

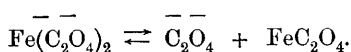
XXIII.—*The Molecular Condition in Solution of Ferrous Oxalate.*

By SAMUEL EDWARD SHEPPARD and CHARLES EDWARD KENNETH MEES.

THE investigation of the development of silver haloid emulsions by means of ferrous oxalate makes a knowledge of its condition in solution very desirable. Ferrous oxalate itself is only slightly soluble in water, and the developing solution is prepared by dissolving it in potassium oxalate. This solution has a reddish-brown colour and powerful reducing properties (Eder, *Monatsh.*, 1880, 1, 137). On treatment with alcohol, a double salt is precipitated having the composition $K_2Fe(C_2O_4)_2 \cdot 2H_2O$. The precipitate sometimes appears as a red oil, which subsequently crystallises, but more frequently it is obtained as a sludge. This substance is extremely soluble in water, but rapidly decomposes even in a dry state.

If aqueous potassium oxalate is added to the requisite amount of ferrous oxalate to form the double salt, the whole of the ferrous oxalate does not go into solution; further, if equimolecular solutions of ferrous sulphate and potassium oxalate are mixed, ferrous oxalate is precipitated. In general, more of the alkaline oxalate is employed than the proportion required to yield the double salt. Hence, an equilibrium must be established in solution between the amounts of iron and oxalate. The iron is not present to any great extent as free ferrous ions, as the blue precipitate with ferricyanide is only slowly formed. It seems to exist chiefly as the complex anion, $Fe(C_2O_4)_2$ (Rieger, *Zeit. Elektrochem.*, 1901, 7, 871), to which the colour of the solution is due.

The double salt, therefore, dissociates into $2K^+$ and $Fe(C_2O_4)_2^-$, and the foregoing equilibrium will be of the form



In the presence of solid ferrous oxalate, the active mass of the latter will be constant, and we shall have as equilibrium equation:

$$KC_1 = K'C_2, \text{ or } C_1/C_2 = K'/K = K, \text{ a constant,}$$

that is, the amount of ferro-oxalanion* in solution bears a constant ratio to the amount of free oxalanion.

To confirm this view and to ascertain the value of the equilibrium

* The ionic terminology employed is that indicated in the English translation of Ostwald's *Anorganische Chemie*.

constant, the solubility of ferrous oxalate in potassium oxalate was determined, the ferrous oxalate being kept in excess; 10 c.c. of a solution containing the molecular weight in grams per litre of potassium oxalate were added, and the whole stirred continuously in a thermostat at 20°.* The potassium oxalate was titrated against $N/10$ potassium permanganate, a similar estimation being subsequently made with the ferrous oxalate mixture. The increase in the titre gave the amount of ferrous oxalate dissolved. Thus, in one estimation, the titrations before and after the addition of ferrous oxalate were respectively 197.8 c.c. and 266.2 c.c. of permanganate. The increase is 68.4 c.c., and the value of

$$K = \frac{C_{\text{Fe}(\text{C}_2\text{O}_4)_2}}{C_{\text{C}_2\text{O}_4}} \text{ is } \frac{102.6}{163.6} = 0.63.$$

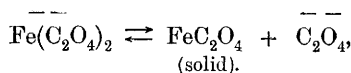
An increase in the time of stirring raised this value to a certain point and then lowered it again. This result is due to saturation only being reached slowly, and then oxidation causing a diminution. The maximum mean value found for

$$K = \frac{C_{\text{FeOx}}}{C_{\text{Ox}}} \text{ was } 0.80 (\mp 0.02 \Delta).$$

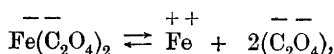
This result was checked by obtaining the equilibrium from the opposite side. Excess of ferrous sulphate in molecular solution was added to potassium oxalate, and, when ferrous oxalate was no longer precipitated, the solution was titrated. The errors in this case are in the opposite direction, as supersaturation will give too high values of K , whilst oxidation will diminish this constant.

Thus, to 5 c.c. of $2N$ potassium oxalate, 2.0 c.c. of $2N$ ferrous sulphate were added, and, after standing in the thermostat, the solution was titrated with $N/10$ permanganate, filtering off the ferrous oxalate. The difference gave the amount of this salt precipitated, and the following values of $K = \frac{C_{\text{Fe}(\text{C}_2\text{O}_4)_2}}{C_{\text{C}_2\text{O}_4}}$ were obtained: 0.84, 0.705, 0.72, 0.68, 1.06, 0.915. The mean gives $K=0.82$. The mean of the first series gave $K=0.80$, whence $K=0.81$ at 20°.

This confirms the view of the equilibrium



but the complex may also dissociate in the following manner:



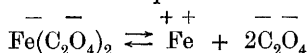
* For apparatus used, see Walker and Lumsden (Trans., 1902, 81, 353).

giving free ferrous ions, which may take part in development (Luther, *Chemische Vorgänge in der Photographie*), although, as already stated, their concentration is small. The proportion cannot be determined analytically, but spectrophotometric measurements will give some idea of it, as the ferro-oxalanion is highly coloured, while the free ferrous ion is practically colourless (F. Peters, *Zeit. physikal. Chem.*, 1898, **26**, 192). The change occurring on dilution was measured in the Hüfner spectrophotometer (*Zeit. physikal. Chem.*, 1889, **3**, 562). In this, the extinction coefficient E is equal to $-\log_e \cos^2 \theta$, where θ is the angle of rotation of the analysing Nicol. For convenience, E is given to base 10. The following measurements were obtained on diluting with water at $\lambda = 5420 \mu\mu$.

Solution strength.	Angle.	E .	Ratio of $E \frac{a}{b}$.
<i>a.</i> $N/10$ FeSO_4 + sat. $\text{K}_2\text{C}_2\text{O}_4$ to 10 c.c....	63.5°	0.700	2.0
<i>b.</i> + Equal vol. H_2O	47.75	0.342	
<i>a.</i> $N/5$ FeSO_4 + sat. $\text{K}_2\text{C}_2\text{O}_4$ to 10 c.c. ...	72.95	1.070	1.84
<i>b.</i> + Equal vol. H_2O	59.2	0.582	
<i>a.</i> $3N/10$ FeSO_4 + sat. $\text{K}_2\text{C}_2\text{O}_4$ to 10 c.c....	81.52	1.662	1.92
<i>b.</i> + Equal vol. H_2O	68.4	0.865	

The measurements were made in a cell of 10 mm. thickness at 17° approximately.

They show that the concentration of the ferro-oxalanion is proportional to the dilution, so that the equilibrium



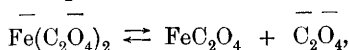
is practically negligible.

The following measurements exhibit the absorption spectrum at three higher concentrations. The extinction-coefficient E was plotted against wave-length. The coefficients E_a , E_b , E_c in the following table correspond with a concentration of ferrous sulphate in a saturated potassium oxalate solution of $N/10$, $N/5$, and $3N/10$ strength respectively.

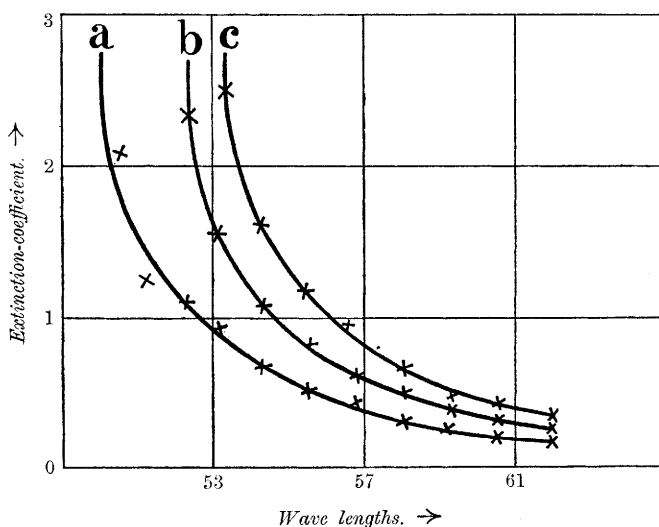
Wave length.	E_a .	E_b .	E_c .	Wave length.	E_a .	E_b .	E_c .
6200	0.144	0.174	0.180	5420	0.700	1.068	1.668
6070	0.153	0.264	0.332	5280	0.852	1.542	2.562
5930	0.184	0.294	0.388	5120	1.142	—	—
5800	0.284	0.366	0.570	5100	1.232	—	—
5670	0.350	0.576	0.892	5020	2.120	—	—
5540	0.504	0.872	1.202	4930	∞	—	—

Influence of Acids.

As all the developing solutions employed were slightly acidified with sulphuric acid, the action of acids is interesting. If increasing quantities of an acid are added to a ferrous oxalate solution, a point is soon reached when ferrous oxalate is precipitated. This must be due to a disturbance of the equilibrium



and on the ionic theory this is obviously due to the removal of the oxalanion according to the equation: $\overline{\text{C}_2\text{O}_4} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{C}_2\text{O}_4$, oxalic



Absorption spectrum of ferrous oxalate in potassium oxalate.

acid, as a "weak" acid, being much less dissociated than its salts. The disturbance therefore increases with the "strength" of the acid, and qualitative tests supported this view. Neglecting any formation of ferrous ions, the equation

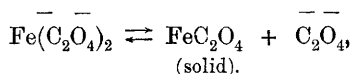
$$\frac{C_{\text{Fe}(\text{C}_2\text{O}_4)_2}}{C_{\text{Fe}(\text{C}_2\text{O}_4)}} = KC_{\text{C}_2\text{O}_4}$$

may be said to measure the complexity ratio (Donnan and Basset, Trans, 1902, 81, 945) of the ferro-oxalanion, and the measurements show that the complex ion is not very stable, since a considerable excess of free oxalate is required to keep the ferro-oxalanion undis-

sociated. It may be pointed out that solutions supersaturated with respect to ferrous oxalate are easily prepared, and this explains the complete solution of the double salt $K_2Fe(C_2O_4)_2 \cdot 2H_2O$ when prepared according to Souchay and Lenssen's method (*Annalen*, 1858, 105, 255). This solution is supersaturated with respect to ferrous oxalate. The molecular condition of ferric oxalate solutions is more complex, as this salt itself is soluble. It is uncertain whether the complex anion has the formula $\overline{\overline{Fe(C_2O_4)_2}}$ or $\overline{\overline{Fe(C_2O_4)_3}}$; double salts corresponding with both are known, and probably both are existent in ferric oxalate solutions. The ferric complexes are probably more stable than the ferrous, in agreement with Abergg and Bodländer's theory of electro-affinity (*Zeit. anorg. Chem.*, 1899, 20, 453).

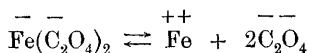
Summary.

(1) The iron is chiefly present as the complex anion $\overline{\overline{Fe(C_2O_4)_2}}$; this, however, is not very stable, and for the dissociation



the equation $\frac{C_{\overline{\overline{Fe(C_2O_4)_2}}}}{C_{\overline{\overline{C_2O_4}}}} = K$ holds, the value found for K being 0.81 at 20°.

(2) Spectrophotometric measurements showed that at moderate concentration the dissociation



is negligible.

(3) The action of acids is to precipitate ferrous oxalate by disturbing the equilibrium in (1).

(4) The absorption spectrum at three concentrations is given.

In conclusion, the authors desire to express their thanks to Professor Sir William Ramsay, F.R.S., for his interest in the work.

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