CCCCXXVIII.—*Stability of Ferrous Sulphate Solutions and their Use in Standardising Permanganate.*

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FOR many years it has been known that dilute, acidified solutions of ferrous sulphate are very resistant at the ordinary temperature to oxidation by free air or oxygen. The first to study the subject systematically appears to have been McBain (*J. Physical Chem.*, 1901, 5, 623), who introduced oxygenated water into bottles containing solutions of ferrous sulphate in an inert atmosphere. He observed that the reaction was approximately unimolecular, the rate of oxidation being proportional to the oxygen concentration, and rising rapidly both with the temperature and with concentration of the ferrous sulphate solution. He also found that sulphuric acid ranging in concentration from $N/50$ to N (referred to as $N/2$ in the text, but apparently by a typographical error) exerted a small but definite retarding action.

Some of these observations have been confirmed and extended by other investigators (see Peters and Moody, *Amer. J. Sci.*, 1901, 12, 369; Phelps, *Z. anorg. Chem.*, 1904, 38, 110; Müller and Kapeller, *Z. Elektrochem.*, 1908, 14, 76; Baskerville and Stevenson, *J. Amer. Chem. Soc.*, 1911, 33, 1104), notably by Ennos (*Proc. Camb. Phil. Soc.*, 1913, 17, 182), who concluded that atmospheric oxidation takes place *via* the un-ionised portion of the ferrous salt, and by Warynski (*Ann. Chim. Analyt.*, 1909, 14, 45) and Banerjee (*Z. anorg. Chem.*, 1923, 128, 343), who have studied the retarding or accelerating influence of dissolved salts and free acids, but in very dilute solution only.

On the other hand, Reedy and Machin (*J. Ind. Eng. Chem.*, 1923, 15, 1271), in contrast to McBain, found that on bubbling air through

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solutions of ferrous sulphate ranging in concentration from 2 to 7%, the rate of oxidation was but little affected by the concentration.

Now, Russell (J., 1926, 497) has shown that titanous sulphate in $4N$-sulphuric acid is very resistant to atmospheric oxidation, and that even vanadous sulphate in $10N$-sulphuric acid in a burette is not measurably oxidised by air within an hour. It seemed probable, therefore, that comparable concentrations of sulphuric acid might exert a powerful retarding effect upon the oxidation of ferrous sulphate solutions. In view of the wide use of ferrous sulphate for standardising permanganate solutions, it was decided to investigate these points more closely.

FIG. 1.

Normality of sulphuric acid.
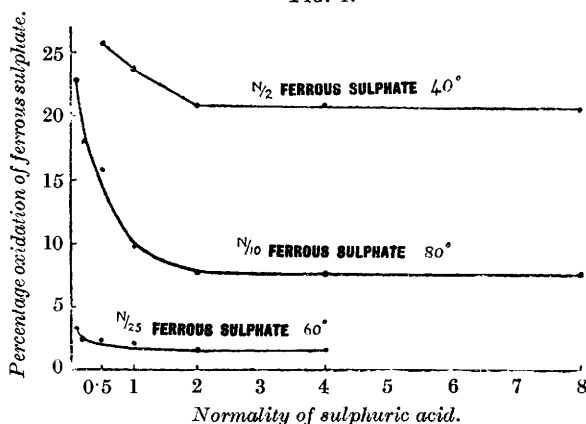
E X P E R I M E N T A L.

Influence of Concentration of Sulphuric Acid.—A slow current of purified air, saturated with moisture, was drawn through a series of flasks containing acid solutions of ferrous sulphate kept in a thermostat. At the conclusion of each run, the unoxidised ferrous sulphate was determined by titration with permanganate.* A few typical results are as follows :

Conc. of FeSO$_4$.	Temp.	Period of aspiration (hours).	Percentage oxidation of ferrous sulphate in sulphuric acid of concentration :						
			$N/10$.	$N/5$.	$N/2$.	N.	$2N$.	$4N$.	$8N$.
$N/25$	60°	33	3·22	2·50	2·32	2·11	1·59	1·63	—
$N/10$	60	33	6·80	5·80	5·19	3·79	2·81	2·79	—
$N/10$	80	33	22·86	17·97	15·91	9·79	7·94	7·68	7·51
$N/2$	40	100	—	—	25·72	23·80	20·91	20·88	20·36

These results are shown in Fig. 1. At all the temperatures studied, increase in concentration of sulphuric acid up to $2N$ greatly

* In all experiments a few drops of manganous sulphate solution were added prior to titration.

increased the resistance to oxidation; beyond this point, however, further increase in acid had but little effect.   If the function of the sulphuric acid were merely to reduce ionisation of the ferrous salt, one would expect, in accordance with the theory of Ennos, an increased oxidation on addition of the acid.

It would appear, therefore, that some complex is formed in solution which is more resistant to oxidation than un-ionised ferrous sulphate alone.

The increased oxidation with rise of temperature is clearly indicated and is in harmony with previous work.

Influence of Concentration of Ferrous Sulphate.—The foregoing results appear to indicate also that the percentage oxidation rises with the concentration of the ferrous sulphate, as noted by McBain (*loc. cit.*).   In view of the contrary statement of Reedy and Machin (*loc. cit.*), however, it seemed desirable to confirm this, since any two of the preceding series may not be strictly comparable owing to the difficulty of ensuring exactly the same conditions of aspiration in two sets of tests.   Further experiments were therefore carried out in which air was drawn through flasks containing solutions of ferrous sulphate of various concentrations in N-sulphuric acid at 40°.   The results were as follows :

Period of aspiration (hours).	Percentage oxidation in ferrous sulphate solution of concentration :			
	$N/3$.	$N/5$.	$N/10$.	$N/25$.
50	12·03	7·67	3·84	2·24
30	7·14	4·55	2·18	0·44

The percentage oxidation is seen to be approximately proportional to the concentration, the oxidation–concentration curve being only slightly concave to the concentration axis.   This supports the view (Ennos, *loc. cit.*) that the reaction is bimolecular at temperatures above atmospheric.

The optimum conditions for stability of ferrous sulphate solutions are thus high dilution, low temperature, and acidity of at least $2N$.

Preparation of Standard Solutions.—McBain concluded that, since dilute solutions of ferrous sulphate manifest relatively high stability, it should be unnecessary, when preparing standard solutions by dissolving iron in sulphuric acid, to observe the classical precaution of allowing the exit tube from the dissolving-flask to dip into sodium carbonate solution in order to prevent inrush of air during cooling. In two experiments he showed that, upon dissolving 1·4 g. of iron wire in 75 c.c. of $3N$-sulphuric acid over the Bunsen flame under continuous aëration, finally cooling rapidly and diluting to 250 c.c., the $N/10$-ferrous sulphate solution thus obtained contained only

0·04—0·05% of ferric iron, an amount usually negligible in ordinary volumetric analysis.

In view of the rapid increase in the rate of oxidation with rise of iron concentration, these results can only be taken, without further data, to apply to the particular concentrations used by McBain. The subject does not appear to have been further investigated, and the use of the carbonate trap is still recommended in modern text-books (see Bassett, " The Theory of Quantitative Analysis," 1925, p. 276).

In order to ascertain the limits within which no special precautions to avoid oxidation need be taken, the following experiments were carried out.   Weighed pieces of iron wire were put into each of several series of round-bottomed flasks of ca. 500 c.c. capacity containing 100—200 c.c. of $4N$-sulphuric acid, and warmed on the water-bath. The first flask in each series was fitted with a carbonate trap ; the others were fitted with vertical tubes through rubber bungs, the tubes being some 20″ in length and of 0·2″ internal diameter.   These functioned mainly as air condensers to prevent mechanical loss of solution with the escaping hydrogen, but also assisted to retain an atmosphere of hydrogen within the flask.   Immediately the iron had completely dissolved, the flasks were rapidly cooled by immersion in a tank of cold water with gentle agitation but avoiding bubble formation.   The contents of each flask were then made up to 250 c.c.,* the suspended carbon allowed to settle—a necessary precaution—and 25 c.c. titrated with permanganate.   The results obtained in three selected series are given below, each titration representing the mean of several agreeing to within 0·03 c.c.

Initial vol. of acid.	200 c.c.	200 c.c.	100 c.c.†
Fe (g.) in 250 c.c.‡	4·3	1·4	1·0
Conc. of $KMnO_4$	$N/3$	$N/10$	$N/10$
	C.c. $KMnO_4$ per 0·43 g. Fe.	C.c. $KMnO_4$ per 0·14 g. Fe.	C.c. $KMnO_4$ per 0·1 g. Fe.
With carbonate trap	23·54	25·20	18·10
With vertical tube	23·57	25·22	18·09

† $6N$-Sulphuric acid.

‡ In all the tests pure Armco iron wire was used.   For analysis, see p. 3232.

The results clearly justify the omission of the carbonate trap when a vertical tube is used, provided that (i) the flask is removed from the water-bath immediately the iron has dissolved, and rapidly cooled in cold water, and (ii) the initial concentration of the sulphuric acid is sufficiently high to exceed $2N$ after the iron has dissolved.   The former condition entails constant supervision of the experiment, which may be more trouble than the use of the carbonate trap.

* Recently-boiled distilled water was used in the experiment with the carbonate trap and ordinary distilled water in those with the vertical tube.

Experiments were therefore carried out to determine if rigid adherence to that condition is necessary. Approximately 1·4 g. of iron were dissolved in 150 c.c. of $4N$-sulphuric acid under various conditions, and the solutions made up to 250 c.c. (see footnote, p. 3230); 25 c.c. were titrated with approximately $N/10$-permanganate with the following results (means of two titrations agreeing to 0·02 c.c.), calculated for exactly 1·400 g. of iron.

		$KMnO_4$, c.c.
1. Carbonate trap		25·69
2. Vertical tube.	Flask removed immediately iron dissolved, and rapidly cooled	25·72
3. Do.	Flask removed immediately iron dissolved, and cooled slowly in air	25·65
4. Do.	Flask kept 20 mins. on water-bath after iron had dissolved; then rapidly cooled	25·71
5. Do.	Flask kept 20 mins. on water-bath after iron had dissolved; cooled slowly in air	25·69
6. Do.	Flask kept 40 mins. on water-bath after iron had dissolved; cooled slowly in air	25·63

These results agree to within 0·4%, which is frequently sufficient for ordinary works practice. The best results are obtained by rapid cooling upon removal from the water-bath, whilst a few minutes extra on the bath after the iron has dissolved do not appreciably influence the result (Expts. 2 and 4).

In almost every case the vertical-tube method, as carried out in Expt. 2, yielded a slightly higher result (ca. 0·1%) than the carbonate-trap method. This would have been attributed to experimental error had it not occurred so persistently. Possibly it was due to traces of dissolved oxygen in the carbonate trap for, as shown below, the results obtained by the vertical-tube method are probably most correct, since they agree very closely with those obtained with sodium oxalate. Experiments with appreciably higher concentrations of ferrous sulphate, viz., $N/5$ upwards, diverged appreciably from the standard under conditions 3, 5, and 6 above. This was to be expected in view of the increased rate of oxidation with rise in concentration. As such concentrations are less frequently used in practice the subject was not pursued further, but the results on p. 3230 show that excellent results are obtainable with even $N/3$ solutions by use of the vertical-tube method, provided that the precautions mentioned are duly observed.

The vertical-tube method of preparing $N/10$-ferrous sulphate solution has been found very useful in our laboratory. It is often more convenient than others because variations in temperature and acidity at the moment of titration do not affect the accuracy (Kolthoff, *Pharm. Weekblad*, 1924, **61**, 1082), whereas ferrous ammonium sulphate crystals vary slightly in composition (Hackl, *Chem. Ztg.*, 1922, **46**, 1065), and the temperature of sodium oxalate requires

regulating (Schröder, *Z. öffentl. Chem.*, 1910, **16**, 270, 290; Kolthoff, *loc. cit.*, p. 561). The last two methods, however, may be made to yield very accurate results agreeing to about 0·05% (McBride, *J. Amer. Chem. Soc.*, 1912, **34**, 393; Kolthoff, *Z. anal. Chem.*, 1924, **64**, 255; Hendel, *ibid.*, 1923, **63**, 321) if suitable precautions are taken. It was thus desirable to ascertain if these methods yielded results identical with the present one, as this does not appear to have been determined hitherto with accuracy. One difficulty is that for accurate work it is, of course, necessary to determine with proportionate exactness the composition of the iron used. This may be less convenient than the preparation of pure oxalates or ferrous salts. Electrolytic iron is frequently recommended, although even such metal is liable to contain appreciable amounts of impurity. A few parallel experiments have been carried out with sodium oxalate and Armco iron wire, the composition of which was as follows : C, 0·025; Si, 0·009; S, 0·033; P, 0·009; Mn, 0·036; Cu, 0·036; Fe (by difference) 99·852%. $N/10$-Solutions of permanganate, sodium oxalate, and ferrous sulphate were prepared, the last-named by dissolving 1·4 g. of iron wire in 200 c.c. of $4N$-sulphuric acid on the water-bath, using the vertical tube, rapidly cooling in a tank of cold water and making up to 250 c.c. The permanganate was then standardised by titration with each of the above solutions. In titrating the sodium oxalate, the precautions mentioned by Schröder (*loc. cit.*) were carefully observed.

The following factors for two approximately $N/10$-permanganate solutions were obtained in two sets of experiments : with oxalate, (1) 0·9915, (2) 0·9878; with iron, (1) 0·9916, (2) 0·9866. Provided, therefore, that the composition of the iron is accurately known, this method of standardising permanganate agrees to within about 0·1% with that by sodium oxalate for $N/10$-solutions.

Conclusion.

In preparing standard solutions of ferrous sulphate by dissolving iron in sulphuric acid, a carbonate trap is not necessary. Very accurate results are obtainable when 150—200 c.c. of $4N$-sulphuric acid and up to 1·4 g. of iron are warmed in a flask, fitted with a vertical tube, on the water-bath, and, immediately the iron has dissolved, rapidly cooled in water, and made up to a minimum of 250 c.c. Provided that the composition of the iron is accurately known, the result of standardising permanganate with such a solution agrees to within 0·1% with the sodium oxalate method.

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