Because of the fact that the activation energy for diffusion rises even above the heat of vaporization of water, we are inclined to believe that the mechanism of diffusion involves the simultaneous breaking of several hydrogen bonds, as many as three in the case of the most concentrated glucose solution. If diffusion takes place by a rotation of a sugar molecule in such a way as to carry a water molecule forward as previously suggested by English and Dole,[2] several hydrogen bonds would have to be broken in as much as the sugar molecule in question would be hydrogen bonded to a number of water molecules which would in turn be partially bonded to other sugar molecules.

The more hydrogen bonds that are broken in the diffusion process, the greater the activation energy and the greater the increase in entropy of the activated state. Referring to eq. (4) it is clear that if $\Delta S^{\ddagger}$ is the same at similar values of $\Delta E^{\ddagger}$ for both glucose and sucrose, the diffusion coefficient of the two substances should be the same at the same $\Delta E^{\ddagger}$. This is not quite the case as the diffusional entropy for the sucrose solutions is less than the entropy of the glucose solutions at the same activation energy.

Acknowledgments.—We wish to acknowledge gratefully the financial support and gift of materials from E. J. Brach and Sons, Inc., Chicago. We continue to be indebted to Dr. K. A. Strand, Director of the Dearborn Observatory at Northwestern University for the use of his dividing engine.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Iron–Thioglycolate Complexes

BY D. L. LEUSSING AND I. M. KOLTHOFF

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In solutions with a *p*H between about 9 and 11, two complexes composed of iron(II) and thioglycolic acid are found: $Fe(OH)(RS)^-$(yellow), and $Fe(RS)_2^=$(red), in which RS denotes $^-OOC—CH_2S^-$. The equilibrium contants $K_{Fe}(II)_1$ and $K_{Fe}(II)_2$ of the reactions: $Fe(OH)(RS)^- + 2H^+ \rightleftarrows Fe^{++} + RSH^- + H_2O$ and $Fe(RS)_2^= + 2H^+ \rightleftarrows Fe^{++} + 2RSH^-$ were found from solubility data to be equal to 1.5×10^{12} and 1.5×10^{10}, respectively, at 25°. The ratio of the two constants was also determined spectrophotometrically and found equal to 0.009 in good agreement with the value found from solubility data. In weakly acid medium slightly soluble FeRS is formed. The activity constant $S_{FeRS} = a_{Fe^{++}}a_{RSH^-}/a_{H^+}$ was found equal to 7. The intensely colored complex of iron and thioglycolate in alkaline medium is derived from ferric iron and does not contain ferrous iron. Ferric iron catalyzes the air oxidation of thioglycolate to the disulfide. From solubility data of ferric hydroxide in ammoniacal thioglycolate solutions, extrapolated to zero time when no reduction of ferric iron by thioglycolate has occurred, it was postulated that the complex has the composition $FeOH(RS)_2$.$^=$ The formation of the complex is given by: $Fe(OH)_3(s) = 2RSH^- \rightleftarrows Fe(OH)(RS)_2^= + 2H_2O$, with an equilibrium constant at 25° $a^2_{RSH}/a_{Fe(OH)(RS)_2^=}$ of 0.020.

Complex formation[1] between iron and thioglycolate has been made of analytical use in the colorimetric determination of iron[2-4] and in the separation of iron from other metals.[5,6] In air-saturated ammoniacal medium a deep purple-red complex is formed regardless, whether the iron was present initially in the ferrous or ferric state.

In alkaline solutions iron(III) oxidizes thioglycolate to dithiodiglycolate, $-O_2CCH_2SSCH_2CO_2-$, with formation of iron(II). Oxygen very rapidly oxidizes the iron(II) in alkaline thioglycolate solutions so the net result is the catalytic oxidation of thioglycolate by oxygen.[7-10] The rate of reduction of iron(III) by thioglycolate increases with the acidity of the solution and in acid solutions is very rapid to form a colorless solution which does not give the deep red color in the presence of oxygen.[9]

Little has been reported on the composition of the ferrous and ferric thioglycolate complexes existing in aqueous solutions. Indeed, even the valence state of iron is in doubt in the deep purple-red complex. Lyons[2] postulates that it is a ferrous complex, Dubsky and Sindelar[11] claim that it is a ferric complex and Mayr and Gebauer[12] state that the highly colored complex contains both ferrous and ferric iron and has the composition KFe(III)[Fe(II)$(SCH_2CO_2)_2]_2$.

Schubert[10] and Mayr and Gebauer[12] have prepared solid ferrous–thioglycolate salts corresponding to the composition $Fe(SCH_2CO_2)$ (yellow) and $M_2Fe(SCH_2CO_2)_2$ (red), where M is an alkali metal. $Fe(SCH_2CO_2)$ is reported to be insoluble but $M_2Fe(SCH_2CO_2)_2$ dissolves in air-free water to form light yellow solutions at low concentrations and raspberry red solutions at higher concentrations. The intensity of the color of these latter solutions is much less than that of air-saturated alkaline solutions containing the same amount of iron.

Michaelis and Schubert[13] have attempted to prepare solid salts of ferric iron and thioglycolate but were unsuccessful because of the reduction of the iron to ferrous. They were able to prepare solid Co(III)–thioglycolate compounds which existed as dimers.

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[1] R. Andreasch, *Ber.*, **12**, 1391 (1879).

[2] E. Lyons, THIS JOURNAL, **49**, 1916 (1927).

[3] H. W. Swank and M. G. Mellon, *Ind. Eng. Chem.*, *Anal. Ed.*, **10**, 7 (1938).

[4] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 2nd ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 378.

[5] C. Mayr and A. Gebauer, *Z. anal. Chem.*, **113**, 189 (1938).

[6] R. A. Hummel and E. B. Sandell, *Anal. Chim. Acta*, **7**, 308 (1952).

[7] P. Claesson, *Ber.*, **14**, 409 (1881).

[8] L. Michaelis, *J. Biol. Chem.*, **84**, 777 (1929).

[9] B. K. Cannan and G. N. Richardson, *Biochem. J.*, **23**, 1242 (1929).

[10] M. P. Schubert, THIS JOURNAL, **54**, 4077 (1932).

[11] J. V. Dubsky and V. Sindelar, *Microchim. Acta*, **3**, 258 (1938).

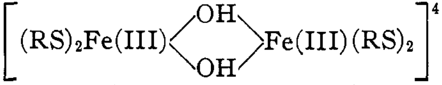
[12] C. Mayr and A. Gebauer, *Z. anal. Chem.*, **116**, 225 (1939).

[13] L. Michaelis and M. P. Schubert, THIS JOURNAL, **52**, 4418 (1930).

TABLE I

ANALYSES OF MIXTURES CONTAINING FERROUS CHLORIDE, THIOGLYCOLIC ACID AND SODIUM HYDROXIDE

Experiment no.	Total mmoles $FeCl_2$	Total mmoles NaOH	Total mmoles TGA	Total vol., ml.	*p*H	Total Fe in supernatant liquid $M \times 10^3$	Total TGA in supernatant liquid $M \times 10^3$	Millimoles Fe in precipitate	Millimoles TGA in precipitate
1	4.81	10.11	9.92	119	4.22	27.3	70.7	1.56	1.50
2	4.77	10.06	8.10	117	4.31	17.6	46.1	2.70	2.70
3	5.00	10.06	6.08	116	4.85	7.88	18.1	4.09	3.98
4	4.97	10.11	4.96	115	(7.07)	2.47	2.02	4.69	4.73
5	5.22	6.07	1.98	72	(7.8)	30.8	<0.5	3.00	1.94
6	5.02	10.24	4.01	74	(7.95)	2.37	2.18	4.84	3.85
7	5.18	10.06	4.05	114	(8.25)	2.41	0.43	4.90	4.00
8	5.23	10.06	3.04	113	(8.37)	3.02	0.45	4.89	2.99
9	5.03	20.12	10.13	120	9.60	42	84.5	No precipitate	
10	5.52	21.5	10.0	92	10.10	60	109	No precipitate	
11	5.00	20.12	8.10	118	10.75	29.4	68.8	1.53	...
12	4.92	15.37	4.01	79	10.88	16.22	48.4	3.64	(0.20)
13	5.22	25.7	10.02	95	11.12	34.1	108.5	1.98	(−0.30)
14	5.17	20.5	6.01	86	11.33	16.65	70.4	3.74	..

the cobalt atoms being joined by an oxygen bridge, Schubert[10] has also prepared analogous compounds of cobalt(III) and cysteine. From these results Martell and Calvin[14] postulate that a complex of ferric iron and thioglycolate should have the composition  $\left[(\mathrm{RS})_2\mathrm{Fe(III)}\begin{matrix}\diagup\mathrm{OH}\diagdown\\ \\ \diagdown\mathrm{OH}\diagup\end{matrix}\mathrm{Fe(III)}(\mathrm{RS})_2\right]^{4-}$ where RS refers to the divalent thioglycolate ion, $-SCH_2CO_2-$.

The present investigation was undertaken to determine the composition and stability of the iron(II) and (III) thioglycolate complexes existing in aqueous medium.

Ferrous–Thioglycolate Complexes. Experimental.—Pure thioglycolic acid reagent was prepared by vacuum distilling Eimer and Amend thioglycolic acid. The analysis, stability, polarography and storage of the reagent are described elsewhere.[15]

0.5 *M* ferrous chloride stock solutions were prepared freshly for each series of experiments under air-free conditions by allowing a slight excess of iron powder (Baker C.P.) to react with 1.0 *N* hydrochloric acid in bottles which were sealed with self-sealing Buna N gaskets. Samples of the solutions were removed by means of hypodermic syringes and were analyzed for iron. Further details are given in a paper on the solubility of ferrous hydroxide.[16]

Sodium hydroxide solutions were freshly prepared each day from a stock solution of 50% sodium hydroxide and were standardized with standard acid.

The ferrous–thioglycolate system was studied in air-free solutions in which the amounts of iron, thioglycolic acid and sodium hydroxide were varied. For the preparation of each mixture the desired amounts of thioglycolic acid, air-free sodium hydroxide solution and water were placed in a 200-ml. narrow-mouth bottle which was then sealed with a Buna N, self-sealing gasket tightly held in place by a screw-cap punched with holes. The solution within the bottle was then bubbled with nitrogen (Linde, 99.99% pure) which was introduced below the surface of the liquid by means of a 6-inch, 20 gage hypodermic needle inserted through the gasket. A smaller needle also was inserted through the gasket in order to allow the escape of the gases. The nitrogen was previously saturated with water. After one-half hour of bubbling the needles were removed and then the desired volume of 0.5 *M* ferrous chloride was taken from the stock bottle by means of a calibrated, hypodermic syringe and injected into the thioglycolate solution. The bottles containing the mixtures were rotated in a water-bath at 25 ± 1°. Iron analyses and *p*H determinations of the supernatant liquids of representative bottles indicated that equilibrium had been attained in four days in all experiments. All bottles were rotated for at least that length of time. The *p*H of samples of the solutions was determined under air-free conditions in the same manner as described previously.[16] After the *p*H determination the bottles were centrifuged, samples withdrawn, and aliquots of these analyzed for total iron and thioglycolate.

The total iron analysis of the supernatant liquids in the concentration range of 0.001 to 0.1 *M* iron was made volumetrically with standard cerate by making the sample 1.5 *M* in sulfuric acid and oxidizing the thioglycolate by adding a concentrated solution of potassium permanganate dropwise to the hot sample until a permanent precipitate of MnO_2 was obtained. The ferric solution was then reduced in the conventional manner with stannous chloride and titrated. In more dilute solutions iron was determined colorimetrically using the thioglycolate method.[2-4]

Total thioglycolate was determined polarographically by measuring the diffusion current at −0.1 volt *vs.* S.C.E. of the anodic thioglycolate wave[15] in a buffer of 0.1 *M* acetic acid−0.1 *M* sodium acetate. In this buffer and at the concentrations useful for a polarographic analysis (< 0.002 *M*) the ferrous–thioglycolate complexes are practically completely dissociated, and the total concentration of thioglycolate in a solution containing the complexes was obtained upon injecting the solution into the acetate buffer.

A summary of the details and results of the series of experiments conducted is given in Table I. The experiments in Table I are arranged in order of increasing *p*H in the equilibrium solutions. For an interpretation the data are roughly divided into three groups: acid, *p*H 4–5; neutral to mildly alkaline, *p*H 7–9; and alkaline, *p*H 10–11.

Acid Range.—In the acid range, yellow solutions of varying intensity were obtained at first upon mixing the constituents in the amounts stated in Table I. Within 24 hours precipitates appeared in these bottles and the supernatant liquids became colorless. Some of the precipitates were colored pink while others were colored yellow. It seems that the pink color is due to slight oxidation as in some cases the originally yellow precipitate turned pink after samples had been removed for a *p*H determination. No doubt traces of oxygen were admitted in this process.

No indication was obtained of the presence of a complex in the supernatant liquids—these were colorless and exhibited no striking red color on brief exposure to the air as did the more alkaline solutions in this series of experiments.

The composition of the precipitate readily can be

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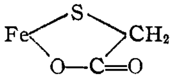
(14) A. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 384.

(15) D. L. Leussing and I. M. Kolthoff, *J. Electrochem. Soc.*, in print.

(16) D. L. Leussing and I. M. Kolthoff, THIS JOURNAL, **75**, 2476 (1953).

calculated from the differences in the amounts of iron and thioglycolic acid present initially and those found in solution at equilibrium. It is seen from the data of Table I that the precipitate contains ferrous iron and thioglycolic acid in a molar ratio of 1:1 within the experimental error. A similar compound has been described by Schubert[10] and Mayr and Gebauer.[12] The compound has the postulated structure



which will be abbreviated as FeRS.

Neutral to Mildly Alkaline Range.—The neutral to mildly alkaline solutions exhibited a slight tendency for the formation of soluble ferrous thioglycolate complexes in solution. When the constituents were first mixed, yellow precipitates and yellow solutions were obtained. At equilibrium the supernatant liquids had become colorless and the precipitates consisted of pure FeRS in experiment 4 in Table I and mixtures of FeRS and $Fe(OH)_2$ in the remainder of the experiments in this *p*H range. Some of the precipitates exhibited the behavior noted earlier of changing from yellow to pink after a sample had been removed. This pink precipitate formed a very pronounced layer beneath the ferrous hydroxide when the bottles were centrifuged. This indicates that neither a solid solution nor mixed crystals are formed between FeRS and $Fe(OH)_2$.

The supernatant liquids in some of the experiments in this *p*H range exhibited a marked sensitivity to air. A deep red color developed immediately when the solution came into contact with the air. Unfortunately this air sensitivity caused the *p*H measurements on these slightly buffered solutions to be incorrect. Traces of oxygen are rapidly reduced and the system is slow to readjust to the slight change in *p*H that occurs during this reaction. This is reflected in the fact that unlike other solutions in this series of experiments the *p*H measurements on the solutions in the mildly alkaline *p*H range fluctuated erratically from day to day. For this reason the *p*H measurements in this range cannot be used in calculations.

Alkaline Range.—Complexes were very clearly present in solutions in the alkaline range. The color of the supernatant liquid varied from red in experiment 9 to yellow in experiment 14 of Table I. The iron concentration in the solutions was much greater than that calculated from the value of the solubility product of ferrous hydroxide.[16]

The precipitates in this range consisted only of ferrous hydroxide.

The complexes present in these solutions apparently catalyze the oxidation of ferrous hydroxide by water. Precipitates of initially white ferrous hydroxide turned green in about 16 hours and became darker with time. In some bottles a dark blue precipitate was obtained beneath a green one upon centrifuging. The extremely air-sensitive supernatant liquids in these alkaline solutions where the complexes are most readily formed show no evidence of oxidation. This indicates that the reaction takes place among the constituents in the bottle and is not due to air leaking in.

The concentration of hydroxyl ions was great enough in these solutions to exert a sufficient buffer capacity to obtain reproducible *p*H measurements.

Calculations and Discussion.—The observations in the present work agree with those reported previously[10,12] that two soluble thioglycolate iron(II) complexes can exist to an appreciable extent in alkaline aqueous solutions. The yellow complex apparently has a smaller ratio of thioglycolate to iron than the red complex. In experiments 9 and 10 of Table I no precipitate of ferrous hydroxide was observed and thus at the *p*H measured in these solutions the activity of free ferrous iron must be negligible compared with the total iron concentration in the solution,[16] *i.e.*, all the iron is present as a complex. Stoichiometric considerations applied to solutions 9 and 10 lead to the conclusion that the red complex has the formula $Fe(RS)_2^{=}$, while the soluble yellow complex must have the formula $Fe(OH)(RS)^-$. Calculations given below further verify the existence of these ions.

The following equations express the relation between the concentrations of the various species present to an appreciable extent in the alkaline solutions

$$[\mathrm{Fe}]_t = [\mathrm{Fe(OH)(RS)^-}] + [\mathrm{Fe(RS)_2^{=}}]$$

$$[\mathrm{TGA}]_t = [\mathrm{RSH^-}] + [\mathrm{RS^{=}}] + [\mathrm{Fe(OH)(RS)^-}] + 2[\mathrm{Fe(RS)_2^{=}}]$$

$$[\mathrm{OH^-}]_t = [\mathrm{OH^-}] + [\mathrm{RSH^-}] + 2[\mathrm{RS^{=}}] + 3[\mathrm{Fe(OH)(RS)^-}] + 4[\mathrm{Fe(RS)_2^{=}}]$$

The quantities in the brackets on the right hand side refer to the equilibrium concentrations in the aqueous phase while $[\mathrm{Fe}]_t$, $[\mathrm{TGA}]_t$ and $[\mathrm{OH^-}]_t$ refer to the total concentrations of iron, thioglycolic acid and sodium hydroxide in the aqueous phase. $[\mathrm{Fe}]_t$ and $[\mathrm{TGA}]_t$ are experimentally determined and the value of $[\mathrm{OH^-}]_t$ is calculated from the initial number of millimoles of hydroxide present minus twice the number of millimoles of ferrous iron which has precipitated.

The values for the activity constants

$$K_{\mathrm{Fe(II)_1}} = \frac{a_{\mathrm{Fe^{++}}} \cdot a_{\mathrm{RSH^-}}}{a_{\mathrm{Fe(OH)(RS)^-}} \cdot a^2_{\mathrm{H^+}}} \text{ and}$$

$$K_{\mathrm{Fe(II)_2}} = \frac{a_{\mathrm{Fe^{++}}} \cdot a^2_{\mathrm{RSH^-}}}{a_{\mathrm{Fe(RS)_2^{=}}} \cdot a^2_{\mathrm{H^+}}}$$

refer to the equilibria

$$\mathrm{Fe(OH)(RS)^-} + 2\mathrm{H^+} \rightleftarrows \mathrm{Fe^{++}} + \mathrm{RSH^-} + \mathrm{H_2O} \text{ and}$$

$$\mathrm{Fe(RS)_2^{=}} + 2\mathrm{H^+} \rightleftarrows \mathrm{Fe^{++}} + 2\mathrm{RSH^-}$$

When solid ferrous hydroxide is in equilibrium with the aqueous phase the ratio $a_{\mathrm{Fe^{++}}}/a^2_{\mathrm{H^+}}$ becomes equal to $S_{2\mathrm{Fe(OH)_2}}/K^2_{\mathrm{w}}$ where $S_{2\mathrm{Fe(OH)_2}}$ is defined as $a_{\mathrm{Fe^{++}}} \cdot a^2_{\mathrm{OH^-}}$. The above equations become

$$K_{\mathrm{Fe(II)_1}} = \frac{S_{2\mathrm{Fe(OH)_2}}}{K^2_{\mathrm{w}}} \cdot \frac{a_{\mathrm{RSH^-}}}{a_{\mathrm{Fe(OH)(RS)^-}}} \text{ and}$$

$$K_{\mathrm{Fe(II)_2}} = \frac{S_{2\mathrm{Fe(OH)_2}}}{K^2_{\mathrm{w}}} \cdot \frac{a^2_{\mathrm{RSH^-}}}{a_{\mathrm{Fe(RS)_2^{=}}}}$$

No precipitate of ferrous hydroxide was obtained in experiment 10 so $K_{\mathrm{Fe(II)1}}$ and $K_{\mathrm{Fe(II)2}}$ cannot be obtained as the activity of the ferrous ion in the solu-

TABLE II

CACULATED CONCENTRATIONS OF THE SPECIES PRESENT IN THE ALKALINE SOLUTIONS OF TABLE I

Exp. no.	$[RSH^-]$ M	$[RS^-]$ M	$[Fe(OH)(RSH)^-]$ M	$[Fe(RS)_2^-]$ M	γ_1	γ_2	$\frac{a_{RSH^-}}{a_{Fe(OH)(RS)^-}}$ [a]	$\frac{a^2_{RSH^-}}{a_{Fe(RS)_2^-}}$ [a]	$\frac{a_{Fe(OH)(RS)^-} \cdot a_{RSH^-}}{a_{Fe(RS)_2^=}}$
10	0.007	0.005	0.023	0.037	0.73	0.39	..	......	0.0059
11	.0056	.0162	.0118	.0176	.76	.41	0.48	3×10^{-3}	.0054
12	.0053	.0207	.0102	.0060	.76	.41	.53	7×10^{-3}	.0127
13	.007	.050	.017	.017	.73	.38	.42	4×10^{-3}	.0096
14	.0039	.044	.0108	.0059	.73	.38	.36	4×10^{-2}	.010
						Avg.	.44	4×10^{-3}	.009

[a] For "green" ferrous hydroxide. When solid ferrous hydroxide is in equilibrium with the aqueous phase this ratio should be constant.

tion is unknown. However, the ratio of these constants can be calculated as

$$\frac{K_{Fe(II)_2}}{K_{Fe(II)_1}} = \frac{a_{Fe(OH)(RS)^-} \cdot a_{RSH^-}}{a_{Fe(RS)_2^=}} = K$$

The results of calculations for the solutions in the alkaline range are presented in Table II. Values of the ionization constants for thioglycolic acid of 2.5 × 10^{-4} and 2.8 × 10^{-11} as calculated from measurements with the glass electrode[17] and values of activity coefficients γ obtained from the tables of Kielland[18] were used. Experiment 9 did not yield values sufficiently accurate for the calculation of K.

The ratios $a_{RSH^-}/a_{Fe(OH)(RS)^-}$ and $a^2_{RSH}/a_{Fe(RS)_2^-}$ are given in Table II for those solutions which are in equilibrium with solid ferrous hydroxide. The average of four experiments is 0.44. The ratio $a^2_{RSH^-}/a_{Fe(RS)_2^-}$ is 4×10^{-3}.

The precipitates of ferrous hydroxide obtained in these experiments were green. Using a value of $S_{2Fe(OH)_2}$ equal to 3.5×10^{-16} for "green" ferrous hydroxide[13] the values are calculated to be $K_{Fe(II)_1} = 1.5 \times 10^{12}$ and $K_{Fe(II)_2} = 1.5 \times 10^{10}$.

The average value of K is about 0.009 including experiment 10 in which no precipitate was obtained.

The equilibria involving the solubility of FeRS are best studied in acid solutions. The above values of $K_{Fe(II)1}$ and $K_{Fe(II)2}$ indicate that the presence of $Fe(OH)(RS)^-$ and $Fe(RS)_2^=$ can be neglected in the acid solutions in this series of experiments. The total iron concentration in these solutions is then equal to the free ferrous ion concentration. The following relations hold at equilibrium

$$[Fe]_t = [Fe^{++}]$$
$$[TGA]_t = [RSH_2] + [RSH^-]$$
$$[OH^-]_t = [RSH^-]$$

The activity constant, S_{FeRS}, can then be calculated for the equilibrium

$$FeRS_s + H^+ \rightleftarrows Fe^{++} + RSH^-$$

where

$$S_{FeRS} = \frac{a_{Fe^{++}} \cdot a_{RSH^-}}{a_{H^+}}$$

The results of these calculations are given in Table III. As a check on the validity of the assumptions the value of pH was calculated making use of the value of the first ionization constant of thioglycolic acid. This calculated value of pH is also presented in Table III. The agreement of the observed value with the calculated value is very good in experiments 1 and 2 and lends support to our interpretation.

TABLE III

CALCULATION OF $S_{FeRS} \frac{a_{Fe^{++}} \cdot a_{RSH^-}}{a_{H^+}}$ FOR THE EQUILIBRIUM: $FeRS(s) + H^+ \rightleftarrows Fe^{++} + RSH^-$

Exp. no.	Fe^{++} (M)	RSH^- (M)	RSH_2 (M)	γ_1	γ_2	pH$_{obs.}$	pH$_{calc.}$[a]	S_{FeRS}
1	0.0273	0.0587	0.0120	0.78	0.42	4.22	4.18	9
2	.0176	.0400	.0061	.80	.44	4.31	4.32	5
3	.0079	.0162	(.002)	.81	.47	4.85	(4.4)	4

[a] Calculated assuming $K_1 = 2.5 \times 10^{-4}$.

For the purposes of further calculation the value of S_{FeRS} equal to 7 was assumed.

Spectrophotometric Evaluation of K.—The complex ion, $Fe(RS)_2^=$, is colored red while $Fe(OH)(RS)^-$ is colored yellow so the constant $K_{Fe(II)2}/K_{Fe(II)1} = K$ can be evaluated spectrophotometrically for the equilibrium $Fe(RS)_2^= + H_2O \rightleftarrows Fe(OH)(RS)^- + RSH^-$. This equilibrium is independent of pH except to the extent that $[RSH^-]$ is affected by the pH.

Solutions were prepared under air-free conditions in sealed bottles. Each bottle was equipped with a cell consisting of a side arm of square glass tubing so that optical measurements could be made upon the solution within the bottle without transferring. Square glass Pyrex tubing with an internal bore of 1 cm. was attached at right angles to the side of a screw-cap Pyrex bottle, 125 ml. The bottle could be placed on its side in a Beckman Model B spectrophotometer so that the cell would fit into the carriage of the spectrophotometer. The bottle slid with the carriage so that the instrument could be balanced against a "blank" of water. A small wooden block was constructed to support the bottle on the side of the spectrophotometer. The entire cell cavity containing the bottle was then covered with a light-tight box. Readings were reproducible to 1% when the bottle was removed and then replaced.

A total volume of solution of 100 ml. was used in these experiments. Fifty ml. of 0.64 M NH_4NO_3, 0.68 M NH_4OH buffer was placed in the flask and then the desired volumes of 0.603 M thioglycolic acid, 0.517 M sodium hydroxide, and sufficient water so that the final volume of the reaction solution would be 100 ml.

The amount of sodium hydroxide added in order to maintain a constant pH was roughly calculated from the extent of the reaction expected from the data found previously. The bottles were then sealed with Buna N gaskets and screw-caps punched with holes and were bubbled out with nitrogen as described in the previous sections. The nitrogen was washed with an ammonia buffer of the same concentration as used in the experiment. After one-half hour of vigorous bubbling, the needles through which the nitrogen was admitted were removed and 4.0 ml. of an air-free 0.5 M $FeCl_2$ solution was injected with a syringe. The bottles were then kept at 25°. Experimental details are given in Table IV.

The solutions in the bottles all exhibited the same reddish yellow color upon first mixing. In 24 hours the solutions became more red in experiments 3 and 4 of Table IV but the solution in experiment 1 remained yellow. A small amount of green ferrous hydroxide separated out of the solution in experiment 1. In 5 days the optical densities measured at 530 and 750 mμ became constant.

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[17] D. G. Bush, unpublished results obtained in this Laboratory.

[18] J. Kielland, THIS JOURNAL, 59, 1675 (1937).

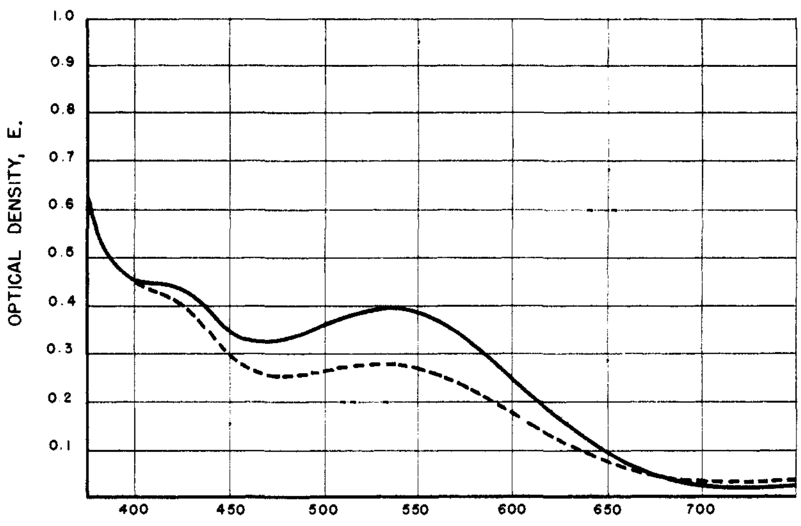

Fig. 1.—Optical density at equilibrium of solutions containing ferrous–thioglycolate complexes, solutions buffered with 0.32 M NH_4NO_3, 0.34 M NH_4NO_3: —·— $[Fe]_t$ = 0.0206 M, $[TGA]_t$ = 0.0500 M; - - - $[Fe]_t$ = 0.0206 M, $[TGA]_t$ = 0.1085 M.

The absorption curves of experiments 2 and 4 of Table IV at equilibrium are given in Fig. 1.

The optical density E of each of the solutions was determined *versus* water at 530 and 750 mμ and this was corrected for the cell "blank" and to a 1.00-cm. cell length. These corrected values are reported in Table IV.

The total iron concentration was determined colorimetrically with thioglycolic acid in the presence of air according to the standard procedure.[4]

The pH of each of these solutions at equilibrium was 9.5.

At equilibrium the solution in experiment 1 was yellow and in the other bottles the color became progressively more red as the total thioglycolic acid concentration became greater. This trend is reflected in the values of optical density at 530 and 750 mμ as reported in Table IV.

TABLE IV

SPECTROPHOTOMETRIC STUDIES OF SOLUBLE FERROUS IRON–THIOGLYCOLIC ACID COMPLEXES

The following reagents were mixed under air-free conditions in a buffer of 0.32 M NH_4NO_3, 0.34 M NH_4OH.

Exp. no.	$[Fe]_t$, M	$[TGA]_t$, M	$[NaOH]_t$, M	E_{530}	E_{750}	$[Fe(OH)(RS)^-]$,[a] M	$[Fe(RS)_2^=]$,[a] M
1	..	0.0362	0.072	0.118	0.047	....	....
2	0.0206	.0500	.093	.293	.044	0.0080	0.0126
3	.0201	.0700	.1138	.349	.028	.0046	.0155
4	.0206	.1085	.145	.395	.025	.0029	.0177

[a] Values of $[Fe(OH)(RS^-)]$ and $[Fe(RS)_2^=]$ were calculated as described in the text assuming the values of activity coefficients to be γ_1 = 0.65 and γ_2 = 0.42 in experiment 4, and γ_1 = 0.67 and γ_2 = 0.39 in experiments 2 and 3.

The following equations were set up in order to calculate the concentrations of the species present.

$$[Fe]_t = [Fe(OH)(RS)^-] + [Fe(RS)_2^=]$$

$$[TGA]_t = [RSH^-] + [RS^=] + [Fe(OH)(RS)^-] + 2[Fe(RS)_2^=]$$

$$E_{530} = \epsilon_{530-1}\cdot[Fe(OH)(RS)^-] + \epsilon_{530-2}[Fe(RS)_2^=]$$

$$K = \frac{[Fe(OH)(RS)^-][RSH^-]}{[Fe(RS)_2^=]}\cdot\frac{\gamma_1^2}{\gamma_2}$$

where ϵ_{530-1} and ϵ_{530-2} represent the extinction coefficients in M^{-1} cm.$^{-1}$ of $Fe(OH)(RS)^-$ and $Fe(RS)_2^=$, respectively.

A method of approximations was used to calculate the values for the concentrations of the species present.

The approximation was made that in experiments 3 and 4 the contribution of $Fe(OH)(RS)^-$ to the optical density is negligible. Experiments 3 and 4 can then very easily be solved simultaneously for a value of K' and ϵ_{530-2}, the extinction coefficient in M^{-1} cm.$^{-1}$ at 530 mμ of $Fe(RS)_2^=$.

An approximate value of ϵ_{530-1}, the extinction coefficient at 530 mμ of $Fe(OH)(RS)^-$, can then be calculated from the experimental data of experiment 2 and the approximate values of K' and ϵ_{530-2}. This approximate value of ϵ_{530-1} is then used in experiments 3 and 4 to find better values of K' and ϵ_{530-2}. This process is repeated until constant values are obtained.

The final values calculated by approximation are $\epsilon_{530-1} = 1.5\ M^{-1}$ cm.$^{-1}$, $\epsilon_{530-2} = 22.1\ M^{-1}$ cm.$^{-1}$ and K = 0.010. This value of K agrees very well with the value of 0.009 found above in the solubility studies.

Approximate values for the extinction coefficients at 750 mμ for $Fe(OH)(RS)^-$ and $Fe(RS)_2^=$ are ϵ_{750-1} = 4.4 and $\epsilon_{750-2} = 0.7\ M^{-1}$ cm.$^{-1}$. The data at this wave length are not very accurate, however.

Ferric Thioglycolate Complexes. Valence State of the Iron in the Intensely Red Complex.—The following experiment was carried out in order to learn quantitatively the effect of the valence state of the iron on the color produced.

A stock solution of 0.0102 M ferrous ammonium sulfate and 3.6 M thioglycolic acid in 0.005 M sulfuric acid was prepared air-free as, also, was a solution of 0.0103 M ferric ammonium sulfate in 0.005 M sulfuric acid. Twenty-five (25.0) ml. of 4 M ammonia and 73 ml. of water were placed in one of the bottles equipped for optical measurements. The bottle was sealed with a Buna N gasket and bubbled out with nitrogen as previously described. One (1.00) ml. of the air-free ferrous iron–thioglycolic acid solution was then injected into the solution in the bottle. The extinction at 530 mμ of this solution was measured to be the same as that of water used for the blank. One (1.00) ml. of the air-free ferric solution was then injected into the bottle. The deep red color was produced immediately. The extinction at 530 mμ was measured to be 0.384, corrected for the blank and to a 1.00-cm. cell length. The extinction remained at this value for about four minutes, then slowly began to decrease to 0.382 in 15 minutes and 0.376 in 24 minutes. The bottle was then opened to the air and shaken well. The extinction at 530 mμ increased to 0.775 (cor.).

TABLE V

EXTINCTION OF SOLUTIONS CONTAINING 0.036 M THIOGLYCOLATE AND 1 M AMMONIA

Initial Fe^{II} (M)	Initial Fe^{III} (M)	Obs. extinction at 530 mμ cor.	Calcd. extinction at 530 mμ[a]	Conditions
1.03×10^{-4}	0.0	0.000	0.000	Air-free
1.02×10^{-4}	1.03×10^{-4}	.384	.384	Air-free
1.02×10^{-4}	1.03×10^{-4}	.775	.765	Air-saturated
0.0	1.03×10^{-4}	.354	.384	Air-free
0.0	1.03×10^{-4}	.372	.384	Air-saturated

[a] Extinction calculated on the basis of the extinction coefficient of the ferric complex being equal to 3.73×10^3 M^{-1} cm.$^{-1}$ as determined in an air-saturated solution.

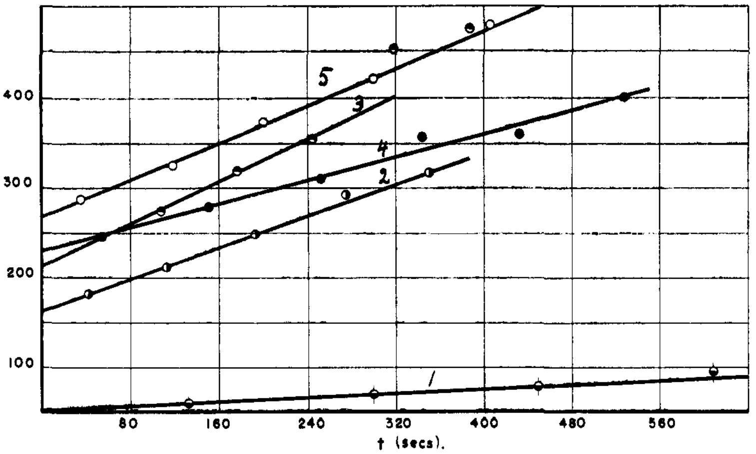

Fig. 2.—Concentration of iron in air-saturated thioglycolate solutions. Solid ferric hydroxide present (see Table VI). Multiply ordinate by 10 for experiment 5.

The experiment was repeated except that the air-free ferric solution was injected into an air-free ammoniacal thioglycolate solution from which the ferrous iron was omitted. The extinction was measured to be 0.354 (cor.) at 530 mμ. This reading was made about one minute after the mixing. The bottle was then opened to the air and shaken well. The extinction was observed to increase to 0.372 (cor.). This agrees with the theoretical value of 0.384 within the error of 2–3% in the iron concentration. A summary of the results is presented in Table V.

The 5% lower extinction of the air-free ferric solution (0.354) compared with the air-saturated ferric solution (0.372) must be due to reduction of the ferric iron before the extinction could be measured.

These results indicate that the intensely colored compound formed in air-saturated alkaline solutions is a ferric complex.

Solubility of Ferric Iron in Ammoniacal Thioglycolate Solutions.—When ferric iron is added in excess to an ammoniacal thioglycolate solution a brown precipitate is obtained. Dubsky and Sindelar[11] suggest that this precipitate could be an insoluble ferric thioglycolate, $Fe_2(RS)_3$, instead of ferric hydroxide. We have found, however, that no thioglycolate was precipitated from solution under our experimental conditions and that the precipitate consisted of ferric hydroxide.

In the following experiments the procedure was to add a slight excess of a ferric ammonium sulfate solution (so that a slight amount of a precipitate of ferric hydroxide was obtained initially) into a solution of a known concentration of thioglycolate in an ammonia–ammonium nitrate buffer. Because of the reduction of iron(III) by thioglycolate the iron concentration was determined as a function of time. The concentrations of ammonia and thioglycolate were varied throughout the series of experiments and the rate of disappearance of ferric iron studied as a function of these quantities.

The rate of decrease of ferric iron concentration was determined in air-saturated and, also, in air-free solutions.

In air-saturated solutions, because of the rapid oxidation of the ferrous complexes by oxygen the iron in solution may be considered to be all ferric. In air-free solutions the ferrous iron formed remains and is not reoxidized. In both cases as thioglycolate is consumed the solubility of iron(III) decreases and more ferric hydroxide precipitates

Air-saturated Solutions.—Thioglycolic acid was weighed into dry bottles of 250-ml. capacity. Known volumes of water and of standard solutions of ammonia and ammonium nitrate were then placed into the bottles. The details of each experiment are given in Table VI-A. Air previously washed with a buffer of the same concentration of ammonia and ammonium nitrate as used in the experiment was vigorously bubbled through the solution in each bottle, and finally the desired volume of 0.103 *M* ferric ammonium sulfate in 0.050 *M* sulfuric acid was added rapidly. The time was measured from this moment and samples of the solution were removed periodically for an iron analysis in the supernatant liquid. Before the analysis the solid ferric hydroxide suspended in the solution was removed by filtering under pressure through glass wool. The filtering required about one second.

The pressure filter consisted of a syringe of 50-ml. capacity that had been about one-third filled with glass wool. The sample was placed in the syringe through the open top and then the plunger was inserted and pushed down forcing the liquid through the glass wool. The time was noted when the liquid was forced through the glass wool.

A known volume of the filtered solution was removed with a pipet and analyzed for iron either by the volumetric method or the colorimetric thioglycolate method.

A blank made without thioglycolic acid showed that in the buffer used the precipitation of ferric hydroxide is rapid and quantitative.

It was found that in the *p*H range 9–10 plots of the reciprocal of the iron concentration *versus* time gave straight lines. However, at a *p*H less than 9 the rate of disappearance of the iron in solution became very great, and the iron concentration decreased linearly with time. Because of the experimental error involved in these rapid reactions only those experiments carried out at a *p*H of 9 or greater were used to obtain by extrapolation a value of $[Fe]_0$, the iron concentration at zero time. The plots by which values of $[Fe]_0$ were obtained are illustrated in Fig. 2 and the experimental details are given in columns 1–4 of Table VI-A.

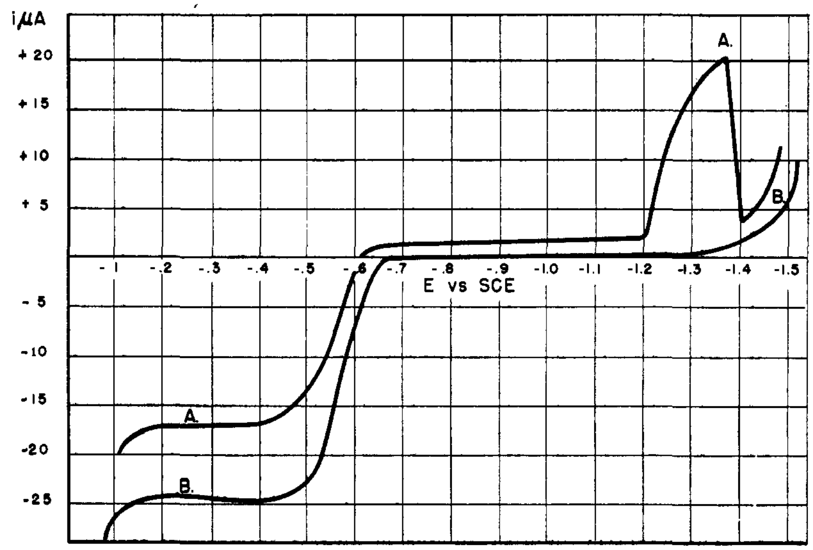

Fig. 3.—Current–voltage curve of TGA in 0.80 *M* NH_3–0.20 *M* NH_4NO_3 buffer: (A) 0.00675 *M* TGA + excess $Fe(OH)_3(s)$, (B) 0.00752 *M* TGA.

Air-free Solutions.—The ferric–thioglycolate complex gives a cathodic wave at the dropping mercury electrode and the diffusion current of this wave was used to determine the instantaneous concentration of the ferric complex in air-free ammoniacal thioglycolate solutions saturated with solid ferric hydroxide.

Current–voltage curves of ammoniacal thioglycolate solutions with and without ferric iron are illustrated in Fig. 3. To obtain the current–voltage curves illustrated in Fig. 3,

TABLE VI

SOLUBILITY AT ZERO TIME OF FERRIC IRON IN AMMONIACAL THIOGLYCOLATE SOLUTIONS AND "APPARENT" CONSTANTS FOR THE EQUILIBRIUM: $Fe(OH)_3 + n RSH^- \rightleftarrows Fe(OH)_{3-n}(RS)_n^{-n} + n H_2O$

Exp. no.	Initial [TGA],[a] M	Total $[Fe^{III}]$, M	$[NH_3]$,[b] M	$[NH_4^+]$,[b] M	$[Fe]_0$,[c] M	$n = 1$ $[RSH^-]$, M	$n = 1$ k_1[d]	$n = 2$ $[RSH^-]$, M	$n = 2$ k_2[e]	$n = 3$ $[RSH^-]$, M	$n = 3$ k_3[f] × 10^6
					A. Air-saturated Solutions						
1	0.0580	0.026	0.68	0.33	0.0196	0.0293	1.5	0.0143	0.010	....	...
2	.0221	.0103	0.15	.25	.0060$_5$	.0149	2.5	.0093	.014	0.0038	0.9
3	.0211$_5$	.0103	1.56	.26	.0043$_5$	.0093	2.1	.0069	.011	.0045	2.1
4	.0192$_5$	.0103	0.34	.26	.0047	.0124	2.6	.0084	.015	.0044	1.8
5	.0041	.0051	0.74	.22	.00037$_2$	.0025	6.8	.0023	.014	.0020	2.5
					B. Air-free Solutions						
6	0.0182	0.0069	0.78	0.26	0.00343	0.0106	3.1	0.0081	0.019	0.0056	5.2
7	.0095	.0030	.82	.22	.00149	.0053	3.6	.0043	.013	.0033	2.5
8	.0071$_3$	.0028	.83	.21	.0008$_8$	.0041	4.7	.0035	.014	.0029	2.8
9	.00478	.0020	.83	.21	.0003$_8$	.0029	7.6	.0026	.018	.0024	3.7

[a] Corrected for the volume of 0.103 M ferric ammonium sulfate added. [b] Corrected for the changes in concentration brought about by precipitation of $Fe(OH)_3$ and neutralization of the hydrogen ion of thioglycolic acid, etc. [c] The value of the iron concentration obtained at zero time. [d] $k_1 = [RSH^-]/[Fe]_0$. [e] $k_2 = [RSH^-]^2/[Fe]_0$. [f] $k_3 = [RSH^-]^3/[Fe]_0$.

25 ml. of a 0.00752 M thioglycolate solution in an ammonia buffer was placed in a polarographic cell, deaerated and a polarogram obtained with the recording Sargent Model XXI Polarograph. Then 2.8 ml. of an air-free solution of 0.103 M ferric ammonium sulfate in 0.05 M sulfuric acid was injected into the solution and another polarogram was started immediately.

Both of the solutions gave the anodic wave of thioglycolate. However, after the iron solution had been injected into the solution in the cell, the thioglycolate wave decreased by more than can be accounted for by dilution or oxidation to dithiodiglycolate during the time of the experiment. Also, a cathodic current was observed at potentials more negative than −0.65 v. *vs.* S.C.E. after the iron was added. The cathodic current is due to the reduction of a ferric complex to a ferrous.

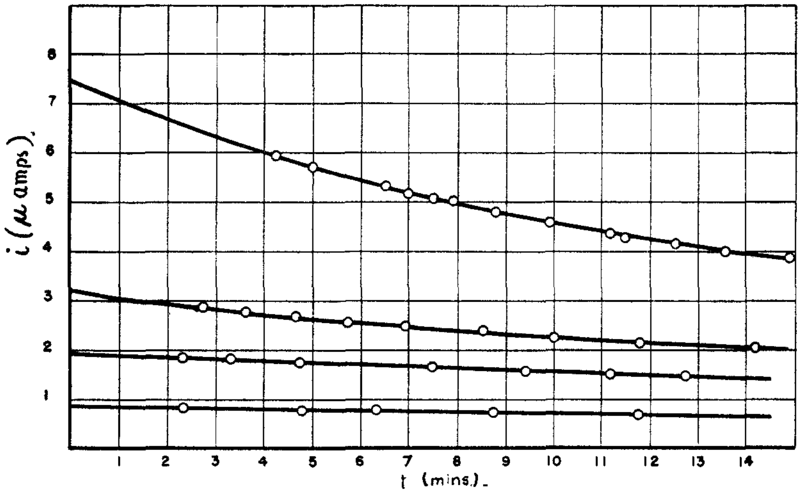

Fig. 4.—The iron(III) diffusion current in air-free ammoniacal thioglycolate solutions. Data are given in Table VIB.

A large increase in current was observed at −1.2 volts, the wave exhibiting a pronounced maximum at −1.34 volts. The discharge of the supporting electrolyte prevented a closer examination of this second "wave." The diffusion coefficient of the ferric complex was evaluated by extrapolation to zero time of the diffusion current observed at −0.80 volt *vs.* S.C.E. in a solution which was 0.0488 M in thioglycolate, 0.84 M in ammonia, 0.20 M in ammonium nitrate and 9.7 × 10^{-4} M in ferric ammonium sulfate (no ferric hydroxide precipitate). The manual polarograph and capillary II described in a previous publication[16] were used. The value of the diffusion coefficient for the ferric complex calculated using the Ilkovic equation[19] and assuming a one electron reduction was 7.0 × 10^{-6} cm.^{2} sec.$^{-1}$ at 25°.

The studies of air-free thioglycolate solutions saturated with ferric hydroxide were carried out as follows.

Twenty-five ml. of a solution of known concentration of thioglycolate in 0.20 M ammonium nitrate and 0.84 M ammonium hydroxide was placed in a polarographic cell and deaerated. The air-free 0.103 M ferric solution was then added to the cell in sufficient amount to produce a slight initial precipitate of ferric hydroxide. The current was measured at −0.80 volt *vs.* S.C.E. as a function of time. The details of this series of experiments are given in Table VI-B.

Before the addition of the ferric solution, the current observed at −0.80 volt for the ammoniacal thioglycolate solution was equal to the residual current obtained in this buffer. Immediately upon the addition of the ferric solution the current increased and then slowly decreased with time as illustrated in Fig. 4.

Various functions of the current were plotted *versus* time in order to obtain a straight line. The following behavior was noted with decreasing concentration of thioglycolate in the initial solution. A straight line was obtained in experiment 6 of Table VI for a plot of the reciprocal of the current *versus* time. This same function also yielded a straight line in experiment 7 for the values obtained within the first seven minutes but after this time the current decreased at a smaller rate. The rate of decrease of the current was even less in experiments 8 and 9. In these last two experiments a straight line was obtained for a plot of the logarithm of the current *versus* time.

The current at zero time was obtained by extrapolation of the linear plots and the concentration of the ferric complex at zero time was then calculated from the diffusion current constant found above. At zero time, when no thioglycolate has been oxidized, the thioglycolate concentration can

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[19] See I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed. Interscience Publishers, Inc., New York, N. Y., 1952, p. 43.

be readily calculated from the amount added.

An analysis of the data of Table VI reveals that $[\mathrm{Fe}]_0$ depends on the initial concentration of thioglycolate (present mostly as RSH^- in the *p*H range studied) but does not depend on the ratio $[\mathrm{NH_3}]:[\mathrm{NH_4^+}]$, *i.e.*, *p*H, to as great an extent as expected for an equilibrium of the type

$$\mathrm{Fe(OH)_{3(s)}} + n\mathrm{RSH}^- \rightleftharpoons \mathrm{Fe(RS)}_n{}^{3-2n} + (3-n)\mathrm{OH}^- + n\mathrm{H_2O}$$

This suggests that the equilibrium between the soluble complex, thioglycolate and solid ferric hydroxide is of the form

$$\mathrm{Fe(OH)_{3(s)}} + n\mathrm{HRS}^- \rightleftharpoons \mathrm{Fe(OH)}_{3-n}\,(\mathrm{RS})_n{}^{-n} + n\mathrm{H_2O} \tag{1}$$

The following equations may then be set up

$$[\mathrm{Fe}]_0 = [\mathrm{Fe(OH)}_{3-n}(\mathrm{RS})_n{}^{-n}] \text{ at zero time} \tag{2}$$

$$[\mathrm{TGA}]_\mathrm{i} = [\mathrm{RSH}^-] + [\mathrm{RS}^=] + n[\mathrm{FeO(H)}_{3-n}\,(\mathrm{RS})_n{}^{-n}] \tag{3}$$

where $[\mathrm{TGA}]_\mathrm{i}$ is equal to the total initial concentration of thioglycolate.

Considering the equilibrium

$$\mathrm{NH_3} + \mathrm{RSH}^- \rightleftharpoons \mathrm{NH_4^+} + \mathrm{RS}^=$$

$$\frac{[\mathrm{RS}^=][\mathrm{NH_4^+}]}{[\mathrm{RSH}^-][\mathrm{NH_3}]}\colon \gamma_2 = \frac{K_2 \cdot K_\mathrm{b}}{K_\mathrm{w}} \tag{4}$$

where K_2 is the second ionization constant of thioglycolic acid, K_b is the basic dissociation constant of ammonia, K_w is the activity product of water and γ_2 is the activity coefficient of the divalent ion.

The following equation is then derived from equations (2), (3) and (4).

$$[\mathrm{RSH}^-] = \frac{[\mathrm{TGA}]_\mathrm{i} - n[\mathrm{Fe}]_0}{1 + \dfrac{K_2 \cdot K_\mathrm{b}[\mathrm{NH_3}]}{K_\mathrm{w} \cdot \gamma_2[\mathrm{NH_4^+}]}} \tag{5}$$

A concentration constant, k_n, can be set up for the reaction represented in equation (1) where

$$k_n = \frac{[\mathrm{RSH}^-]^n}{[\mathrm{Fe}]_0} \tag{6}$$

Apparent values of k_n can be calculated by assuming the likely values of n equal to one, two or three in equation (5) to obtain an apparent value of $[\mathrm{RSH}^-]$, which can be inserted in equation (6). Values of $K_2 = 2.8 \times 10^{-11}$, found in this Laboratory,[17] $K_\mathrm{b} = 1.81 \times 10^{-5}$ from Latimer[20] and $K_\mathrm{w} = 10^{-14}$ were used in solving equation (5). The value of γ_2 was taken to be 0.38 in all of the experiments as the minimum in the activity coefficient curve occurs in the range of ionic strength (0.25–0.35) of the present experiments; also, the denominator in equation (5) can allow a slight variation in γ_2 without changing its value significantly.

The apparent values of k_n and $[\mathrm{RSH}^-]$ calculated according to the above procedure are also given in Table VI. Values of k_1 calculated assuming n equal to one show a trend as the thioglycolate concentration increases. Values of k_2 assuming n equal to two are reasonably constant while values of k_3 assuming n equal to three show a trend in the more concentrated solutions. In experiment 9 the amount of thioglycolate present was insufficient to form a complex of the formula, $\mathrm{Fe(RS)_3}^{---}$. Even allowing for experimental error the value of k_3 obtained would indicate a much more stable complex than do the values of k_3 calculated from the other experiments in this series. The most likely formula for the complex is, therefore, $\mathrm{Fe(OH)(RS)_2}^-$. The empirical formula of the complex ion postulated by Martell[14] is the same as that found in the present work. The calculation from the present data of an "apparent" concentration constant assuming the dimeric formula of Martell results in a "constant" that varies greatly with the concentration of thioglycolate. Also, the value of 7.0 × 10⁻⁶ cm.² sec.⁻¹ calculated above for the diffusion coefficient of the ferric complex agrees well with those reported for other monomeric iron complexes.

The average of the concentration constant

$$k_2 = [\mathrm{RSH}^-]^2/[\mathrm{Fe(OH)(RS)_2}^-]$$

from all experiments is 0.014 at 25°.

Assuming a value of γ_1 equal to 0.73 and γ_2 equal to 0.38 for the solutions of ionic strength 0.25 the activity constant

$$a^2_{\mathrm{RSH}^-}/a_{\mathrm{Fe(OH)(RS)_2}^-}$$

becomes equal to 0.020. If the value reported by Latimer[21] for the solubility product of ferric hydroxide of 6×10^{-38} is accepted the constant $K_{\mathrm{Fe(III)}}$ is calculated to be equal to 1.2×10^3 for the equilibrium

$$\mathrm{Fe(OH)(RS)_2}^- + 3\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{+++} + 2\mathrm{RSH}^- + \mathrm{H_2O}$$

where

$$K_{\mathrm{Fe(III)}} = \frac{a_{\mathrm{Fe}^{+++}} \cdot a^2_{\mathrm{RSH}^-}}{a_{\mathrm{Fe(OH)(RS)_2}^-} \cdot a^3_{\mathrm{H}^+}}$$

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[20] W. M. Latimer, "Oxidation Potentials" 2nd ed., Prentice-Hall Inc., New York, N. Y., 1952, p. 354.

[21] W. M. Latimer, ref. 20, p. 224.