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THE POTENTIAL OF INERT ELECTRODES IN SOLUTIONS OF SULFUROUS ACID AND ITS BEHAVIOR AS AN OXIDIZING AND REDUCING AGENT

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I. Introduction

Certain reducing substances such as sulfurous acid, formic acid or oxalic acid show in their chemical behavior a much smaller reducing power than that calculated from the free-energy changes attending their conversion into their ordinary oxidation products (sulfuric acid or carbon dioxide and water). This is especially well known in the case of sulfurous acid, whose chemical reducing power is much less than corresponds to the potential (-0.14 volt) calculated for the conversion of SO_2(1 atm.) to SO_4^{--} (1 m.) in the presence of H^+ (1 m.).

The probable nature of the electrode process in a sulfite cell had been considered by Carter and James.[1] In view of the obvious discrepancy with the calculated sulfite–sulfate potential they attributed the observed potential to the tendency of the sulfur dioxide to be reduced rather than oxidized. The reduction product might be sulfur, but since their experiments showed that the addition of sulfur to the electrode vessel did not improve the constancy or reproducibility of the potential (which varied over 0.05 volt), they concluded that an intermediate reduction product of sulfurous acid was concerned. This product they considered to be probably dithionous acid,[2] $H_2S_2O_4$, since their experiments showed that this acid was produced by the cathodic reduction of sulfurous acid in acid solution.

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[1] Carter and James, *J. Chem. Soc.*, **125**, 2231–2240 (1924).

[2] This acid of formula $H_2S_2O_4$ is called by many authors hydrosulfurous acid, and by many others hyposulfurous acid. The first of these names is conventional and without theoretical significance; the second, although recommended by the Nomenclature Committee of the American and London Chemical Societies (see Crane and Patterson "Literature of Chemistry," p. 180), is distinctly irrational, since logically the name hyposulfurous acid should be applied (as it sometimes is) to the acid H_2SO_2 (of which derivatives only have been prepared). This last acid is, however, commonly called sulfoxylic acid. The confusion could be avoided and a rational system of nomenclature for these sulfur acids introduced by giving the acid H_2SO_2 its logical name, hyposulfurous acid, and giving the disulfur acid $H_2S_2O_4$ the new name dithionous acid, which would indicate that it stands in the same relation to sulfurous acid (and hyposulfurous acid) as dithionic acid stands to sulfuric acid (and sulfurous acid). These series of sulfur acids would then be: H_2SO_2, hyposulfurous; $H_2S_2O_4$, dithionous; H_2SO_3, sulfurous; $H_2S_2O_6$, dithionic; H_2SO_4, sulfuric. In the interest of the introduction of this rational nomenclature, the names "dithionous acid" and "dithionite" are used throughout this article.

This paper is a further contribution to the interpretation of this potential of sulfur dioxide, and of its behavior as an oxidizing and reducing agent. The experiments refer chiefly to the potentials exhibited at a platinized platinum electrode by a half-cell with various concentrations of sulfite and hydrogen ion in the presence of various other substances, and under different conditions of agitation and temperature. This half-cell was measured in combination with a hydrogen half-cell in which nearly the same hydrogen-ion concentration prevailed.

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II. Hypotheses as to the Electrode Process in the Sulfite Half-Cell and the Thermodynamic Relations Involved

In order to facilitate the appreciation of the somewhat complex effects to be described in the following sections of this article, there may be presented in advance the following hypotheses, of whose adequacy to explain the phenomena the reader can judge as these are described. To the chemical equations numerical values are appended which show the free-energy decreases[3] attending the reactions at 25° when all the ions involved have a concentration of 1 molal.

1. The potential produced when a platinum electrode is placed in a solution of sulfurous acid arises from the tendency of this acid to reduce to a lower oxidation state, not from its tendency to oxidize to sulfuric acid in accordance with the electrode reactions

$$HSO_3^- + H_2O = SO_4^{--} + 3H^+ + 2E^- - 4245 \text{ cal. or} \quad (1)$$
$$SO_2(g) + 2H_2O = SO_4^{--} + 4H^+ + 2E^- - 6545 \text{ cal.} \quad (2)$$

If the potential were determined by these reactions, the expressions for it would be

$$E = -0.092 - 0.0296 \log \frac{(SO_4^{--})(H^+)^3}{(HSO_3^-)} = -0.142 - 0.0296 \log \frac{(SO_4^{--})(H^+)^4}{p_{SO_2}} \quad (3)$$

2. The sulfurous acid undergoes slight spontaneous decomposition into

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[3] These free-energy decreases were calculated from the following data: $1H_2O$ (l), −56,560 cal.; $1HSO_3^-$ (1 m.), −123,920 cal.; $1SO_2$ (1 atm.), −69,660 cal.; $1SO_4^{--}$ (1 m.), −176,235 cal.; $1S_2O_3^{--}$ (1 m.), −121,345 cal.; $1S_2O_4^{--}$ (1 m.), −134,305 cal. The first three values are those given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 607. That for $1SO_4^{--}$ was obtained by Sherrill and Noyes, This Journal, **48**, 1871 (1926), through revision of the value computed by Lewis and Randall. The free energy of $1S_2O_3^{--}$ at 25° was computed from that of $1HSO_3^{--}$ and from the equilibrium constant 0.013 at 11° determined by Foerster and Vogel, *Z. anorg. allgem. Chem.*, **155**, 189 (1926), for the reaction $HSO_3^- + S(s) = H^+ + S_2O_3^{--}$, neglecting the difference in temperature. That for $1S_2O_4^{--}$ was derived from the reduction potential (+0.009 volt) which was determined electrometrically by Jellinek, *Z. Electrochem.*, **17**, 163 (1911), for the electrode reaction $S_2O_4^{--} + 2H_2O = 2HSO_3^- + 2H^+ + 2E^-$, assuming the acid $H_2S_2O_4$ to be completely ionized, as the other disulfur acids $H_2S_2O_3$ and $H_2S_2O_6$ appear to be.

sulfuric acid and a lower reduction product, namely, dithionous acid $H_2S_2O_4$, in accordance with the reaction

$$3HSO_3^- = SO_4^{--} + S_2O_4^{--} + H^+ + H_2O - 4660 \text{ cal.} \qquad (4)$$

3. The sulfurous acid and the so produced dithionous acid are (as concluded by Carter and James) the electromotively active substances to which the electrode quickly responds and of which the concentrations determine its potential, so that the actual electrode reaction is

$$S_2O_4^{--} + 2H_2O = 2H^+ + 2HSO_3^- + 2E^- + 415 \text{ cal. or} \qquad (5)$$

$$S_2O_4^{--} = 2SO_2(g) + 2E^- + 5015 \text{ cal.} \qquad (6)$$

The corresponding expression for the electrode potential is

$$E = +0.009 - 0.0296 \log \frac{(HSO_3^-)^2(H^+)^2}{(S_2O_4^{--})} = +0.109 - 0.0296 \log \frac{(p_{SO_2})^2}{(S_2O_4^{--})} \qquad (7)$$

4. The dithionous acid itself gradually decomposes in solutions of large hydrogen-ion concentration according to the equation

$$2S_2O_4^{--} + H^+ + H_2O = S(s) + 3HSO_3^- + 46{,}590 \text{ cal.} \qquad (8)$$

or, more strictly, since sulfur rapidly unites with sulfurous acid to form thiosulfuric acid until this attains a considerable concentration, the dithionous acid decomposes in accordance with the equation

$$2S_2O_4^{--} + H_2O = S_2O_3^{--} + 2HSO_3^- + 44{,}015 \text{ cal.} \qquad (9)$$

5. The above-given free-energy values show that Reactions 4, 8 and 9 tend to take place in the direction in which they are written (when the other ion concentrations are 1 molal) in case the $S_2O_4^{--}$ concentration has the following values

Reaction 4, when it is less than 0.0004 molal.
Reaction 8, when it is greater than 10^{-17} molal.
Reaction 9, when it is greater than 10^{-16} molal.

These conditions are probably fulfilled under the actual conditions, as shown at the end of Section VII.

6. A fairly definite concentration of dithionite ion and a fairly definite potential establish themselves as a result of a steady state in which the quantity of this ion being produced by Reaction 4 is equal to that being destroyed by Reaction 9. Certain plausible mechanisms can be formulated from which a steady state would result, but they are so hypothetical that they will not be reproduced here.

7. The possibility should also be considered that sulfur, not dithionous acid, is the reduction product which in association with sulfurous acid determines the electrode potential; for sulfur could be produced by the decomposition of sulfurous acid, as a result of the successive occurrence of Reactions 4 and 8, in accordance with the equation

$$3HSO_3^- = S(s) + 2SO_4^{--} + H^+ + H_2O + 37{,}270 \text{ cal.} \qquad (10)$$

Indeed, not only is this reaction thermodynamically possible, but spontaneous decomposition of solutions of sulfurous acid into sulfur and sulfate has been observed at 100–180° by many investigators.[4] The sulfur so produced would, however, be expected to determine the electrode potential in the case, and only in the case, that Reaction 8 takes place so rapidly that its equilibrium conditions are substantially maintained. In that case the electrode potential would have a definite value corresponding to the electrode reaction

$$S(s) + 3H_2O = HSO_3^- + 5H^+ + 4E^- - 45{,}760 \text{ cal. or} \qquad (11)$$

$$S(s) + 2H_2O = SO_2(g) + 4H^+ + 4E^- - 43{,}460 \text{ cal.} \qquad (12)$$

Hence

$$E = -0.496 - 0.0296 \log (HSO_3^-)^{1/2}(H^+)^{5/2} = -0.471 - 0.0296 \log (p_{SO_2})^{1/2}(H^+)^2 \qquad (13)$$

It has, however, already been stated that James and Carter concluded that sulfur was not the active reduction product, and confirmation of this conclusion is afforded by the measurements presented in this paper.

III. Solutions, Apparatus and Experimental Procedure

In the earlier experiments the electrode vessel could not be conveniently agitated, and the sulfur dioxide was introduced in solution. This plan was employed only in the experiments with the half-cell containing sulfite and dithionate, and in those upon the effect of the initial condition of the electrode. In all the later work sulfur dioxide gas was introduced into the cell and maintained at the desired partial pressure by bubbling through the cell a known mixture of this gas with nitrogen or other diluent. This gave better control and furnished a convenient means of agitation.

In the earlier procedure air-free sulfurous acid solution was prepared by bubbling sulfur dioxide, generated by displacement from sodium bisulfite, through boiled distilled water kept under nitrogen. Dithionic acid was made from a solution of the pure barium salt (prepared for us by Mr. R. D. Pomeroy) by adding the equivalent amount of sulfuric acid and filtering off the precipitated barium sulfate. This solution was also kept under nitrogen. By a simple arrangement the solutions could be admitted to nitrogen-filled burets without exposing them to the air at any time. The burets were then used for analyzing the solutions and for filling the cell. This was done by extending the buret tips through the stopper of a nitrogen-filled mixing vessel into which the desired amounts of solution were run and mixed by shaking. The mixing vessel communicated with the electrode chamber, which had been swept out with nitrogen. Both acids were analyzed prior to use, but the sulfite concentration in the cell solution was always determined after taking down the cell, since an error might otherwise result due to the appreciable vapor pressure of the sulfur dioxide.

The potential measurements in all of the work were made by means of a Type K Leeds and Northrup potentiometer. The sulfite half-cell was joined through a stopcock with a hydrogen half-cell containing sulfuric or hydrochloric acid. It was especially important to keep the two solutions separated, for the presence of a small

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[4] See Foerster, Lange, Drossbach and Seidel, *Z. anorg. allgem. Chem.*, **128**, 245 (1923), who in an account of their own extensive research on this subject include a bibliography of previous work. See also Jungfleisch and Brunel, *Compt. rend.*, **156**, 1719 (1913), and Bassett and Durrant, *J. Chem. Soc.*, **131**, 1401 (1927), who regard dithionous acid as the intermediate product; also K. Jellinek and E. Jellinek, *Z. physik. Chem.*, **93**, 325 (1919), who showed that dithionite decomposes in accordance with Reaction 8.

amount of sulfite poisoned the hydrogen electrodes. Each half-cell was equipped with two platinum foil electrodes, one centimeter square, sealed into glass stoppers placed about one centimeter apart and completely immersed in the cell solution. All electrodes were platinized (unless otherwise stated), those in the sulfite half-cell being replatinized for each set-up. Fig. 1 is a diagram of the hydrogen half-cell as it was used in all experiments. This was of a type used in former investigations in this Laboratory.[5] The side vessel is a saturator which was filled with some of the cell solution. The entering gas bubbled up through the helix, entered the bottom of the electrode vessel and passed out through the side trap. The hydrogen electrodes were considered to be operating satisfactorily when the difference of potential between them was not more than 0.1 millivolt and was not fluctuating; but this difference was usually less than 0.02 millivolt. The sulfite half-cell equipped for gas bubbling, which was used in the later work, was a duplicate of the hydrogen half-cell. The cell was kept in an oil thermostat.

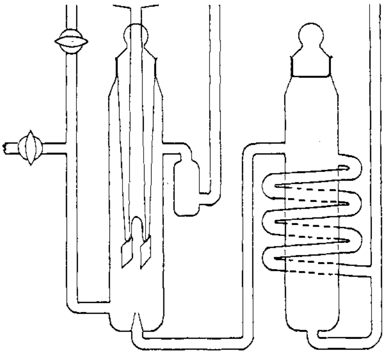

Fig. 1.—Hydrogen half-cell.

The apparatus for mixing the gases is shown diagrammatically in Fig. 2. Nitrogen was the diluent in most of the experiments. The gas from a cylinder was first purified from oxygen by bubbling it through two towers filled with copper turnings immersed in a mixture of equal volumes of concentrated ammonium hydroxide and saturated ammonium chloride solution. From these towers it passed through two wash bottles containing diluted and concentrated sulfuric acid to remove ammonia and water vapor. It passed through the capillary of a flow meter and was mixed with the current of sulfur dioxide. The sulfur dioxide was admitted from a gas cylinder, dried with concentrated sulfuric acid but not otherwise purified,[6] and passed through a flow meter. After the two streams joined, thorough mixing was insured by passing

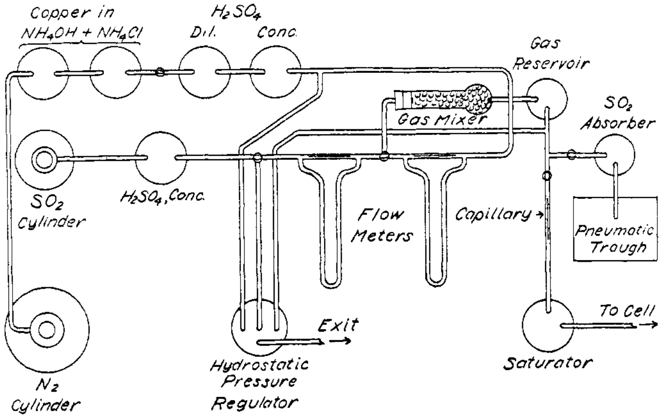

Fig. 2.—Apparatus for gas control.

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[5] Schuhmann, THIS JOURNAL, **46**, 52 (1924).

[6] See L. Moser, *Z. anorg. allgem. Chem.*, **110**, 141 (1920).

the gas through a vessel filled with glass beads. The gas was then admitted to a small reservoir, passed thence to a saturator filled with the cell solution and finally led into the saturator which comprised part of the cell. The flow of gas was kept constant by means of by-passes to hydrostatic pressure exits arranged as shown in the figure and consisting of tubes whose depth of immersion in a well of transil oil could be varied. Gas was kept bubbling from them so that constant pressures were maintained. Nujol was used in the flow meters and their sensitivity was increased by inclining the gages. The various parts of the apparatus were joined with rubber tubing.

The gas mixtures corresponding to the gage settings adopted were analyzed by passing them slowly into an absorption vessel filled with standard iodine solution (to remove the sulfur dioxide) and then into a pneumatic trough, where the nitrogen was collected over water. The excess of iodine was titrated with thiosulfate solution. The agreement of the analyses is shown by the following data: for one gage setting the mixtures were found to contain 7.23, 7.29 and 7.32% of SO_2; for another setting, 23.8, 24.1 and 24.1% of SO_2.

IV. Behavior of a Platinum Electrode in Sulfurous Acid Solutions

When a half-cell that consists of a platinized electrode in an air-free solution of sulfurous acid containing also some stronger acid is allowed to stand at 25° for some hours without bubbling or other agitation, there is established a tolerably constant and reproducible potential, namely, one which as a rule changes by less than two centivolts during several days. This potential has a value of about -0.37 volt, referred to that of the molal hydrogen electrode as zero. If now a mixture of nitrogen and sulfur dioxide (at a partial pressure equal to its vapor pressure in the solution) is bubbled steadily through the solution, so as to mix the liquid surrounding the electrode with the rest of the solution, the potential immediately increases in negative value—an increase which in the course of half an hour usually amounts to two to four centivolts. It then reverts to less negative values, rapidly during the first two hours and then more slowly, attaining after some five or six hours a fairly constant value which may be one or two centivolts more negative than that exhibited before the solution was agitated. When the bubbling is stopped, the potential attains within twenty minutes substantially the value which it had previous to the agitation. If after standing for several hours the bubbling is resumed, the same sequence of phenomena is observed. Thus after a few hours of bubbling the same fairly constant value is obtained as before, usually differing from it by only two or three millivolts; and on quiet standing nearly the same final value results as before. The two duplicate electrodes in the cell then usually check within one or two millivolts, though occasionally they differ by as much as five or six millivolts. The constancy and reproducibility of the electrodes under quiet conditions are shown in detail by the data in Tables III and IV considered below.

The behavior just described is illustrated by Fig. 3, in which graphs for typical half-cells are drawn by plotting as ordinates the potential of the whole cell (with a hydrogen electrode in its other half-cell) and as abscissas the elapsed time in hours. Broken lines are used to indicate periods during which gas was bubbling through the cell; solid lines, periods when there was no agitation.

It will be seen from Fig. 3 and the above statements that four different effects are to be accounted for: (1) production under quiet conditions of a fairly reproducible potential of about -0.37 volt; (2) production by short agitation of the solution of a much more negative potential varying much with the conditions, thus one of about -0.410 and -0.393 in the cells considered; (3) production by long agitation of a potential steadily decreasing in negative value and slowly approaching a value not much larger than that in the quiet state; thus in the two cells after nine to thirteen hours' bubbling the values were -0.370 and -0.373; (4) reëstablishment of the original quiet-state value when the agitation is stopped, and reproduction of a much higher negative value when the stirring is resumed.

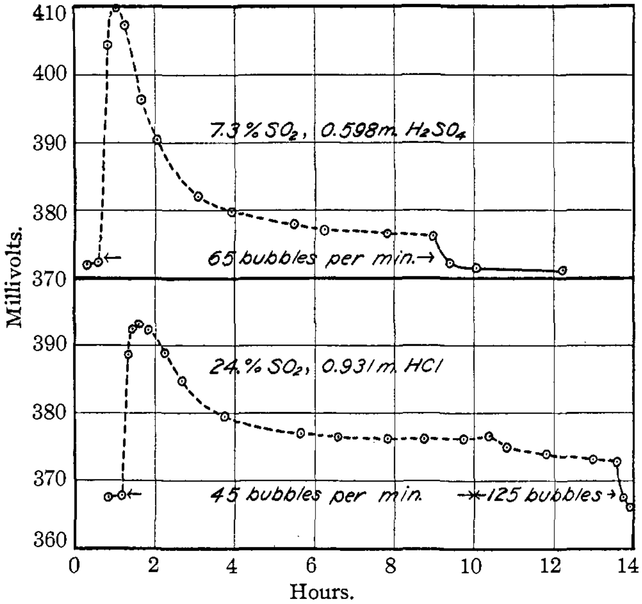

Fig. 3.—Effect of agitation of the sulfite solution upon the electromotive force.

We are not able to present evidence for specific explanations of these agitation phenomena, but they seem to be due to a combination of catalytic and adsorption effects at the electrode, which give rise at its surface to concentration changes that are distributed by stirring the solution.

V. Effect of Preliminary Treatments of the Sulfite Electrode

The following experiments were made in order to establish more fully the conclusion that the potential arises from sulfurous acid and a decomposition product and not from some accidental initial condition of the electrode. One series of experiments was made in which the electrode was treated in various ways before it was placed in the solution; another was made in which a small current was passed through the half-cell in one direction or the other, whereby the electrode would be charged with hydrogen or oxygen gas.

The first series was made with a half-cell with platinum electrodes in a mixture of 0.037–0.046 *N* sulfurous acid and 0.047 *N* dithionic acid, which will later be shown to have no specific effect on the potential, the other half-cell containing sulfuric acid (at 0.078–0.081 *N*) of about the same hydrogen-ion activity. The electromotive force of these cells after successive intervals of quiet standing is shown in Table I. In Expt. 1 platinized electrodes were used but in the other experiments the electrodes were deplatinized. In Expts. 1 and 2 the electrodes were charged with hydrogen by electrolysis in a sulfuric acid solution and then immediately put into the cell. In Expts. 3 and 4 they were allowed to stand overnight in concentrated sulfurous acid solution and in dithionic acid solution, respectively.

Table I

Effect of Various Initial Treatments of the Electrode on its Potential

Expt. no.	Electrode initially treated with	Electromotive force in millivolts after 10–20 min.	1 day	Several days
1	Hydrogen	...	415	447
2	Hydrogen	...	513	477
3	H_2SO_3	475	465	...
4	$H_2S_2O_6$	459	454	...

In a second series of experiments a current was passed through the cell, making the sulfite electrode in some cases the anode and in others the cathode. Somewhat similar experiments had already been made by Carter and James.[1] Our experiments were all made with a half-cell con-

Table II

Electromotive Force of the Cell after Polarization

Expt. no.	Sulfite electrode made	Applied potential Volts	Applied potential Minutes	Before polarization	Electromotive force at various times after polarization 1-2 min.	5 min.	10 min.	20 min.	1 hr.	2 hrs.	1 day
5	Cathode	0[a]	5	434	304	340	400	435	439	434	...
6	Cathode	0[a]	5	427	314	344	389	432	441	433	429
7	Anode	1.6	3	427	484	465	455	449	438	...	427
8	Cathode	65[b]	3	433	250	...	...	444	456	460	460
9	Cathode	65[b]	20	460	220	...	275	305	327[c]	333	435[d]
10	Anode	65[b]	20	425	...	585	530	495	468	461	453

[a] In these cases the cell circuit was closed but no external voltage was applied.

[b] The resulting current was 0.01 ampere.

[c] Thirty minutes after polarization, when the electromotive force was about 340 mv., the cell was shaken; this stopped the rise of the electromotive force for a time.

[d] After two days.

taining platinized electrodes in a mixture containing sulfurous acid at 0.043 *N* (corresponding to a sulfur dioxide pressure of 0.014 atm.) and sulfuric acid at 0.068 *N;* the other half-cell with the hydrogen half-cell contained sulfuric acid at 0.081 *N*, which has about the same hydrogen-ion activity as the mixture of the two acids. The results are shown in Table II.

It will be seen that although the polarization produced great differences in the initial values of the electromotive force, all the final values are of about the same magnitude (430–460 millivolts).

These two series of experiments clearly show that a platinum electrode in sulfurous acid solutions establishes a fairly reproducible potential which is independent of variations in the initial condition of the electrode.

VI. Sulfite Half-Cells with Dithionic Acid

It had been shown by previous investigators that the potential observed with solutions of sulfurous and sulfuric acids is not much affected by the concentration of sulfate ion, showing that this ion is not electromotively active. It was thought possible, however, that the intermediate oxidation product, dithionic acid ($H_2S_2O_6$), might establish with sulfurous acid a definite potential. Cells were, therefore, set up in which the electromotive force observed when sulfurous acid was present with dithionic acid could be compared with that produced when the latter acid was replaced by sulfuric acid. The results are shown in Table III. All potentials are expressed in millivolts.

Since it took several hours or more for the duplicate electrodes in the sulfite half-cell to come to such equilibrium as to check each other well, values were usually not recorded until the following day after starting a run; after this the duplicate electrodes almost always checked to within one or two millivolts.

TABLE III

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SULFUROUS, SULFURIC AND DITHIONIC ACIDS

	Sulfite half-cell					Hydrogen half-cell		
	Normality of							
Expt. no.	H_2SO_3	H_2SO_4	$H_2S_2O_6$	Press. of SO_2, atm.	Molal activity of H^+	Normality of H_2SO_4	Molal activity of H^+	Calcd. potential
1	0.043	0.068	None	0.014	0.045	0.081	0.047	79
2	.046	None	0.047	.015	.044	.081	.047	79
3	.057	0.019	.016	.017	.032	.050	.031	89

SAME EXPERIMENTS CONTINUED

	Electromotive force of cell after successive days						
Expt. no.	1	2	3	4	7	9	Potential of sulfite half-cell
1	428	433	433	...	...	...	−354
2	415	...	...	447	449	...	−370
3	479	474	470	470	466	459	−370

In calculating the potential of the sulfite half-cell no allowance was made for liquid potential; for the acid used in the hydrogen half-cell was of a strength calculated to have about the same hydrogen-ion activity as that of the mixture in the other half-cell. Hydrogen-ion activities were calculated with the aid of the data published by Sherrill and Noyes.[7] In estimating the ionic strength the dithionic acid was considered to be completely dissociated. Conductivity data show it to be a very strong acid.[8] Equilibrium pressures of sulfur dioxide were calculated by Henry's law, correction being made for the dissociation of the sulfurous acid.

It will be seen that the potential is not much different whether the acid present with the sulfurous acid is sulfuric or dithionic, showing that the electrode process which determines the potential does not directly involve either of these acids.

To establish completely the conclusion that the potential is not dependent upon these oxidation products of sulfurous acid, a series of cells was set up in which sulfur dioxide was the only sulfur compound added and the desired acidity was produced by hydrochloric acid. In this work sulfur dioxide gas diluted with nitrogen was bubbled through the cell, to establish a definite activity of sulfurous acid and to provide efficient stirring; the electromotive force was read, however, only after a long period of quiet standing. In order that the comparison might be direct, a similar series was made in which sulfuric acid was again used. The results which are presented later (in Table IV) show that, provided the hydrogen-ion concentration is nearly the same, hydrochloric acid and sulfuric acid produce (in association with sulfurous acid) substantially the same electromotive force.

VII. The Potential of Sulfite Half-Cells and the Effect upon it of the Concentration of Sulfurous Acid and of Hydrogen Ion

The series of comparative experiments with hydrochloric and sulfuric acids (referred to in Section VI), in which a definite concentration of sulfurous acid was attained by bubbling sulfur dioxide diluted with nitrogen through the cell and measuring the electromotive force after periods of quiet standing, also served to determine to what extent the potential depends upon the activity of sulfurous acid and upon that of hydrogen ion. A pair of comparative experiments at 25 and 50° was also made to determine the effect of temperature.

The results are presented in Table IV. The electromotive forces are those of cells of the type Pt + H_2 (1 atm.), HCl or H_2SO_4 (with H^+ at c_H), $\{SO_2$ (at p) + HCl or H_2SO_4 (with H^+ at $c_H)\}$, Pt. The electromotive forces and separate potentials are all expressed in millivolts. The recorded values

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[7] Sherrill and Noyes, This Journal, **48**, 1861 (1926).

[8] See Abegg's "Handbuch der anorganischen Chemie," IV, 1, 539 (1926).

of the electromotive force of the cell are the daily averages of readings taken at intervals of one, two or three hours throughout the day during which the sulfur dioxide was not bubbling through. An asterisk indicates that after taking the reading the gas mixture was bubbled for several hours through the cell, which was then allowed to stand quietly overnight.[9]

TABLE IV

ELECTROMOTIVE FORCE OF CELLS WITH SULFUROUS, SULFURIC AND HYDROCHLORIC ACIDS

		Sulfite half-cell			Hydrogen half-cell		
		Molality					
Expt. no.	Temp., °C.	H_2SO_4	HCl	SO_2 in gas, %	Molal acid	Activity of H^+	Potential calcd.
1	25	0.598	0.0	1.5	0.598	0.599	13
2	25	.598	.0	7.3	.598	.599	13
3	25	.598	.0	24.0	.598	.599	13
4	25	.0	.931	7.3	.931	.955	1
5	25	.0	.931	24.0	.931	.955	1
6	25	.0	.931	100.0	.931	.955	1
7	25	.0	.205	7.3	.205	.170	46
8	50	.0	.931	7.3	.931	.955	1

	Electromotive force of whole cell after successive days as follows								
Expt. no.	1 8	2 9	3 10	4 11	5 12	6 13	7 14	Best value	Sulfite half-cell potential
1	468.1*	...	394.5*	389.2*	384.1*	381.1*	384.5	...	...
	395.0	...	393.0*	393.0	379.4	377.6*	374.6	...	...
2	372.2*	371.7*	372.2*	372.3	377.5	...	378.9	372	−359
	377.5*	371.3	...	...	...	...	...		
3	370.7*	369.1	...	...	...	...	382.6*	370	−357
	370.5*	369.1	370.6	...	...	...	...		
4	368.2*	370.5	370.7*	370.9	370.5	370.2*	369.4	370	−369
5	367.5*	366.5*	366.4	366.8	...	...	366.4	366	−365
6	364.7*	...	...	...	...	...	...	365	−364
7	436.5*	425.6*	...	396.5*	389.8*	390.4*	388.0*	386	−340
	388.2*	385.5*	...	386.0*	385.5*	386.3*	386.4*		
	392.2*	387.8*	381.4	382.3	381.0	...	...		
8	360.4*	357.6*	357.4	355.1*	363.7*	374.7	372.5*	358	−357

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[9] In cases where an experiment consisted merely in increasing the pressure of sulfur dioxide, the initial value recorded is that obtained on the first or second day after making such an increase, when it was believed that the equilibrium concentration had been established. In experiments which were the first of a series, where the air had to be displaced from the cell and the sulfurous acid concentration built up from an initial value of zero, the first recorded figures are in most cases those obtained after several days of gas bubbling, during which time the negative potential was decreasing from that corresponding roughly to an oxygen electrode; for although the electrodes were initially charged with hydrogen, the initial conditions in the cell were such as to establish a highly negative potential. Bubbling was not continued overnight, as it was not desirable to allow the gas to flow so long without observation. Prior to Expts. 1 and 4 the air in the cell was displaced with nitrogen before any sulfur dioxide was admitted. In the other independent experiments the gaseous mixture was started through at once. In Expt. 7 the third row of readings were those after 15, 16, 17, 18 and 19 days.

The hydrogen-ion activity of the hydrogen half-cell and its corresponding potential were calculated from the data given by Lewis and Randall[10] in the cases where hydrochloric acid was used, and from the data of Noyes and Stewart[11] where sulfuric acid was employed. The potential of the sulfite half-cell was obtained by subtracting the calculated value of that of the hydrogen half-cell from the "best value" of the electromotive force of the whole cell, no allowance being made for the liquid potential, which must have been small, since the hydrogen-ion concentrations had been made approximately equal.

Before considering the effects of concentration, it may be pointed out that the results confirm the previous statement that about the same electromotive force is produced with hydrochloric as with sulfuric acid, since the values of the potential obtained with the latter fit in with those obtained with hydrochloric acid both at higher and lower hydrogen-ion activities. There can therefore be no doubt that sulfuric acid is not electromotively active in establishing the potential.

Coming now to concentration effects, it is seen from Expts. 2 and 3 or from Expts. 4–6 that increasing 3.3-fold, or even 14-fold, the partial pressure of the sulfur dioxide has little, if any, effect upon the value of the potential.

It will also be seen that decrease in the hydrogen-ion activity produces a less negative value of the potential. Thus from Expts. 4 and 7 it is seen that a 5.6-fold decrease (from 0.955 to 0.170 molal) causes a decrease of 29 mv., while $^1/_2$ (H^+) per faraday would require a decrease of 22 mv. To express the observed results, the function of (H^+) which occurs in that electrode potential equation should therefore be $(H^+)^{4/3}$.

It is also important to note the absolute value of the potential of the sulfite half-cell. It will be seen that its mean value of 25° at a hydrogen-ion activity of 0.96 N is -366 mv., or -0.37 volt within the error of the measurements. The experimental values of the sulfite potential are therefore expressed by the empirical equation

$$E = -0.37 - 0.0296 \log(H^+)^{4/3} \tag{14}$$

The effect of temperature is shown by Expts. 4 and 8, which were made at 25 and 50°, respectively. The best value of the potential is seen to be only 12 mv. less negative at 50 than at 25°. This shows that the same electrode process is involved at both temperatures, and confirms the conclusion that the potential is not an accidental one. The small change observed, based as it is on one experiment, should not be considered to indicate even the direction of the effect of temperature.

Regarding this -0.37 volt as a sulfite–dithionite potential, it shows,

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[10] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 336.

[11] Noyes and Stewart, THIS JOURNAL, **48**, 1870 (1926).

when considered in relation to the molal potential +0.009 of that combination as expressed by Equation 7, that the $S_2O_4^{--}$ concentration in the assumed steady state, when (H^+) and (HSO_3^-) are 1 molal, is only $10^{-12.8}$ molal. Even this minute concentration is, however, about 20,000 times larger than the $S_2O_4^{--}$ concentration ($10^{-17.1}$ molal) that is shown by Equation 8 to be in equilibrium with solid sulfur and sulfurous acid when (H^+) and (HSO_3^-) are 1 molal.

VIII. Half-Cells with Sulfurous Acid and Sulfur

The experiments described in Sections VI and VII clearly showed that neither the usual oxidation product of sulfur dioxide, sulfuric acid, nor the intermediate oxidation product, dithionic acid, is electromotively active in association with sulfurous acid. Yet it has been seen that the potential set up in a solution of sulfurous acid is a characteristic, not an accidental, one. Attention must therefore be directed toward its reduction products.

A natural reduction product to consider is solid sulfur—a possibility which was suggested in Section II. If it were the electromotively active substance, the electrode potential established would be that corresponding to Equation.[13] This requires an increase of 15 mv. in the negative value of the potential for a ten-fold increase in the pressure of the sulfur dioxide, and an increase of 59 mv. for a ten-fold increase in hydrogen-ion activity. The results of Table IV showed that in fact variation of the pressure of the sulfur dioxde has little or no effect, and that increase in hydrogen-ion activity has only about two-thirds of the required effect. Although these results with sulfur dioxide are not divergent enough to prove that sulfur is not the active substance involved in the electrode process, yet the absolute value of the molal electrode potential is hardly reconcilable with this assumption, for the observed value is only −370 mv., while that calculated from the free-energy data by Equation 13 is −471 mv. Thus there is a difference of 100 mv., which is about ten times as great as the variation in constancy and reproducibility shown by the data when the conditions are those of strong acidity and moderate pressure of sulfur dioxide. This shows that much more strongly reducing conditions prevail than would be caused by solid sulfur, and therefore that dithionite (or some other strongly reducing substance) is present at higher concentration than that which is in equilibrium with sulfur and sulfurous acid according to Equation 8.

Nevertheless, it seemed worth while to test further the possibility that sulfur is the active substance by depositing it in finely divided form on the electrode. The presence of this added sulfur should give a more constant and reproducible potential and one more nearly of the calculated magnitude if this substance is really electromotively active.

These experiments were first carried out at 50° with Cell 8 of Table IV after taking the readings there recorded. At 50° a cell of this composition should have an electromotive force of approximately 430 mv. if sulfur and sulfur dioxide are the electromotively active substances. The free-energy decrease that attends Reaction 12 at 50° is calculated from that at 25° and from the heat-content decrease at 37.5° (−67,400 cal.) to be −41,460 cal., and the corresponding electrode potential equation is

$$E = -0.449 - 0.0321 \log p_{SO_2}{}^{1/2}(H^+)^2 \qquad (15)$$

The two electrodes in the sulfite cell were removed and one of them was given a shaggy coating of free sulfur by electrolysis in a solution of sodium polysulfide. They were then soaked in hot water for a couple of hours, rinsed thoroughly and returned to the cell. The gas mixture was bubbled through the half-cell for several hours on the first and second days, after which the contents were no longer agitated. After standing overnight the electromotive force returned approximately to that (358 mv.) shown before the sulfur treatment, the two electrodes checking within 2 mv.; but during the next five days it gradually became more negative, after which it showed no consistent trend, though subject to daily fluctuations of 5–6 mv. It showed an average value of 412 mv. at the sulfur-treated electrode, and of 425 mv. at the other electrode.

The electrodes were again removed, cleaned and replatinized. One of them was coated with a thick, sirupy solution of sodium polysulfide and sulfur was precipitated from it by fuming it with concentrated hydrochloric acid overnight. The electrodes were then subjected to a very thorough washing and leaching with warm water; they were returned to the cell and gas was bubbled through it to replace any air. After standing quietly overnight the electromotive force of the cell was 396 mv. at the sulfur-treated electrode and 410 mv. at the other. The values rose over a period of six days, and then remained constant within 3 mv. for four days more at 444 mv. and 440 mv., respectively. These values are seen to be approximately equal to the calculated value (430 mv.), and indicate that at 50° the presence of sulfur on or near the electrode tends to establish the potential required by electrode Reaction 12 involving sulfur and sulfur dioxide.

In view of these results it seemed desirable to investigate the effect of the addition of sulfur at 25° also. The results so obtained are shown in Table V. One electrode was untreated but the other was coated with sulfur by the second method above described, and after the reading first recorded in the table some powdered rhombic sulfur was added to the sulfite half-cell.

It will be seen that the values obtained at 25° with the uncoated electrode are apparently not changed by adding solid sulfur to the solution,

TABLE V

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SOLID SULFUR ADDED

HCl in each half-cell, 0.829 *M;* H^+ activity, 0.804 *M;* calculated potential of hydrogen half-cell, +6 mv.

Sulfite half-cell Electrode sulfur treated	% SO_2 in dry gas	Electromotive force of cell after successive days as follows								Best value	Potential of sulfite half-cell
		1	2	4	5	6	8	9	11		
No	7.3	380.0[a]	374.0[a]	372.9[a]	375.6	375.5	375.5[a]	375.2	376.9	375	−369
Yes	7.3	396.0[a]	387.5[a]	375.2[a]	390.6	387.9	389.0[a]	376.0	377.9	385	−379
No	24.0	373.4[a]	373.3	...	...	...	...	...	...	373	−367
Yes	24.0	380.6[a]	379.4	...	...	...	...	...	...	380	−374

[a] After this reading the gas mixture was bubbled for several hours through the cell, which then stood quietly overnight.

and even the values obtained at the sulfur-treated electrode differ from those at the untreated electrode by only 10 mv. in many cases, and show no tendency to deviate more than this.

These facts show that at 25° the additional sulfur does not determine the potential of the half-cell and that sulfur would have little effect even if it were formed on the electrode through decomposition of the sulfurous acid in cases where sulfur was not added. This presumably arises from the facts that it has much less electromotive activity than dithionite, and that the decomposition of the dithionite by Reaction 8 is not rapid enough, even though it may be catalyzed by solid sulfur, to reduce its concentration to that corresponding to the equilibrium conditions of Reaction 8. The result at 50° showing that the addition of sulfur causes the theoretical sulfur potential to be approximated is probably due to the fact that at this higher temperature the decomposition of the dithionite is rapid enough in the presence of sulfur to establish approximately the equilibrium conditions of Reaction 8.

IX. Sulfite Half-Cells in the Presence of Oxygen

An extensive investigation was carried out some years ago by Edgar, and reported later by Lewis, Randall and Bichowsky,[12] in which sulfur dioxide diluted with air was bubbled through a half-cell containing sulfuric acid solution and an iridized platinum electrode. The electrode potential of this half-cell was measured against a half-cell having a mercury–mercurous sulfate electrode and containing sulfuric acid at a concentration equal to that in the sulfite half-cell. Reproducibility to within about 1 mv. was obtained.

The electromotive forces directly observed by Edgar were calculated by us over to the molal hydrogen electrode with the aid of the values of Randall and Cushman[13] for the cell H_2 (1 atm.), H_2SO_4, $Hg_2SO_4(s)$ + Hg, so as to obtain the electromotive forces of the cell H_2 (1 atm.), H_2SO_4 (*c*),

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[12] Lewis, Randall and Bichowsky, THIS JOURNAL, **40**, 360 (1918).

[13] Randall and Cushman, *ibid.*, **40**, 393 (1918).

H_2SO_4 (*c*) + SO_2 (g). By subtracting from these the calculated values for the potential of the hydrogen half-cell, the potentials of the sulfite half-cell were obtained.

Table VI shows the results obtained by Edgar with the moderately concentrated solutions of sulfuric acid. The concentration of the sulfuric acid in the hydrogen half-cell was always the same as that in the sulfite half-cell. The potentials are as usual expressed in millivolts. The values in the last column were obtained from those in the preceding one by subtracting 0.0296 log p_{SO_2}. These values correspond to the assumption that the change in potential is determined by an electrode reaction including among the reduced substances $\frac{1}{2}SO_2$ per faraday. This fact was naturally interpreted by the earlier investigators as indicating that the observed quantity was a sulfite–sulfate potential established in accordance with Equation 3 of Section II.

TABLE VI

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SULFUR DIOXIDE AND AIR

(Calculated from Edgar's data)

	Sulfite half-cell		Hydrogen half-cell			Sulfite half-cell	
Expt. no.	Molality of H_2SO_4	Pressure, SO_2 atm.	Activity H^+	Potential calcd.	E.m.f. of cell	Potential	SO_2 at 1 atm.
1	0.5009	0.00689	0.497	18	458	−440	−376
2	.5009	.01328	.497	18	445	−427	−373
3	.5009	.02479	.497	18	437	−419	−372
4	.5009	.05080	.497	18	430	−412	−372
5	.5009	.1091	.497	18	422	−404	−376
6	.5125	.969	.508	17	371	−354	−354

The results shown by Table VI may be summed up as follows. When little or no oxygen is present, as in Expt. 6, the sulfite potential has the value −354 mv., which corresponds closely to that (−358 mv.) required by our empirical Equation 14 of Section VII. But when, as in Expts. 1–5, oxygen is present and a considerable acid concentration prevails (this perhaps enabling the oxygen to cause oxidation) the potential is more negative (−404 to −440 mv.). This signifies that the reducing substance (the dithionite) involved in the steady state determining the potential is being destroyed not only by the spontaneous decomposition expressed by Equation 9 but also by oxidation by the air. Moreover, the negative value is increased by decreasing the concentration of the sulfite; that is to say, the potential becomes more oxidizing on diminishing the concentration of what is here regarded as the oxidizing substance. To explain this anomaly, one must assume that the concentration of the reducing substance (the dithionite) is decreased in still greater proportion when a lesser quantity of sulfurous acid is present from which it can be regenerated.

To study further the effect of oxygen, a series of experiments was made in which gas mixtures of air with sulfur dioxide were bubbled through a sulfite half-cell. The results are shown in Table VII.[14]

TABLE VII

ELECTROMOTIVE FORCE AT 25° OF CELLS WITH SULFUR DIOXIDE AND AIR

Expt. no.	Sulfite half-cell Molal. H_2SO_4	Sulfite half-cell SO_2 in gas, %	Hydrogen half-cell Activity of H^+	Hydrogen half-cell Potential, calcd.	Electromotive force of whole cell 1	2	3	4	5	6	7	Best value	Sulfite half-cell potential
1	0.590	1.5	0.594	13	512[a]	506[a]	491[a]	...	...	485[a]	491	489	−476
2	.590	7.3	.594	13	443	438[a]	437[a]	431	...	...	...	437	−424
3	.590	7.3	.594	13	498[a]	486[a]	490[a]	487[a]	477[a]	481[a]	477	483	−470
4	.590	24.0	.594	13	459[a]	453	425[a]	440[a]	435[a]	422	...	430	−417
5	.590	24.0[b]	.594	13	466[a]	465[a]	...	460[a]	470	...	...	465	−452

[a] After this reading the gas mixture was bubbled for several hours through the cell, which then stood quietly overnight before the next reading was made.

[b] In this experiment the SO_2 was diluted with oxygen, instead of air.

It will be seen that the experiments presented in Table VII do not show the constancy or agreement with one another exhibited by those of Edgar. It is evident that our conditions, probably especially those prevailing at the sulfite electrode, were not nearly as favorable as those in Edgar's experiments. Our results are cited here, not to cast doubt upon the previous ones, but only to show how capricious the potential may be when the electrode process is complicated by the presence of oxygen.

X. The Oxidizing and Reducing Properties of Sulfurous Acid

Finally, reference should be made to the chemical behavior of sulfurous acid in relation to its electrode potential. An extensive series of researches on the oxidizing and reducing action of this substance has recently been carried out by Wardlaw, Carter and their associates.[15]

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[14] The method of recording the data is the same as that in Table IV. Immediately following Expt. 1 the electrodes were removed and resaturated with hydrogen before being replaced. This appeared to produce a permanent decrease in the electromotive force of the cell, as was shown by the character of the bubbling curve and by the non-bubbling value obtained the following morning (455 mv.). The sulfur dioxide pressure was then changed to 7.3% in Expt. 2. Expts. 3, 4 and 5 form a new series in which a fresh solution was taken.

The air used in these experiments was drawn from the laboratory compressed air lines and was passed through a solution of sodium hydroxide and then through concentrated sulfuric acid. Oxygen was drawn from a gas cylinder and passed through the same solutions. After taking down the cells the solution was analyzed by first titrating with thiosulfate for sulfite content and then with sodium hydroxide for total acidity. The increase in the molality of the sulfuric acid was calculated to be about 0.004 mole, although this cell was in operation for twenty days.

[15] Wardlaw and Clews, *J. Chem. Soc.*, **117**, 1093–1103 (1920); Wardlaw and Carter, *ibid.*, 1241–1247 (1920); Wardlaw and Pinkard, *ibid.*, **121**, 210–221 (1922); Carter and Clews, *ibid.*, **125**, 1880–1888 (1924); Carter and Lea, *ibid.*, **127**, 499–510 (1925); Carter and Robinson, *ibid.*, **130**, 1921–1923 (1927). For a summary of the results see Carter, *J. Soc. Chem. Ind.*, **45**, 207-210 (1926); Wardlaw, *ibid.*, **45**, 210–214 (1926).

These investigators have studied the effect at 95° or above of sulfurous acid, both as an oxidizing agent and as a reducing agent, on various combinations having a series of reduction potentials, namely, on different mixtures of ferrous and ferric chlorides, of ferrous and ferric phosphates, of cuprous and cupric chlorides, and of mercurous and mercuric chlorides, in the presence of the corresponding acid at widely varied concentrations. They have thus qualitatively determined the combinations which have near 95° such reduction potentials as cause them to be barely oxidized and such as cause them to be barely reduced by sulfurous acid at different acid concentrations. They have found in general: (1) that sulfurous acid, because of its tendency to undergo two entirely different reactions, behaves either as a reducing agent or an oxidizing agent depending on the nature of the combination acted upon and on the strength of the acid, (2) that at a given acid concentration the reduction potential of the combination acted upon need be varied by only a relatively small amount (say by 20 to 40 mv.) in order to change the action of sulfurous acid from a reducing one to an oxidizing one, and (3) that increase in acid concentration makes sulfurous acid a less powerful reducing agent, and also (to about the same extent) a more powerful oxidizing agent.

From a theoretical standpoint this chemical behavior of sulfurous acid may now be interpreted in the following way more quantitatively than was done by the English investigators.

Sulfur dioxide at 25° at 1 atm. in an aqueous solution containing hydrogen ion at 1 molal may be expected to behave toward other oxidation–reduction combinations of substances in three different ways according as the reduction potential of the latter (a) is more negative than -0.37 volt; (b) lies between -0.37 volt and -0.14 volt; (c) is more positive than -0.14 volt. (It may be recalled that the value -0.37 is the potential which sulfur dioxide has, under the specified conditions, with respect to its conversion into dithionite ion $S_2O_4^{--}$ as it exists in the steady reaction state, and that -0.14 is the potential which it has with respect to its conversion to sulfate ion, SO_4^{--}, at 1 molal.) For it is evident that sulfur dioxide may oxidize any combination with a reduction potential more reducing (less negative) than -0.37 volt, and that it may reduce any combination which has a potential more oxidizing (more negative) than -0.14 volt. Therefore it may either oxidize or reduce any combination with a potential between -0.37 and -0.14 volt, and which of these two possible effects actually occurs will depend on the relative rates of the oxidizing reaction and of the reducing reaction. For example, sulfur dioxide (at 25° and 1 atm. and with H^+ at 1 molal) can only reduce Fe^{++}(1 m.), Fe^{+++} (1 m.) for which E is -0.75 volt, or I^-(1 m.), I_2(s) for which E is -0.54 volt; and it can only oxidize Pb (s), Pb^{++} for which E is $+0.12$ volt, or H_2 (1 atm.), H^+ (1 m.), for which $E = \pm 0$. But it might either oxidize or reduce Hg (l) + Cl^-(1 m.), Hg_2Cl_2(s) for which E is −0.27 volt, or Cu(s), Cu^{++} (1 m.) for which E is −0.34 volt. In fact, however, in such cases the oxidizing effect of sulfur dioxide (whereby it is converted to dithionite) seems to be more rapid than its reducing effect (whereby it is converted to sulfate), so that within the interval −0.37 to −0.14 volt it probably acts ordinarily as an oxidizing agent. If this is the case, the potential which a combination actually must have in order that it may be reduced by sulfur dioxide is −0.37, not −0.14, thus accounting for the condition mentioned in the Introduction that sulfur dioxide seems to be reducing through a narrower range than thermodynamic relations permit.

Increase of hydrogen-ion concentration, according to empirical Equation 14, extends the region (to more negative values than −0.37) within which sulfur dioxide can act oxidizing, and, according to theoretical Equation 3, it narrows the region (requiring more negative potentials than −0.14 in the combination acted upon) within which sulfur dioxide can act reducing. Thus increase of acidity should make sulfur dioxide more oxidizing, but less reducing, as the English investigators found.

XI. Summary

Experiments have been described in this article showing the electromotive force developed in various cells of the general type Pt, H_2SO_3 + HA at c_1, HA at c_2, H_2 + Pt, where c_1 and c_2 are so related that the hydrogen-ion concentration is nearly the same in the two solutions (thus largely eliminating the liquid potential), and where HA is sulfuric acid, dithionic acid or hydrochloric acid.

It is shown that fairly definite electromotive forces result when and only when the cells are allowed to stand quietly for many hours or for several days, since agitation immediately causes a large increase in the negative value of the electromotive force. This definite electromotive force is nearly independent of the concentration of the sulfurous acid and does not depend on whether the acid associated with it is sulfuric, dithionic or hydrochloric acid, thus proving that the anion of none of these acids determines the potential. At 25° the potential E of the sulfite half-cell (obtained by subtracting from the electromotive force the calculated potential of the hydrogen electrode) is approximately given by the empirical expression $E = -0.37 - 0.03 \log (H^+)^{4/3}$.

It is shown that the results are satisfactorily explained by the assumption, earlier made by Carter and James, that the sulfite potential arises from association with the sulfurous acid of one of its spontaneously produced reduction products, probably the acid $H_2S_2O_4$ (for which the rational name dithionous acid is proposed, in place of the conventional names hydrosulfurous or hyposulfurous acid used in the literature). It is suggested that the fairly definite potential is the result of a steady state in which the quantity of this acid produced per minute by the decomposition of sulfurous acid (into $H_2S_2O_4$ and H_2SO_4) becomes equal to the quantity of it destroyed per minute by its spontaneous decomposition (into H_2SO_3 and S or into $H_2S_2O_3$).

It is shown that the reduction product which determines the potential is not sulfur itself, for thermodynamic calculations require that the potential then be about 0.10 volt more negative than the observed value of −0.37 volt; moreover, experiments in which finely divided sulfur was added to the sulfite half-cell showed that it is not active enough to change the potential in the required direction. This is true at any rate at 25°, but there are indications that at higher temperatures, where the sulfur is more active and the rate of decomposition of the dithionous acid more rapid, sulfur may be the reduction product which determines the potential.

As an aid in the interpretation of the results the free energies and electrode potentials corresponding to all the sulfur reactions possibly involved have been derived from existing theremodynamic data and formulated (in Section II).

The existence of the definite steady-state potential (−0.37 volt at 25°) between sulfurous acid and its reduction product considered in connection with the thermodynamically known potential (−0.14 volt) of sulfite–sulfate, enables the behavior of this acid as an oxidizing agent and as a reducing agent to be predicted; namely, it is shown that a solution of sulfurous acid at 25° (when the corresponding pressure of sulfur dioxide is 1 atm. and the H^+ concentration is 1 molal) may oxidize any other oxidation–reduction combination which has a reduction potential more reducing (less negative) than −0.37 volt, and that it may reduce any combination which has a potential more oxidizing (more negative) than −0.14 volt. Therefore it may either oxidize or reduce any combination with a potential between −0.37 and −0.14 volt; which of these two possible effects actually occurs will depend on the relative rates of the oxidizing reaction and the reducing reaction.

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