

82. *Equivalence Changes in Oxidation-Reduction Reactions in Solution: Some Aspects of the Oxidation of Sulphurous Acid.*

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Stoichiometries have been found in the oxidation of sulphurous acid in aqueous solution by various reagents, and the results are compared with those previously obtained in the oxidation of hydrazine by the same reagents. For both reducing agents the nature of the products formed depends principally upon whether the oxidising agent favours a 1- or a 2-equivalent reaction. It is concluded that the mechanisms of oxidation of these reducing agents are similar.

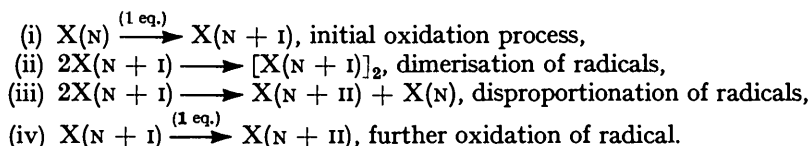
Confirmation of the mechanism of oxidation of sulphurous acid by 1-equivalent reagents has been obtained by a kinetic study of the system, sulphurous acid-iron(III)-copper(II).

The factors which determine whether a given oxidation-reduction reaction is of the 1- or 2-equivalent type are discussed.

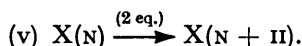
WHEN oxidised or reduced in homogeneous solution, several inorganic compounds derived from non-metallic elements give proportions of products which vary with the oxidising or reducing agent used. A fairly complete interpretation of such observations in terms of a reaction mechanism is available only in the oxidation of hydrazine in aqueous acid.¹⁻⁶ Two types of mechanism operate, and oxidising agents have been divided into three classes depending on whether their reactions indicate one, the other, or both of these mechanisms. The three classes have previously been termed "mono-, di-, and poly-de-electronators,"¹ and also "1-, 2-, and 1,2-electron-transfer reagents."³ These terms may appear to imply that oxidation-reduction necessarily occurs through an electron-transfer mechanism, rather than by an atom-transfer or other mechanism. Since this aspect of the oxidation-reduction process is unimportant for our purposes, we shall use the terms "1-equivalent, 2-equivalent, and 1,2-equivalent oxidising agent."

The mechanisms first advanced in the oxidation of hydrazine can be represented simply in the form:

Reaction with a 1-equivalent oxidising agent:



Reaction with a 2-equivalent oxidising agent:



1,2-Equivalent oxidising agents react according to both these mechanisms. If it is assumed that this scheme can be applied in the oxidation of compounds other than hydrazine, $X(N)$ represents a simple compound of a non-metallic element in oxidation state N , for example, a hydride or hydroxide, or an ion derived from one of these. If $X(N)$ is a normal molecule, the initial product of 1-equivalent oxidation, $X(N+1)$, must be a free radical and can disappear by various competing reactions. Three of the more important

¹ Kirk and Browne, *J. Amer. Chem. Soc.*, 1928, **50**, 337.

² Audieth and Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, 1951, Chap. VI.

³ Higginson, Sutton, and Wright, *J.*, 1953, 1380.

⁴ Higginson and Sutton, *J.*, 1953, 1402.

⁵ Higginson and Wright, *J.*, 1955, 1551.

⁶ Cahn and Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2568.

are included above. These mechanisms therefore imply that while 2-equivalent reagents should oxidise $X(N)$ to $X(N + II)$ only, 1-equivalent oxidising agents should produce $[X(N + I)]_2$ and $X(N + II)$ in proportions varying with the concentrations of the reactants. In simple cases $[X(N + I)]_2$ and $X(N + II)$ will be end-products, although this is not so in the oxidation of hydrazine where the corresponding molecules, $(N_2H_3)_2$ and N_2H_2 respectively, undergo further reactions.

It is of interest to determine whether reducing substrates other than hydrazine show a similar differentiation between oxidising agents and hence follow the mechanism suggested above. In this paper we present evidence to show that the major features of the oxidation of sulphurous acid, a compound otherwise unrelated to hydrazine, are in accord with this general mechanism. The experimental work is in two parts. First, we have observed the stoichiometries of the oxidation of sulphurous acid by various oxidising agents, in order to make a comparison with results previously obtained in the oxidation of hydrazine.³ Secondly, we have investigated certain aspects of the kinetics of oxidation of sulphurous acid by iron(III) in the presence of copper(II), thus obtaining more quantitative evidence about the mechanism of oxidation by 1-equivalent reagents.

STOICHEIOMETRIES IN THE OXIDATION OF SULPHUROUS ACID

There is an extensive literature on the estimation of sulphurous acid by oxidation methods, much of it referred to in a recent review.⁷ The only common products of the oxidation of sulphurous acid and its related anions appear to be sulphate and dithionate ions, these corresponding respectively to $X(N + II)$ and $[X(N + I)]_2$. Hence if the behaviour of sulphurous acid on oxidation can be accounted for solely in terms of the general mechanism given above, all oxidising agents should lead to the formation of sulphate, but dithionate should be formed only in oxidations by 1-equivalent reagents. Similar, but not identical, conclusions have been reached by Bassett and his co-workers,^{8,9} but these depend upon experiments involving relatively few oxidising agents, in some cases under heterogeneous conditions. In Table 1 we summarise the stoichiometries we have observed in the oxidation of sulphurous acid at room temperature by various oxidising agents at similar concentrations. Where possible, experiments were done at pH values of approx. 0.5, 5, and 9; the principal sulphur(IV) species present in these solutions are respectively H_2SO_3 plus SO_2 , HSO_3^- , and SO_3^{2-} . In those cases where no stoichiometry is recorded, either no reaction took place, or precipitation, or complex formation between the oxidising agent and sulphurous acid occurred. For comparison we include stoichiometries previously observed under similar conditions in the oxidation of hydrazine in acid solutions.³ The stoichiometry, defined as the number of equivalents of the oxidising agent consumed per substrate molecule or ion, can vary between the limits 1.0 and 2.0 for sulphurous acid oxidations, and 1.0 and 4.0 when hydrazine is the substrate.

It is seen that, with a few exceptions, the oxidising agents fall into the same three classes whether sulphurous acid (or its anions) or hydrazine is the reducing substrate. We consider that these results show that in most respects the oxidation of sulphurous acid and its anions is in accord with the predictions of the reaction scheme suggested above. However, there is also evidence that other reactions must be occurring to a limited extent. In contrast to their simple behaviour with hydrazine, several 2-equivalent oxidising agents give stoichiometries slightly below the maximum in their reactions with sulphurous acid. This effect is most marked at pH 5, at which the metabisulphite ion¹⁰ is present in greater relative concentration than at pH 0.5 or 9. The side reaction responsible for these deviations in stoichiometry below 2.0 may thus be $S_2O_5^{2-} \xrightarrow{(2 \text{ eq.})} S_2O_6^{2-}$, a reaction already

⁷ Rao and Rao, *Analyt. Chim. Acta*, 1955, **13**, 313.

⁸ Bassett and Henry, *J.*, 1935, 914.

⁹ Bassett and Parker, *J.*, 1951, 1540.

¹⁰ Simon and Waldman, *Z. anorg. Chem.*, 1955, **281**, 113, 135; 1956, **283**, 359; **284**, 36, 47.

suggested by Bassett and Henry.⁸ Alternatively, dithionate formation could occur by a reaction analogous in mechanism to that of the iodine-thiosulphate reaction,¹¹ *i.e.*, $\text{SO}_3^{2-} + \text{Y}(\text{N} + \text{II}) \longrightarrow (\text{SO}_3 \rightarrow \text{Y})^{2-}$, $\text{SO}_3^{2-} + (\text{SO}_3 \rightarrow \text{Y})^{2-} \longrightarrow \text{S}_2\text{O}_6^{2-} + \text{Y}(\text{N})$, where $\text{Y}(\text{N} + \text{II})$ and $\text{Y}(\text{N})$ represent respectively the oxidised and reduced forms of a 2-equivalent reagent. Two reagents, bromate and chloroplatinate, show distinctly different behaviour with hydrazine and sulphurous acid; we shall discuss these anomalies below.

Our investigations can be regarded as an extension of those of Bassett and his co-workers and we accept most of their conclusions. There are certain differences which we now consider.

First, Bassett and Henry conclude that free sulphite ions (SO_3^{2-}) are always oxidised to sulphate, no dithionate being formed. However, we have found that, in the range pH 7.0—12.3, ferricyanide gives a stoicheiometry of 1.2—1.3 under our conditions. The rate of reaction varied by less than a factor of two over this range of pH, showing that SO_3^{2-} is the sulphur(IV) species undergoing oxidation. Ferricyanide, which is the only common 1-equivalent reagent capable of oxidising sulphite in alkaline solution, was not investigated by these authors. Thus their conclusion depends upon their results with 2-equivalent reagents and the complex oxidising agents, permanganate and dichromate, which even in acid solution give relatively little dithionate.

Secondly, these authors, by using permanganate and dichromate in acid solutions, obtained invariant stoicheiometries of 1.81 and 1.96 respectively. On the other hand we have found that the stoicheiometry varied over a limited range with the method of mixing. If our mechanism is correct the latter behaviour is to be expected since both these oxidising agents, which belong to the class of 1,2-equivalent reagents, should give a stoicheiometry varying with the conditions of reaction, but higher than that obtained with 1-equivalent reagents.

Finally, Bassett and Parker,⁹ in discussing the oxidation by metal cations, regard as important the formation of complex ions between these metal ions and sulphite ions. A considerable increase in the complexity of our mechanism would be necessary to take into account the various specific reactions which these complex ions are thought to undergo. Accordingly we have restricted measurements involving simple metal ions to conditions in which the proportion of such complex ions is likely to be small, and we believe that specific reactions involving these ions are unimportant under these conditions.

SOME KINETIC ASPECTS OF THE OXIDATION OF SULPHUROUS ACID BY 1-EQUIVALENT REAGENTS

In principle it is possible to establish the mechanism of oxidation of sulphurous acid by a 1-equivalent reagent by studying the dependence of the relative rates of formation of products upon reactant concentrations. This method has been used previously in investigations of the mechanism of oxidation of hydrazine by iron(III).^{5, 6} Our attempts to use the method in the study of the iron(III)-sulphurous acid reaction mechanism failed since our measurements were insufficiently accurate, for the range of stoicheiometries observed, to permit a unique kinetic interpretation. However, we have been able to extend the range of our experiments by using the catalytic effect of copper(II) upon this reaction.¹² Although the complexity of the system is thereby increased, it becomes possible to test various kinetic relations deduced from our general mechanism, and so to establish its validity. Catalysis by copper(II) has also been studied in the iron(III)-hydrazine system,⁶ and occurs owing to the greater reactivity of copper(II) than of iron(III) in oxidising the radical N_2H_3 [$\text{X}(\text{N} + \text{I})$] in our general mechanism) to N_2H_2 [$\text{X}(\text{N} + \text{II})$].

Preliminary experiments showed that iron(II)• retards the rate of the iron(III)-sulphurous acid reaction, an effect similar to that observed in the iron(III)-hydrazine reaction.

¹¹ Awtrey and Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1341.

¹² Kuzmínkykh and Bomshtein, *J. Appl. Chem. (U.S.S.R.)*, 1953, **26**, 1.

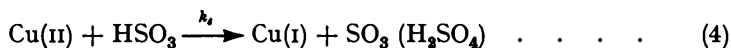
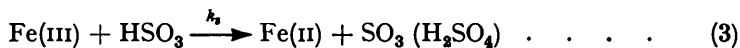
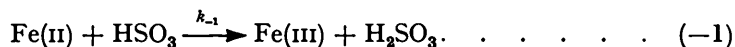
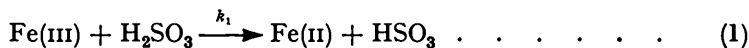
TABLE 1. *Stoichiometries in the reaction of oxidising agents with hydrazine and sulphurous acid.*

Oxidising agent	Hydrazine pH 0—1	Sulphurous acid		
		pH 0.5	pH 5 (HSO ₃ ⁻)	pH 9 (SO ₃ ⁻)
<i>1-Equivalent reagents.</i>				
Ce(SO ₄) ₂	1.05—1.4	1.27—1.44	—	—
Co ₂ (SO ₄) ₃	1.03—1.15	1.04—1.37	—	—
K ₂ Co(CO ₃) ₂	—	—	1.02—1.12	—
CoN(CH ₂ CO ₂) ₃	Not studied	1.26 (SR)	—	—
Fe ₂ (SO ₄) ₃	1.1—1.35	≈ 1.2 (SR)	—	—
K ₂ Fe(CN) ₆	—	—	—	1.32 (SR)
Na ₂ Mn(H ₂ P ₂ O ₇) ₂	1.05	≈ 1.24	1.19 (SR)	1.03 (SR) *
OH	1.07—1.96	Not studied	Not studied	Not studied
<i>2-Equivalent reagents.</i>				
I ₂	4.00	2.00	1.93—2.00	1.96—2.00
Br ₂	4.00	1.98—2.00	1.98—2.00	—
HBrO	—	—	—	1.99—2.00
Cl ₂	4?	1.99—2.00	—	—
HClO	—	—	1.99—2.00	2.00
KIO ₃	4.00	2.00	1.98—2.00	—
KBrO ₃	4.00	1.77—1.95	—	—
H ₂ O ₂	—	2.00	1.92—2.00	2.00
Tl ₂ (SO ₄) ₃	4.00	2.00	—	—
<i>1, 2-Equivalent reagents.</i>				
K ₂ Cr ₂ O ₇	3—4	1.84—1.95	1.67—1.85	—
KMnO ₄	1.45—2.2	1.55—1.80	—	—
K ₂ PtCl ₆	≈ 3.7	2.00 (SR)	—	—
(VO ₂) ₂ SO ₄	3.5—4	1.57 (SR)	—	—

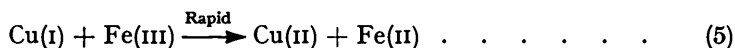
SR = Slow reaction.

* Experiment at pH 8.

By analogy, this observation suggests that the reaction corresponding to (i), $\text{Fe(III)} + \text{H}_2\text{SO}_3 = \text{Fe(II)} + \text{HSO}_3$, is reversible. We also conclude that the radical-disproportionation reaction (iii), in this case $2\text{HSO}_3 \rightarrow \text{H}_2\text{SO}_3 + \text{SO}_3$ (H_2SO_4), is unimportant under our conditions of reaction since stoichiometries as low as 1.04 can be obtained in oxidations by 1-equivalent reagents (Table 1). Taking these features of the reaction into account, we suggest the following mechanism:



followed by



For convenience we represent all sulphur species as uncharged molecules or radicals, since we are concerned only with the oxidation state of the sulphur and not with the acid-base character of these molecules or radicals. In sections I—IV, below, we derive from this mechanism four relations between the rates of formation of the products and the reactant concentrations. The kinetic experiments performed to test these relations are summarised in Tables 2 and 3. In them, and subsequently, $R(\text{Fe})$ is used for $-d[\text{Fe(III)}]/dt = d[\text{Fe(II)}]/dt$; in other cases $R(Z)$ represents $d[Z]/dt$, and St represents $R(\text{Fe})/R(\text{H}_2\text{SO}_3)$, the instantaneous stoichiometry. In Table 2, two concentration figures are quoted for each reactant. The first denotes the concentration present at half the total amount of reaction

TABLE 2. $[H^+] = 0.08M$; ionic strength = 2.0; temp. = 25°.

Expt.	Dur- ation (min.)	$10^3[Fe(III)]$	$10^3[Fe(II)]$	$10^3[Cu(II)]$	$10^3[H_2SO_3]$	$10^6R(Fe)$	$10^6R(H_2S_2O_6)$	$10^6R(H_2SO_4)$	St
		(M)	(M)	(M)	(M)	(all in mole l. ⁻¹ min. ⁻¹)			
1	319	8.51 (9.0)	1.486 (1.0)	0	19.59 (20.0)	3.36	1.178 ±0.052	0.502 ±0.137	1.176
2	5,760	8.70 (10.0)	11.30 (10.0)	0	19.05 (20.0)	0.458	0.108 ±0.006	0.121 ±0.021	1.362
3	585	3.49 (4.0)	1.51 (1.0)	0	39.55 (40.0)	1.711	0.710 ±0.035	0.146 ±0.075	1.093
4	1,484	7.11 (8.0)	2.89 (2.0)	0.025	19.21 (20.0)	1.344	0.399 ±0.017	0.273 ±0.057	1.254
5	1,653	7.00 (8.0)	3.00 (2.0)	0.05	19.25 (20.0)	1.236	0.314 ±0.019	0.304 ±0.059	1.327
6	585	7.74 (8.5)	2.26 (1.5)	0.10	19.45 (20.0)	2.57	0.609 ±0.026	0.676 ±0.106	1.359
7	675	7.00 (8.0)	3.00 (2.0)	0.25	19.40 (20.0)	2.88	0.336 ±0.045	1.104 ±0.145	1.621
8	445	6.98 (8.0)	3.02 (2.0)	0.50	19.43 (20.0)	4.59	0.375 ±0.060	1.92 ±0.21	1.719
9	332	6.96 (8.0)	3.04 (2.0)	1.0	19.47 (20.0)	7.66	0.443 ±0.040	3.39 ±0.29	1.792
10	177	7.00 (8.0)	3.00 (2.0)	1.5	19.46 (20.0)	11.23	0.432 ±0.040	5.18 ±0.39	1.857
11	123	7.01 (8.0)	2.99 (2.0)	2.5	19.47 (20.0)	17.3	0.455 ±0.045	8.21 ±0.53	1.902
12	102	7.03 (8.0)	2.97 (2.0)	3.5	19.47 (20.0)	23.0	0.391 ±0.055	11.11 ±0.76	1.934
13	90	7.00 (8.0)	3.00 (2.0)	5.0	19.50 (20.0)	25.3	0.266 ±0.013	12.38 ±0.76	1.959
14	35	7.01 (8.0)	2.99 (2.0)	15.0	19.50 (20.0)	60.0	0.167 ±0.015	29.8 ±1.8	1.989

TABLE 3. $[H^+] = 0.08M$; St ≈ 2.0; ionic strength = 2.0; temp. = 25°.

Expt.	Time (min.)	$10^3[Fe(III)]$	$10^3[Fe(II)]$	$10^3[Cu(II)]$	$10^3[H_2SO_3]$	$10^6R(Fe)$	
		(M)	(M)	(M)	(M)	(mole l. ⁻¹ min. ⁻¹)	
13	0	8.0	2.0	5.0	20.0	—	
	10	7.62	2.38			19.81	3.48
	20	7.31	2.69			19.65	2.99
	30	7.02	2.98			19.51	2.63
	50	6.56	3.44			19.28	2.12
14	0	8.0	2.0	15.0	20.0	—	
	5	7.59	2.41			19.79	7.70
	10	7.22	2.78			19.61	6.95
	15	6.90	3.10			19.45	6.10
	20	6.60	3.40			19.30	5.40
	25	6.36	3.64			19.18	4.65
15	0	10.0	0	5.0	18.8	—	
	3	9.52	0.48			18.56	12.8
	7.5	9.06	0.94			18.33	8.4
	15	8.59	1.41			18.09	5.7
16	0	8.09	1.91	15.0	17.84	4.6	
	3	10.0	0			18.8	—
	7.5	9.43	0.57			18.52	18.0
	12	8.70	1.30			18.15	13.1
		8.22	1.78		17.91	8.5	

measured. The second, in parentheses immediately below the first, gives the initial concentration of the reactant. The rates of reaction given in this Table are those found at half-reaction, *i.e.*, they correspond to the upper of the two concentration figures.

I. For any given experiment in Table 2,

$$R(H_2S_2O_6) = \frac{1}{2}k_2[HSO_3]^2 \dots \dots \dots (6)$$

and

$$R(H_2SO_4) = k_3[Fe(III)][HSO_3] + k_4[Cu(II)][HSO_3] \dots \dots (7)$$

whence, by eliminating $[HSO_3]$,

$$R(H_2SO_4) \div \sqrt{R(H_2S_2O_6)} \{ [Fe(III)] + k_4k_3^{-1}[Cu(II)] \} = k_3\sqrt{2/k_2} \dots (8)$$

Fairly consistent values of the left-hand side of eqn. (8) can be calculated from the results in Table 2 by assuming $k_4k_3^{-1} = 110 \pm 10$. These values are shown in Table 4, and were obtained by using $k_4k_3^{-1} = 110$.

TABLE 4.

Expt.	1	2	3	4	5	6	7
$10^3k_3\sqrt{2/k_2}$	5.43	4.22	4.97	4.38	4.34	4.62	5.47
Expt.	8	9	10	11	12	13	14
$10^3k_3\sqrt{2/k_2}$	5.04	4.35	4.58	4.32	4.53	4.30	4.38

II. By making the stationary state assumption $R(\text{HSO}_3) = 0$,

$$k_1[\text{Fe(III)}][\text{H}_2\text{SO}_3] - k_{-1}[\text{Fe(II)}][\text{HSO}_3] - k_2[\text{HSO}_3]^2 - k_3[\text{Fe(III)}][\text{HSO}_3] - k_4[\text{Cu(II)}][\text{HSO}_3] = 0 \quad (9)$$

also,

$$R(\text{Fe}) = k_1[\text{Fe(III)}][\text{H}_2\text{SO}_3] - k_{-1}[\text{Fe(II)}][\text{HSO}_3] + k_3[\text{Fe(III)}][\text{HSO}_3] + k_4[\text{Cu(II)}][\text{HSO}_3] \quad (10)$$

From (9) and (10) we derive :

$$R(\text{Fe}) = k_2[\text{HSO}_3]^2 + 2k_3[\text{Fe(III)}][\text{HSO}_3] + 2k_4[\text{Cu(II)}][\text{HSO}_3] \quad (11)$$

and elimination of k_2 , by using eqn. (6), gives

$$R(\text{Fe}) = 2R(\text{H}_2\text{S}_2\text{O}_6) + 2k_3[\text{Fe(III)}][\text{HSO}_3] + 2k_4[\text{Cu(II)}][\text{HSO}_3] \quad (12)$$

Under conditions where $R(\text{Fe}) \gg R(\text{H}_2\text{S}_2\text{O}_6)$, as a good approximation,

$$R(\text{Fe}) = 2k_3[\text{Fe(III)}][\text{HSO}_3] + 2k_4[\text{Cu(II)}][\text{HSO}_3] \quad (13)$$

From (10) and (13),

$$k_1[\text{Fe(III)}][\text{H}_2\text{SO}_3] - k_{-1}[\text{Fe(II)}][\text{HSO}_3] - k_3[\text{Fe(III)}][\text{HSO}_3] - k_4[\text{Cu(II)}][\text{HSO}_3] = 0 \quad (14)$$

whence

$$[\text{HSO}_3] = k_1[\text{Fe(III)}][\text{H}_2\text{SO}_3] \div \{k_{-1}[\text{Fe(II)}] + k_3[\text{Fe(III)}] + k_4[\text{Cu(II)}]\} \quad (15)$$

Eliminating $[\text{HSO}_3]$ from eqn. (13) by using eqn. (15), and rearrangement gives

$$[\text{Fe(III)}][\text{H}_2\text{SO}_3]/R(\text{Fe}) = \frac{1}{2}k_1^{-1} + \frac{1}{2}k_1^{-1}k_{-1}k_4^{-1}[\text{Fe(II)}] \div \{[\text{Cu(II)}] + k_3k_4^{-1}[\text{Fe(III)}]\} \quad (16)$$

Hence, for experiments in which the above approximation can be made, a plot of the left-hand side of eqn. (16) against $[\text{Fe(II)}] \div \{[\text{Cu(II)}] + k_3k_4^{-1}[\text{Fe(III)}]\}$ should be linear and enable k_1 and $k_1k_4^{-1}$ to be found. (The value of $k_3k_4^{-1}$ which is required in evaluating the term in braces has already been found to be 1/110, see section I.) Fig. 1 shows this plot, constructed from the results summarised in Table 3. We find $k_1 = 0.71 \pm 0.06$ l. mole⁻¹ min.⁻¹, and $k_1k_4^{-1} = 11.1 \pm 0.8$. In this treatment we have assumed that reaction between copper(II) and sulphurous acid can be neglected. In a series of experiments in which the initial concentrations of reactants other than copper(II) were constant, the rate of reaction tended to an upper limit with increasing copper(II) concentration. Also, we were not able to detect any reaction in the absence of iron(III) under our conditions. We therefore conclude that this assumption is justified.

III. If the rate of disappearance of HSO_3 radicals by reaction (-1) is sufficiently greater than the sum of the rates of reactions (2), (3), and (4), we have, as an approximation,

$$[\text{HSO}_3] = K[\text{Fe(III)}][\text{H}_2\text{SO}_3]/[\text{Fe(II)}] \quad (17)$$

where $K = k/k_{-1}$.

By combining (7) and (17), and eliminating k_4 by using $k_4 k_3^{-1} = 110$, we find :

$$R(\text{H}_2\text{SO}_4) = k_3 K \{ [\text{Fe(III)}] + 110[\text{Cu(II)}] \} [\text{Fe(III)}] [\text{H}_2\text{SO}_3] / [\text{Fe(II)}] \quad (18)$$

The expression $R(\text{H}_2\text{SO}_3) \div \{ k_1 [\text{Fe(III)}] [\text{H}_2\text{SO}_3] - R(\text{H}_2\text{SO}_3) \}$, represented by $R(2, 3, 4)/R(-1)$, gives the ratio of the rate of disappearance of HSO_3 radicals by reactions (2), (3), and (4) to the rate of disappearance by reaction (-1), and its value can be used to indicate whether eqn. (17) is an allowable approximation. From the results of a similar treatment applied in the oxidation of hydrazine,⁵ we conclude that eqn. (18) should hold well provided that $R(2, 3, 4)/R(-1)$ does not greatly exceed 0.03. This ratio can be

FIG. 1. Plot of (X) $[\text{Fe(II)}] \div \{ [\text{Cu(II)}] + k_4 k_3^{-1} [\text{Fe(III)}] \}$ against (Y) $[\text{Fe(III)}] [\text{H}_2\text{SO}_3] / R(\text{Fe})$ (mole l.⁻¹ min.).

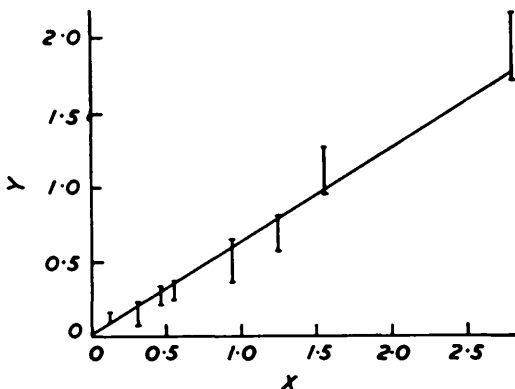
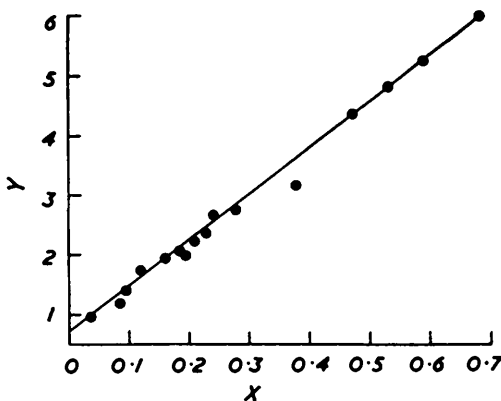


FIG. 2. Plot of (X) $10^3 \{ [\text{Fe(III)}] + 110[\text{Cu(II)}] \} [\text{Fe(III)}] [\text{H}_2\text{SO}_3] / [\text{Fe(II)}]$ (mole³ l.⁻³) against (Y) $10^4 R(\text{H}_2\text{SO}_4)$ (mole l.⁻¹ min.⁻¹).

evaluated for the experiments in Table 2 since $R(\text{H}_2\text{SO}_3) = 2R(\text{H}_2\text{S}_2\text{O}_6) + R(\text{H}_2\text{SO}_4)$, and k_1 has already been found. In experiments 1-8, $R(2, 3, 4)/R(-1)$ is less than 0.03, and Fig. 2 shows a test of eqn. (18) for these experiments. From the gradient of this plot we find $k_3 K = (6.5 \pm 0.4) \times 10^{-4}$ l. mole⁻¹ min.⁻¹.

IV. Under conditions where eqn. (17) holds, eqn. (6) becomes

$$R(\text{H}_2\text{S}_2\text{O}_6) = \frac{1}{2} k_2 K^2 [\text{Fe(III)}]^2 [\text{H}_2\text{SO}_3]^2 / [\text{Fe(II)}]^2 \quad (19)$$

Fig. 3 shows a test of equation (19) for experiments 1-8. It is clear that, although the experimental points lie fairly close to a straight line, this line does not pass through the origin as it should were eqn. (19) to hold.

Discussion.—In sections I-III we have shown that our results fit reasonably well certain kinetic equations deduced from the mechanism suggested above. However, the relation deduced in section IV, between the rate of formation of dithionic acid and the reactant concentrations is not in satisfactory accord with these results. Further, it can be seen from Table 2 that $R(\text{H}_2\text{S}_2\text{O}_6)$ increases in the series of experiments 5, 7-11, for which

the concentrations of reactants other than copper(II) are almost constant. Since therefore the stationary-state concentrations of intermediate species will be almost constant, we should expect $R(\text{H}_2\text{S}_2\text{O}_6)$ to remain constant. These anomalies suggest that in addition to the main reaction sequence, (1)—(5), a side-reaction involving the formation of dithionic acid occurs to a limited extent. Our results are in fairly good quantitative agreement with kinetic equations deduced from the above mechanism with the additional assumptions that metabisulphite ions, probably present in our reaction solutions, can be oxidised by iron(III) to HS_2O_5 , and that such radicals can then be oxidised by either iron(III) or copper(II) to dithionic acid. However, we consider that more precise results than ours would be necessary to establish the nature of this side-reaction with certainty.

We conclude that our results provide satisfactory evidence that under our conditions the course of 1-equivalent oxidation of sulphurous acid follows in its main essentials the general mechanism advanced at the beginning of this paper. Optical evidence suggested that the concentration of complex ions between iron(III) and sulphur(IV) species is negligible, and we have been unable to interpret our kinetic results by assuming that reactions of such complex ions are of major importance. Under other conditions of reaction the

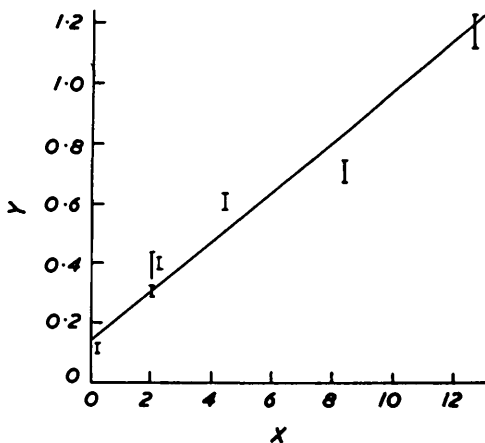


FIG. 3. Plot of (X) $10^3[\text{Fe(III)}]^2[\text{H}_2\text{SO}_5]^2/[\text{Fe(II)}]^2$ (mole² l.⁻²) against (Y) $10^4R(\text{H}_2\text{S}_2\text{O}_6)$ (mole l.⁻¹ min.⁻¹).

formation of such complex ions must be taken into account,⁹ and it is possible that they may take part in the side-reaction discussed above, and that our alternative suggestion concerning the oxidation of metabisulphite ions is incorrect.

FACTORS DETERMINING THE EQUIVALENCE CHANGE IN OXIDATION-REDUCTION REACTIONS

As we have seen, the main features of the oxidation of sulphurous acid, and hydrazine in acid solution, can be interpreted in terms of a common mechanism which differentiates between 1- and 2-equivalent oxidising agents. Although this mechanism may be applicable in some other instances where the products of oxidation of a substrate depend upon the oxidising agent used, we do not consider that all such cases can be so interpreted. For example, bromine and iodine give different products in their reactions with thiosulphate ions in acid solution¹³ although both reactions are almost certainly of the 2-equivalent type. On the other hand, substrates are known which give a single product, irrespective of whether the oxidising or reducing agents used are of the 1- or 2-equivalent type. Thus, the oxidation of iodide ions to iodine by hydrogen peroxide is thought to occur by a 2-equivalent mechanism,^{14, 15} whereas the oxidation of iodide by iron(III) occurs in two 1-equivalent steps.¹⁶ Again, the reduction of thallium(III) to thallium(I) by mercury(I)

¹³ Yost and Russell, "Systematic Inorganic Chemistry," Oxford Univ. Press, 1946, p. 389.

¹⁴ Baxendale, "Advances in Catalysis," Academic Press Inc., New York, Vol. 4, 1952, p. 43.

¹⁵ Symons, J., 1955, 273.

¹⁶ Fudge and Sykes, J., 1952, 119.

probably involves a 2-equivalent reaction,¹⁷ but the reduction by iron(II) occurs in 1-equivalent steps.¹⁸ We consider that these and many other observations can be summarised as follows:

(a) Oxidation-reduction reactions between two transition-metal ions, simple or complex, usually occur in 1-equivalent steps.

(b) Oxidation-reduction reactions between simple compounds or ions derived from two non-transition elements, whether metallic or non-metallic, usually occur in 2-equivalent steps.

(c) Oxidation-reduction reactions between transition-element ions and compounds or ions derived from non-transition elements may occur in either 1- or 2-equivalent steps. The 1-equivalent mechanism occurs more often.

(d) If one of the reactants is a free radical, a 1-equivalent reaction is the more probable.

These conclusions apply only in cases where two species undergo oxidation-reduction in a given step. Reactions in which more than two species undergo oxidation-reduction simultaneously in a single transition complex are rare, although a few examples are known.^{19, 20}

In support of these generalisations we may note first that many reactions in class (b) are considered to follow a common mechanism which involves 2-equivalent oxidation-reduction steps.²¹ Similar conclusions have also been reached for reactions in this class where one of the non-metallic species is an organic compound.²² Secondly, from a recent review of inorganic free radicals,²³ it is apparent that the most common modes of formation of such radicals are by 1-equivalent oxidation-reduction reactions of non-metallic substrates with a transition-metal ion, or with another free radical. (A third possibility is by homolysis of a weak bond.) The numerous examples of these 1-equivalent reactions provide evidence for (c) and (d). In class (c) 2-equivalent reactions are thought to occur in a few cases, *e.g.*, in the reactions of dichromate, permanganate, and vanadium(V) with hydrazine³ and with sulphurous acid. Definite evidence concerning reactions in class (a) is frequently lacking, although a 1-equivalent change is the most obvious interpretation in most cases. References to many oxidation-reduction reactions between metal ions are given in recent reviews.^{24, 25}

We believe that these generalisations can be understood qualitatively by considering the relative stabilities of the various oxidation states of the principal elements present in the compounds taking part in a given reaction, and it is assumed that the less endothermic reaction, whether 1- or 2-equivalent, will be the more probable. The oxidation numbers of stable states of a non-transition element, excluding that of the free element, usually differ by units of two in simple compounds or ions. Hence, in oxidation-reduction reactions between two such molecules or ions, a 1-equivalent change would lead to two relatively unstable species and so seems unlikely compared with a 2-equivalent change. The principal exceptions are likely to occur in the reactions of bromine, chlorine, and nitrogen compounds. Since these elements form oxides which are free radicals, each possesses a series of stable states differing in oxidation number by unity. Thus, certain compounds of these elements may be able to undergo 1-equivalent reactions in systems involving compounds of non-transition elements only. For example, the reaction $\text{NO}_2^- + \text{I}_2 + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 2\text{I}^- + 2\text{H}^+$ is considered to involve 1-equivalent steps.²⁶

¹⁷ Armstrong, Halpern, and Higginson, *J. Phys. Chem.*, in the press.

¹⁸ Ashurst and Higginson, *J.*, 1953, 3044.

¹⁹ George, *J.*, 1954, 4349.

²⁰ Webster and Halpern, *J. Phys. Chem.*, 1956, **60**, 280.

²¹ Edwards, *Chem. Rev.*, 1952, **50**, 455.

²² Levitt, *J. Org. Chem.*, 1955, **29**, 1297.

²³ Uri, *Chem. Rev.*, 1952, **50**, 375.

²⁴ Amphlett, *Quart. Rev.*, 1954, **8**, 219.

²⁵ Zwolinski, Marcus, and Eyring, *Chem. Rev.*, 1954, **55**, 157.

²⁶ Durrant, Griffith, and McKeown, *Trans. Faraday Soc.*, 1936, **32**, 999.

On the other hand, several reactions yielding free-radical products do not necessarily proceed through 1-equivalent steps. In the reactions $3\text{HNO}_2 \longrightarrow 2\text{NO} + \text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O}$, and $3\text{HClO}_3 \longrightarrow 2\text{ClO}_2 + \text{H}^+ + \text{ClO}_4^- + \text{H}_2\text{O}$, it is possible that 2-equivalent reactions occur forming molecules (N_2O_2 or Cl_2O_4 respectively) which rapidly dissociate. Another exception to (b) can occur when a reactant or intermediate dissociates forming free radicals which take part in 1-equivalent reactions. Examples include the reaction between peroxydisulphate and thiosulphate ions in the absence of transition-metal ions,²⁷ and the oxidation of nitrous acid by hydrogen peroxide.²⁸

In oxidation-reduction reactions involving ions of transition elements, for most of which the oxidation numbers of successive stable states differ by unity, both 1- and 2-equivalent steps may occur. However, for many of the ions of common transition metals 2-equivalent reactions are improbable. For the oxidising agents, cerium(IV), cobalt(III), and iron(III), and the reducing agents, titanium(III), and vanadium(IV), the oxidation states which would be formed if 2-equivalent reactions occurred are unknown. For oxidising agents including titanium(IV) and vanadium(IV), and reducing agents including chromium(II), copper(I), and iron(II), most 2-equivalent reactions would be so highly exothermic that they can be disregarded. Consequently, in oxidation-reduction reactions between two transition-metal ions, few instances are likely to occur where a 2-equivalent mechanism is the more probable. One such case is the reaction $\text{Pt(IV)} + \text{U(IV)} \longrightarrow \text{Pt(II)} + \text{U(VI)}$. However, in respect of the stability of their intermediate states, Pt(III) and U(V), platinum and uranium resemble non-transition metals rather than transition elements.

In an oxidation-reduction reaction between an ion of a transition element and a compound or ion derived from a non-transition element, the formation of a free radical or unstable oxidation state from the second reactant by a 1-equivalent reaction is likely in some cases to be a more endothermic process than the corresponding 2-equivalent reaction. Thus the occurrence of 2-equivalent reactions in class (c) is to be expected. However, as we have noted above, many of the ions of common transition elements are capable only of undergoing 1-equivalent reactions, and so the predominance of 1-equivalent reactions in this class is not surprising.

Although most reactions in class (d) are of the 1-equivalent type, some exceptions occur, e.g., $\text{NO}_2 + \text{H}_2\text{SO}_3 \longrightarrow \text{NO} + \text{H}_2\text{SO}_4$ is probably a 2-equivalent reaction. In only a few cases is sufficient known about the energetics of the alternative 1- or 2-equivalent reactions to predict which is the more probable.

Some further comments may now be made upon the observations summarised in Table 1 on the oxidation of sulphurous acid and hydrazine. The stoichiometries obtained in the reactions of vanadium(V) with these reducing agents show that this ion is unusual in being able to undergo both 1- and 2-equivalent reactions with the same substrate. On the other hand, platinum(IV) undergoes only a 2-equivalent reaction with sulphurous acid, while with hydrazine a small proportion of the total reaction presumably occurs through a 1-equivalent step involving the formation of platinum(III) as an intermediate. We consider that a reagent capable of undergoing 1- and 2-equivalent reactions need not necessarily show the same behaviour in its reactions with different substrates, although we should expect relatively small variations when the substrates are of similar type. Bromate may provide another example where a 2-equivalent oxidising agent shows a weak 1-equivalent tendency in its reactions with certain non-metallic substrates. However, in this case sulphurous acid is the substrate and an alternative explanation is possible: the side-reaction forming dithionic acid may be of the 2-equivalent type previously suggested, being similar to, but occurring to a greater extent than, that taking place with other 2-equivalent reagents.

²⁷ Sorum and Edwards, *J. Amer. Chem. Soc.*, 1952, **74**, 1204.

²⁸ Halfpenny and Robinson, *J.*, 1952, 928.

EXPERIMENTAL

Materials and Solutions.—Hydrogen peroxide free from stabiliser was obtained from Laporte Ltd. Metallic iron was Hilger's H.H.P. quality. Other reagents were of "AnalaR" grade or were otherwise available in a pure state. Iron(II) and iron(III) sulphate solutions were prepared as described previously.⁵ Cobalt(III) sulphate solutions in dilute sulphuric acid were prepared from the solid compound obtained by the electrolytic oxidation of cobalt(II) sulphate in solution in 7*M*-sulphuric acid. Thallium(III) sulphate solutions were prepared by dissolving pure dithallium trioxide in an excess of sulphuric acid. Cobalt(III) and manganese(III) complex ions were prepared in solution by standard methods immediately before use.

Solutions of oxidising agents and sodium sulphite were standardised immediately before use. The stock solutions of 0.1*M*-sodium sulphite used in the stoichiometry experiments also contained 10⁻³*M*-ethylenediaminetetra-acetate, added as the disodium dihydrogen salt. The presence of this reagent greatly improves the stability of sodium sulphite solutions to atmospheric oxidation. In the kinetic experiments this reagent was not present, and freshly prepared sodium sulphite solutions were used.

Procedure in the Stoichiometry Experiments.—Experiments were done at pH 0.5 in the presence of sulphuric acid, pH 5 (acetate buffer), and pH 9 (borate buffer). Except where reaction was slow, as indicated in Table 1, three ways of mixing the oxidising agent and sodium sulphite solutions were used. (i) The oxidising agent solution (0.1*N*) was slowly added from a burette to a mechanically stirred mixture of 0.1*M*-sodium sulphite (25 ml.) and an appropriate quantity of sulphuric acid or buffer solution. (ii) The oxidising agent and sodium sulphite solutions (about 25 ml.) were rapidly mixed in the presence of acid or buffer solution. (iii) The sulphite solution (0.1*M*) was slowly added to a mechanically stirred mixture of 0.1*N*-oxidising agent (25 ml.) and an appropriate quantity of sulphuric acid or buffer. For a given oxidising agent, method (i) usually gave the lowest stoichiometry, and method (iii) the highest. In experiments at pH 0.5 by method (i) the titrations were conducted in long-necked flasks. Blank experiments showed that the loss of sulphur dioxide from the acid solutions was negligible under these conditions. When the reaction was slow, the solutions were mixed rapidly, and kept under nitrogen in stoppered flasks. All these experiments were done at room temperature (approx. 18°). Except for the oxidising agents mentioned below, quantities were so chosen that a small excess of sulphite remained at the end of the reaction. This excess was determined by titration with iodine. The titrations with permanganate and iodine were completed by using the colour of these reagents to indicate the end-point. Starch was added just before the end-point in the case of iodine. Bromate and iodate were used in excess. At the end of the addition, iodide was added and the iodine liberated was titrated. In the reaction between hydrogen peroxide and sulphite, experiments were done with either reagent in excess. Bromine was then added in excess to oxidise the remaining hydrogen peroxide or sulphite, followed by the addition of iodide and titration of the iodine liberated. When thallium(III) was the oxidising agent, sulphite was in excess. The reaction was shown to be complete by the absence of a dithallium trioxide precipitate when a sample of the mixture was made alkaline. The sum of the thallium(I) and remaining sulphite concentrations was then determined by titration with iodate (Andrews's conditions). The stoichiometry of the reaction can be calculated from this titration, the initial concentrations of reactants being known. A similar procedure was used in the reaction between potassium chloroplatinate and sulphite. In this case the reaction required several days for completion, which was established by comparing the absorption spectrum of the mixture with that of a similar mixture of potassium chloroplatinite and sulphite between 220 and 330 $m\mu$. Owing to the low solubility of potassium chloroplatinate, the concentration of this reagent in the reaction mixture was about 0.02*N*, about half the concentration of oxidising agent present in other cases. We estimate an error of ± 0.01 in the stoichiometry values quoted in Table 1.

Kinetic Experiments.—In kinetic experiments on the iron(III)-sulphurous acid system the value of the hydrogen-ion concentration is critical. At concentrations greater than about 0.2*M* the oxidation-reduction reaction is extremely slow at 25°. At pH 2 or greater, optical and kinetic evidence showed that complexes between iron(III) and sulphur(IV) species are present in significant concentrations and greatly increase the complexity of the reaction mechanism. We finally adopted a hydrogen-ion concentration of 0.08*M* at 25° and ionic strength 2.0; the concentration of iron(III)-sulphur(IV) complex ions appears to be negligible under

these conditions. After the contribution to the ionic strength by the principal reactants had been taken into account, sufficient sodium sulphate and sodium hydrogen sulphate were used to give a total ionic strength of 2.0. To maintain the initial hydrogen-ion concentration constant in different experiments, the ratio $[\text{SO}_4^{2-}]/[\text{HSO}_4^-]$ was 1.04 in all cases. Since in most experiments the copper(II) concentration only was varied, the SO_4^{2-} and HSO_4^- concentrations were approximately constant and about 0.45M. In these solutions iron(III) is present mainly as $\text{Fe}(\text{SO}_4)_2^-$ and FeSO_4^+ , less than 1% being in the form Fe^{3+} .²⁹ The second dissociation constant of sulphuric acid, used in calculating the hydrogen ion concentration, was found to be 0.083 ± 0.010 mole l^{-1} under these conditions. An indicator method was used, similar to that previously described;³⁰ both picric acid and *o*-cresol-red were used as indicators.

Reaction mixtures were made up by bubbling pure nitrogen for 20 min. through a mixture of all the constituents apart from the sodium sulphite solution, and then adding the latter. Samples for analysis were withdrawn as required by pipette. Precautions were taken to prevent access of air to the reaction mixture during sampling. Blank experiments showed that negligible loss of sulphurous acid occurred during this procedure. Iron(II) was estimated by measurement of the optical density of the tris-*o*-phenanthroline complex.³¹ Ammonium fluoride was added to prevent further reaction between iron(III) and sulphite during these measurements. In these and other optical measurements a Unicam SP 500 spectrophotometer was used. In most of the experiments about eight estimations of the iron(II) concentration were made covering the first quarter of the reaction. The remaining three-quarters of the reaction was not investigated. The extent of the measurements can be gauged from Table 2 in which the upper and the lower figure for a particular reactant give respectively its concentration after the occurrence of half the amount of reaction investigated, and its initial concentration.

Dithionic acid was estimated in separate 20 ml. samples by a modification of Glasstone and Hickling's method.³² 7.5N-Sulphuric acid (20 ml.) was added to the sample, arresting reaction, and sulphur dioxide was removed by bubbling carbon dioxide through the mixture for 20 min. in the absence of air. Iron(II) was then oxidised to iron(III) by the addition of just less than the theoretical quantity of dichromate, followed by titration of the remaining iron(II) with permanganate. A known volume of standard dichromate solution was added, and the solution was made 2N in sulphuric acid and refluxed gently for 1 hr., oxidation of dithionic acid being then complete. The dichromate remaining was estimated by the addition of a small excess of iron(II) followed by back-titration with cerium(IV) (ferroin, *i.e.*, tris-*o*-phenanthroline, indicator).

Values of $R(\text{Fe})$ were obtained by plotting iron(II) concentrations against the time of sampling and taking the gradients. We estimate that $R(\text{Fe})$ can be obtained within $\pm 6\%$. A similar method could not be used to obtain $R(\text{H}_2\text{S}_2\text{O}_6)$ since the accuracy of the dithionic acid estimations is not sufficiently great. Accordingly, the average rate of dithionic acid formation over the amount of reaction studied was found as the mean of three parallel estimations of dithionic acid made on samples taken at approximately the same time as the last sample for iron(II) estimation. We have assumed that this average rate, $\Delta(\text{H}_2\text{S}_2\text{O}_6)/\Delta t$, is equal to $R(\text{H}_2\text{S}_2\text{O}_6)$ at reactant concentrations corresponding to half the amount of reaction studied. From the velocity constants found above, values of $R(\text{H}_2\text{S}_2\text{O}_6)$ can be calculated for a given experiment, and $\Delta[\text{H}_2\text{S}_2\text{O}_6]$ obtained from them by graphical integration. We find that the ratio $\Delta[\text{H}_2\text{S}_2\text{O}_6]/\Delta t : R(\text{H}_2\text{S}_2\text{O}_6)_{\frac{1}{2}\text{reaction}}$ is almost constant in our experiments and is slightly less than unity. We conclude that for our purpose $\Delta[\text{H}_2\text{S}_2\text{O}_6]/\Delta t$ is a sufficiently good approximation for $R(\text{H}_2\text{S}_2\text{O}_6)$.

The values of $R(\text{H}_2\text{SO}_4)$ shown in Table 2 were obtained by using the relation $R(\text{Fe}) = 2R(\text{H}_2\text{S}_2\text{O}_6) + 2R(\text{H}_2\text{SO}_4)$. Owing to the assumption made about $R(\text{H}_2\text{S}_2\text{O}_6)$, these values of $R(\text{H}_2\text{SO}_4)$ are subject to a small and unimportant systematic error.

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³⁰ Ashurst and Higginson, *J.*, 1956, 343.

³¹ Brandt and Smith, *Analyt. Chem.*, 1949, 21, 1313.

³² Glasstone and Hickling, *J.*, 1933, 5.