5. *The Influence of Acid Concentration on the Oxidation–Reduction Potential of Mixtures of Ferric and Ferrous Sulphates in Sulphuric Acid Solution.*

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It has been shown by Peters (*Z. physikal. Chem.*, 1895, **26**, 193) and by Carter and Clews (J., 1924, **125**, 1880) that the potential of mixtures of ferrous and ferric chloride in hydrochloric acid becomes less positive as the concentration of the acid is increased. The present investigation concerns the effect of sulphuric acid concentration upon the oxidation–reduction potential of mixtures of ferric and ferrous sulphates.

Experimental.

Preparation of Solutions.—The $FeSO_4$ and $Fe_2(SO_4)_3$ solutions were prepared by dissolving the requisite quantities of pure Fe wire and $Fe_2(SO_4)_3$ respectively in H_2SO_4 of the necessary concn. These solutions were mixed in various proportions, and analysed both before and after the potential measurements. The ferric iron was estimated by reduction

with $TiCl_3$ (KNCS being the indicator), and the ferrous iron was then oxidised with dil. $KMnO_4$ aq. and the total Fe estimated as before. Total sulphate was estimated as $BaSO_4$.

Construction of Cells.—The oxidation half-element consisted of a glass vessel containing about 100 c.c. of the $Fe^{\cdot\cdot}$–$Fe^{\cdot\cdot\cdot}$–H_2SO_4 solution, over which was enclosed an atmosphere of CO_2. The vessel was furnished with four recently platinised Pt electrodes, any of which, if it disagreed by more than 0·2 mv. from the others, was replaced by a new one. The acid iron solution at the oxidation–reduction electrode was connected with a standard electrode by a chain of three intermediate vessels, the two adjacent to the oxidation–reduction half-element containing the same solution as this half-element, and the other vessel the same solution as the standard electrode. The component parts of the cell were connected with syphons to the top of which were attached short vertical tubes. The syphons were filled, and any bubbles which collected removed, by suction through those tubes, which were then closed with glass plugs. The limbs of the syphon connecting the third intermediate vessel with the next were about 5 in. apart to allow the two parts of the cell (as required for the measurement of E_f; see below) to be placed in two different thermostats. This syphon was fitted with a tap which was open only whilst a potential measurement was being taken.

The N-Hg_2SO_4 electrode was chosen as standard, but as the *E.M.F.*'s of the oxidation–reduction cells were very low when compared with this electrode, and also changed from a positive to a negative value as the acid concn. increased, it was decided to take *E.M.F.* observations with the N-Hg_2Cl_2 electrode in addition for comparison.

Potential Measurements.—The cell was kept for *ca.* ½ hr. in the 20° thermostat, and, by means of a Tinsley potentiometer and a galvanometer, its *E.M.F.* was observed every 2 or 3 min. until it was const. The cell was then removed to the 60° thermostat and the *E.M.F.* at this temp. measured in the same way. Finally, the standard electrode and adjacent intermediate vessel were placed in the 20° thermostat, while the oxidation–reduction half-element and the other two intermediate vessels remained in the 60° thermostat, and the *E.M.F.* of the cell thus arranged was then measured. The three *E.M.F.*'s thus obtained are denoted by E_b, E_d, and E_f, respectively.

Concns. throughout are denoted by the use of square brackets.

Variation of Potential with Variation of (a) *the* $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ *Ratio and* (b) H_2SO_4 *Concentration.*—These data are given in Table I. The values of E_0 (cols. 5 and 6) are calc. from the equation $E = (RT/nF) \log f_o[\text{oxidant}]/f_r[\text{reductant}]$ (where f_o and f_r are activity factors), by substituting for f_o[oxidant] and f_r[reductant] the concns. of the ferrous and ferric iron respectively. Since the ratio $f_o[\text{oxidant}]/f_r[\text{reductant}]$ is not equal to the ratio $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$, the E_0 values thus obtained have been termed " apparent " (abbreviated to " appt.") to distinguish them from the true E_0 values as defined by the thermodynamic logarithmic formula.

Comparison of Cell E.M.F. *Values obtained from Calomel Electrode with those from Mercurous Sulphate Electrode.*—In order to effect this comparison, the *E.M.F.*'s (E_x, in volts) of the cells of the type set out diagrammatically below were measured; they are given in Table II, x being the normality of the H_2SO_4.

$$\text{Hg} \left| \begin{matrix} Hg_2SO_4 \\ N\text{-}H_2SO_4 \end{matrix} \right| x N\text{-}H_2SO_4 \left| \begin{matrix} Hg_2Cl_2 \\ N\text{-KCl} \end{matrix} \right| \text{Hg}$$

If these values are subtracted from the mean " apparent " E_0 values for the same acid concn. and temp. based on the N-calomel electrode (see Table I, cols. 5 and 6), the E_0 values based on the N-Hg_2SO_4 electrode are obtained. The values so derived are in Table III (cols. 4 and 5); they agree closely with those obtained by direct observation (cols. 6 and 7). The latter, being probably the more accurate, have been used in the subsequent calculations.

Potential of the N-*Mercurous Sulphate Electrode.*—The following *E.M.F.* values (E_c, in volts) were obtained at 20° for three independent cells of the type represented diagrammatically below. The arrow indicates the direction of the current inside the cell. The N-Hg_2SO_4 electrode potential values are all based on the value 0·560 for the N-Hg_2Cl_2 electrode at 18°.

$$\underset{\leftarrow}{\text{Hg}} \left| Hg_2SO_4,\ N\text{-}H_2SO_4 \right| N\text{-}H_2SO_4 \left| \underset{\rightarrow}{N\text{-KCl}} \right| N\text{-KCl},\ Hg_2Cl_2 \left| \underset{\rightarrow}{\text{Hg}} \right.$$

$$E_m \qquad\qquad 0{\cdot}0232 \qquad\qquad 0{\cdot}560 + 0{\cdot}00061\ (t - 18)$$

$$\leftarrow\!\!\!

TABLE I.

Fe‴ iron, %.	*E.M.F.* at 20° (E_b).	*E.M.F.* at 60° (E_d).	E_f.	E_{b_0} (appt.).	E_{d_0} (appt.).	10^4 × Temp. coeff. of *N*-Hg_2SO_4 electrode.*
			$[H_2SO_4] = 0{\cdot}1N$; standard electrode, *N*-mercurous sulphate.			
24·91	0·0106	0·0215	0·0321	0·0385	0·0532	2·65
48·85	0·0364	0·0526	0·0633	0·0377	0·0546	2·70
50·00	0·0400	0·0545	—	0·0400	0·0543	—
50·00	0·0400	0·0553	0·0653	0·0400	0·0553	2·50
31·35	0·0170	0·0283	—	0·0368	0·0508	—
76·15	0·0707	0·0875	0·0989	0·0415	0·0543	2·85
				Mean 0·0391	0·0538	2·68
			$[H_2SO_4] = 1N$; standard electrode, *N*-mercurous sulphate.			
14·43	−0·0434	−0·0209	−0·0097	−0·0001	0·0285	2·80
26·07	−0·0257	−0·0001	—	−0·0003	0·0297	—
49·28	−0·0005	0·0284	0·0401	0·0012	0·0293	2·90
51·11	0·0008	0·0291	0·0401	−0·0003	0·0282	2·75
75·00	0·0300	—	—	0·0012	0·0300	—
75·19	0·0280	0·0615	0·0727	0·0000	0·0297	2·80
				Mean 0·0003	0·0292	2·81
			$[H_2SO_4] = 5N$; standard electrode, *N*-mercurous sulphate.			
15·35	−0·0687	−0·0448	−0·0349	−0·0266	0·0040	2·48
51·34	−0·0265	0·0046	—	−0·0251	0·0031	—
50·00	−0·0269	0·0011	0·0129	−0·0269	0·0011	2·95
81·30	0·0102	0·0424	—	−0·0270	0·0009	—
90·64	0·0181	0·0517	—	−0·0283	−0·0013	—
				Mean −0·0268	0·0015	2·72
			$[H_2SO_4] = 10N$; standard electrode, *N*-mercurous sulphate.			
13·86	−0·0822	−0·0604	−0·0492	−0·0361	−0·0080	2·80
26·01	−0·0607	−0·0367	−0·0254	−0·0343	−0·0069	2·82
41·70	−0·0432	−0·0172	−0·0060	−0·0346	−0·0074	2·80
50·00	−0·0337	−0·0064	0·0030	−0·0337	−0·0064	2·42
51·24	−0·0332	−0·0061	—	−0·0344	−0·0075	—
73·31	−0·0066	0·0226	0·0349	−0·0321	−0·0062	3·08
83·90	0·0092	0·0401	—	−0·0319	−0·0071	—
				Mean −0·0339	−0·0071	2·79
			$[H_2SO_4] = 0{\cdot}1N$; standard electrode, *N*-calomel.			
56·63	0·3921	0·4007	—	0·3854	0·3931	—
50·00	0·3850	0·3970	—	0·3850	0·3971	—
50·00	0·3872	0·3963	—	0·3872	0·3963	—
75·58	0·4114	0·4300	0·4490	0·3830	0·3989	—
				Mean 0·3852	0·3964	—
			$[H_2SO_4] = 1N$; standard electrode, *N*-calomel.			
25·82	0·3455	0·3725	0·3843	0·3722	0·4028	—
37·00	0·3575	0·3825	0·3965	0·3710	0·3978	—
50·42	0·3737	0·3998	0·4123	0·3734	0·3993	—
68·68	0·3916	0·4251	0·4403	0·3718	0·4026	—
74·48	0·4013	0·4347	0·4440	0·3743	0·4041	—
				Mean 0·3725	0·4013	—
			$[H_2SO_4] = 5N$; standard electrode, *N*-calomel.			
26·79	0·3240	0·3537	0·3667	0·3504	0·3826	—
49·42	0·3533	0·3784	0·3949	0·3539	0·3789	—
51·34	0·3585	0·3872	—	0·3572	0·3857	—
73·92	0·3815	0·4102	0·4242	0·3567	0·3825	—
				Mean 0·3546	0·3824	—
			$[H_2SO_4] = 10N$; standard electrode, *N*-calomel.			
25·67	0·3312	0·3507	0·3627	0·3580	0·3815	—
50·00	0·3525	0·3785	0·3917	0·3525	0·3785	—
51·24	0·3545	0·3822	—	0·3538	0·3808	—
75·00	0·3815	0·4112	0·4257	0·3538	0·3796	—
84·16	0·3968	0·4289	0·4437	0·3546	0·3809	—
				Mean 0·3545	0·3803	—

* Uncorrected for contact potential (see p. 13).

TABLE II.

x	0·1	1·0	5·0	10·0
E_x at 20°	0·3461	0·3718	0·3830	0·3900
E_x at 60°	0·3415	0·3701	0·3843	0·3901

TABLE III.

	E_0 (appt.), from N-Hg_2Cl_2 electrode (from Table I).		E_0 (appt.), from N-Hg_2SO_4 electrode (calc. from cols. 2 & 3).		E_0 (appt.), from N-Hg_2SO_4 (obs.).	
$[H_2SO_4]$.	E_{t0}.	E_{d0}.	E_{b0}.	E_{d0}.	E_{b0}.	E_{d0}.
0·1	0·3852	0·3964	0·0391	0·0549	0·0391	0·0538
1·0	0·3725	0·4013	0·0007	0·0312	0·0003	0·0292
5·0	0·3546	0·3824	−0·0284	−0·0017	−0·0268	0·0015
10·0	0·3545	0·3803	−0·0355	−0·0098	−0·0338	−0·0071

The potential of the N-Hg_2SO_4 electrode at 20°, represented by E_m, is given by the equation $E_m = E_c + 0{\cdot}0232 + 0{\cdot}5612$, and, by substituting the mean value for E_c, *viz.*, 0·3718, in this equation E_m is found to be 0·9562 volt.

The potential of this electrode as obtained by Wilsmore (*Z. physikal. Chem.*, 1900, **35**, 291) is 0·9566 at 25°; if the temp. coeff. of the N-Hg_2SO_4 electrode is taken as $2{\cdot}83 \times 10^{-4}$ (see below), this value becomes 0·9546, and the observed value 0·9556, at 18°. Hence the mean value at 18° may be taken as 0·9551 (cf. Makio, *Researches Electrotech. Lab. Japan*, No. 114, 1926).

Temperature Coefficient of the Potential of the N-*Mercurous Sulphate Electrode.*—A direct determination of the temp. coeff. of the N-Hg_2SO_4 electrode was obtained by measuring the *E.M.F.* of the cell $Hg|Hg_2SO_4$, N-$H_2SO_4|N$-H_2SO_4, $Hg_2SO_4|Hg$, one half being maintained at 20° and the other at 60°; the *E.M.F.* was 0·0116 volt, whence temp. coeff. $= 2{\cdot}90 \times 10^{-4}$ volt. This, in conjunction with the values obtained in presence of N-H_2SO_4 (Table I, col. 7; these require no correction for contact potential, since N-H_2SO_4 is present throughout), gives a mean of $2{\cdot}83 \times 10^{-4}$ volt (cf. Makio, *loc. cit.*).

Diffusion Potentials in the Oxidation Cells.—Using Henderson's formula (*Z. physikal. Chem.*, 1907, **59**, 118; 1908, **63**, 325) and assuming N-H_2SO_4 to be completely dissociated into $H^{\cdot}$ and HSO_4' ions (cf. Small, *ibid.*, 1894, **14**; Sauer, *ibid.*, 1904, **47**, 146; Noyes and Stewart, *J. Amer. Chem. Soc.*, 1910, **32**, 1133), we calculate a contact potential of 0·0232 volt for the N-H_2SO_4–N-KCl junction, whereas Sauer, by an application of the Planck formula, obtained 0·026 volt.

For the junctions N-$H_2SO_4|0{\cdot}1N$-H_2SO_4 and $0{\cdot}1N$-$H_2SO_4|N$-KCl, contact potentials of 0·0074 and 0·0399 volt respectively were calculated by using Henderson's formula. The following values for the concns. (g.-equiv./l.) at 20° of the ions in $0{\cdot}1N$-H_2SO_4 were used in the Henderson formula: $H^{\cdot} = 0{\cdot}0638$, $HSO_4' = 0{\cdot}0302$, $SO_4'' = 0{\cdot}0336$; they were obtained by interpolation from the values obtained at 0° and 25° by Noyes and Stewart (*loc. cit.*).

The contact potentials thus calculated are confirmed to some extent by the *E.M.F.* value observed for the cell diagrammatically shown below. The arrows indicate the direction of the current inside the cell.

$$\underset{\leftarrow}{Hg}\,|\,Hg_2SO_4,\ N\text{-}H_2SO_4\,|\,\underset{\rightarrow}{0{\cdot}1N\text{-}H_2SO_4}\,|\,\underset{\rightarrow}{N\text{-KCl},\ Hg_2Cl_2}\,|\,\underset{\rightarrow}{Hg}$$

$$0{\cdot}955 + 2{\cdot}83 \times 10^{-4}\,(t - 18) \qquad \pi_1 \qquad \pi_2 \qquad 0{\cdot}560 + 6{\cdot}1 \times 10^{-4}\,(t - 18)$$

$$\longleftarrow\!\!\!

cell. They show that, unlike the temp. coeff. of the $FeCl_2$–$FeCl_3$ electrode in HCl, which falls progressively as the HCl concn. increases (Carter and Glover, *J. Physical Chem.*, 1932, **36**, 679), the temp. coeff. of the $FeSO_4$–$Fe_2(SO_4)_3$ electrode increases as the H_2SO_4 concn. increases from $0{\cdot}1N$ to $1N$, and then remains practically const. up to $10N$.

TABLE IV.

$[H_2SO_4]$.	E_{b0}.	E_{d0}.	$10^4 \times$ Temp. coeff. of cell.	$10^4 \times$ Temp. coeff. of oxidation–reduction electrode.
0·1	0·0391	0·0538	3·68	6·51
1·0	0·0003	0·0292	7·22	10·05
5·0	−0·0268	0·0015	7·08	9·91
10·0	−0·0339	−0·0071	6·70	9·53

Heat of Reaction, from Potential–Temperature Measurements.—The heat of the reaction occurring in the cell has been calc. from the Gibbs–Helmholtz equation $U = EnF - TnF \cdot dE/dT$, the values of E at 20° and 60° being obtained by subtracting (since the contact potential acts to increase the $E.M.F.$ of the cells) the appropriate contact potential from E_{b0} and E_{d0} respectively. These values of U show that the reaction is endothermic, the heat absorption increasing as the acid concn. increases from $0{\cdot}1N$ to N.

$[H_2SO_4]$.	$E_{20°}$.	$E_{60°}$.	U, cals.
0·1	−0·0008	0·0139	−2503
1·0	0·0003	0·0292	−4877

Substitution of the values for E_0 at 20° and 60° for the cell in which $[H_2SO_4] = N$ in the equation $E_0 = RT/nF \cdot \log K$ gives $\log K = 0{\cdot}0052$ at 20° and 0·4420 at 60°. The const. K previously inadvertently taken to be the equil. const. of the cell reaction (*J. Physical Chem.*, 1932, **36**, 685) is really only of empirical significance.

Variation of Oxidation Potential of the Ferrous–Ferric Sulphate Electrode with Concentration of Sulphuric Acid.—The following oxidation–reduction electrode potentials have been calc. from the $E.M.F.$'s (E_{b0} and E_{d0}, Table III, cols. 6 and 7) of the corresponding oxidation cells with N-Hg_2SO_4 electrode, by correcting, if necessary, for the contact potential operating in the cells and adding the potential, $0{\cdot}955 + 2{\cdot}83 \times 10^{-4}\,(t - 18)$, of the N-Hg_2SO_4 electrode :

	Oxidation–reduction electrode potential, volts.	
$[H_2SO_4]$.	20°.	60°.
0·1	0·9548	0·9798
1·0	0·9559	0·9961

They increase very slightly at 20°, and more markedly at 60°, as the concn. of H_2SO_4 changes from $0{\cdot}1N$ to $1N$; they thus change in the opposite sense to those of the $FeCl_2$–$FeCl_3$ electrode (Carter and Glover, *loc. cit.*). The potentials of the $FeSO_4$–$Fe_2(SO_4)_3$ electrode for higher concns. of H_2SO_4 cannot be calc. from the cell potential, since the values of the contact potentials operating in the cells are unknown; but as their temp. coeff. is const. over the range 1—$10N$ (Table IV), it is probable that the electrode oxidation–reduction potential remains fairly const. over this range.

DISCUSSION.

It has been suggested (Carter and Clews, *loc. cit.*) that the fall in potential of mixtures of ferric and ferrous chlorides in hydrochloric acid with increasing acid concentration takes place in consequence of a change in the ratio $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$, which, it was suggested, is due to the disappearance of ferric ions owing to the formation of a complex between the ferric chloride and hydrogen chloride. If this explanation is applied to the mixtures of ferric and ferrous sulphates in sulphuric acid, it indicates that as the acid concentration is increased from $0{\cdot}1N$ to $1N$ at 20°, if there is complex formation it is such that there is no appreciable change in the $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$ ratio. At 60°, however, complex formation may take place, the removal of ions being such that the $[Fe^{\cdot\cdot\cdot}]/[Fe^{\cdot\cdot}]$ ratio increases with acid concentration over this range.

As an alternative explanation, the hypothesis (which in some respects may be regarded as a development of the foregoing) is now advanced that in mixtures of ferric and ferrous chlorides in hydrochloric acid and also, when temperature and acid concentration con-

ditions are suitable, in mixtures of the sulphates in sulphuric acid, the ferric and ferrous ions combine with other ions or undissociated substances to form complex ferric and ferrous ions, thus forming a new oxidation–reduction system in which the complex ferric ion and the complex ferrous ion form the oxidant and reductant respectively. This system may displace the original ferric–ferrous ion system either partially or (if the complexes formed dissociate to such a slight extent that only a relatively small proportion of simple ferrous or ferric ions is present) wholly. The amount or composition of these complex ions may vary with acid concentration, and so the oxidation–reduction potential of the ferrous–ferric mixture will vary accordingly. Variations of this kind in the composition of the mixture at the oxidation–reduction electrode would also be associated with variation in the heats of reaction taking place in the corresponding oxidation–reduction cells.

The influence of acid concentration (if acids of equal molar concentration be regarded as comparable) on the oxidation–reduction potential of mixtures of ferrous and ferric chlorides in hydrochloric acid (Carter and Glover, *loc. cit.*) is greater than on that of mixtures of the sulphates in sulphuric acid. The fact that potential measurements indicate that at 20° on increasing the acid concentration from 0·1*N* to 1·0*N* there is no appreciable change in $[Fe^{\cdots}]/[Fe^{\cdot\cdot}]$ ratio would suggest that at this temperature, as a result of this change in acid concentration, no further complex formation takes place. In this regard, it is significant that the marked colour changes with increase of acid concentration which occur in the case of ferrous or ferric chloride in hydrochloric acid do not take place with the corresponding sulphates in sulphuric acid.

SUMMARY.

(1) The *E.M.F.*'s of cells in which the oxidation–reduction half-element consists of mixtures of ferric and ferrous sulphates in sulphuric acid varying in concentration from 0·1*N* to 10*N* have been measured at 20° and 60°.

(2) A logarithmic relation between the *E.M.F.* of the cell and the ratio of ferric to ferrous iron has been shown to hold at both temperatures.

(3) From experimentally determined and collected data, mean values have been found for the potential at 18° and for the temperature coefficient of the *N*-mercurous sulphate electrode.

(4) The heat of the reaction for the ferric–ferrous sulphate oxidation cells in 0·1*N*- and *N*-sulphuric acid has been calculated.

(5) Values have been found for the oxidation–reduction potential of mixtures of ferrous and ferric sulphates in 0·1*N*- and 1·0*N*-sulphuric acid at 20° and 60°.

(6) An hypothesis has been put forward to account for the variation with acid concentration of the oxidation–reduction potential of mixtures of ferric and ferrous chloride in hydrochloric acid and of mixtures of the sulphates in sulphuric acid, and also for the variation with acid concentration of the heats of reaction taking place in the oxidation–reduction cells corresponding with these mixtures.

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