plotting both the left- and right-hand members against arbitrary values of N_2, their intersection can usually be determined from three or four substitutions.

Summary

1. An equation for the calculation of the solubility from the properties of the pure components has been tested for a large number of solutions of iodine, stannic iodide, sulfur and phosphorus and found to hold even better than could be expected in view of the approximations involved. Departure from spherical symmetry and presence of dipole moment do not necessarily vitiate the calculations.

2. The uncertainty on the basis of the London theory regarding the relation between the attraction constants of like and unlike molecules, $k_{12} \leqq (k_{11}\,k_{22})^{1/2}$, seems to be greatly diminished by experimental indications that the inequality is small.

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The Equilibrium of the Reaction between Ferric Ion and Silver

BY WALTER C. SCHUMB AND SUMNER B. SWEETSER

The equilibrium of the reaction $Fe^{+++} + Ag \rightleftarrows Fe^{++} + Ag^{+}$ is one of the comparatively few reactions in which at equilibrium the concentration of reactants and products can be determined by ordinary methods of chemical analysis. It is of interest also because the determination of the equilibrium constant affords an accurate method for obtaining the molal ferric–ferrous electrode potential and may also be of use in obtaining the activity of ferric ion when the activities of the ferrous and silver ions are known more accurately. The commonly accepted value of the equilibrium constant is 0.128, which was obtained by Noyes and Brann.[1] Later determinations of the ferric–ferrous electrode potential by Popoff and Kunz,[2] and Popoff, Fleharty and Hanson[3] also afford a means of calculating the equilibrium constant of the above reaction.

Noyes and Brann used nitrate as the acid constituent and plotted the calculated values of K against total nitrate concentration. However, their points were widely scattered so that the result of the extrapolation to zero concentration was somewhat uncertain. The present investigation was undertaken with the purpose of obtaining a more accurate value of the equilibrium constant by selecting conditions which would give points on a smooth curve and by carrying on the reaction over a wider range of concentration in order to lessen the amount of extrapolation necessary.

Reagents.—Perchlorates were used in this work in preference to the nitrates because a higher concentration of perchloric than of nitric acid could be used without attacking the powdered silver. Ferric perchlorate was prepared by dissolving hydrated ferric sulfate in water, precipitating with a slight excess of ammonium hydroxide, washing the precipitate repeatedly by decantation, and then digesting the ferric hydroxide with reagent quality 60% perchloric acid. The solution was decanted from the undissolved hydroxide, concentrated, and violet crystals of $Fe(ClO_4)_3 \cdot 6H_2O$ obtained, which were repeatedly recrystallized. The hexahydrate rather than the nonahydrate was employed, as the latter tended to be soft and pasty and retained a large amount of solution.

Finely divided silver was prepared by slowly adding a hot solution of ammonium formate to a hot 35% solution of silver nitrate. The ammonium formate was obtained by the addition of 50% formic acid to concentrated ammonium hydroxide until the solution reacted acid to litmus.

Reagent grade chemicals were used for all analytical work.

Methods of Analysis.—Tenth normal permanganate solution was standardized against Bureau of Standards ingot iron (99.85% Fe).[4] The equivalence point of the titration was obtained potentiometrically using a bright platinum gauze electrode and a saturated calomel electrode. Popoff and Kunz[2] found that failure to remove the precipitated mercurous chloride formed in the oxidation of the excess stannous chloride caused an error in the titration. However, this error was only about one part per thousand so was neglected in this work.

The iron content of ferric perchlorate solutions was determined by the same method as that used to standardize the permanganate, employing perchloric acid in place of hydrochloric acid.

Popoff, Fleharty and Hanson[3] determined the quantity of free acid in ferric perchlorate solution by adding an ex-

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(1) Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).

(2) Popoff and Kunz, *ibid.*, **51**, 382 (1929).

(3) Popoff, Fleharty and Hanson, *ibid.*, **53**, 1643 (1931).

(4) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., 1929, p. 305.

cess of standard sodium hydroxide, filtering the solution while hot, thoroughly washing the precipitated ferric hydroxide with hot water, and then titrating the filtrate with standard hydrochloric acid, using methyl orange indicator. This method has the disadvantage that it is difficult to wash the precipitated ferric hydroxide free from the excess base that is occluded. The method used in this work was to heat 75 to 100 cc. of water to boiling and add a sample of the ferric perchlorate solution containing the free perchloric acid by means of a pipet. The solution was then titrated immediately with tenth normal sodium hydroxide using phenolphthalein indicator. It was found that the ferric hydroxide precipitated completely and in the hot solution coagulated before the indicator turned pink. By allowing the precipitate to settle for a few seconds after each addition of base near the equivalence point, this point could be quite readily determined. In a comparison of the two methods the normality of the acid in a ferric perchlorate solution was found to be 0.1614 by the former method and 0.1613 by the new method.

The equilibrium mixtures were analyzed potentiometrically for ferrous iron and silver. A silver electrode could not be used because of the possibility that it would be attacked by the ferric iron in the solution. It was found that a bright platinum gauze electrode could be used as an indicator electrode for both the ferrous iron and the silver. Thus a portion of the equilibrium mixture could be titrated for ferrous iron with permanganate and then with potassium thiocyanate for the silver without changing solutions or electrodes. The thiocyanate was used in preference to the chloride because of the greater insolubility of silver thiocyanate and also because the ferric iron in the solution acted as an indicator for the thiocyanate, so that a check for the equivalence point obtained potentiometrically was available. The platinum electrode did not give as abrupt a change in voltage at the equivalence point for the silver determination as for the ferrous iron. The drop of 20 to 40 millivolts at the equivalence point could be easily detected, however. In this titration the voltage had a tendency to fluctuate, probably from the adsorption of silver ion on the precipitated silver thiocyanate. The addition of 10 to 15 cc. of concentrated nitric acid to the solution before the titration with thiocyanate prevented this fluctuation. The platinum electrode had to be heated in a flame frequently or it ceased to function as an indicator electrode for silver. The calomel electrode used was of the type described by Kolthoff and Furman;[5] the part of the bridge which dipped into the solution to be analyzed was filled with potassium nitrate and agar instead of potassium chloride in order to prevent precipitation of silver chloride from the solution. The thiocyanate solution was standardized potentiometrically against standard silver nitrate solution.

The ferric iron in the equilibrium mixtures was determined as the difference between the total iron in the solution and the ferrous iron found in the equilibrium mixtures. Since theoretically the concentrations of ferrous iron and silver in the equilibrium mixtures should be the same, these concentrations were averaged and subtracted from the total ferric perchlorate to get the ferric iron in the equilibrium mixtures.

Experimental Procedure

About 5 g. of finely divided silver was placed in a 250-cc. glass-stoppered bottle and 150 to 200 cc. of ferric perchlorate solution was added. The air was displaced from the bottle by passing in a slow stream of nitrogen. The slightly lubricated stopper was then pressed in firmly, sealed with melted paraffin, and taped down.

The bottles were rotated overnight in a thermostat at 25 ± 0.01°, although Noyes and Brann[1] stated that four hours was usually sufficient to attain equilibrium. To reach equilibrium from the "hot side" the bottles, after being rotated overnight in the thermostat, were heated at 40 to 50° in a water-bath for half an hour with occasional shaking. They were then put back in the thermostat for at least another four hours before analysis. In approximately half the experiments equilibrium was approached from both the "hot" and the "cold" sides, and the results so obtained were in good agreement.

The bottles were removed from the thermostat and let stand for five minutes to allow the silver to settle. This made filtration unnecessary and the danger of loss by adsorption on the filter paper was avoided. Before the titration with permanganate a sample of the equilibrium mixture was diluted to 150 cc. and 7 to 8 cc. of 60% perchloric acid added, in the case of the more concentrated solutions, or 5 cc. in the more dilute ones. Popoff and Kunz[2] found that there was no appreciable oxidation of the ferrous iron by the atmosphere during the time taken for a titration, so that it seemed unnecessary to carry out the titration in a reducing atmosphere. Blank titrations were made and corrections applied when appreciable.

It was desired to carry out the experiments over a range of concentrations in such a manner that when the values of *K*, or some function thereof, calculated from the experimental data, were plotted, a smooth curve would result. The method employed by Popoff, Fleharty and Hanson[3] for this purpose involved an extrapolation in each of four curves. It seemed possible to accomplish the same result with one curve, by keeping a constant ratio of perchloric acid to ferric perchlorate throughout a series of experiments. Therefore, in starting a series of experiments a solution of known concentration of ferric perchlorate was made up with the addition of a known amount of perchloric acid, sufficient to make it perfectly colorless, and the different lower concentrations of this solution were obtained by dilution in calibrated volumetric apparatus. When more dilute permanganate and thiocyanate solutions were needed for titrating the equilibrium mixtures, they were prepared by diluting standard tenth normal solutions. These solutions were freshly prepared on the day of use.

Two series of experiments were carried out. Although there was no indication of hydrolysis in even the most dilute solutions of the first series, the ratio of acid to ferric perchlorate was made larger in the second series as a precautionary measure.

The data for these two series of experiments are given in Table I. The equilibrium constant

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[5] Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., 1931, p. 80.

TABLE I

EXPERIMENTAL DATA AND RESULTS

Original mixture (F.W. per liter)		Equilibrium mixtures (F.W. per liter)					
$Fe(ClO_4)_3$	$HClO_4$	Fe^{++}	Ag^+	Fe^{+++}	K	μ	Log $K + 2.02\ \mu^{1/}$
			Series 1				
0.1244	0.4673	0.07387	0.07363	0.05065	0.1074	1.0663	1.128
.09952	.3738	.06292	.06256	.03678	.1070	0.8456	0.888
.08293	.3115	.05509	.05496	.02790	.1085	.6994	.724
.08024	.3014	.05368	.05363	.02658	.1083	.6754	.697
.06220	.2336	.04457	.04450	.01766	.1123	.5178	.505
.04147	.1558	.03282	.03256	.00878	.1217	.3394	.265
.02073	.07788	.01840	.01824	.00241	.1393	.1657	− .032
			Series 2				
0.1045	0.9255	0.06529	0.06546	0.0391	0.1092	1.4215	1.4468
.08360	.7404	.05504	.05509	.02854	.1063	1.1319	1.1755
.06270	.5553	.04420	.04435	.01842	.1064	0.8428	0.8812
.04180	.3702	.03223	.03232	.00952	.1094	.5563	.5455
.02090	.1851	.01811	.01813	.00278	.1181	.2742	.1300
.008360	.07404	.007976	.007981	.000381	.1672	.1082	− .1124

was calculated in terms of concentrations from the expression: $K = (Fe^{++})(Ag^+)/(Fe^{+++})$. In the first series some experiments were carried to lower concentrations than the table indicates. The values of K for these experiments were unreliable, because the ferric iron in the equilibrium mixtures was determined by difference of the total iron and the ferrous iron, and, as the table indicates, the concentration of ferric iron diminishes much more rapidly than that of the ferrous iron. Therefore, a small error in the analysis of the ferrous iron was magnified many times in determining the concentration of ferric iron. Because of the uncertainty thus introduced, the points at the lowest concentrations were excluded from the table.

As was predicted, when K was plotted against total perchlorate concentration or against μ, the ionic strength, a smooth curve for each series was obtained. However, the slope of the curves was increasing so rapidly with decreasing concentration that a satisfactory degree of precision in extrapolation could not be attained. When plotted[6] as log $K + 2.02\ \mu^{1/2}$ against μ the data gave curves which were much more suitable for extrapolation The curves for the two series were very nearly superimposable, as shown in Fig. 1.

The equations of the curves for the two series were calculated separately by the method of least squares. These gave K the values 0.539 and 0.523 at zero ionic strength. If the two series are averaged, the equation for the resulting curve is found to be

$$\log K + 2.02\ \mu^{1/2} = -0.275 + 1.645\ \mu - 0.316\ \mu^2$$

This gives K the value 0.531, which is taken as the true value of equilibrium constant at 25°.[7]

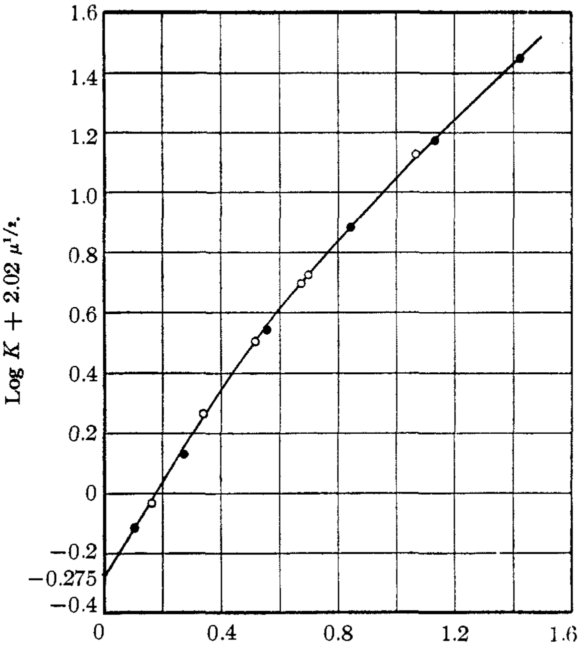

Fig. 1.—Series 1, ○; Series 2, ●; at zero ionic strength, $K = 0.531$.

The value of Randall and Young[8] for the molal potential of the silver electrode is 0.7985 ± 0.0010 volt. From this figure and our value of 0.531 for the equilibrium constant the molal

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(6) $2.02 = (2^2 + 1^2 - 3^2)(-0.505)$ as derived from the Debye-Hückel theory.

(7) In obtaining the equations by the method of least squares, the last point recorded in Table I in the first series was given half weight. In the second series points 1 and 5 were given half weight and point 6 one-third weight. All others were given unit weight.

(8) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

ferric–ferrous electrode potential is calculated to be 0.782 ± 0.001 volt at 25°.

Although our values for K and the ferric–ferrous electrode potential are considerably higher than the commonly accepted values for these constants, there is evidence other than that presented here to indicate that the higher values are correct. Thus, Bray and Hershey[9] developed a method for calculating the amount of hydrolysis in a solution of ferric ion, and with the aid of this hydrolysis correction they have recalculated the data of Noyes and Brann[1] and concluded that K should have the value 0.363 instead of 0.128. Similarly they concluded that the value of Popoff and Kunz[2] for the molal ferric–ferrous electrode potential should be raised from 0.748 to 0.772 volt. Their recalculated values for these constants thus agree more closely with our values than with the previously accepted ones.

The method of Bray and Hershey[9] for hydrolysis correction was applied to the data obtained in this investigation. The correction, however, was appreciable only for the last point on the curve in both series; furthermore, application of the correction would have changed the slope in this region of the curves upward in an unaccountable manner. Consequently such an hydrolysis correction was omitted.

The suggestions and assistance of Professor George Scatchard of this Institute in the interpretation of our data are gratefully acknowledged.

Summary

The equilibrium constant of the reaction $Fe^{+++} + Ag \rightleftarrows Fe^{++} + Ag^{+}$ has been redetermined with perchlorate as the acid constituent. Two series of experiments have been conducted at 25° with a different constant ratio of perchloric acid to ferric perchlorate in each series. The data have been plotted as $\log K + 2.02\,\mu^{1/2}$ against μ and extrapolated to zero ionic strength. The mean value thus determined for K is 0.531. From this value of K the molal ferric–ferrous electrode potential has been calculated as 0.782 volt.

CAMBRIDGE, MASS. RECEIVED MARCH 15, 1935

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[9] Bray and Hershey, THIS JOURNAL, **56**, 1889 (1934).

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Ultraviolet Absorption Spectrum of Pepsin

BY GEORGE I. LAVIN AND JOHN N. NORTHROP

Introduction

Recent investigations of Lavin, Northrop and Taylor[1] and of Gates[2] have shown that pepsin has an absorption band in the ultraviolet at 2500–3000 Å. This band is typical of the proteins and has been attributed to the absorption of the aromatic amino acids, tyrosine and tryptophan. Thus Stenström and Reinhard[3] found that gelatin, which contains very little tyrosine and no tryptophan, did not show this absorption band.

A large amount of work has been done on the absorption spectra of the amino acids and most of the results indicate that only the aromatic acids have selective or band absorption in the region 2500–3000 Å. Where the investigators have determined the extinction coefficients, using the usual photometers and line sources, they have, in general, found only one wide band. However, if a continuous light source is used, it is possible to show that tyrosine, tryptophan and phenylalanine have narrow absorption bands as well as the well-known broad band.

Among others, Ross[4] has found that tyrosine has two absorption bands, one at 2840 Å. and another at 2760 Å. In the case of tyrosine, Stenström and Reinhard have shown that the position of the bands is dependent on the hydrogen ion content of the solvent. Ross also found that tryptophan has a narrow band at 2900 Å. and a broad region of absorption from 2850 to 2600 Å. The absorption of phenylalanine was found to consist of five narrow bands at 2680, 2640, 2585, 2525 and 2480 Å.

Since our work on the absorption spectrum of pepsin had shown the presence of narrow bands, an attempt has been made to explain the absorption in this region in terms of the individual aromatic amino acids.

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[1] Lavin, Northrop and Taylor, THIS JOURNAL, **55**, 3497 (1933).

[2] Gates, *J. Gen. Physiol.*, **17**, 797 (1933–34).

[3] Stenström and Reinhard, *J. Biol. Chem.*, **66**, 819 (1925).

[4] Ross, *ibid.*, **104**, 531 (1934).