

THE POTENTIAL OF INERT ELECTRODES IN SULFUROUS ACID SOLUTIONS

Thesis by

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## THE POTENTIAL OF INERT ELECTRODES IN SULFUROUS ACID SOLUTIONS

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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 fact is especially pronounced in the case of sulfurous acid, where a fairly definite electrode-potential (about -0.4 volts) results, which is in much better agreement with its known chemical behavior than is the potential (-0.14 volts) calculated for the conversion of  $\text{SO}_2$  (1 atm.) to  $\text{SO}_4^{=}$  (1 m.)

The probable nature of the electrode process has been considered by Carter and James.<sup>1</sup> In view of the apparent discrepancy with the calculated sulfite-sulfate potential, they considered the observed potential to be due to the tendency of the sulfur dioxide to be reduced rather than oxidized, an assumption which is also justified by its chemical behavior, which will be discussed later. Since experiments in which sulfur was added to the electrode vessel did not improve the constancy or reproducibility of the potential (which varied over 0.05 volts), they concluded that the sulfur was without effect, and that an intermediate reduction-product of sulfurous acid was concerned, which their experiments on the cathodic reduction in acid solution led them to believe was hydrosulfurous acid,  $\text{H}_2\text{S}_2\text{O}_4$ .

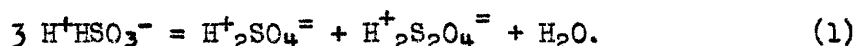
The present work is a further contribution to the interpretation of this sulfur dioxide potential. It is concerned chiefly with the potentials exhibited at a platinized platinum electrode in a half-cell containing sulfur dioxide in acid solution under various conditions of concentration, temperature, and agitation, and in the presence of certain other substances.

This investigation was carried on under the supervision of Professor A. A. Noyes to whom the writer is indebted for much helpful advice and cooperation. It was assisted financially by a grant to Professor Noyes from the Carnegie Institution of Washington.

## II. Hypothesis as to the Electrode Process in the Sulfite Half-Cell

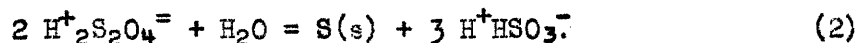
In order to facilitate the appreciation of the somewhat complex effects to be described in the following sections of this article, there may be presented in advance, but without laying stress on the validity of the assumptions, especially with respect to the specific sulfur reduction-products considered, the following hypothesis, of whose adequacy to explain the phenomena the reader can judge as they are described.

1. The sulfurous acid undergoes slight spontaneous decomposition into sulfuric acid and a lower reduction-product, probably hydrosulfurous acid,  $\text{H}_2\text{S}_2\text{O}_4$ , in accordance with the reaction:

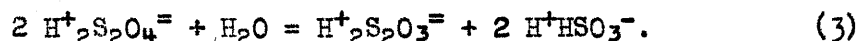


2. The sulfurous and hydrosulfurous acids are (as concluded by Carter and James) the electromotively active substances to which the electrode quickly responds and of which the concentrations determine its potential.

3. The hydrosulfurous acid is itself gradually decomposed in solutions of large hydrogen-ion concentration according to the equation

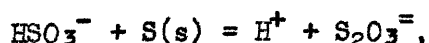


Or more strictly, since sulfur rapidly unites with sulfurous acid to form a complex acid, thiosulfuric acid, until a considerable concentration of the latter is reached, the hydrosulfurous acid decomposes in accordance with the equation



4. A fairly definite concentration of hydrosulfurous acid and a fairly definite potential establishes itself as a result of a stationary state where the quantity of the acid being destroyed by reaction (2) or (3) becomes equal to that being produced by reaction (1).

It can be shown from free-energy data that each of these reactions tends to take place in the direction in which it is written under the conditions of concentration which doubtless prevail. Namely, Lewis and Randall<sup>2</sup> give as the free energy at 25° of  $\text{HSO}_3^-$  (1 m.) the value -123,920 cal., and Sherrill and Noyes<sup>3</sup> give as a revision of the value of Lewis and Randall for  $\text{SO}_4$  (1 m.) the value -176,235 cal. From this value for  $\text{HSO}_3^-$  and the equilibrium-constant 0.013 determined by Foerster and Vogel<sup>4</sup> for the reaction



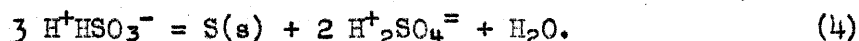
the free energy of  $\text{S}_2\text{O}_3^{2-}$  (1 m.) is found to be -121,345 cal. And from the reduction potential (+0.009 volt) determined electrometrically by Jellinek<sup>5</sup> for the electrode reaction



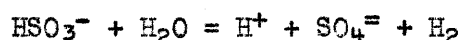
the free energy of  $\text{S}_2\text{O}_4^{2-}$  (1 m.) is found to be -134,305 cal.\* From these values the free-energy decreases attending the above reactions when all the ions are 1 m. are as follows: reaction (1), -4,660 cal.; reaction (2), +46,590 cal.; reaction (3), +44,015 cal. It may then readily be calculated that, when the other ions are all 1 m., the reactions tend to take place in the directions written under the following conditions: reaction (1) when  $(\text{S}_2\text{O}_4^{2-})$  is less than 0.0004 m.; reaction (2) when  $(\text{S}_2\text{O}_4^{2-})$  is greater than  $10^{-17}$ ; and reaction (3) when  $(\text{S}_2\text{O}_4^{2-})$  is greater than  $10^{-16}$  m.

\* Lewis and Randall<sup>2</sup> give -56,560 cal. as the free energy at 25° of  $\text{H}_2\text{O}(l.)$

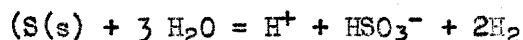
The net result of reactions (1) and (2) would be expressed by the equation



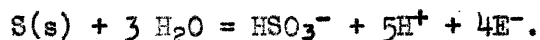
And the free-energy decrease attending this reaction at 25° when the  $\text{H}^+$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_4^-$  ions are at 1 molal is +37,370 cal. Therefore, if reaction (2) was practically instantaneous, sulfurous acid and sulfur might be the electromotively active substances, determining the potential. However the free-energy decrease attending the reaction



is -4245 cal. (which corresponds to a potential of -0.092 for the electrode process  $\text{HSO}_3^- + \text{H}_2\text{O} = \text{SO}_4^- + 3\text{H}^+ + 2\text{E}^-$ ); so that by subtraction there is found for the reaction



a free-energy decrease of -45,760 cal. which corresponds to a reduction-potential of -0.496 volt for the electrode process



Yet, as will be shown below, the observed potential of the sulfite half-cell in the quiet state is only -0.37, and even on agitation is only a few centivolts more negative, making it evident that a much more reducing substance than sulfur must compensate the oxidizing action of sulfurous acid, and therefore that not sulfurous acid and sulfur, but sulfurous acid and an intermediate reduction-product, such as hydrosulfurous acid, are the electromotively active substances, as was assumed above.

Not only are reactions (1) and (3) thermodynamically possible, but spontaneous decomposition of solutions of sulfurous acid to sulfur

and sulfate as end-products has been observed at 100°-180° by many investigators.\* Jungfleisch and Brunel<sup>7</sup> and Bassett and Durrant<sup>8</sup> regard hydrosulfurous acid as the initial reduction product; and K. Jellinek and E. Jellinek<sup>9</sup> have found that hydrosulfite decomposes in accordance with reaction (3).

### III. Solutions, Apparatus, and Procedure

In the earlier experiments the electrode vessel was not equipped for convenient agitation, and the sulfur dioxide was introduced in solution. This plan was only employed in experiments which dealt with the possibility of a reversible sulfite-dithionate electrode, and with the effect of the initial condition of the electrode. But 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 controlled 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

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\*Foerster, Lange, Drossbach, and Seidell in accounts of their own researches on this subject include descriptions of previous work.<sup>6</sup>



filling the cell. This was done by extending the buret tip 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 hydrosulfuric acid. It was especially important to keep the two solutions separated; for the presence of a small 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 in the case of the sulfite half-cell 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. Figure I 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.<sup>10</sup> The side vessel is a saturator which was filled with some of the cell solution. The entering gas bubbled up through its spiral, was admitted at 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 in excess of 0.1 millivolt and was not subject to

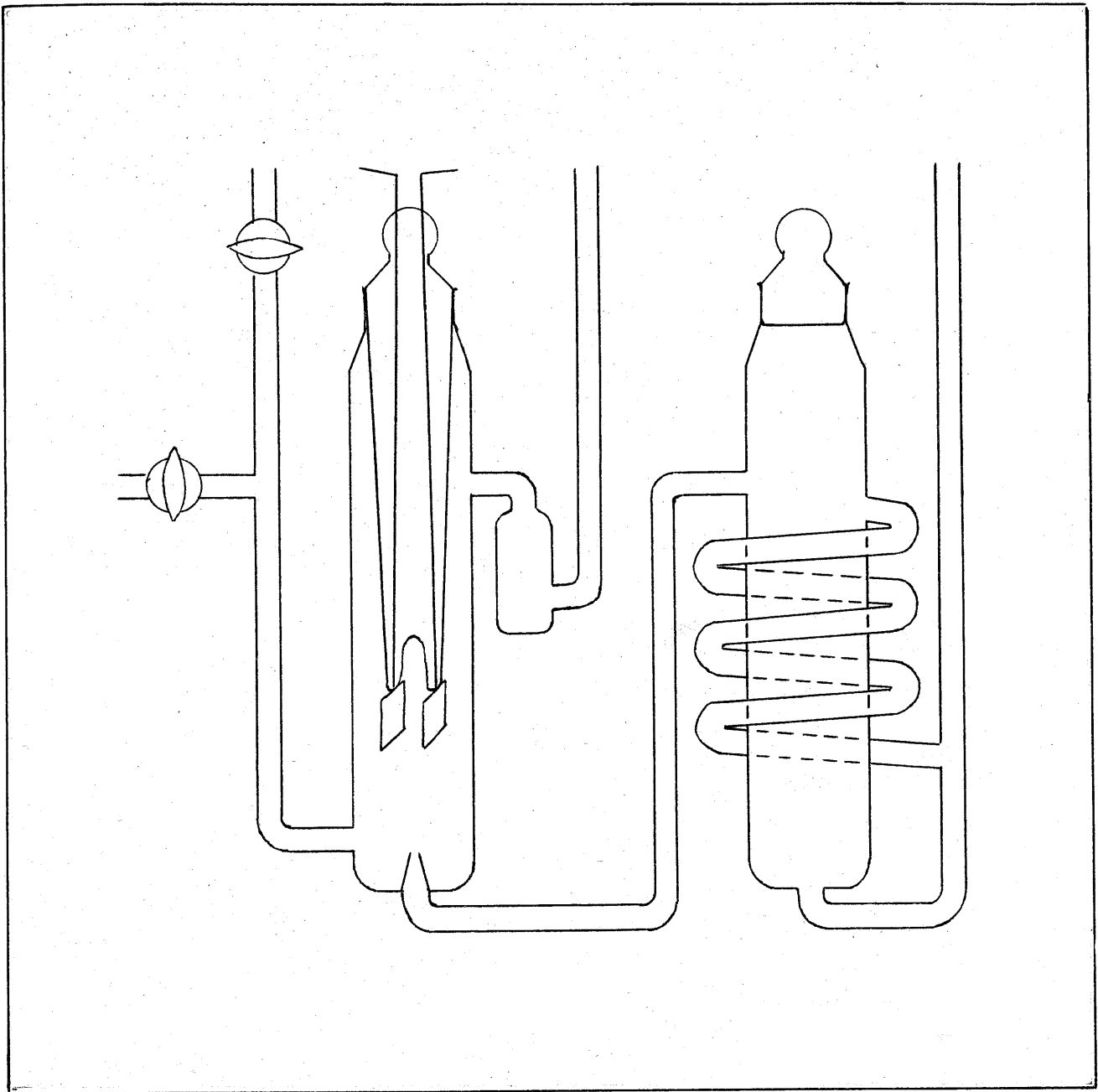


FIGURE I  
Hydrogen Half-Cell

fluctuation; but this difference was usually less than 0.02 millivolt. The sulfite half-cell (equipped for gas bubbling) that was used in the later work was a duplicate of the hydrogen half-cell. The cell was kept in an oil thermostat.

The apparatus for mixing the gases is shown diagrammatically in Figure II. 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,<sup>11</sup> and then passed through a flow meter. After the two streams joined, thorough mixing was insured by passing the gas through a vessel filled with glass beads. The gas was then admitted to a small reservoir, passed from there 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 bypasses 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 heads of pressure were maintained. Nujol was used in the flow meters, and their sensitivity was increased by inclining the gauges. The various parts of the apparatus were joined with rubber tubing.

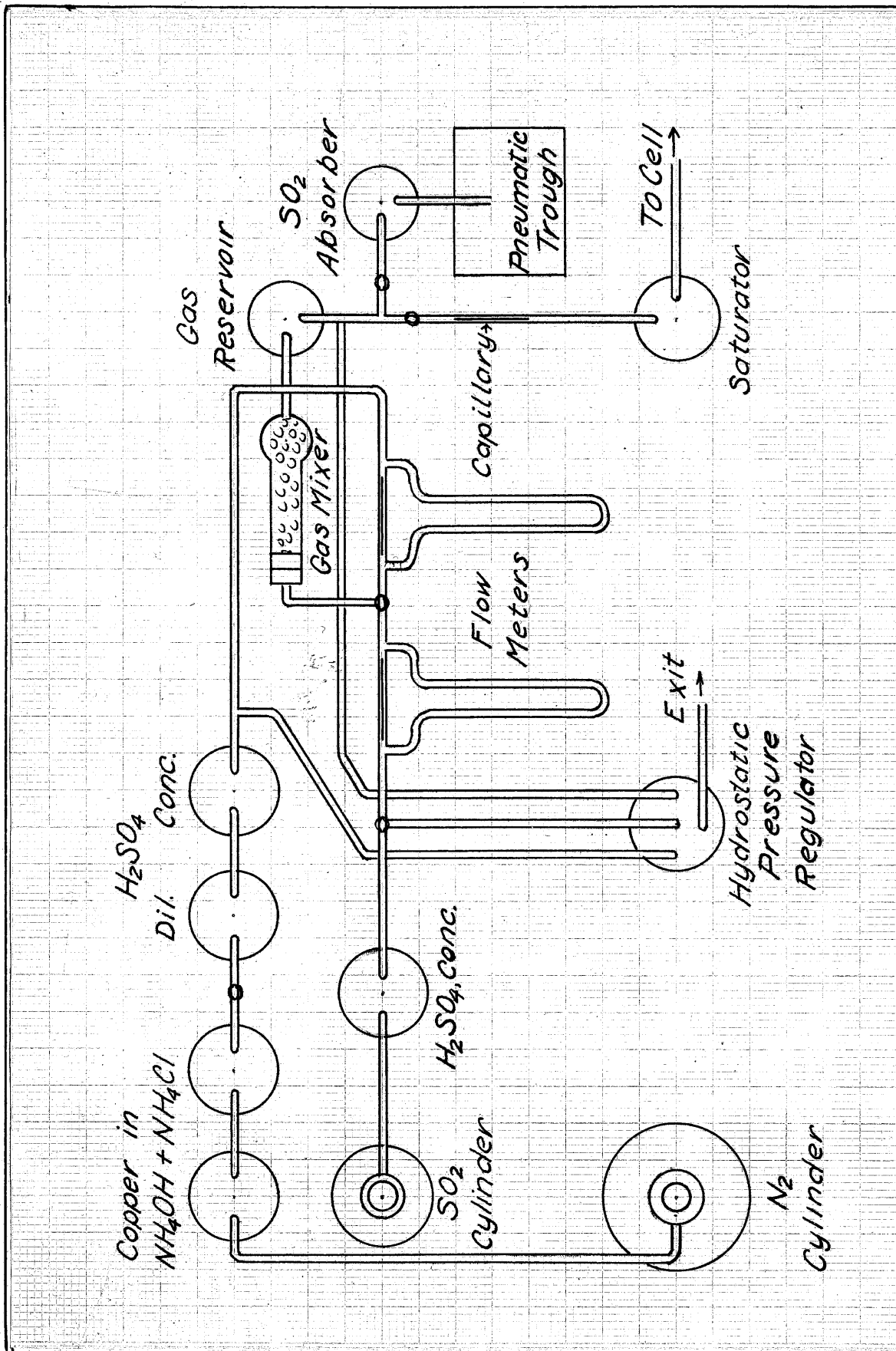


FIGURE II.

Diagram of Apparatus for Gas Control

The gas mixtures corresponding to the gauge 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 gauge-setting the mixtures were found to contain 7.23, 7.29, and 7.32% of  $\text{SO}_2$ ; for another setting, 23.8, 24.1, and 24.1% of  $\text{SO}_2$ .

#### 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  $25^\circ$  for some hours without bubbling or other agitation there is established a fairly constant and reproducible potential, namely, one which as a rule changes by less than two centivolts over 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 shows an immediate increase in its negative value - an increase which in the course of half an hour usually amounts to two to four centivolts. It then reverts to more positive 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 disturbance. If after standing several hours the bubbling is resumed, the same series 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 below.

The behavior above described is illustrated by Figure III in which graphs for selected 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.

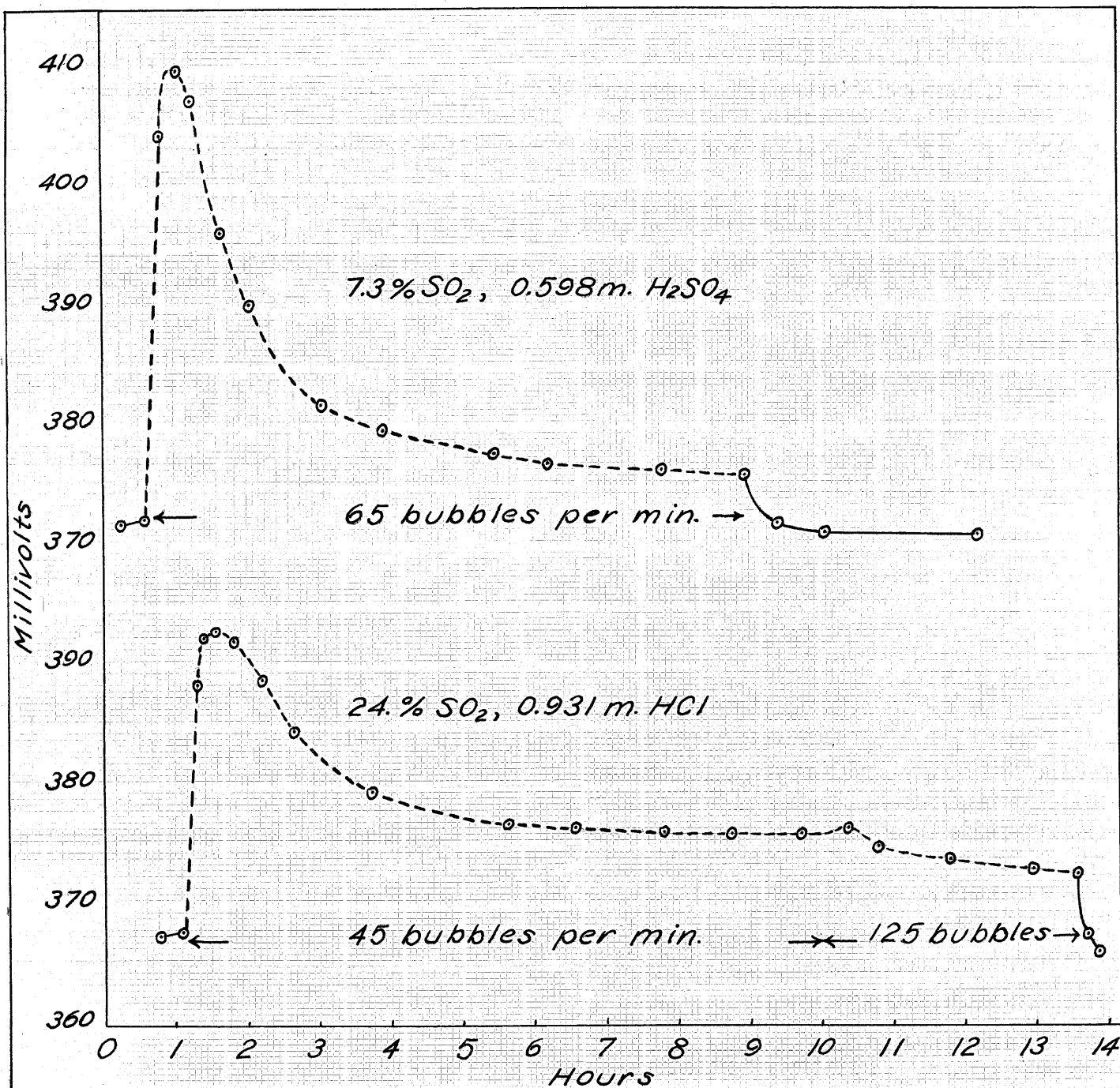


FIGURE III

Influence of Agitation of the Sulfite Solution  
upon the  
Electromotive Force of the Cell

It will be seen from Figure III 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 about  $-0.410$  and  $-0.393$  in the two 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 cases after 9 to 13 hours' bubbling the values  $-0.376$  and  $-0.373$ ).

(4) Reestablishment of the original quiet-state value when the agitation is stopped; and reproduction of a much higher negative value when the stirring is resumed.

We are not able to present evidence for any specific explanation of these agitation phenomena, which would 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 the stirring of 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; and 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 0.073 - 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 Experiment 1 platinized electrodes were used, but in the other experiments they were deplatinized. In experiments 1 and 2 the electrodes were charged with hydrogen by electrolysis in a sulfuric acid solution, and then immediately put into the cell. In experiments 3 and 4, they were allowed to stand over night in concentrated sulfurous acid solution and in dithionic acid solution, respectively.

TABLE I

Effect on the Potential of Various Initial Treatments of the Electrode

Expt. No.	Electrode		Electromotive Force in Millivolts after		
	Platinized	Initially treated	10-20 min.	1 day	Several days
1	Yes	with hydrogen	--	415	447
2	No	with hydrogen	--	513	477
3	No	with H <sub>2</sub> SO <sub>3</sub>	475	465	--
4	No	with H <sub>2</sub> S <sub>2</sub> O <sub>6</sub>	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 (Ref. 1, p. 1). Our experiments were all made with a half-cell containing platinized electrodes in a mixture of sulfurous acid at 0.068 N (corresponding to a sulfur-dioxide pressure of 1.014 atm.) and sulfuric acid at 0.068 N; the other half-cell with the hydrogen electrode containing 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.

TABLE II

## Electromotive Force of the Cell after Polarization

Exp. Number	Applied Potential		Electromotive Force at Various Times after the Polarization							
	Sulfite Electrode made	Volts	Minutes	1-2 min	5 min	10 min	20 min	1 hr.	2 hrs.	1 day
5	Cathode	0 <sup>a</sup>	5	304	340	400	435	439	434	--
6	Cathode	0 <sup>a</sup>	5	314	344	389	432	441	433	429
7	Anode	1.6	3	484	465	455	449	438	--	427
8	Cathode	65. <sup>b</sup>	3	250	--	--	444	456	460	460
9	Cathode	65. <sup>b</sup>	20	220	--	275	305	327 <sup>c</sup>	333	435 <sup>d</sup>
10	Anode	65. <sup>b</sup>	20	--	585	530	495	468	461	453

<sup>a</sup>In these cases the cell circuit was closed, but no external voltage was applied.

<sup>b</sup>The resulting current was 0.01 ampere.

<sup>c</sup>30 minutes after polarization, when the electromotive force was about 340 mm., the cell was shaken; and this stopped the rise of the electromotive force for a time.

<sup>d</sup>After 2 days.

## 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 ( $\text{H}_2\text{S}_2\text{O}_6$ ) 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 which the duplicate electrodes almost always checked to within one or two millivolts.

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 mixed solution in the other half. Hydrogen-ion activities were calculated with the aid of data published by Sherrill and Noyes.<sup>12</sup> In estimating the ionic strength the dithionic acid was considered to be completely dissociated. Conductivity data show it to be a very strong acid.<sup>13</sup> Equilibrium pressures of sulfur dioxide were calculated by Henry's law, correction being made for the dissociation of the sulfurous acid.



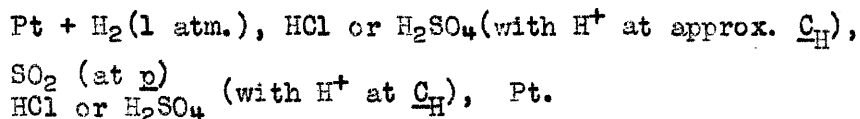
It will be seen that the potential is not much different whether the acid present with the sulfurous acid is sulfuric or dithionic acid, showing that the electrode process which determines the potential does not directly involve either of these acids.

To confirm completely the conclusion that the potential is not dependent upon these more oxidized sulfur compounds, 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 being read, however, only after a long period of quiet standing. In order that the comparison might be complete, a similar series was made in which the 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. Effect of the Concentration of Sulfurous Acid and of Hydrogen-Ion and of Temperature on the Potential of Sulfite Half-Cells

The series of comparative experiments with hydrochloric and sulfuric acids (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



The electromotive forces and separate potentials are all expressed in millivolts.

The recorded values 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 readings the gas mixture was bubbled for several hours through the cell, which was then allowed to stand quietly over night.\*

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\*For foot-notes see next page.

The hydrogen-ion activity of the hydrogen half-cell and the corresponding potential were calculated from the data given by Lewis and Randall<sup>14</sup> in the cases where hydrochloric acid was used, and from the data of Noyes and Stewart<sup>15</sup> 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.

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\*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 experiments 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.



TABLE IV

## Electromotive Force of Cells with Sulfurous, Sulfuric and Hydrochloric Acids

Ex. No.	Sulfite Half-Cell		Hydrogen Half-Cell		Electromotive Force of Whole Cell							Sulfite Half-Cell Potential			
	Temp.	Molality	% SO <sub>2</sub> in gas	H <sub>2</sub> SO <sub>4</sub>	HCl	1	3	4	5	6	7	14	Best Value		
1	25	0.598	0.0	1.5	0.598	0.599	468.1*	394.5*	389.2*	384.1*	381.1*	394.5	372	-359	
2	25	0.598	0.0	7.3	0.598	0.599	372.2*	371.7*	372.2*	372.3	377.5	378.9	370	-357	
3	25	0.598	0.0	24.	0.598		377.5*	371.3				382.6*	370	-357	
4	25	0.0	0.931	7.3	0.931	0.955	370.7*	369.1					370	-369	
5	25	0.0	0.931	24.	0.931	0.955	370.5*	369.1	370.6				370	-369	
6	25	0.0	0.931	100.	0.931	0.955	368.2*	370.5	270.7*	370.9	370.5	370.2*	370	-369	
7	25	0.0	0.205	7.3	0.205	0.170	369.4						370	-369	
8	50	0.0	0.931	7.3	0.931	0.955	367.5*	366.5*	366.4	366.8	366.4	366.4	366	-365	
							364.7*						365	-364	
							436.5*	425.6*		396.5*	389.8*	390.4*	388.0*		
							388.2*	385.5*		386.0*	385.5*	386.3*	386.4*		
							392.2*	387.8*		382.3	381.0		386	-340	
							360.4*	357.6*	357.4	355.1*	363.7*	374.7	372.5*	358	-357

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 that a change in the partial pressure of the sulfur dioxide has little, if any, effect upon the value of the potential. It is also evident that decrease in the hydrogen-ion activity produces a more positive value, and it is readily estimated that through the range studied, 0.955 to 0.170 molal, the magnitude of the potential change is about two-thirds that which would attend the participation of one  $H^+$  per faraday in the electrode reaction.

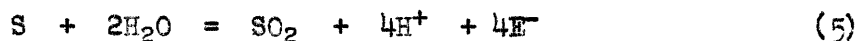
The effect of increase in temperature is shown by experiments 4 and 8 made at 25° and 50°. Thus taking the first four readings of experiment 8 as most representative, the potential is only about 12 millivolts lower at 50° than at 25°. It is evident that the same electrode process is involved at both temperatures, and that all the reactants concerned are not greatly changed in relative activity.

Finally, it is important to note the absolute value of the potential of the sulfite half-cell. It will be seen that its mean value at 25° at a hydrogen-ion activity of 0.30-0.96 N is -0.367 volt, or -0.37 volt within the error of the measurements.

## VIII. Half-Cells with Sulfurous Acid and Sulfur

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

A natural reduction-product to suspect is sulfur, a possibility which was suggested in Section II. Its low solubility would require the formation of only a small amount to provide a constant activity. And it might establish the electrode-potential corresponding to the equation.



This requires the participation of only one mol of sulfur dioxide per four faradays of electricity, which means only a small change in electromotive force with change in the pressure of the sulfur dioxide. Increase in hydrogen-ion activity should produce a more negative potential, the magnitude of the change corresponding to the participation of one mol of hydrogen-ion per faraday. Although these requirements are not conformed to exactly by the experimental sulfite potential, yet the results of Table IV show a rough agreement with them. But as stated in Section II the absolute value of the molal electrode potential is hardly reconcilable with this electrode process; for the observed value

is only -370 millivolts, while that calculated from free-energy data is -471 millivolts. Thus there is a difference of 100 millivolts, which is about ten times as great as the variation in constancy and reproducibility shown by the data of Table IV for conditions of strong acidity and moderate pressures of sulfur dioxide. Furthermore, the deviation is in the direction which would indicate supersaturation with respect to sulfur to an unbelievably large extent; thus the activity of the sulfur, even assuming that it exists only at the immediate surface of the electrode, would have to be more than  $10^6$  times its activity at saturation.

Nevertheless, it seemed worth while to try to test more accurately than was done by Carter and James the possibility that sulfur is the active substance by depositing it in finely divided form on the electrode. If there were supersaturation with respect to it this should then be quickly eliminated; and the presence of solid sulfur should give a more constant and reproducible potential of the calculated magnitude if this substance is really electromotively active.

Such 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 give an electromotive force of approximately 430 millivolts if sulfur and sulfur dioxide are the electromotively active substances. 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 over night the electromotive force returned approximately to that (358 mv.) shown before the sulfur treatment, the two electrodes checking within two millivolts; but during the next five days it gradually became more negative, after which it showed no constant trend, though subject to daily fluctuations of 5-6 mv., but showed on the average a value of 412 mv. at the sulfur-treated electrode, and 425 mv. at the other electrode.

The electrodes were again removed, cleaned, and replatinized. One of them was coated with a thick syrupy solution of sodium polysulfide, and sulfur was precipitated from it by fuming with concentrated hydrochloric acid over night. The electrodes were then subjected to very thorough washing and leaching with warm water and were returned to the cell; and the gas was bubbled through to replace any air. After standing quietly over night 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 stayed constant within 3 mv. for four days more at 444 mv. and 440 m., 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 (5) 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 data 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 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; and even the values obtained at the sulfur-treated electrode differ from those at the untreated electrode by only about a centivolt in many cases, and show no tendency to deviate more than this.

These facts indicate that at 25° sulfur has little electromotive activity; and that, even if it were formed on the electrode through decomposition of the sulfurous acid, it would not determine the potential of the half-cell, at any rate so long as a more active reduction-product, such as hydrosulfurous acid, were present. The fact that at 50° in the presence of sulfur the theoretical sulfur potential is approximated may be due to its greater electromotive activity at this higher temperature.

TABLE V

Electromotive Force at 25° of Cells with Solid Sulfur Present

HCl in each half-cell 0.829 M.; H<sup>+</sup> activity, 0.804 M.;  
calculated potential of hydrogen half-cell, +6 mv.

Sulfite Half-Cell Electrode sulfur treated	Sulfite Electrode % SO <sub>2</sub> in dry gas	Electromotive Force of Cell after Successive days as follows									Best Value	Potential sulfite Half-cell
		1	2	4	5	6	8	9	11	11		
No	7.3	380.0*	374.0*	372.9*	375.6	375.5	375.5*	375.2	376.9	375	-369	
Yes	7.3	396.0*	387.5*	375.2*	390.6	387.9	389.0*	376.0	377.9	385	-379	
No	24.0	373.4*	373.3	--	--	--	--	--	--	373	-367	
Yes	24.0	380.6*	379.4	--	--	--	--	--	--	380	-374	

\* After this reading the gas mixture was bubbled for several hours through the cell,  
which then stood quietly over night.

## IX. Sulfite Half-Cells with Thiosulfate and Hydrosulfite Added

The effects upon the potential of adding to the sulfite half-cell sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$  and hydrosulfite  $\text{Na}_2\text{S}_2\text{O}_4$  were also investigated.

To the sulfite half-cell used in Experiment 3 of Table V., subsequent to taking the last reading of 373 mv., there was added a strong solution of sodium thiosulfate in such amount that, had it not decomposed, it would have made the solution 0.05 molal in this salt. In order to stir up the solution and remove oxygen which might have entered during the addition of the thiosulfate, the gas mixture was bubbled for several hours. After standing quietly over night the non-bubbling value was 334 mv. at the electrode not coated with sulfur. Gas was then bubbled through the day; and the following morning the value was 341 mv. at the non-coated electrode and about 320 mv. at the sulfur-coated electrode.\*

Sodium hydrosulfite was added to a cell containing 0.591 molal  $\text{H}_2\text{SO}_4$ , through which a gas mixture with 1.5% of  $\text{SO}_2$  was passed; a cell like that used in experiment 1 of Table IV, which had been slow in reaching equilibrium. The gas mixture was bubbled through the cell for five hours on one day and an hour and a half on the succeeding day, after which the electromotive force was 446 mv. and was decreasing at

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\* In the previous experiments, the effect of bubbling was to increase the electromotive force; but when thiosulfate was added bubbling always decreased it by about 1 centivolt; the value holding almost constant throughout the period of bubbling; but upon discontinuing the bubbling, the electromotive force returned quickly to its former value.



a rate of about 4 mv. per hour. Then 5 mg. of  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  powder were added. The electromotive force dropped quickly to 363 mv., but rose in the course of two hours to 386 mv., and then slowly declined. After standing over night without bubbling the value was 372 mv. During the following period the gas was bubbled during the day but not during the night; on successive mornings the electromotive force was 367, 368, and 368 mv. There then were added 45 mg. more of the sodium hydrosulfite, and the gas was bubbled. The electromotive force dropped from 372 to 272 mv. but the value rose to 327 mv. in two hours, after which time the gas was turned off. On succeeding days the value was 342, 344, and 344 mv. Then, with the gas bubbling, a further addition of 44 mg. of the salt was made. The value dropped from 329 to 245 mv. then rose to 323 mv. in three hours, at which time the gas was turned off. The next morning the value was 336 mv. The two electrodes in the sulfite half-cell checked well until the 45 mg. of salt were added, after which a difference of about 10 mv. developed. The values just given are the lower ones.\*

It will be seen that the addition of thiosulfate and of hydrosulfite give rise after standing to nearly the same electromotive force of about 340 mv., which corresponds to a potential of -327 mv. for the sulfite half-cell. This potential is about 30 mv. more reducing than that shown when there is no addition. The fact that the two salts have

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\*The effect of the bubbling after the first addition of 5 mg. was to increase the electromotive force as in the experiments in which no salt was added, but not so greatly (only about 10 mv.); while after the addition of the 45 mg. the effect was to decrease the electromotive force.

nearly the same effect indicates that there is a fairly rapid conversion of them into one another, presumably in accordance with equation (3) of Section II. The more reducing potential indicates that in the steady state a larger concentration of hydrosulfite persists when it has been once produced by the addition of either substance.

#### X. Half-Cells with Sulfurous Acid in the Presence of Oxygen

Up to this point there has not been mentioned an extensive piece of work carried out by Arthur Edgar, and reported by Lewis, Randall and Bichowsky,<sup>16</sup> in which sulfur dioxide diluted with air was bubbled through sulfuric acid solution in the half-cell. An iridized platinum electrode was employed and the electromotive force was measured against a mercury-mercurous-sulfate electrode. Reproducibility to within about a millivolt was obtained. The anticipated cell reaction was

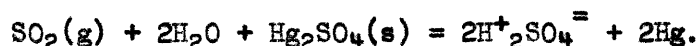
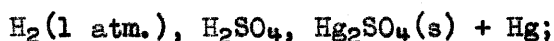
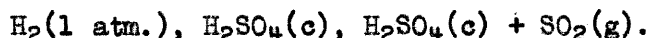


Table VI shows the results obtained with the more dilute solutions of sulfuric acid. The electromotive forces directly observed by Edgar were calculated over to the molal hydrogen electrode with the aid of the values of Randall and Cushman<sup>17</sup> for the cell



so that they represent the electromotive forces of the cell



By subtracting from these the calculated values (shown in the table) for the potential of the hydrogen half-cell, the potentials of the sulfite half-cell were obtained.

TABLE VI

Electromotive Force of Cell  $H_2(1 \text{ atm}), H_2SO_4(c), H_2SO_4(c) + SO_2(g) + SO_2(g)$  at  $25^\circ$ 

Calculated from Edger's Data

Expt. No.	Sulfite Half-Cell		Hydrogen Half-Cell		E.M.F. of Cell	Potential of Sulfite Half-Cell	
	Molality $H_2SO_4$	Pressure $SO_2$ atm.	Molality $H_2SO_4$	Activity $H^+$		Observed	calc. for $SO_2$ 1 atm
1	0.5009	.00689	0.5009	0.497	458	-440	-376
2	0.5009	.01328	0.5009	0.497	445	-427	-373
3	0.5009	.02479	0.5009	0.497	437	-419	-372
4	0.5009	.05080	0.5009	0.497	430	-412	-372
5	0.5009	0.1091	0.5009	0.497	422	-404	-376
6	0.5125	0.969	0.5125	0.508	371	-354	-354
7	0.0531	.00689	0.0531	0.045	458	-378	-315
8	0.0531	.01328	0.0531	0.045	452	-372	-317

It will be seen from the last column of the table that the potential varies with the pressure of sulfur dioxide between the limits of 0.007 and 0.109 atmospheres as required by the above-given reaction. A comparison of the electromotive forces of the cells in experiments 1 and 7 or in experiments 2 and 8 shows that this electromotive force does not vary with the concentration of the sulfuric acid. This would signify that the potential of the sulfite half-cell is independent of the sulfate-ion concentration provided it be assumed that the potentials of the two half-cells vary in the same degree with the hydrogen-ion concentration.

Our results presented previously are in accord with this last conclusion but not with the effects observed by Edgar of varying the pressure of the sulfur dioxide. To determine whether the presence of oxygen accounted for Edgar's results, 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.\*

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\* The method of reporting electromotive force values is the same as that adopted in Table IV. Immediately following experiment 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 the non-bubbling value obtained the following morning (455 mv.). The sulfur dioxide pressure was then changed to 7.3 percent for experiment 2. Experiments 3, 4, and 5 form a new series in which fresh solution was taken.

The air used in these experiments was drawn from the laboratory compressed air line 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 cell its solution was analyzed by first titrating with thiosulfate for sulfite content and then with sodium hydroxide for total acidity. Analyses were made in triplicate and checked reasonably well. The specific gravity of the solution was determined and the increase in the molality of the sulfuric acid was calculated to be about 0.004 mols. This cell was in operation for twenty days and the fact that the increase in sulfate content was so small is no doubt attributable to the high acidity.

TABLE VII

## Electromotive Force at 25° of Cells with a Gas Phase of Sulfur Dioxide and Air

Ex. No.	Sulfite Half-Cell Molality SO <sub>2</sub> , % H <sub>2</sub> SO <sub>4</sub> dry gas	Hydrogen Half-Cell Activity Potent. H <sup>+</sup>	Electromotive Force of Cell in Millivolts					Sulfite Half-Cell Best Value	Poten.		
			1	2	3	4	5			6	7
1	0.590 1.5	0.0594	13	512*	506*	491*	431*	485*	491	489	-476
2	0.590 7.3	0.0594	13	443	438*	437*	431*	437*	437	437	-424
3	0.590 7.3	0.0594	13	498*	486*	490*	487*	477*	481*	483	-470
4	0.590 24.0	0.0594	13	459*	453	425*	440*	433*	422	430	-417
5	0.590 24.0**	0.0594	13	466*	465*	460*	470	470	465	465	-452

\*After this reading the gas mixture was bubbled for several hours through the cell, which then stood quietly over night.

\*\*In this experiment the SO<sub>2</sub> was diluted with oxygen.

Steady and reproducible potential values were not obtained, there was no such regularity in the results as in those obtained by Edgar, and increase in the partial pressure of the oxygen influenced the values. For a proportionate change in sulfur dioxide pressure the change in electromotive force was much greater in these experiments than in those of Edgar. It appears that Edgar's results, while undoubtedly due in part to the presence of oxygen, are highly dependent upon the technique employed. The two series of investigations have this in common, that the presence of oxygen makes the electrode potential more negative. This indicates that if the potential is set up between sulfur dioxide and a reduction product the oxygen diminishes the concentration of the latter, which is quite reasonable to expect.

#### XI. Summary of Experimental Results

The preceding section concludes the account of the experimental work done in this Laboratory. Before proceeding to the further discussion of the electrode process it has seemed desirable to summarize the results of these experiments as follows:

1. In the absence of oxygen, in a solution having a hydrogen ion activity of one molal, and under a partial pressure of sulfur dioxide of about ten percent of an atmosphere, a platinized platinum electrode attains a potential of  $-370 \pm 5$  millivolts. Stirring the solution influences the potential in the manner exhibited in Figure III, showing that there are concentration effects at the electrode.

2. Preliminary treatment of the platinum electrode with hydrogen, concentrated sulfurous acid, dithionic acid, or with the anodic or cathodic products of electrolysis of the solution does not permanently affect the potential, showing that its value is not dependent upon initial surface conditions.

3. The potential is not much different whether the acid present with the sulfurous acid is sulfuric, dithionic, or hydrochloric, showing that the electrode process which determines the potential does not directly involve any of these acids.

4. Change in the partial pressure of sulfur dioxide and the corresponding change in concentration of the sulfurous acid has little if any effect on the electromotive force.

5. The potential is dependent upon the hydrogen-ion activity, becoming more reducing as the acidity is decreased. Over the moderate range studied, 0.955 to 0.170 molal, the magnitude of the potential change is about two thirds that which would attend the participation of one  $H^+$  per faraday in the electrode reaction. The potential is steadier at the higher acidities.

6. Between 25° and 50°C the temperature coefficient of the electrode reaction is a little less than +0.5 mv. per degree, which is a good indication that over this temperature range the character of the electrode process does not change.

7. At 25°C the presence of sulfur is without effect upon the potential whereas a reversible sulfur - sulfur dioxide electrode should register a value about one tenth volt less reducing. At 50°C

the addition of sulfur does slowly produce a less reducing potential in the neighborhood of that which would be established at a reversible sulfur - sulfur dioxide electrode. The manner of its establishment, however, argues against the potential which is established before sulfur is added being determined by the tendency of the sulfur dioxide to reduce directly to sulfur.

8. Addition of sodium thiosulfate makes the potential a few centivolts more reducing.

9. Addition of sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , produces a more reducing potential. The limit of the change which can be effected by the addition of successive moderate amounts to the acid solution is about four centivolts.

10. In the presence of oxygen gas, a less reducing and, under the conditions of the writer's experiments, a less definite and less reproducible potential results.



## XII. 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 those who have been associated with them.<sup>18</sup>

These investigators, as a result of the researches, have shown in a plot of reduction-potential against acidity of solution, the region in which sulfur dioxide neither oxidizes nor reduces. It appears as a narrow strip, showing that the limits of the oxidizing and reducing reactions of sulfur dioxide are practically the same.\* This strip is compared with a curve showing the experimental sulfur dioxide electrode also in relation to the acidity of the solution. The two are closely similar in contour and agree well in their position on the plot for solutions under two normal in hydrochloric acid. Divergence which develops above this acidity amounts to but seven centivolts in seven normal hydrochloric acid.

From a theoretical standpoint the interpretation of the chemical behavior of the substance is now clearly indicated assuming hydrosulfite to be the electromotively active intermediate reduction product as has been done by these investigators.

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\* The curve which marks the limiting values for sulfur dioxide as an oxidizing agent is well defined. There is but one point shown on the other limiting curve. However there is evidence of not so quantitative a nature which indicates that the two curves do lie close together for at least a part of their length.

Namely, sulfurous acid spontaneously decomposes into sulfuric acid and a reduction-product, probably hydrosulfurous acid  $\text{H}_2\text{S}_2\text{O}_4$ . This product, because of its great tendency in strongly acid solutions to decompose, probably into thiosulfuric acid  $\text{H}_2\text{S}_2\text{O}_3$  and sulfurous acid, never attains in such acid solutions more than a very small concentration - one probably of the order of  $10^{-18}$  molal. This suffices, however, to establish in association with sulfurous acid at moderate concentrations, a fairly definite reduction-potential of the order of  $-0.37$  volt referred to the hydrogen standard; and accordingly, sulfurous acid possesses an oxidizing power corresponding to this potential. It therefore tends to act oxidizing on any combination (like liquid  $\text{Hg} + 1 \text{ m. Cl}^-$ , solid  $\text{Hg}_2\text{Cl}_2$  for which the potential at  $25^\circ$  is  $-0.27$ ) which has a more reducing potential than  $-0.37$ , but not on any combination (like  $1 \text{ m. I}^-$ , Solid  $\text{I}_2$  with a potential of  $-0.54$ ) which has a potential less reducing than  $-0.37$  volt.

On the other hand, the known free energy values show that sulfurous acid has with reference to its conversion into sulfuric acid (when both are at moderate concentrations) a reduction-potential of  $-0.16$  volt. It should therefore tend to act reducing at  $25^\circ$  on any combination which (like the two above cited) has a more oxidizing potential than  $-0.16$ , but not on any combination (like solid  $\text{Cu} + 1 \text{ m. Cl}^-$ , solid  $\text{CuCl}$ , with a potential of  $-0.12$ ) which has a more reducing potential than  $-0.16$ .

It will be seen that there is an intermediate region, between  $-0.15$  and  $-0.37$  volt, where any combination (like liquid  $\text{Hg} + 1 \text{ m. Cl}^-$ , solid  $\text{Hg}_2\text{Cl}_2$ ) having a reduction-potential between these limits would

tend to be both reduced and oxidized by sulfurous acid. Which one of these two effects actually take place will then depend on the comparative rates of the two reactions; since in fact combinations with potentials within the stated limits seem usually to be oxidized rather than reduced, it seems to be true that sulfurous acid is commonly reduced more rapidly than it is oxidized.

### XIII. Evidence in Support of Hydrosulfite as the Active Product

Further justification may now be made for the assumption of hydrosulfurous acid as the active reduction product. It has been shown how a small, constant concentration of this acid may be accounted for by the spontaneous decomposition of the sulfurous acid solution. There are, however, other intermediate reduction products which are formed. Such are thiosulfate\* and the thionic acids. However, it has been seen (Section II) that several investigators favor hydrosulfite as the initial reduction product.\*\* It, then, is reasonable to assume that it also is the primary reduction product at the electrode, and, therefore, that one which could establish the potential.

There is, however, more direct evidence that hydrosulfite may well be the agent involved. K. Jellinek and E. Jellinek<sup>21</sup> have shown that hydrosulfite is the product of the cathode reduction of bisulfite solutions and there is no evidence of an intermediate stage, or of other initial products. Moreover, K. Jellinek<sup>22</sup> has shown that

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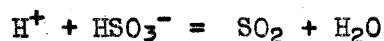
\* and \*\* for footnotes see next page, 41a.

\* K. Jellinek concluded from his work that thiosulfate is not electroactively active with sulfite.<sup>19</sup>

\*\* Foerster and his associates<sup>20</sup> have assumed that hyposulfurous acid,  $\text{H}_2\text{SO}_2$ , is the initial reduction product, but Bassett and Durrant<sup>8</sup> believe the assumption of hydrosulfurous acid to be in agreement with the former's data. Neither free hyposulfurous acid,  $\text{H}_2\text{SO}_2$ , nor its salts are known, the radical having been obtained only as the aldehyde derivatives.

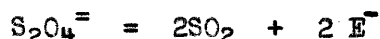
hydrosulfite does set up a reversible potential against sulfite in slightly acid solution (in which there is only slow decomposition of hydrosulfite) and it is the only substance for which a reversible potential against sulfurous acid has ever been established experimentally. Carter and James found that the cathodic decomposition potentials of strongly acid sulfite solutions (comparable to those reported in this paper) were in accord with the assumption that hydrosulfite was produced.

The data of Karl Jellinek enable the calculation of the concentration of hydrosulfite which would correspond to the potentials obtained in the writer's experiments. Thus, in a solution under a pressure of 0.24 atmosphere of sulfur dioxide, which gives a potential of -365 mv. as in experiment 5 of Table IV, if the potential is due to a sulfite - hydrosulfite system the concentration of hydrosulfite is about  $6 \times 10^{-18}$  molal or about  $4 \times 10^3$  molecules per cubic centimeter. This concentration is quite in accord with the very slow decomposition of the sulfite and the known absence of appreciable amounts of decomposition products. Moreover, if constant in amount it is probably capable of establishing a reasonably steady potential as it is known that other substances at extremely low concentrations give reliable reversible potentials. It is also in agreement with the thermodynamic requirements of Section II. For the free energy of  $\text{HSO}_3^-$  corresponding to 0.24 atm. of  $\text{SO}_2$  may readily be calculated from the reaction

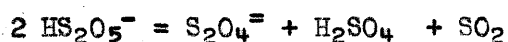


by means of the Lewis and Randall free energies; that for  $\text{SO}_2$  (1 atm.) being -69,660 cal. This value is -126,220 cal. corresponding to an activity for  $\text{HSO}_3^-$  of .02 m. At this activity when the other ions are 1 m. reaction (1) tends to take place in the direction written if  $\text{S}_2\text{O}_4^{2-}$  is less than  $3 \times 10^{-9}$ ; reaction (2) if  $\text{S}_2\text{O}_4^{2-}$  is greater than  $3 \times 10^{-20}$ ; and reaction (3) if  $\text{S}_2\text{O}_4^{2-}$  is greater than  $2 \times 10^{-18}$ . If the activity of  $\text{S}_2\text{O}_3^{2-}$  is that which exists in equilibrium with sulfur and  $\text{HSO}_3^-$  then, as for reaction (2), reaction (3) tends to take place if  $\text{S}_2\text{O}_4^{2-}$  is greater than  $3 \times 10^{-20}$ .

It was found that change in sulfur dioxide pressure produced very little effect upon the potential, but that it became more negative with increase in hydrogen-ion activity, the magnitude of the change corresponding to about two-thirds of that which would attend the participation of one  $\text{H}^+$  per faraday. It may not at once be evident how the sulfite - hydrosulfite electrode reaction which may be written as



would lead to such results. However, it is possible to conceive of a number of different mechanisms by which they could be achieved. One of these is presented here, not that the writer feels that it is the correct one or that the experimental evidence is sufficient to say with any certainty what the true mechanism is, but simply to show that such evidence is not contradictory to the assumptions made. Consider such a decomposition as



a bimolecular reaction between ions of pyrosulfurous acid which are be-

lieved to be present in sulfite solutions<sup>23</sup> (this radical being chosen to make the reaction bimolecular), which reaction results in the formation of sulfate, hydrosulfite, and more sulfur dioxide, and is not in disagreement with experimental findings. Then if the rate of this decomposition is independent of the concentrations of its products, and if in turn the same is true of the decomposition of hydrosulfite (the Jellineks have shown that at higher concentration in less acid solution this obtains<sup>9</sup>) when a steady state is reached

$$\frac{d(S_2O_4^{2-})}{dt} = k_1 (HS_2O_5^-)^2 = -\frac{d(S_2O_4^{2-})}{dt} = k_2 (S_2O_4^{2-})^2$$

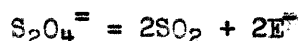
for the decomposition of hydrosulfite is bimolecular.<sup>21</sup> But

$$(HS_2O_5^-) = K \frac{[SO_2]^2 (H_2O)}{(H^+)}$$

hence

$$k_2 (S_2O_4^{2-})^2 = k_1 K^2 \frac{[SO_2]^4 (H_2O)^2}{(H^+)^2}$$

The electrode reaction as written above



gives as the electromotive force equation

$$E = E_0 - \frac{RT}{2F} \ln \frac{[SO_2]^2}{(S_2O_4^{2-})}$$

which, upon substituting for  $(S_2O_4^{2-})$  the value just obtained, becomes

$$E = E_0 - \frac{RT}{2F} \ln \frac{(H^+)}{(H_2O)}$$

which is in reasonable agreement with experiment.

The theory of the maintenance of an exceedingly small steady concentration of hydrosulfite in the cell solution necessarily assumes that it has a very high specific decomposition rate under the given conditions. The fact that the addition of successive amounts of hydrosul-

fite did not permanently change the potential by more than four centivolts whereas the sulfite - hydrosulfite potential, when both reactants are present in appreciable amounts, is much more reducing (having a molal value of +0.009 volt) furnishes strong support to the theory.

#### XIV. Conclusion

In view of the preceding considerations it is the opinion of the writer that the hypothesis formulated in Section II is substantially correct and that the potential established at an inert electrode in sulfurous acid solution is due to the tendency of sulfurous acid to reduce to hydrosulfurous acid (as was previously concluded by Carter and James), that there is a minute concentration of the latter present in the solution due to the slow spontaneous decomposition of the sulfurous acid, and that this concentration remains reasonably constant because the hydrosulfurous acid also decomposes and a steady state is established in which its rate of formation is equal to its rate of decomposition.



## XV. Summary

There is presented an experimental study of the potential of platinum electrodes in sulfurous acid solutions, under varied conditions, the results of which are summarized in Section XI.

These results are discussed from the standpoint of determining what electrode reaction is operative.

It is concluded, in agreement with Carter and James that the potential is probably due to the tendency of sulfurous acid to reduce to hydrosulfurous acid,  $\text{H}_2\text{S}_2\text{O}_4$ .

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