31.7° between these two hydrates in contact with saturated solution in such a way that *d* is stable at lower and *b* at higher temperatures. The range for the stable existence of the *d* is thus limited to the range of temperature lying between 30° and 31.7°, but *d* was observed and its solubility measured at temperatures as high as 38.6°. Thus between 31.7° and 38.6° the *d* exists in a superheated state. As is well known, this is a very rare phenomenon. It is possible that, since the three transition points at 30°, 30.5° and 31.7° lie so close together, we have been deceived as to their exact location, but this seems hardly probable.

The chief value of the curves at present is that they define very exactly the fields of supersaturation and supercooling for the forms already studied. To interpret the curves briefly, we see that at temperatures below 31.5° (on *a* curve) a fused pentahydrate is supersaturated or supercooled in respect to all forms considered in this paper. Above 31.5° supersaturation in regard to *a* ceases. At 34.5° supercooling in regard to $\beta$ ceases, while above 39.5,° 49.5° and 53° supercooling or supersaturation as to *d*, $\alpha$ and *b*, respectively, ceases. The detailed interpretation need not be given here, as any one interested can make it for himself.

We shall extend the investigation to all the remaining forms, including the anhydride.

STANFORD UNIVERSITY, CAL.,
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# A STUDY OF REVERSIBLE OXIDATION AND REDUCTION REACTIONS IN SOLUTIONS.

BY EUGENE P. SCHOCH.

Received August 4, 1904.

## INFLUENCE OF THE CONCENTRATIONS OF THE COMPONENTS UPON THE EQUILIBRIUM IN ACIDIFIED SOLUTIONS OF IODINE, POTASSIUM FERROCYANIDE, POTASSIUM FERRICYANIDE AND POTASSIUM IODIDE.

THE investigation here described was undertaken for the purpose of studying a reversible oxidation reaction in solution. The reaction used was selected on the basis of the following considerations:

(1) The action should be simple.

(2) Each component should be present in relatively large amount, so that its concentration could be varied to a large extent.

(3) The approach to equilibrium from either side should take place with a measurable velocity.

I selected, for investigation, the reversible reaction between iodine and potassium ferrocyanide in acidified solution because (1) the action is probably simple, since it appears to be a mere transfer of ionic charges as per the equation

$$2Fe(CN)_6'''' + I_2 \rightleftarrows 2Fe(CN)_6''' + 2I' ;$$

(2) each component may have its concentration varied between wide limits; (3) the action starting with either iodine and ferrocyanide or iodide and ferricyanide, requires one and a half to two hours to obtain equilibrium.

In addition to fulfilling these conditions, this reaction presented the following advantages: (1) The potentials of ferrocyanide-ferricyanide solutions[1] and of iodine-potassium iodide solutions[2] had been measured; and (2) the state in which iodine exists in the potassium iodide solutions had been clearly explained and determined by Jakowkin.[3]

Equilibrium in a reversible reaction is considered to be the result of two opposite actions having equal velocities, and the observed velocity of change of a mixture which reacts reversibly is proportional to the difference of the velocities of the two opposing reactions. The effect of the concentration of any constituent, according to this view, is evidently the same whether the mixture is in or out of equilibrium,[4] and since equilibrium conditions are usually more accurately determinable, it was decided to obtain these before making any velocity determinations. I present below the results obtained in the study of the equilibrium conditions, trusting to be able to follow this soon with another paper presenting the velocity determinations.

*Chemicals, Preparation of Solutions, Etc.*—The potassium iodide employed was obtained from Kahlbaum, and was found to be free from iodate. A normal solution was prepared practically every day on which it was used.

Potassium ferrocyanide and potassium ferricyanide were both Kahlbaum's "for quantitative work." Half-normal solutions of

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[1] Fredenhagen : *Ztschr. anorg. Chem.*, **29**, 396.

[2] Crotogino : *Ibid.*, **24**, 225.

[3] Jakowkin : *Ztschr. phys. Chem.*, **20**, 20.

[4] Van't Hoff's "Vorlesungen Theor. Phys. Chem.," 1, 182.

these were prepared by weighing out the required amount of salt. The strength of these solutions was also checked by titration with a decinormal solution of iodine, according to Rupp and Schiedt's[1] method, which method I had tested carefully. Both solutions decomposed very slowly;[2] hence fresh solutions were prepared frequently.

For the iodine solution, Kahlbaum's resublimed iodine was employed. Potassium iodide in amount to make exactly a decinormal solution, and iodine for approximately the same concentration, were weighed out and dissolved. The exact titer of the iodine was then found and checked frequently during the progress of the work.

More dilute solutions were prepared from the above as occasion demanded.

*Some Preliminary Determinations by Means of Electromotive Force Measurements.*—Of the substances put into the reaction mixture—namely, potassium ferrocyanide, potassium ferricyanide, potassium iodide, iodine and hydrochloric acid—only the following are involved in the action: Ferrocyanidions, iodine, ferricyanidions and iodions; and the others (potassions and hydrochloric acid) are *quasi* foreign ingredients. While the main problem is the determination of the influence of the concentration of the main ingredients, it is evidently also necessary to know the influence of the concentrations of these other substances. To determine their influence, electromotive force measurements were made, because the potentials of ferrocyanide-ferricyanide solutions and of iodine-potassium iodide solutions are easily and accurately determinable. The method used was the well-known Poggendorff compensation method. A large accumulator was used as the working element, and its current was passed through two equal resistance boxes of 500 ohms each. An Ostwald capillary electrometer was used for a zero instrument; it was sensitive to 0.0001 volt and less. For comparison, two normal cadmium cells were employed. They had been prepared at different times, and since they agreed to within 0.0001 volt, and the measurements in this paper are only comparative, comparisons with a standard cell were not made. Two normal calomel electrodes were prepared which agreed exactly with each other, and hence were con-

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[1] Rupp and Schiedt: *Ber. d. chem. Ges.*, **35**, 2430.

[2] Mathuschek: *Chem. Ztg.*, **25**, 601.

sidered to be correct. They were frequently exchanged in making the measurements, thus guarding against temporary defects in either one. The calomel electrodes, as well as the other electrode vessels and platinized electrodes, were prepared according to directions in Ostwald-Luther's "Hand- und Hilfsbuch."

*Influence upon the Potential of Iodine-potassium Iodide Solutions.*—As shown by Crotogino,[1] the potential of the iodine-potassium iodide electrode depends upon the fraction of the total iodine which is not combined with the potassium iodide. The per cent. of dissociation in any case may be calculated with the aid of Jakowkin's formula.[2] There appears to be no reason why acidifying the solution should have any influence upon the potential; at most, there might be a slight influence, since the thermic dissociation of hydriodic acid is slightly less than the thermic dissociation of potassium triiodide. Crotogino found this latter to be the case. I also found only a very small difference. A solution, N/4 in potassium iodide and N/100 in iodine, gave 0.001 volt less after acidifying with hydrochloric acid (N/20) than before.

The influence of potassions upon iodine-potassium iodide solutions need evidently not be considered, since the quantity of potassions introduced by the ferrocyanide and the ferricyanide is very small in comparison with that introduced by the potassium iodide.

*Influence of Potential of Ferrocyanide-ferricyanide Solutions.*—(1) Influence of concentrations of potassions; *à priori*, it is to be expected that large variation in the concentrations of the potassions will cause, at least, some variation in the ionization of the ferrocyanide and ferricyanide, and hence change the potential. Such is the case, but the variation is small. The addition of potassium chloride to ferrocyanide-ferricyanide mixtures in amounts varying from N/2 to N/8 in the resulting solutions produced less than 0.005 volt difference.

(2) *Influence of Acidification.*—The potentials of the neutral ferrocyanide-ferricyanide solutions were first investigated by Schaum, and afterward by Fredenhagen,[3] both of whom applied the results and formula obtained by Peters,[4]

$$\pi = \text{A} + \frac{\text{RT}}{n\text{F}}\, ln \frac{\text{C (ferricyanide)}}{\text{C (ferrocyanide)}}.$$

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[1] Crotogino: *Ztschr. anorg. Chem.*, **24**, 225.
[2] Jakowkin: *Ztschr. phys. Chem.*, **20**, 20.
[3] Fredenhagen: *Ztschr. anorg. Chem.*, **29**, 396.
[4] Peters: *Ztschr. phys. Chem.*, **26**, 193.

In this formula A is the value of $\pi$ when the two substances are present in the same concentration, since the log. of unity is zero. R, T, *n* and F have the usual significance. The formula enables the calculation of the potential of neutral solutions, the results agreeing to millivolts with the observed values. The formula is evidently based upon the idea that 1 ferrocyanidion changes to 1 ferricyanidion, since the first power of the concentration of both is employed. Hence all mixtures which contain ferrocyanide and ferricyanide in the same ratio should have the same electromotive force, irrespective of the volume of the solution.

Fredenhagen has shown that the potentials of solutions of ferrocyanide-ferricyanide do not change when *slightly* acidified. Nothing is stated anywhere about the effects of stronger acidification. I found that the potential of ferrocyanide-ferricyanide electrodes measured against a normal calomel electrode increases very largely upon acidification, as may be seen from the following trial:

A solution containing 0.01538/N ferrocyanide, 0.00962/N ferricyanide, and 0.50/N potassium chloride, when *neutral,* gave electromotive force = 0.1795 volt; when acidified (= N/20 hydrochloric acid), gave electromotive force = 0.2667 volt.

Though the concentration of the potassions has but little influence upon the potential, yet it was thought best to add them in the form of potassium chloride to correspond to potassions introduced by the potassium iodide in the equilibrium experiments given later on.

Since both $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ are strong acids, about equally dissociated, it was somewhat difficult to understand why acidification should cause this great difference in potential. Hence it was determined to investigate this further by varying the concentrations should not affect the potential as long as the ratio to our present knowledge of these substances, variations in concentrations should not affect the potential as long as the ratio of the molecules or ions remains the same; in other words, the potential depends only upon the *ratio* of the quantities of ferrocyanide and ferricyanide. Such has been found to be the case in neutral solutions. In acidified solutions (= N/20 hydrochloric acid) the concentration was found to effect the potential extensively, and it appeared that the effect is entirely due to the ferrocyanide. When the concentration of the ferrocyanide is kept constant and the concentration of the ferricyanide is varied, the potentials observed agree fairly well with those calculated from the formula,

$$\pi = A + 0.0575 \log. \frac{C \text{ (ferricyanide)}}{C \text{ (ferrocyanide)}}.^{1}$$

TABLE I.—POTENTIALS OF SOLUTIONS CONTAINING 0.50/N POTASSIUM CHLORIDE, 0.05/N HYDROCHLORIC ACID, 0.005/N FERROCYANIDE, AND FERRICYANIDE AS IN COLUMN 1.

| Ferricyanide. | Electromotive force observed. | Electromotive force calculated. |
|---|---|---|
| 0.0025/N | 0.259 | 0.254 |
| 0.0050/N | 0.2709 | Value of A in formula |
| 0.0125/N | 0.294 | 0.2938 |
| 0.0250/N | 0.3108 | 0.311 |
| 0.0375/N | 0.321 | 0.321 |
| 0.0500/N | 0.3276 | 0.328 |

TABLE II.—POTENTIALS OF SOLUTIONS CONTAINING 0.50/N POTASSIUM CHLORIDE, 0.05/N HYDROCHLORIC ACID, 0.0125/N FERROCYANIDE, AND FERRICYANIDE AS IN COLUMN 1.

| Ferricyanide. | Electromotive force observed. | Electromotive force calculated. |
|---|---|---|
| 0.004/N | 0.233 | 0.233 |
| 0.00625/N | 0.2436 | 0.244 |
| 0.0125/N | 0.2625 | Value of A in formula |
| 0.0250/N | 0.279 | 0.2798 |
| 0.0375/N | 0.2868 | 0.288 |
| 0.050/N | 0.294 | 0.296 |

With a still larger quantity of ferrocyanide than was used in the second series above, say, 5 cc. N/2 ferrocyanide solution per 100 cc. total solution, the electromotive force obtained with different concentrations of ferricyanide diverge somewhat from those calculated. When, on the other hand, the ferricyanide is kept constant and the concentration of the ferrocyanide is varied, there is no agreement between the observed results and those calculated with the formula.

TABLE III.—POTENTIALS OF SOLUTIONS CONTAINING 0.50/N POTASSIUM CHLORIDE, 0.05/N HYDROCHLORIC ACID, 0.0125/N FERRICYANIDE, AND FERROCYANIDE AS IN COLUMN 1.

| Ferrocyanide. | Electromotive force observed. | Electromotive force calculated. |
|---|---|---|
| 0.004/N | 0.2979 | 0.2904 |
| 0.00625/N | 0.285 | 0.279 |
| 0.0125/N | 0.2625 | Value of A in formula |
| 0.025/N | 0.224 | 0.244 |
| 0.0375/N | 0.1974 | 0.2355 |
| 0.050/N | 0.1806 | 0.227 |

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[1] This formula is derived from the one mentioned before by substituting numerical values for R, T, F, and $n$ and changing to Brigg's logarithms.

The disagreement between the observed results and those calculated with the formula is shown most strikingly by the following series of electromotive force measurements in which the ratio of ferrocyanide to ferricyanide is kept constant, but the concentration of both together is varied. Theoretically the same electromotive force should be obtained in all cases.

TABLE IV.—POTENTIALS OF SOLUTIONS CONTAINING 0.50 N POTASSIUM CHLORIDE, 0.05 N HYDROCHLORIC ACID, FERRICYANIDE AND FERROCYANIDE IN EQUIVALENT AMOUNTS AS GIVEN IN COLUMN I.

| Concentration of ferrocyanide and of ferricyanide. | Electromotive force observed. |
|---|---|
| 0.005 N | 0.2709 |
| 0.0084 N | 0.2667 |
| 0.0125 N | 0.2625 |
| 0.025 N | 0.2415 |
| 0.050 N | 0.2205 |

The indications are that the effect of the ferrocyanide varies as some power of its concentration other than the first—probably the second power. The above figures, however, agree only very roughly with any such calculations, and since the results obtained further on show better agreement, no definite conclusions are based on the above.

*Equilibrium Determinations.*—To investigate the influence on equilibrium of the members of the reversible reaction under consideration, the concentrations necessary for one equilibrium mixture were first accurately determined. Then, in turn, two of the four substances were kept constant, a third changed to one-half, double, or treble the amount in the first equilibrium mixture and the quantity of the fourth, which is necessary for equilibrium, was then found by trial.

The mixtures were analyzed by determining the amount of iodine present. In general, it is not possible to do this by titration, because more iodine is generated as soon as some iodine is removed. In very dilute solutions, however, iodine and ferrocyanide react *completely*, irrespective of any iodide and ferricyanide present. Hence for every mixture of the four substances there must be an intermediate dilution at which iodine is practically not produced, or a small quantity not absorbed. Theoretically, this is the dilution in which one drop or less of iodine is in equilibrium with the ferrocyanide, ferricyanide and iodide present. Such dilutions were found experimentally by taking different ratios of ferrocyanide to ferricyanide and different concentrations of potassium iodide in such dilutions that the mixtures would not generate or absorb more iodine in an hour than corresponds to one drop of decinormal solution. Any solution approximating these concentrations will fulfil the above conditions. The following table, V, gives the results thus obtained, and these figures were used in this work:

TABLE V.—SOLUTIONS OF FERROCYANIDE, FERRICYANIDE, POTASSIUM IODIDE, AND HYDROCHLORIC ACID, WHICH PRACTICALLY DO NOT GENERATE OR ABSORB IODINE.

| Total volume in cc. | No. cc. N/1 KI solution. | No. cc. N/2 ferrocyanide solution. | No. cc. N/2 ferricyanide solution. | No. cc. N/1 HCl. |
|---|---|---|---|---|
| 375 | 25 | 2.5 | 2.5 | 5.0 |
| 435 | 25 | 2.0 | 3.0 | 5.0 |
| 235 | 25 | 3.0 | 2.0 | 5.0 |
| 160 | 25 | 3.5 | 1.5 | 5.0 |
| 535 | 25 | 1.5 | 3.5 | 5.0 |
| 560 | 50 | 2.5 | 2.5 | 5.0 |
| 326 | 16.6 | 2.5 | 2.5 | 5.0 |
| 175 | 12.5 | 2.5 | 2.5 | 5.0 |
| 340 | 25 | 2.5 | 2.5 | 10.0 |
| 122 | 25 | 2.5 | 2.5 | 2.0 |

That thiosulphate in such solutions can be titrated back accurately with iodine was tested carefully. Amounts of thiosulphate, varying from 10 to 25 cc. decinormal solution, were put into each one of the mixtures given in the table above, and titrated back with decinormal iodine solution. It was also ascertained that small quantities of iodine are not taken up by reaction in these solutions. Thus 5 to 15 cc. centinormal solution of iodine were added to each of the mixtures, and when titrated back after a lapse of 5 to 7 minutes, only a negligible loss was observed.

The actual procedure in any titration was as follows: By reference to the table the amount of water necessary for diluting 100 cc. of the solution to be examined was estimated. This amount was put into a beaker, N/10 thiosulphate solution in amount exceeding about 10 cc., the amount necessary for the iodine, was added, the measured amount of sample added quickly with constant stirring and the excess of thiosulphate solution determined with starch and decinormal iodine solution. In all cases the resulting mixture was tested to see if it had been properly diluted.

TABLE VI.—RESULTS OF EQUILIBRIUM EXPERIMENTS WITH ACIDIFIED (= N/20 HCl) SOLUTIONS OF POTASSIUM IODIDE, FERROCYANIDE, FERRICYANIDE, AND IODINE.

| | Concentrations (in terms of N/normal solution.) | | | | | | Values (4) of | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt. No. | Ferrocyanide. | Ferricyanide. | Potassium iodide. | Iodine. | Per cent. dissociated iodine. (1) | Total free iodine in terms of 0.0001 N. | $\frac{I_2\ (\text{free})}{(K_3Fe(CN)_6)^2}$. | $\frac{I_2\ (\text{free})}{(KI)^4}$. | $\frac{[K_4Fe(CN)_6]^2}{K_3Fe(CN)_6}$. | $[K_4Fe(CN)_6]^4.I_2\ (\text{free})$. | $K_3Fe(CN)_6.KI$. | $\frac{[K_4Fe(CN)_6]^2}{KI}$ | Values of $10^{5} \times K$ from $K = \frac{[K_3Fe(CN)_6]^4.I_2\ (\text{free})}{[K_4Fe(CN)_6]^2.(KI)^2}$. (3) |
| 1 | 0.01 | 0.0072 | 0.26 | 0.00973 | 0.54 | 0.525 | 1.0135 | 0.00078 | 0.0140 | $5254 \times 10^{-16}$ | 0.001872 | 0.000385 | 150 |
| 2 | 0.01 | 0.01 | 0.26 | 0.01946 | 0.55 | 1.070 | 1.0703 | ...... | ..... | ........ | ....... | ....... | 158 |
| 3 | 0.01 | 0.0123 | 0.26 | 0.02919 | 0.565 | 1.649 | 1.0900 | ...... | ..... | ........ | ....... | ....... | 161 |
| 4 | 0.01 | 0.0072 | 0.125 | 0.001123 | 1.145 | 0.013 | ..... | 0.00082 | ..... | ........ | ....... | ....... | 159 |
| 5 | 0.01 | 0.0072 | 0.3744 | 0.0292 | 0.393 | 1.148 | ..... | 0.00082 | ..... | ........ | ....... | ....... | 159 |
| 6 | 0.03 | 0.0615 | 0.26 | 0.00973 | 0.54 | 0.525 | ..... | ..... | 0.0146 | ........ | ....... | ....... | 166 |
| 7 | 0.0076 | 0.0072 | 0.26 | 0.02919 | 0.565 | 1.649 | ..... | ...... | ..... | $4945 \times 10^{-16}$ | ....... | ....... | 157 |
| 8 | 0.01 | 0.0144 | 0.13 | 0.00487 | 1.17 | 0.565 | ..... | ...... | ..... | ........ | 0.001872 (2) | ....... | 162 |
| 9 | 0.0148 | 0.0072 | 0.52 | 0.01946 | 0.27 | 0.525 | ..... | ...... | ..... | ........ | ....... | 0.000421 | 179 |
| 10 | 0.00709 | 0.0072 | 0.13 | 0.00487 | 1.17 | 0.565 | ..... | ...... | ..... | ........ | ....... | 0.000387 (2) | 164 |

Since with the proper dilution all the iodine is taken up by the thiosulphate, and at no moment the iodine in the dilute solution was present in sufficient amount to react appreciably with the ferrocyanide, it is certain that the quantity of iodine in the equilibrium mixture is thus accurately determined.

The equilibrium experiments were carried out by measuring into calibrated 100 cc. flasks the required amount of these substances, filling up to the mark, mixing thoroughly and leaving the flasks in a thermostat from two and one-half to three hours. The thermostat maintained a temperature of 25° C., with variations not exceeding 0.05°. The flasks were almost entirely filled with the solution, and were closed with ground glass stoppers.

In all cases a series of trials with separately prepared mixtures was made until the proportion was found with which the amount of iodine put in remained unchanged. When this had been found, at least one more trial was made with the proportions on the side of equilibrium beyond that from which it was approached. Each final equilibrium determination was duplicated. The results are given in the accompanying table, VI.

NOTES TO TABLE VI.

(1) The concentration of effective iodine, *i. e.*, the portion not combined with the iodine, is found with the aid of Jakowkin's formula

$$\frac{(a-l-x)x}{v(l-x)}=k\ ;$$

where $v$ = volume in liters of 1 gram-molecule of iodine;

$a$ = number of KI gram-molecules in $v$ volume; and

$x$ = fraction of total iodine which is not combined with KI to form $KI_3$. The mean value for $k$ is 0.00138. However, this value is not absolutely constant, and must be properly changed according to the concentration.

(2) The concentration of free iodine in this experiment is not quite the same as in Expt. 1. This must be borne in mind in comparing results.

(3) At first sight the values of this K do not appear to be as nearly constant as might be desired, but we must not neglect to consider several factors which probably account for this variation:

(*a*) Ferrocyanide and ferricyanide solutions are decomposed by sunlight and other influences.[1] A very small change in the

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[1] Mathuschek: *Chem. Ztg.*, **25**, 601.

concentration of either, and particularly in the concentration of the ferrocyanide causes a large difference in the numerical result. Thus, if in Expt. 9 the stock solution of ferrocyanide used had decomposed so as to be 4 per cent. weaker, the value for K would have been 0.000000015.

(*b*) An error is introduced by calculating the thermic dissociation of iodine upon the assumption that only $KI_3$ is present, whereas the dissociation is undoubtedly influenced by the presence of the acid, so that the quantity of dissociated iodine is probably slightly less, corresponding to the presence of some $HI_3$. Both of these causes probably operate to produce the extreme value in Expt. 9. I believe, in view of this, the agreement among the values of K is fairly satisfactory.

(4) The selection of the powers of the concentrations to be employed for the products and quotients in columns 8 to 13 was easily done by inspection. The products and quotients give the equilibrium formula,

$$\frac{C^4\,(\text{ferrocyanide})\;C\,(\text{free iodine})}{C^2\,(\text{ferricyanide})\;C^2\,(\text{potassium iodide})} = K.$$

From the equation for the reaction

$$2Fe(CN)_6'''' + I_2 = 2Fe(CN)_6''' + 2I'.$$

The *second* power of the concentration of the ferrocyanide should appear in the equilibrium formula. But since all independent variations possible (see Expts. 6, 7, 9 and 10) require the second power of the concentration of the ferrocyanide in place of the first (hence the fourth power in place of the second), there can be no doubt of the correctness of the formula arrived at. It should also be recalled that electromotive force measurements point to the same result.

## SUMMARY.

(1) In this paper has been presented the influence upon equilibrium of the concentrations of potassium ferrocyanide, potassium ferricyanide, potassium iodide, and iodine in dilute acid solutions (N/20 hydrochloric acid). The formula expressing the conditions of equilibrium in such solutions at constant temperatures is

$$\frac{C^4\,(\text{ferrocyanide})\;C\,(\text{free iodine})}{C^2\,(\text{ferricyanide})\;C^2\,(\text{iodide})} = K.$$

(2) Both electromotive force measurements and chemical equilibrium determinations show that the effect of ferrocyanide in acidified solutions is proportional to the square of its concentration where theoretically it *should be proportional to the first power.*

Work on this problem will be continued.

In the experimental work of this paper I have been assisted by Mr. R. C. Pantermühl of this laboratory. I gladly take this occasion to express my appreciation of his assistance.

# EQUILIBRIUM IN THE SYSTEM $BeO : SO_3 : H_2O$.

BY CHARLES LATHROP PARSONS.

Received August 9, 1904.

THE sulphates of beryllium were first studied by Berzelius in 1815,[1] although Vauquelin, in 1798,[2] had already produced a gummy basic sulphate. It was Berzelius who first found the necessary conditions to produce the neutral tetrahydrate, which he considered to be of an acid nature. He also produced basic substances to which he gave the formulas $3BeO.SO_3$, $2BeO.SO_3$ and $6BeO.SO_3 + 3H_2O$. Awdejew,[3] in 1842, first proved the neutral character of $BeSO_4.4H_2O$, carefully purified it and studied its properties in connection with his atomic weight determinations. Weeren,[4] in 1854, again used this salt for the same purpose and claimed that it loses one-third of its water of crystallization as low as 35°. Debray,[5] in the following year, used the properties of the basic sulphates as a means of separation from aluminum and states that the precipitated basic sulphate, on continued washing, left nothing but the hydroxide.

In 1869, Klatzo[6] took up the study of the sulphates and claimed to prepare the salt $BeSO_4.7H_2O$. Atterberg, 1873-74, in his extended study of the compounds of beryllium,[7] again prepared $BeSO_4.4H_2O$ and $BeSO_4.2H_2O$, and assigned the following formulas to the basic compounds prepared by him. $BeSO_4.Be(OH)_2$

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[1] Schweigger : *J. Chem. Phys.*, **15**, 296.

[2] *Allgem. Jour. der Chem. Scheerer*, **1**, 590.

[3] Pogg. *Ann.*, **56**, 101.

[4] *Ibid.*, **92**, 91.

[5] *Ann. chim. phys.* (3), **44**, 1.

[6] Inaugural dissertation, Dorpat, *Ztschr. Chem.*, **12**, 129.

[7] *Kongl. Svenska Vet. Akad. Hand.*, **12**, 1 ; also *Bull. Soc. Chim.* (2), **19**, 497, and (2), **21**, 157.