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FREE ENERGY OF THE THIOSULFATE ION

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In order to determine the free energy of formation of the thiosulfate ion from its elements, three reactions are suggested as suitable for study.

The first, $S_5^{--} + H_2O = S_2O_3^{--} + 3H_2S$, is known to go, at moderate temperatures, largely in the direction written, and though the reverse reaction has not been described, preliminary experiments show that it takes place to a measurable extent even at 100°. If equilibrium can be reached and can be measured, this reaction gives a new and important means of obtaining not only the free energy of formation of thiosulfate ion but also of sulfur dioxide.[2]

The second reaction, which appears suitable, is the familiar reaction, $S_2O_3^{--} + H^+ = S + HSO_3^-$. This reaction is known to be reversible, the reverse reaction being one of the usual methods of preparing thiosulfates. However, at acid concentration where the equilibrium is measurable the reaction is very slow at room temperatures, while at higher temperatures difficulties of analysis and the uncertainties of the degree of ionization of the substances involved render this method unsuitable.

The third reaction, $S_2O_3^{--} = S + SO_3^{--}$, is really the same as the second, except that instead of using hydrogen ion to keep the concentration of the sulfite ion low, other means are used to control the concentration of the sulfur or sulfite ion. Biltz[3] found that copper reacts with the fused

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[1] National Research Fellow. This research was begun at the Geophysical Laboratory, Washington, D. C., and completed while the writer was National Research Fellow at the University of California.

[2] By means of the chain of reactions: $4S + HS^- = S_5^{--} + H^+$; $H_2S = HS^- + H^+$; $H_2S = S_r + H_2$; $S_5^{--} + 3H_2O = S_2O_3^{--} + 3H_2S$; $SO_2 + H_2O = SO_3^{--} + 2H^+$; $S_2O_3^{--} = S + SO_3^{--}$, the last of these being the reaction actually measured in this investigation.

[3] Biltz, "Laboratory Methods in Inorganic Chemistry," Wiley and Sons, **1909**, p. 131.

hydrate of sodium thiosulfate to give cuprous sulfide and sodium sulfite. This reaction is apparently irreversible. It suggests, however, that at high temperatures sodium thiosulfate dissociates into sulfite and sulfur. If this is so, the vapor pressure of sulfur in the equilibrium mixture must be very low, as prolonged heating of either the anhydrous or hydrated sodium thiosulfate in a high vacuum failed to show any distillation of sulfur into the cold parts of the tube, and the reaction mixture, when cooled, failed to give any test for sulfite. At very high temperatures (red heat and above) the reaction, $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$, takes place in preference. It is possible that some metal besides copper might be used, but if the reaction is to be studied in solution, the number of such metals is rather limited.

Moreover, the other alternative, namely, lowering the sulfite concentration by using the thiosulfate of some element whose sulfite is very slightly soluble, would be more satisfactory theoretically, as it would avoid the difficulty of analyzing mixtures of thiosulfates and sulfites, as well as the difficulties of the thermodynamic treatment of such solutions. A number of elements form soluble thiosulfates and insoluble sulfites. The thiosulfates of calcium and barium were chosen for experimental investigation because these elements are divalent, thus eliminating the formation of intermediate ions, they do not readily form thiosulfate complexes, they are not easily hydrolyzed, they exist in only one oxidation stage, and their sulfides are soluble.

Preliminary experiments showed that up to 200° saturated solutions of barium thiosulfate dihydrate which is only slightly soluble, do not dissociate. 2.0 Molar solutions of calcium thiosulfate were partly decomposed into sulfur and calcium sulfite dihydrate,[4] when heated for 4 days at 150°, leaving the solution about 0.4 *M*. Some hydrogen sulfide and sulfate were formed but no gypsum or anhydrite could be detected in the solid material. The reverse reaction was then tried, that is, calcium thiosulfate dehydrate and sulfur were heated with water for 4 days at 140°. The unaltered sulfur and sulfite were removed and the solution was analyzed; 100 cc. contained 0.01958 mole of calcium ion, 0.01945 mole of thiosulfate ion, 0.0001 mole of sulfide ion, approximately 0.0001 mole of hydrogen ion, and approximately 0.0001 mole of sulfate ion; no sulfite and no polythionate could be detected. It is therefore evident that equilibrium is established at 140° between the separate phases, liquid sulfur, solid calcium thiosulfate dihydrate, and a solution containing only calcium ion and thiosulfate ion at some concentration between 0.4 and 0.19 molar. More careful determinations were, therefore, undertaken.

Preparation of Calcium Thiosulfate Hexahydrate.—Calcium thiosulfate

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[4] Determined microscopically by Mr. Merwin of the Geophysical Laboratory, Washington, D. C.

is an extremely soluble salt, a saturated solution at 25° containing 2.28 moles of $CaS_2O_3.6H_2O$ per 1000 g. of solution (new determination). It can readily be prepared in solution by adding a concd. solution of calcium chloride to a cold concd. solution of sodium thiosulfate, when sodium chloride separates. The crystals of calcium thiosulfate can then be fractionally crystallized by adding alcohol, redissolving the precipitate in water and reprecipitating with alcohol. This method works well with small quantities if a trace of alcohol is no objection. For large quantities, the best method is to dissolve 510 g. of crystallized sodium thiosulfate in 465 g. of water, then add, with constant stirring, 350 g. of finely crystallized calcium chloride dihydrate. The temperature of the solution should not rise above 60° during this process. The solution is allowed to stand overnight, the clear solution is decanted through a large filter, and cooled to 0° or —10° and allowed to crystallize. Prepared in this way, the crystals contain only a small amount of sodium chloride as an impurity, from which they can be freed by recrystallization. The solid salt dehydrates rapidly at room temperature, also decomposing into sulfur and sulfite at the same time. In contact with its saturated solution it is stable for several weeks at 25°. At 0° it is apparently indefinitely stable. The 2 *M* solution is stable up to about 35° and is the most convenient form in which to keep the salt. The solutions used in this investigation were free from excess of calcium and contained less than 0.1% of sodium chloride.

Calcium Sulfite.—The dihydrate was prepared (1) by precipitation of fresh sodium bisulfite with calcium chloride, (2) by recrystallization of commercial calcium sulfite from a solution of sulfurous acid, (3) by partial oxidation of calcium thiosulfate with hydrogen peroxide in alkaline solution (a new reaction), (4) by thermal decomposition of solutions of calcium thiosulfate. These samples varied strikingly in crystalline habit, but had nearly the same refractive index, and no difference in behavior was noted among them. The material used in the final experiments was all prepared by Method 1. Above temperatures somewhere near 160° the dihydrate is unstable in contact with water, presumably forming the semihydrate, $CaSO_3.{}^1/_2H_2O$, analogous to $CaSO_4.{}^1/_2H_2O$.

The sulfur used was the common purified substance.

Equilibrium Measurements.—Two sets of sealed Pyrex tubes were made up, each of the first containing about 15 cc. of *M* calcium thiosulfate solution to which a little powdered sulfur and calcium sulfite dihydrate were added; each of the second, 15 cc. of water and an excess of sulfur and calcium sulfite dihydrate. These were heated side by side in an air thermostat, constant to 0.5° of the temperature desired. From time to time one from each set was withdrawn, cooled, filtered through a dry filter into a weighed flask containing a few drops of a solution of cadmium acetate to precipitate any hydrogen sulfide present. The flask was then weighed again, and its contents filtered through a dry filter to remove cadmium sulfide. The precipitate was washed until the washings did not affect the titer and the filtrate was titrated with 0.1 *N* iodine solution; weighed burets were used. If equilibrium were reached the concentration of both tubes should be the same. In the case where special care was taken, as in the experiment at 141°, the values from above and below did not differ by 0.1%, and there is apparently no reason why this accuracy should not be reached, if needed, at any temperature. At 174° equilibrium was not reached, the titer of the tubes starting with the thiosulfate side remaining constant at 0.118 *M* per 1000 g. of solution, and those from the water side slowly changing at a concentration of about 0.158 *M* per 1000 g. solutions, even after 2 weeks' heating. Microscopic examination showed that in the first case the solid phase was not calcium sulfite dihydrate, but presumably the semihydrate. In the tubes containing water the solid material was largely the dihydrate with some semihydrate present. An accident prevented the completion of the run at 120° and the results are not accurate. The results of a typical run are presented in Fig. 1.

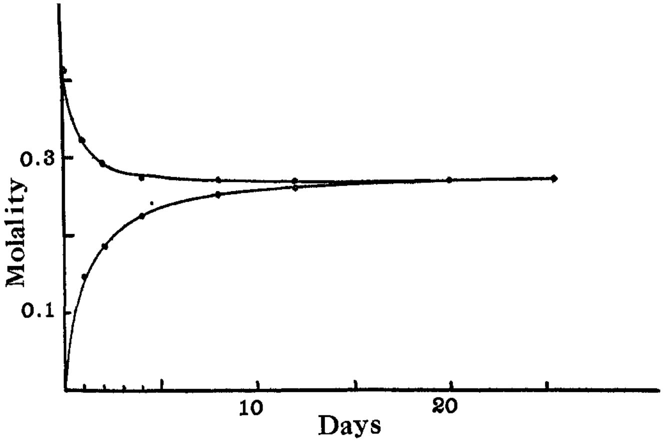

Fig. 1

At temperatures below 110° the reaction was too slow to allow this method to be used. So, instead of starting with pure water or a concentrated solution of thiosulfate, solutions of known strength, say 1.2, 1.00, 0.80, 0.60 *M* were prepared and heated in the presence of calcium sulfite dihydrate and sulfur in sealed Pyrex bulbs in a vapor bath. Samples were withdrawn after a week and analyzed, and it was noted whether the strength of the calcium thiosulfate had decreased or increased. Thus it could be determined that the equilibrium concentration lay between, say, 1.00 and 0.80. By making up a new set of tubes with concentrations of 1.00, 0.95, 0.90, 0.85, 0.80, *M* the process could be repeated and the equilibrium limits narrowed still more. Table I gives the results of one such run.[5] Final values for the equilibrium concentrations are given in Table II, where Line I gives the temperature, Line 2, the concentration in moles per 1000 g. of water, and Line 3, the form of sulfur stable at the temperature in question.

Table I

Sample Equilibrium Determination

Original concentration	After 6 days	After 14 days	After 30 days	After 50 days
1.427	1.17	1.12	...	...
1.142	1.12	1.076	1.026	1.025
0.950	0.964	0.990	1.006	1.010
0.660	0.713	0.757	...	...
0.478	0.598	0.695	...	...

Table II

Equilibrium Concentrations

Temp., °C.	141	122	110	100	79.8
Concn.	0.2665	0.417	0.618	0.713	1.120
Form of sulfur	$S_{\lambda\mu}$	$S_{\lambda\mu}$	S_m	S_m	S_r

In order to use these equilibrium data to calculate the free-energy change at the standard temperature and concentration it is necessary to know the heat of the reaction, the heat of dilution of these concentrated solutions, the heat capacity of all substances involved and the free energy of dilution of the thiosulfate solution.

The Heat of Reaction.—No direct determination of this quantity was available, and though it may be calculated from the equilibrium measurements themselves, the calculation is so involved in this case that it was thought advisable to determine this factor calorimetrically. In theory this may readily be done by treating in a calorimeter a solution of calcium thiosulfate with an excess of acid and then, under identical conditions, an equivalent amount of calcium sulfite dehydrate with the same amount of the same acid. The chief chemical difficulty lies in the fact that the sulfur formed by the action of acids on thiosulfate solutions is not rhombic sulfur but a mixture of S_λ and S_μ.[6] Under the conditions of these experiments the change of these substances into rhombic sulfur is slow and the heat involved in that process must be allowed for. A rough approximation

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[5] It will be noted that the rate of the reactions by which thiosulfate is formed is quite different (being between two different phases) from the rate at which it decomposes, though, of course, the slope of the two curves in Fig. 1 must be equal at equilibrium. At any given time short of equilibrium the one reaction is thrice as far from equilibrium as the other.

[6] Brownlee, This Journal, **29**, 1032 (1907).

of the heat involved may be made from existing data.[7] Under the conditions of the experiments the value estimated was 110 cal. per mole. Fortunately, in one case, the sulfur could be isolated, washed, and treated with ammonium hydroxide in the calorimeter and this value determined directly. The value found was 200 calories per mole.

The apparatus used in our calorimetric experiments, except those in the heat capacity of calcium sulfite dihydrate, is shown in Fig. 2. The calorimeter was submerged up to the stopper in a large, stirred water-bath, the heavy copper parts serving to keep the top at approximately the temperature of the bath. At the beginning of the experiment, the stopper Ba and appurtenances were inverted, the stopper Ba adjusted, and the vessel B filled with a known weight of 1:1 hydrochloric acid. Stopper Bb was then adjusted, the Dewar flask A filled with a known weight of water and of calcium sulfite or of calcium thiosulfate solution of equivalent strength. The stopper Ba and appurtenances were then put in place. The thermel, E (in most cases a 15 junction thermel belonging to Dr. White) was inserted, the calorimeter placed in the bath, and the run begun,[8] using all the usual precautions of the fore period and stirring described in Dr. White's paper.[9] At the moment of mixing, stirring was stopped and the stoppers Ba and Bb were pushed out by means of rod Bc, the stopper Bb swinging back against the wall of the Dewar flask on the platinum wire hinge Be. Stirring was then started and the run completed in the usual manner. The heat capacity was determined electrically, using the heater D. The current and the voltage were read on a White double potentiometer, the time being controlled by a very accurate interval switch belonging to Dr. White. The final values for the two reactions are: for Reaction (1), 0.0638 mole of CaS_2O_3 in 302 g. of soln. + 64.02 g. of 1:1 HCl solution = 205.51 calories of heat absorbed. The sulfur formed

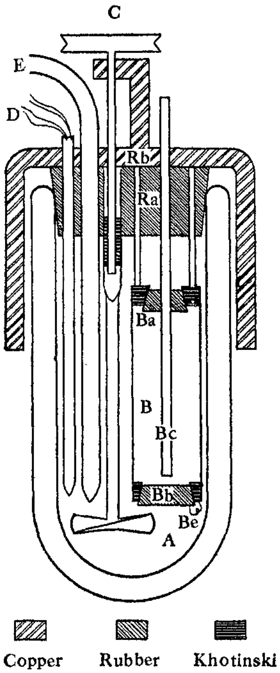

Fig. 2

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[7] Lewis and Randall, "The Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Co., **1923**, p. 532. The nomenclature of these authors is adopted throughout this paper.

[8] All of the calorimetric determinations except those starred were carried out in Dr. White's laboratory in the Geophysical Laboratory in Washington, D. C., often with Dr. White's personal assistance. I wish here to express my gratitude to Dr. White for these many courtesies.

[9] White, THIS JOURNAL, **40**, 1872 (1918).

contained 10.1% S_μ. (2)* 0.06374 mole of CaS_2O_3 in 302 g. of solution + 63.99 g. of 1:1 HCl = 206.60 calories of heat absorbed. In this run the calorimeter was washed, 0.5 *M* ammonium hydroxide added to the vessel B and water added to the vessel A. When these were mixed there was a quick evolution of heat, followed by a slow evolution of heat amounting to about 10 calories, or 200 calories per mole of sulfur present. Calculation gives 110 calories per mole for the reaction $S_{\lambda\mu} = S_r$, on the assumption that the sulfur is "hardened" before the run began, and 365 calories on the assumption that it is not. (3) 0.06382 mole of $CaSO_3.2H_2O$ (10.381 g.) and 290.1 g. of H_2O + 64.00 g. of 1:1 HCl solution = 212.5 calories of heat evolved. (4) 0.0639 mole of $CaSO_3.2H_2O$ and 290.3 g. of water + 64.05 g. of 1:1 HCl solution = 212.2 calories of heat evolved. (5)* Another sample of calcium sulfite dihydrate calculated to the same weight gave 215.0 cal. We shall take for the reaction CaS_2O_3 (0.2127 mole per 1000 g. of soln.) = $CaSO_3.2H_2O + S_r$, $\Delta H = -6300$. It is believed that the total error due to heat losses, etc., does not amount to over 10 calories per mole, but due to the slowness of the reaction involving thiosulfate and sulfur the error in the total heat of reaction may be many times this, say, 1000 calories per mole.

Heat of Dilution.—Using the same apparatus, the heats of the following reactions were determined. (1) (1 mole of CaS_2O_3 in 33.50 moles of H_2O) + (197.4 moles of H_2O) = (1 mole of CaS_2O_3 in 230.4 moles of H_2O); ΔH = 408.5 cal. (2)* (1 mole of CaS_2O_3 in 33.4 moles of H_2O) + 197 moles of H_2O = (1 mole of CaS_2O_3 in 230.4 moles of H_2O); ΔH = 407.9 cal. (3) (1 mole of CaS_2O_3 in 33.5 moles of H_2O) + (0.734 moles of CaS_2O_3 in 164.8 moles of H_2O) = (1.724 moles of CaS_2O_3 in 198.3 moles of H_2O); ΔH = 177.5 cal. (4)* (1 mole of CaS_2O_3 in 33.5 moles H_2O) + (320 moles of H_2O) = (1 mole CaS_2O_3 in 353.5 moles of H_2O); ΔH = 353 cal. It would have been better to carry out measurements in even more dilute solutions but the advantage of this was not realized until the apparatus was no longer available. Reaction 3 can be combined with Reaction 1 giving Reaction 3a, that is, (1 mole of CaS_2O_3 in 33.5 moles of water) + (83 moles of H_2O) = (1 mole of CaS_2O_3 in 116 moles of H_2O); ΔH = 274 cal. It will be noted that of Equations 1, 3a and 4, each gives the heat effect of adding *x* moles of water to a thiosulfate solution of the same strength. It happens that the data for these experiments fall on an hyperbola whose equation is $\Delta H = \dfrac{N'_1}{0.163 + 0.00168\,N'_1}$ where N'_1 is the number of moles of water added to 1 mole of calcium thiosulfate dissolved in 33.5 moles of H_2O. Changing units we obtain[6] $\Delta H = \dfrac{N_1 - c}{E + BN_1}$ where N_1 is the number of moles of water in the final solution to 1 mole of calcium thiosulfate. E = 0.107; c = 33.5 and b = 0.00168. Now $\dfrac{\partial H}{\partial N_1}$

= $\bar{L}_1$ the partial molal heat content of the water of the solution and $N_1 \frac{\partial \bar{L}_1}{dN_1} = \partial \bar{L}_2$. Or, carrying out the indicated transformation, $\bar{L}_1 = \frac{E + bc}{(E + bN_1)^2}$ and $\bar{L}_2 = \frac{E + bc}{b}\left\{\frac{E + 2bN_1}{(E + bN_1)^2}\right\}$. Values of $\bar{L}_1$ and $\bar{L}_2$ for the mol ratio N_1 given in Col. 1 are tabulated in Table III.

Table III

Heat Content of Solution

N_1	208	141.3	89.8	77.9	49.5
$\bar{L}_1$	0.785	1.38	2.45	2.88	4.52
L_2	−376	−487	−597	−635	−735

Specific Heat of Solutions of Calcium Thiosulfate.—Incidental to determining the heat of dilution, the specific heats of the various concentrations of calcium thiosulfate were determined. The values found were 0.704, 0.769, 0.840, 0.918, 0.954 for solutions whose concentrations were 1.750, 1.3234, 0.888, 0.447 and 0.213 *M*, respectively. Using the method of intercepts, the values of $\bar{c}_{p_1}$ and $\bar{c}_{p_2}$ were determined. These values for the concentrations used in the equilibrium experiments are given in Table IV, Lines 2 and 3, respectively. Line 1 gives the concentration in moles per 1000 g. of water.

Table IV

Partial Molal Heat Capacity

Concn.	0.1625	0.2665	0.393	0.618	0.713	1.120
$\bar{c}_{p1}$	18.00	17.99	17.98	17.95	17.90	17.70
$\bar{c}_{p2}$	−3.4	−3.4	−3.3	−3.2	−3.1	−2.6

Heat Capacity of Calcium Sulfite Dihydrate.—A preliminary estimate of the change of heat capacity of the equilibrium reaction based on known data and a value for $c_p/CaSO_3.2H_2O$ based on Kopp's law showed that the Δc_p term in the free-energy equation would have quite exceptional importance. No value of the specific heat of calcium sulfite dihydrate, $CaSO_3.2H_2O$, being available in the literature, determinations were undertaken, using a simple calorimeter, and the drop method. Quartz was used as a comparison substance. Using two different samples of calcium sulfite, almost identical values were obtained, namely 0.274 and 0.273 calories per g. or 42.7 calories per mole. Kopp's law gives 41.1 calories per mole.

Free Energy of Dilution of Solutions of Calcium Thiosulfate.—In order to obtain the free energy of dilution of solutions of calcium thiosulfate, several series of freezing-point curves were made. The set in which most confidence can be placed was made with an apparatus similar to that described by Rodebush,[10] and Rodebush's original 4-junction thermel.

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[10] Rodebush, This Journal, **40**, 1204 (1918).

Values of the concentration in moles per 1000 g. of solution and Δt are: $m = 1.260$, $\Delta t = -3.96$; $m = 0.810$, $\Delta t = -2.106$; $m = 0.578$, $\Delta t = -1.414$; $m = 0.264$, $\Delta t = -0.623$; $m = 0.0674$, $\Delta t = -0.160$. Besides these, the following values at lower concentrations appear to possess some meaning: $m = 0.02045$, $\Delta t = -0.0482$; $m = 0.0106$, $\Delta t = -0.0282$; $m = 0.00553$, $\Delta t = 0.0156$. As far as these determinations go, the activity coefficient seems to be about that found by Lewis and Randall for bivalent sulfates. The best estimate appears to make the activity coefficient 0.40 at 0.01 M. Using this value as a basis, and following the methods of calculation used by Lewis and Randall,[7] the values for γ, the activity coefficient at 25° of solutions of calcium thiosulfate for the equilibrium concentrations, were obtained. The heat capacity and the heat of dilution and its change with concentration were not neglected in this calculation. $m = 0.01$, $\gamma = 0.40$; $m = 0.20$, $\gamma = 0.165$; $m = 0.163$, $\gamma = 0.149$; $m = 0.2665$, $\gamma = 0.127$; $m = 0.393$, $\gamma = 0.113$; $m = 0.618$, $\gamma = 0.0995$; $m = 0.713$, $\gamma = 0.0972$; $m = 1.117$, $\gamma = 0.0964$.

With these data at hand, it is now possible to calculate ΔF_{298} for the reaction $CaSO_3.2H_2O + S_r = CaS_2O_3$ aq. $+ 2H_2O$, directly from the equilibrium measurements. It is convenient, however, instead, to modify the usual procedure somewhat, and calculate the activity of each of the solutions employed at the temperature of equilibrium. This is the true equilibrium constant of the actual reaction at that temperature.

The results for the logarithm of the equilibrium constant are: $T = 414$, $\log K = -2.971$; $T = 393$, $\log K = -2.630$; $T = 383$, $\log K = -2.334$; $T = 373$, $\log K = -2.221$; $T = 352$, $\log K = -1.881$. This is the equilibrium constant for the reaction in which the sulfur is in the form stable at the temperature of the measurement, that is, the form given in Table I, Col. 4. The equilibrium constant for the reaction $CaSO_3.2H_2O + S_r = CaS_2O_3$ aq. $+ 2H_2O$ is slightly different from this. This correction may be calculated from the free energies of the various reactions: $S_r = S_{\lambda\mu}$, $\Delta F_{447} = -90$, $\Delta F_{414} = -35$, $\Delta F_{398} = -20$; $S_r = S_m$, $\Delta F_{383} = -2$, $\Delta F_{373} = -1$, as given by Lewis and Randall.[11] Using the data on the heat capacity of H_2O and S_r given by Lewis and Randall,[12] together with the data obtained in this paper, the change of heat content for this reaction is: $\Delta H = -1945 - 14.02T - 0.00235T^2$ or $-RI \ln K = -1945 + 14.02T \ln T + 0.00235T^2 + IT$. From this equation it may be calculated for $T = 414$, $I = -67.1$, $T = 393$, $I = -67.8$; $T = 383$, $I = -69.7$; $T = 373$, $I = -69.7$; $T = 353$, $I = -69.9$. There appears to be a trend in the values of I, due presumably to a faulty value of the heat of reaction and also in part to the unsatisfactory freezing-point data. The best value appears to be $I = -68.6$. For the reaction S_r

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[11] Ref. 7, p. 532.

[12] Ref. 7, pp. 102, 531.

+ $CaSO_3.2H_2O$ = CaS_2O_3 (M) + $2H_2O$, therefore, $\Delta F° = 1310$ calories. The error here is probably not over 300 calories and might easily be decreased, given better thermal and activity data.

Solubility of Calcium Sulfite Dihydrate.—The solubility of this substance has been determined by Weisberg[13] and by van der Linden.[14] Their results are 0.057 g. per liter at 18° and 0.065 g. per liter at 25°, respectively. However, it is difficult to prepare calcium sulfite dihydrate free from gypsum, the presence of which would affect the solubility very greatly. Van der Linden notes that his sulfite was not free from sulfate and hence presumably contained gypsum. At any event, the solubilities determined above are not consistent with the solubility of calcium sulfite dihydrate in a solution saturated with gypsum as determined by van der Linden, namely, 0.032 g. per liter. A series of determinations was therefore undertaken with various samples of calcium sulfite, in which the solution was saturated at 25° and titrated with 0.001 N iodine solution. Contrary to the common opinion, even more dilute solutions of iodine can be used without an abnormal blank correction, provided the solution is kept 0.1 N in iodide ion. The sulfite used was prepared, (1) by precipitating the salt from solutions of calcium chloride by the addition of sulfur dioxide and sodium hydroxide simultaneously, (2) by dissolving calcium sulfite dihydrate in a pure solution of sulfurous acid and precipitating the salt by boiling off the sulfur dioxide in a vacuum, (3) by washing the commercial salt with air-free distilled water. None of these samples was quite free from sulfate. The values for the solubility obtained were, respectively, 0.000202, 0.000107, 0.000087 mole per liter. The solubility of Samples 1, 3, and the commercial salt in the presence of solid gypsum were 0.0000371, 0.0000367, 0.0000372 mole per liter or 0.029 g. per liter, agreeing closely with the value of van der Linden. Taking 0.000037 as the final value and applying the principle of ionic strength,[7] the mean activity of the sulfite and calcium ions in a saturated solution of calcium sulfite dihydrate at 25° is 0.000261; that is, for the reaction $Ca^{++} + SO_3^{--} + 2H_2O = CaSO_3.2H_2O$, $\Delta F_{298}° = —9740$ or, adding $\Delta F_{298}°$, = —8430 for the reaction $SO_3^{--} + S_r = S_2O_3^{--}$. Now, Lewis and Randall give for the free energy of formation of the sulfite ion, $\Delta F_{298}° = —116{,}680$. Therefore, the free energy of formation of the thiosulfate ion in solution of unit activity is —125110 calories.

Summary

A complete thermodynamic study has been made of the reaction, S + $CaSO_3.2H_2O$ = CaS_2O_3 aq. + $2H_2O$. This reaction has been proved to be reversible and the equilibrium constant has been measured at various temperatures. The heat of the reaction has been determined experi-

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[13] Weisberg, *Bull. soc. chim.*, [3] **15,** 1097.

[14] Van der Linden, *Arch. Sukerind.*, **24,** 1113 (1916).

mentally as have the specific heat, freezing point and heat of dilution of solutions of calcium thiosulfate of various strengths. The solubility of calcium sulfite dihydrate and its specific heat have also been measured. Using these and other data, the free energy of formation, $\Delta F_{298}°$ of the thiosulfate ion has been calculated to be —125,110 calories.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CATALYTIC COMBINATION OF ETHYLENE AND HYDROGEN IN THE PRESENCE OF METALLIC COPPER

II. MEASUREMENTS OF REACTION VELOCITY AT 150°, 200° AND 250°

BY ROBERT N. PEASE

RECEIVED MAY 31, 1923

In a recent paper[1] the author has recorded results which indicate that the combination of ethylene and hydrogen in the presence of copper at 0° and 20° is, in its first stages, approximately monomolecular with respect to hydrogen, while ethylene in excess acts as an inhibitor. Grassi[2] has studied this reaction to some extent at temperatures between 150° and 275° and reports that in this region the reaction is bimolecular, as would be expected from the chemical equation. Grassi also found that the temperature coefficient between 150° and 275° was very small and decreased with rising temperature whereas between 0° and 20°, the author found the temperature coefficient to be in the neighborhood of 1.6 per 10°, which is of the same order as that for many uncatalyzed reactions. These marked differences in the characteristics of the reaction in the two temperature regions made it important to repeat a part of Grassi's work, especially as this investigator carried his determinations over only a small fraction of the total reaction.

The apparatus and method were the same as those used in the previous determinations at 0° and 20°, except that the temperature was maintained by means of an electrically heated air-bath. The copper catalyst in the state in which it was used for the runs at the lower temperature was much too active for use in the neighborhood of 200°. Partial de-activation was accomplished by heating it to 500–550° in a vacuum. During this treatment, the catalyst shrank about 15% of its original apparent volume and turned from a dirty red-brown to a salmon pink.

Reaction Velocity at 200°

The catalyst in the latter stage of activity was used for a series of runs at 200°. The results of this series, which are shown graphically in Figs. 1 and 2, indicate that the reaction is not exactly bimolecular as Grassi

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[1] Pease, THIS JOURNAL, 45, 1196 (1923).

[2] Grassi, *Nuovo cimento*, [6] 11, 147 (1916).