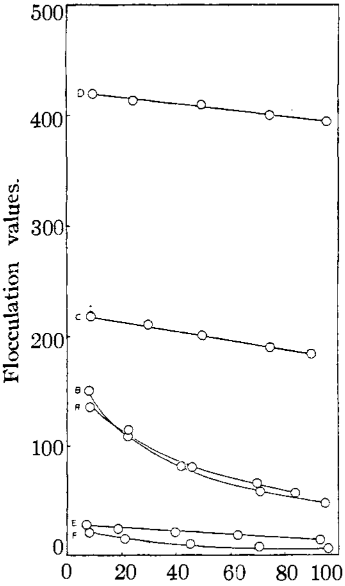
Inasmuch as the ferric oxide hydrosols prepared in this Laboratory[5] seem to be different from ferric oxide sols previously investigated, it was deemed important to study the influence of change of concentration of sol upon the flocculation values of electrolytes with this particular colloid.

Preparation and Purification of Sol.—The chloride-free sol was prepared and purified in accordance with the method already described.[5] In its final purified state it contained 3.042 g. of iron per liter.



A, NaCl; C, KCl; D, $KBrO_3$; E, $K_4Fe(CN)_6$; F, NaCl.

Fig. 1.—Variation of flocculation values of monovalent ions with sol concentration.



A, $NaNO_3$; B, $AgNO_3$; C, $Al(NO_3)_3$; D, $ThCl_4$; E, KCl; F, NaCl.

Fig. 2.—Variation of flocculation values of monovalent anions accompanied by cations of different valences.

Coagulation Studies.—The classical method of adding electrolyte directly to the sol and noting the concentration required to cause complete coagulation after a given length of time, being the method upon which the previously mentioned conclusions were based, was employed. The details of this method were as follows. Exact volumes of sol placed in pyrex test-tubes were diluted to ten cubic centimeters with solutions of electro-

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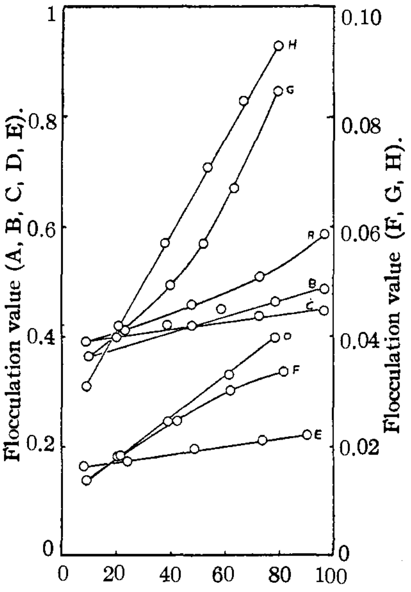
[3] Weiser and Nicholas, *J. Phys. Chem.*, **25**, 742 (1921).

[4] Boutaric and Perrean, *J. chim. phys.*, **24**, 496 (1927).

[5] Sorum, This Journal, **50**, 1263 (1928).

lyte of varying concentrations. The minimum final electrolyte concentration required to cause complete clearing after two hours was taken as the flocculation value. The flocculation value is recorded as millimoles of electrolyte per liter of final solution. The original undiluted sol, containing 3.042 g. of iron per liter, was taken as the 100% sol. The different percentage dilutions were calculated on the basis of the final volume of the flocculation mixture.

The results of the flocculation studies are summarized graphically in Figs. 1, 2 and 3. They emphasize the fact that the ferric oxide sol studied followed the rule of Burton and Bishop.



A, K_2SO_4; B, $K_2C_2O_4$; C, Na_2SO_4; D, $K_2Cr_2O_7$; E, Ag_2SO_4; F, $K_4Fe(CN)_6$; G, $K_3Fe(CN)_6$; H, $NaKC_4H_4O_6$.

Fig. 3.—Variation of flocculation values of polyvalent anions accompanied by monovalent cations.

Reference to Fig. 2 will show that the concentration of monovalent anion required to cause complete flocculation depends to a marked degree upon the valence of the cation with which it is associated; the higher the valence of the cation the greater the flocculation value of the given anion. This is in agreement with Weiser's conclusions.[6]

A comparison of these flocculation values with those reported by other investigators working with the same electrolytes and similar ferric oxide sols[7] will show that the latter are uniformly higher.

The behavior of potassium ferrocyanide as shown in Curves 3F and 1E is typically irregular. In 3F the sol is positive and shows flocculation values consistent with its behavior toward a high-valence negative ion. Higher concentrations of ferrocyanide have reversed it to a negative sol in 1E, where its behavior is typical of that of a negative sol toward a monovalent positive ion.

The Influence of Ferric Chloride on Flocculation Values of Sodium Chloride.—In reviewing the results of the study up to this point, it is to be noted that the sol under observation has three features which seem to distinguish it from other ferric oxide sols. First, it contains no detect-

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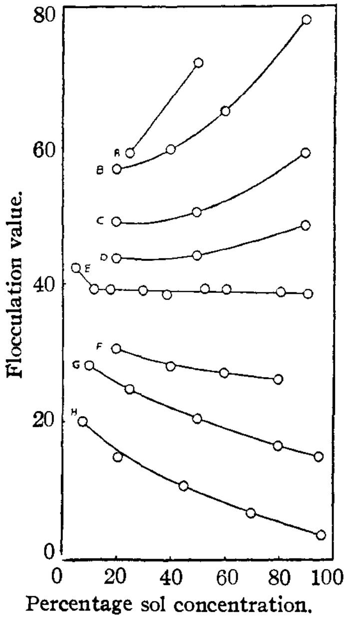
[6] Weiser, "Colloid Symposium Monograph," **1926**, Vol. IV, p. 354.

[7] Kruyt and van der Spek, *Kolloid-Z.*, **25**, 1 (1919).

able chloride ion; second, it requires uniformly lower concentrations of electrolyte to cause coagulation; third, it follows the Burton–Bishop rule. The immediate inference would be that the first feature, that is, freedom from chloride, is responsible for the second and third. To test this inference, ferric chloride was added in varying amounts to the pure sol and the flocculation values for sodium chloride obtained as before. The results are summarized in Fig. 4.



Millimoles of $FeCl_3$ added per liter: A, Kruyt's values; B, 0.16; C, 0.12; D, 0.10; E, 0.09; F, 0.06; G, 0.03; H, 0.00.

Fig. 4.—Influence of $FeCl_3$ on variation of flocculation values of sodium chloride.

They indicate very definitely that flocculation values and flocculation behavior are a function of the purity of the sol. They suggest that the failure of ferric oxide sols to follow the Burton–Bishop rule is due to lack of purity of the sol. They seem to justify the claim that the ferric oxide sols prepared in this Laboratory are more pure, more nearly free from electrolyte, than the ferric oxide sols that have been studied elsewhere. These pure sols obey the Burton–Bishop rule; also, they give lower flocculation values. On being treated with ferric chloride they cease to obey the above rule, and the flocculation values immediately become higher. Apparently, they obey the Burton–Bishop rule and have low flocculation values because the amount of impurity present is quite low.

As previously noted the sol contained 3.042 g. of iron per liter. This corresponds to 4.34 g., or 27.125 millimoles of iron oxide per liter. By consulting Curve B, Fig. 4, it will be noted that when 0.16 millimole of ferric chloride per liter was added, both the actual flocculation value for sodium chloride and the relation of flocculation value and sol concentration come very close to the values given by Kruyt,[7] (Curve A, Fig. 4). The ratio of the number of millimoles of ferric oxide to millimoles of ferric chloride added is 169.5. This ratio comes reasonably close to the values claimed by investigators who have made a study of the chloride content of carefully purified sols.[8]

Summary

1. A chloride-free ferric oxide hydrosol was prepared by high-temperature hydrolysis and dialysis of ferric chloride.

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[8] Pauli and Rogan, *Kolloid-Z.*, **35**, 131, 1924.

2. Flocculation values for a number of electrolytes were determined by the classical method.

3. The chloride-free ferric oxide sol prepared was found to differ from ferric oxide sols prepared and studied by other investigators in that it followed the Burton–Bishop coagulation rule. Furthermore, it gave uniformly lower flocculation values than did these sols. By adding chloride to this chloride-free sol its behavior could be made to conform to that displayed by similar sols prepared by other investigators. The conclusion was drawn that the striking behavior of this sol was due to the absence of detectable chloride. This behavior serves to emphasize the fact that the variation of the flocculation value of anions with dilution of the sol is a function of the purity of the sol; that is, the validity or invalidity of the Burton–Bishop rule is apparently determined by the purity of the sol.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

THE SOLUBILITY, SPECIFIC GRAVITY AND INDEX OF REFRACTION OF AQUEOUS SOLUTIONS OF FUMARIC, MALEIC AND *i*-MALIC ACIDS

BY N. A. LANGE AND M. H. SINKS

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The stereoisomerism of these acids makes any data on them of theoretical interest. The physical properties are scattered throughout the literature, mostly as isolated observations; the latest and most comprehensive list of values are those reported by Weiss and Downs.[1] The present investigation was undertaken with a view of obtaining a more complete series of values—the solubility in water at rather close intervals of temperature, the density of aqueous solutions and the refractive index of aqueous solutions. The values for the solubility are in good agreement with those reported by Weiss and Downs with the exception of the solubility of maleic acid at 60°; the value at this temperature as reported by them was found to be very close to the solubility at 50°.

The acids used in these determinations were the commercial grades which were subjected to a further purification. After two crystallizations from water it was found that the melting points of maleic and fumaric acids remained constant. Malic acid, which is very soluble in water, was purified by a crystallization from water, filtering, digesting the crystals with hot acetone, cooling to room temperature, filtering and air drying at room temperature. The three acids were then dried *in vacuo* at room temperature; the melting points of maleic, fumaric and malic acids thus obtained were found to be 130, 284 and 128.5°, respectively. Weighed samples when dis-

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[1] J. M. Weiss and C. R. Downs, THIS JOURNAL, **45**, 1003 (1923).