[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

A Study of the Passivity of Iron and Aluminum

BY W. H. CONE AND H. V. TARTAR

In previous work in this Laboratory[1] on the speed of a reaction in a heterogeneous system, *viz.*, colloidal aluminum hydroxide with hydrochloric acid, it was found that the presence of certain anions had a marked effect. It seemed an advisable extension of the investigation to study the effect of these anions on the rate of solution of passive iron and aluminum in nitric acid. As the work progressed, it has gradually been enlarged until it is, we believe, a contribution to the literature on the passivity of these metals.

The object of this paper is to present experimental results on the following topics: (a) the passivity of iron and aluminum in nitric acid, (b) the passivity of iron in concentrated chromic acid, (c) the passivity of iron in silver nitrate solutions.

Experimental

Materials and Apparatus

The iron was No. 30 wire used "for standardizing," Fe 99.84%.

The aluminum was in the form of thin foil: Fe, 0.50%, and SiO_2 0.40%. The presence of these impurities had no influence on the experimental results.

The nitric acid was purified by distillation. The stock solution had sp. gr. 1.42, and was free from chlorine, sulfate, phosphate and heavy metals.

The phosphoric acid was "C. P. analyzed grade," 85%, and contained only traces of other acids. The acid content was checked by analysis.

The chromic acid was of best quality obtained from Merck and contained approximately 85% CrO_3. The e. m. f.'s of the cell: metal, acid solution, normal KNO_3, normal KCl, HgCl + Hg, were read to within 1 millivolt with a Leeds and Northrup student type potentiometer. This was sufficiently accurate for measuring the slightly varying e. m. f.'s under consideration. The e. m. f. of cells of the type formulated above was considered positive when negative electricity flowed from right to left. The single potentials, metal against acid solutions, were calculated by taking the potential difference of the normal calomel electrode (electrode, electrolyte) to be −0.282 volt.[2] No correction was made for the liquid–liquid potentials, which remained essentially constant, because only changes in potential difference were of significance. The single potential differences designated in the tables are the e. m. f.'s of the half cell: metal, acid solution, normal KNO_3.

The experiments were made in apparatus kept in a thermostat held at 25° ± 0.1.

Experiments with Iron in Nitric Acid.—To determine the effect of phosphoric acid on the rate of solution of iron in nitric acid, weighed pieces of iron wire 32 mm. long and 0.2 mm. in diameter were placed in small bottles containing 10 cc. of mixtures of concentrated nitric acid (sp. gr. 1.42) and phosphoric acid (85%). The bottles were stoppered and placed in a thermostat at 25°, without shaking, for twenty-four hours. The acid was then poured off the wire and the bottle held in a stream of water to quickly wash free of acid. The wires were then dried with a soft cloth and weighed.

The e. m. f.'s of cells using iron in mixtures of the same concentration as those used for the dissolution tests were measured. The e. m. f.'s were not steady, usually becoming more negative for a few minutes and then more positive rather rapidly for two or three hours, after which the changes were rather small. The changes of e. m. f. with time for three typical runs are given in Fig. 1. When the concentration of phosphoric acid was greater than 0.058 mole per mole of nitric acid, the carefully cleaned iron wire did not become passive; the e. m. f. of the cell changed in an instant to about 0.2 volt and the rate of solution was very rapid.

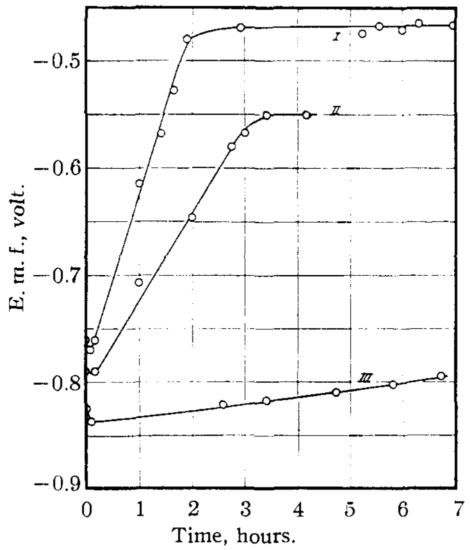

Fig. 1.—Change of e. m. f. with time: (1) 5.58 × 10^{-2} mole of H_3PO_4 per mole of HNO_3; (2) 2.29 × 10^{-2} mole of H_3PO_4 per mole of HNO_3; (3) iron in nitric acid, 1.42 sp. gr.

The changes of potential difference of metal–solution and of the dissolution in nitric acid with increasing concentration of phosphoric acid are shown in Table I and Fig. 2. For convenience, the moles of phosphoric acid have been multiplied by the factor 10^2.

When the ratios of the acids were 0.0824 and 0.185, dissolution measurements could only be obtained by first making the iron passive in concentrated nitric acid before

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[1] Tartar, Bryan and Shinn, THIS JOURNAL, **55**, 2266 (1933).

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 407.

TABLE I

THE POTENTIAL AND DISSOLUTION OF IRON IN MIXTURES OF NITRIC ACID (SP. GR. 1.42) AND PHOSPHORIC ACID, 85% AT 25°

Moles H_3PO_4 × 10^2/mole HNO_3	0.0	0.94	1.52	2.29	3.09
Mg. iron dissd. in 24 hours	0.2	0.9	2.1	2.2	2.8
Potential, metal-soln., after 3 hours	−1.102	−0.991	−0.960	−0.862	−0.837
Moles H_3PO_4 × 10^2/mole HNO_3	3.83	4.73	5.58	8.24	18.5
Mg. iron dissd. in 24 hours	3.2	3.8	4.0	5.5	7.5
Potential, metal-soln., after 3 hours	−0.807	−0.756	−0.749	.....	.....

placing in the phosphoric acid mixture. This treatment results in a much slower drop in the potential and evidently accounts for the change in the slope of the curve, Fig. 2.

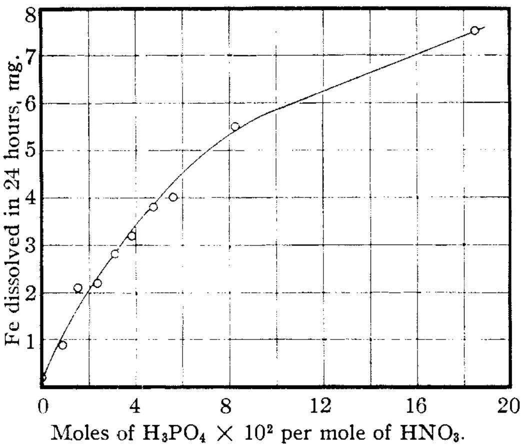


Fig. 2.—Influence of H_3PO_4 on the dissolution of iron.

The influence of the dilution of the nitric with phosphoric acid on the potential difference is shown in Fig. 3. The change approaches a linear function of ratio of the phosphoric to the nitric acid.

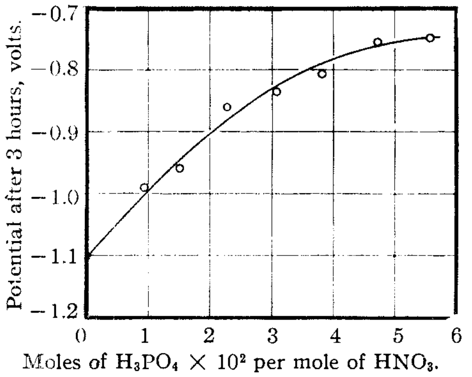


Fig. 3.—Influence of H_3PO_4 on potential difference.

The effect of phosphate on the dissolution and potential of iron in concentrated nitric acid was also determined using potassium dihydrogen phosphate, KH_2PO_4, to avoid dilution and to obviate great reduction in hydrogen-ion concentration. The results were similar to those obtained using the phosphoric acid solution; the data from a typical run are given in Table II.

TABLE II

THE POTENTIAL AND DISSOLUTION OF IRON IN NITRIC ACID (SP. GR. 1.42) CONTAINING KH_2PO_4

Moles KH_2PO_4 × 10^2/mole HNO_3	0.0	0.14	0.28	0.57	1.41	2.83
Mg. iron dissd. in 15 hrs.	0.1	0.2	0.3	0.4	1.7	2.4
Potential, metal-soln., after 3 hrs.	1.102	−1.066	−1.021	−1.013	−0.807	−0.775

From the rapid change in e. m. f. shown in Fig. 1, it was suspected that most of the metal was dissolved during the first two or three hours. Several experiments showed that this was not the case. The results of a typical run on the rate of solution of iron in concentrated nitric acid containing 0.0383 mole of phosphoric acid per mole of nitric acid are reported in Table III and Fig. 4.

TABLE III

RATE OF SOLUTION OF IRON IN HNO_3 + H_3PO_4 MIXTURE

Time, hours	5 sec.	5	10	15	20	25
Mg. of Fe dissd.	0.2	2.2	2.9	3.7	4.3	5.7

The deviations were no more than would be expected due to the impossibility of reproducing in a short interval the same passive condition in each iron sample when variations in surface conditions have so great an influence.

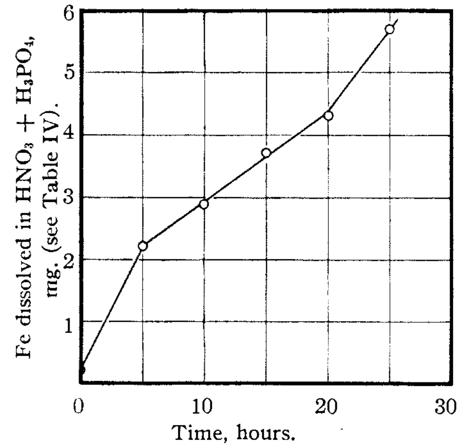


Fig. 4.—Rate of solution of iron in HNO_3 + H_3PO_4 mixtures.

With concentrations of phosphoric acid as high as that used in this test the time of passivation is two to five seconds. During this period solution is very rapid. The average of a number of determinations showed the amount dissolved in this short time interval to be approximately 0.2 mg. In some extreme cases it was as large as 0.4 mg. Figure 4 shows that the amount of iron dissolved is approximately proportional to the time.

Measurements were also made using sodium sulfate instead of the potassium phosphate. Since sodium sulfate is only sparingly soluble in concentrated nitric acid, the acid was diluted in the ratio nine parts by volume of acid to one part of water to increase the solubility of the sulfate. The dissolution of the iron was found to increase and the potential to become less negative with increasing concentrations of sulfate; see Table IV.

TABLE IV

EFFECT OF SULFATE ON DISSOLUTION AND POTENTIAL OF IRON IN NITRIC ACID (SP. GR. 1.39)

Moles $Na_2SO_4 \times 10^2$/mole HNO_3	0.0	0.51	1.54
Mg. Fe dissd. in 24 hrs.	.4	.7	0.9
Potential, metal-soln., after 3 hrs.	−1.089	..	−1.032

Some experiments were tried on the influence of pressure on the passivity of iron in nitric acid. When an iron wire, partially immersed in concentrated nitric acid, was brought under reduced pressure (20 mm.) the metal became active, first at the surface of the liquid and then gradually downward until finally the whole wire was active. When air was then admitted and the pressure permitted to increase, immediate passivity resulted. Activation did not take place with reduced pressure when the iron was immersed completely in the acid.

Experiments with Iron in Chromic Acid.—Iron which had been exposed to air and then placed in concentrated chromic acid (50% CrO_3 or higher) exhibited extreme passivity and no measurable amount of dissolution took place. This passivity was prevented or destroyed, however, by the addition of small amounts of electrolytes to the acid or by simply dipping the iron wire in the electrolyte solution before placing in the acid. The molar concentrations of some substances which are just sufficient to produce activity in concentrated chromic acid solutions (50 to 65% CrO_3), whether dissolved in the chromic acid or used as separate solutions, were found to be as follows: KH_2PO_4, 0.008 *M;* H_3PO_4, 0.008 *M;* NaCl, 0.016 *M;* NaF, 0.016 *M;* Na_2SO_4, 0.03 *M;* $FeSO_4$, 0.03 *M* and KNO_3, 2.0 *M*. The concentration of the electrolyte at the surface of the iron when first brought in contact with the chromic acid determined whether the iron was active or passive. Once active, the iron continued to react until complete dissolution took place. The concentrated chromic acid does not exert a passivifying effect on active iron.

Air-exposed iron was made active toward concentrated chromic acid by keeping the metal under reduced pressure (20 mm.) for about an hour before bringing in contact with the acid. The iron was also activated by placing for five minutes in an atmosphere of hydrogen. Activation of the iron was readily effected by connecting for a few minutes to an active piece of iron in the same solution of chromic acid. The direction of the electric current showed the passive metal to be the cathode. When the air-exposed iron was partially immersed in the chromic acid and then activated in any manner and then more of the wire immersed, the entire immersed portion became active, due to local action between the active and passive portions.

Some experiments were made to determine whether a coating of iron oxide would make the iron passive in concentrated chromic acid. Iron which was permitted to rust until well covered with ferric oxide or heated in air and oxidized to give a bluish color, was, after exposing to air, placed in the concentrated chromic acid. The oxide readily dissolved, leaving passive metal with a bright, clean surface. When the oxidized iron was put under reduced pressure (20 mm.) for an hour, however, and then the chromic acid admitted, the iron oxide dissolved and the metal was active and underwent total dissolution.

The electrical potential difference between active and passive iron in concentrated chromic acid (65% CrO_3) was found to be approximately 1.3 volts. The air-exposed iron always gave against active iron a potential lower than this when first introduced into the solution, the initial potential depending on previous treatment. If the potential difference was above 0.7 volt, the passive metal became more positive, the maximum value being reached in a few minutes. When the initial potential difference was slightly below 0.7 volt the iron did not remain passive but became active in two or three minutes.

Passivity of Iron in Silver Nitrate Solutions.—Carefully cleaned polished iron exposed to air was passive when placed in 0.1 *M* silver nitrate solution and remained passive for many hours if left undisturbed. When sufficient nitric acid was added to the silver nitrate, the iron became active and silver was rapidly deposited. With the molar concentration of the silver nitrate as large as one-eighteenth that of the molar concentration of the nitric acid, iron polished in air remained passive for hours when carefully immersed in the solutions, even when the concentration of the nitric acid was as high as six molar. When the concentration of silver nitrate was much less than one-eighteenth that of the nitric acid, however, the iron immediately became active. The passivitiy in any of these nitric acid–silver nitrate mixtures may be destroyed by keeping the iron in a hydrogen atmosphere for a few minutes before lowering into the solution. The air-exposed iron was active in 6 *M* and lesser concentrations of nitric acid alone.

Experiments with Aluminum.—The dissolution of aluminum in concentrated nitric acid containing varying amounts of phosphoric acid was determined in the same way as with iron using thin pieces of aluminum foil three centimeters long and one centimeter wide. The results are given in Table V.

TABLE V

DISSOLUTION OF ALUMINUM IN CONCENTRATED NITRIC ACID CONTAINING PHOSPHORIC ACID

Moles $H_3PO_4 \times 10^2$/mole HNO_3	0.00	1.48	2.97	3.53	5.93	7.42
Mg. Al dissd. in 5.5 hrs.	1.0	6.5	10.8	14 2	16.4	18.4

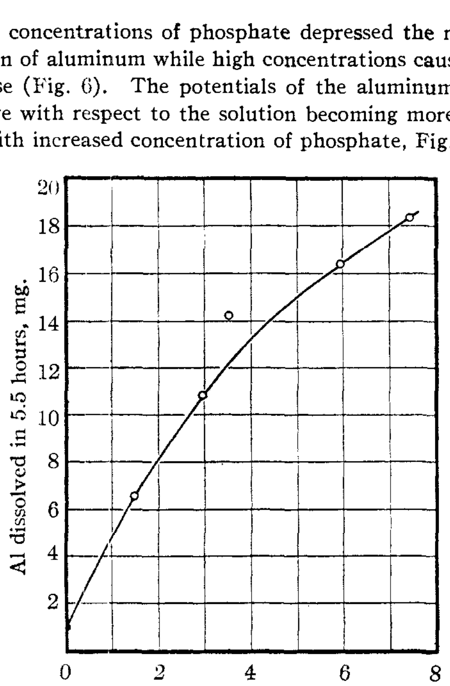
Aluminum, unlike iron, is not rapidly attacked by dilute nitric acid. Determinations were made using 2 *N* nitric acid and KH_2PO_4 as the source of phosphate. The data are reported in Table VI and graphed in Figs. 5 and 6.

TABLE VI

DISSOLUTION OF ALUMINUM IN 2 NORMAL NITRIC ACID CONTAINING KH_2PO_4

Moles $KH_2PO_4 \times 10^2$/mole HNO_3	0.00	3.67	7.35	14.7	22.1	29.4	36.8	73.5
Mg. Al dissd. in 24 hrs.	9.6	5.9	7.1	8.7	10.8	13.3	15.8	18.1
Potential, metal-soln., after 2 hrs.	0.189	0.242	0.348	0.406	0.408	0.414	0.415	0.426

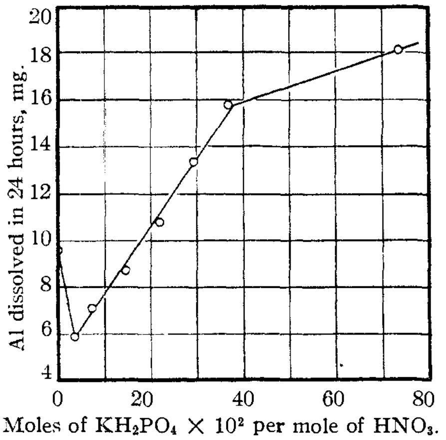
Low concentrations of phosphate depressed the rate of solution of aluminum while high concentrations caused an increase (Fig. 6). The potentials of the aluminum were positive with respect to the solution becoming more positive with increased concentration of phosphate, Fig. 7.



Moles of $H_3PO_4 \times 10^2$ per mole of HNO_3.

Fig. 5.—Influence of H_3PO_4 on the dissolution of aluminum.

The influence of reduced pressure on the activation of aluminum was studied. Freshly cleaned or polished aluminum metal when placed under a pressure of less than 1 mm. did not react with copper nitrate solution or with very clean mercury. Passing hydrogen for some time over the metal to remove oxygen did not make the metal active.



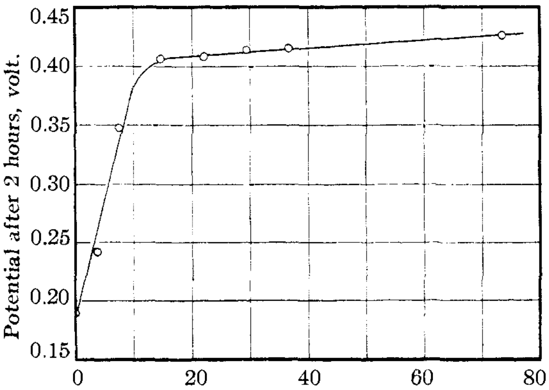
Moles of $KH_2PO_4 \times 10^2$ per mole of HNO_3.

Fig. 6.—Influence of KH_2PO_4 on the dissolution of aluminum.

Discussion of Results

These experiments show that the presence of phosphate, except in small concentrations with aluminum, and of sulfate accelerates the dissolution of these metals in nitric acid. The increase in rate of solution is roughly proportional to the concentration of the phosphate or sulfate. The presence of these also modifies the potential difference between the metal and the solution, the metal becoming more electronegative with respect to the solution. The increase in rate of solution is roughly proportional to the change in potential difference. The data also show clearly that there is no abrupt change from the passive to the active state and *vice versa*. Any rate of dissolution in nitric acid from that of the active metal to that of the very passive state can be obtained by merely varying the phosphate concentration.

The oxide theory of passivity seems not to afford a satisfactory explanation of these data. Both ferric oxide and aluminum oxide, even in colloidal condition, are soluble in nitric acid and more readily soluble in nitric acid containing sulfate or phosphate. Also ferric and aluminum phosphates are readily soluble in nitric acid and would not be precipitated.



Moles of $KH_2PO_4 \times 10^2$ per mole of HNO_3.

Fig. 7.—Influence of KH_2PO_4 on potential difference.

The writers believe that the results are best explained by assuming that the passivity of iron and aluminum in acids is due to an adsorbed oxygen film on the surface of the metals. This assumption is especially applicable in the case of iron. With aluminum the oxygen is held much more tenaciously.

The influence of sulfates and phosphates on the dissolution or iron and aluminum in nitric acid is evidently due to adsorption on the oxygen layer which produces passivity. Colorimetric determinations made in this Laboratory show that iron adsorbs the phosphate from a concentrated nitric acid solution containing two parts per million of phosphorus. Five grams of finely divided iron in 15 cc. of the nitric acid–phosphate mixture adsorbed 20% of the phosphate present.

No explanation is offered of the phenomenon of the passivity of air-exposed iron in nitric acid (6 *M* or less) containing silver nitrate.

Summary

1. The presence of phosphates (except small quantities with aluminum) and of sulfates accelerates the rate of dissolution of iron and aluminum in nitric acid.
2. The presence of phosphate or sulfate modifies the electrical potential difference of passive iron against nitric acid, making the metal more electronegative with respect to the solution.
3. There is no abrupt change with these metals in nitric acid, between the active and the passive states.
4. The effectiveness of anions accelerating dissolution is attributed to the adsorption of these ions at the oxygen film–solution interface.
5. Air-exposed iron is passive in concentrated chromic acid solution. This passivity may be destroyed by reduced pressure, a hydrogen atmosphere, or by wetting with solutions of electrolytes of sufficient concentration.
6. Dilute nitric acid can be made inactive toward air-exposed iron by the addition of silver nitrate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Accelerated and Retarded Diffusion in Aqueous Solution[1]

BY JAMES W. MCBAIN AND CHARLES R. DAWSON

Graham[2] observed that in a mixture of salts the more rapidly diffusing salt diffuses even more rapidly than when diffusing alone into water. In 1874 Marignac[3] recorded a lengthy table of such data, most of which have not yet been accorded quantitative theoretical treatment, nor have his experiments been repeated. Nernst's fundamental paper[4] rests upon the assumption that the diffusion of ions depends not only upon the concentration gradient but also upon the electrostatic forces which are set up in maintaining the law of electroneutrality when ions possess unequal mobilities. Thus even for a single electrolyte such as hydrochloric acid diffusing into water neither ion can exhibit its proper diffusion coefficient (8.05 for H^+, 1.73 for Cl^-) but instead both ions diffuse at the same rate (2.84 at 25°). Planck's papers[5] constitute a more formal statement of the principles utilized by Nernst.

Arrhenius[6] first applied these principles to mixtures of more than two ions. Many later writers have recorded similar work, usually without reference to the earlier originators.

The present paper brings illustrative data of several striking kinds, using the simplest possible materials, potassium chloride and hydrochloric acid. It further reveals hitherto unsuspected possibilities in the field of diffusion by discovering extremely great acceleration of all the constituents, reacting and non-reacting, in experiments with hydrochloric acid and glycine.

A. Experimental Method

The method of employing constant diffusion columns confined within a porous membrane of sintered glass between two homogeneous bodies of liquid affords one of the simplest, quickest, and yet most precise means of studying diffusion in any field of science. The technique has already been described.[7] The temperature was 25.0°. An important improvement for future work is the use of a symmetrical cylindrical cell divided into two equal compartments by the porous disk and provided at each end with two tubes closed with stopcocks, so that after diffusion columns have been established during the first few hours, fresh solutions of original strength may be placed in each compartment. Solutions were analyzed by means of a Zeiss interferometer supplemented by gravimetric determinations or titrations.

Potassium chloride "Kahlbaum for Analysis" was used, and hydrochloric acid diluted from con-

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(1) Read at the meeting of the Pacific Intersectional Division at Salt Lake City, June 13, 1933.

(2) T. Graham, *Phil. Trans. Roy. Soc.* (London), 805 (1850).

(3) C. Marignac, *Ann. chim. phys.*, [5] **2**, 546 (1874).

(4) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(5) M. Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890); *Sitzb. preuss. Akad. Wiss.*, p. 285 (1927); p. 9 (1929); p. 367 (1930); p. 113 (1931).

(6) S. Arrhenius, *Z. physik. Chem.*, **10**, 51 (1892).

(7) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929); J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931); M. E. Laing McBain, *ibid.*, **55**, 545 (1933); C. R. Dawson, *ibid.*, **55**, 432 (1933).