

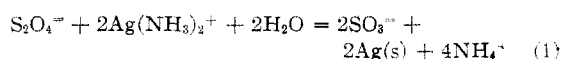
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Thermodynamic Constants of the Dithionite (Hydrosulfite) Ion

BY W. G. McMILLAN, JR., JOHN D. ROBERTS AND CHARLES D. CORYELL

Latimer¹ has pointed out a discrepancy in the literature in the thermodynamic constants for the dithionite (hydrosulfite) ion ($S_2O_4^{2-}$). The calculated value for the free energy of formation of the ion from the calorimetric data of Berthelot² on its oxidation (to bisulfite ion) by oxygen is -126 kcal., obtained by Latimer with the aid of an estimated molal entropy of 8 cal./deg. The value calculated by him from a derived electrode potential given by Jellinek³ for the dithionite-bisulfite couple is -138 kcal.

The data of Berthelot are probably useless in thermodynamic calculations since Meyer⁴ showed that the products of the reaction contain a large amount of sulfate. Indeed, Berthelot noticed that less than one-half of the heat was given off rapidly and the remainder over a long period of time, indicating the complexity of the reaction. For the determination of the heat content of the ion we have selected the reaction studied by Smith⁵ for the quantitative analysis of dithionite preparations



since the reaction is fast and heat data are known for all other participants.⁶ Calculations indicate that under our experimental conditions a small fraction of the ammonia in the unused diamminesilver complex is replaced by sulfite ion, but the heat of this reaction (estimated with the aid of the entropy effect in the analogous thiosulfate complex formation) is found to be negligible.

The decrease in heat content observed at 22° for reaction (1) is 58.2 ± 0.5 kcal. per mole of dithionite ion, correcting for the heat of solution of the substances in ammonia of the same concentration. Assuming that the silver precipitate (observed to be fairly coarse) is essentially in its standard state, neglecting the change in the above determined heat on going to 18° , and taking the remaining heat data from Bichowsky and Ros-

sini,⁶ we calculate the molal heat content of the ion to be -178.7 kcal.

Experimental

The heat of reaction (1) was determined by noting the temperature rise when a weighed sample of sodium dithionite (Eastman Kodak Co.) was introduced rapidly into an excess of ammoniacal silver nitrate solution (0.365 m. in ammonia and 0.1024 m. in diamminesilver nitrate) contained in a liter vacuum-jacketed calorimeter having a heat capacity of 21 cal.

The heat of solution of the salt was measured in 300 g. of an ammonia solution of concentration equal to that of the total ammonia concentration of the ammoniacal silver nitrate. It was found that an average temperature rise of 0.003° was produced per gram of the salt dissolved.

The sodium dithionite, analyzed by the method of Smith,⁵ was found to have a percentage purity (calculated as the anhydrous salt) of 88.9, 89.6%; average 89.3%. The thermal data are summarized in Table I.

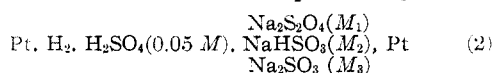
TABLE I
HEAT OF OXIDATION OF DITHIONITE ION BY THE SILVER-AMMONIA COMPLEX

Sodium dithionite, g.	Ag(NH ₃) ₂ ⁺ - NH ₃ soln., g.	Δt (cor.), ^a °C.	Heat cap. of final solution, cal./deg.	$-\Delta H$ per mole S ₂ O ₄ ²⁻ (22°C.)
0.912	300.0	0.885	291.5	59.2 kcal.
1.690	301.2	1.593	292.7	57.7
1.909	300.0	1.802	291.8	57.7
Average value				58.2 kcal.

^a Corrected for heat of solution of salt.

The heat capacity of the final solution was estimated from apparent molal heat capacities of the ions taken or calculated from data given by various investigators.⁷

Our attempts to measure the potentials with smooth platinum electrodes in cells containing air-free solutions of dithionite, sulfite, and bisulfite ions gave unsteady values soon markedly affected by the total destruction of the unstable dithionite. Because of the importance of verifying the calculation of the free energy of the dithionite ion we have recalculated in Table II Jellinek's data² for the cell measured at practically 20°



Jellinek reported concentrations in normality; internal evidence in the paper indicates that he

(7) (a) M. Randall and F. D. Rossini, *THIS JOURNAL*, **51**, 323 (1929); (b) F. T. Gucker and K. H. Schminke, *ibid.*, **54**, 1358 (1932); **55**, 1013 (1933); (c) "Int. Crit. Tables," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1927.

(1) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938, p. 69.

(2) M. Berthelot, *Ann. chim. phys.*, **10**, 389 (1877).

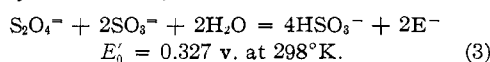
(3) K. Jellinek, *Z. Elektrochem.*, **17**, 147 (1911).

(4) J. Meyer, *Z. anorg. Chem.*, **34**, 43 (1903).

(5) J. H. Smith, *THIS JOURNAL*, **43**, 1301 (1921).

(6) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Pub. Co., New York, N. Y., 1936.

used oxidimetric normality rather than acidimetric normality for sodium bisulfite. The first column of Table II indicates the number of cells averaged, the next three give the molarities of sulfur compounds, the fifth gives the potential measured, the sixth gives Jellinek's calculation of the liquid junction potential by the Henderson equation⁸ (which, in view of the high concentrations, must be looked upon as an empirical treatment), and the last column gives the (large) values of the ionic strength μ in the dithionite half-cells. In the seventh column is given the formal electrode potential E'_0 (uncorrected for activity coefficients) for the half cell



in which the concentration of hydrogen ion in the reference cell is taken as 0.058 *M* including some secondary ionization of the sulfuric acid. We have followed the standard physico-chemical conventions of sign.¹

TABLE II

FORMAL ELECTRODE POTENTIAL OF THE DITHIONITE-SULFITE COUPLE, RETREATMENT OF THE DATA OF JELLINEK³ AT 20°

No. of cells	Na ₂ S ₂ O ₄ <i>M</i> ₁	NaHSO ₃ <i>M</i> ₂	Na ₂ SO ₃ <i>M</i> ₃	<i>E</i> _{obs.} v.	<i>E</i> _L v.	<i>E</i> ' ₀ v.	μ
1	0.050	0.0233	0.0225	0.280	0.022	0.319	0.24
1	.100	.0233	.0225	.288	.018	.314	.39
4	.050	.0232	.223	.345	.011	.314	.84
2	.050	.0212	.219	.352	.011	.317	.83
2	.050	.233	.233	.234	.010	.318	1.08

The values of E'_0 in Table II are quite constant in spite of the large range in ionic strength, although it is to be expected that they should fall noticeably with its increase. Consequently the average value 0.316 v. might be considered as a lower limit. Taking into account the temperature coefficient +0.00226 v./deg., the value becomes 0.327 v. at 25°.

Employing values for the free energies of bisulfite ion (-126.13 kcal.) and sulfite ion (-116.3 kcal.) consistent with the ionization constants for sulfurous acid reported by Tartar and Garretson⁹ (based on Latimer's value for sulfurous acid) and taking from Latimer¹ free energies of the other participants in reaction (3), we obtain (as a lower limit) for the free energy of formation of the dithionite ion -143.4 kcal. at 25°.

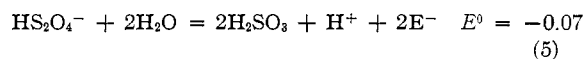
(8) P. Henderson, *Z. physik. Chem.*, **63**, 325 (1908).

(9) H. V. Tartar and H. H. Garretson, *THIS JOURNAL*, **63**, 808 (1941).

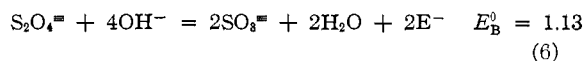
From Jellinek's observed temperature coefficient of e. m. f. (+0.00226 v./deg.) for the cell (2) above, the increase in heat content for the cell reaction (3) is calculated to be 16.0 kcal., and the molal heat content of the dithionite ion, -178.3 kcal. This value is in excellent agreement with our thermal data (-178.7).

The entropy change attending reaction (3) is readily calculated from ΔH and E'_0 to be 104 cal./deg. Employing molal entropy values summarized by Latimer,¹ and using 15.6 cal./deg. as the molal entropy of E^- in solution,¹⁰ the molal entropy of the dithionite ion becomes 18 cal./deg. compared with Latimer's estimate of 8 cal./deg. It is difficult to assess the reliability of this figure.

Taking into account Jellinek's³ value for the second ionization constant of dithionous acid ($pK_2 = 2.45$) and assuming the first ionization is complete, the standard molal electrode potential in acid solution is calculated to be



The couple in basic solution is calculated to be



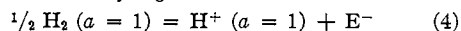
and is thus 0.30 volt more positive than the hydrogen couple in molal hydroxide solution.

Summary

The molal heat content in dilute solution of dithionite ion ($\text{S}_2\text{O}_4^{2-}$) is found to be -178.7 kcal. A reëxamination of Jellinek's potentiometric data gives -178.3 kcal. for the heat content and -143.4 kcal. for the free energy of formation of the ion.

LOS ANGELES, CALIFORNIA RECEIVED OCTOBER 21, 1941

(10) The assignment of zero electrode potential and temperature coefficient to the molal hydrogen half cell



together with the conventional assignment (refs. 1 and 6) of values of ΔF^0 , ΔH^0 , and $S_{298.1}$ to H_2 (0, 0, and 31.23 cal./deg., respectively) and to H^+ (0, 0, and 0, respectively) lead directly to numerical values of the thermodynamic constants for the solvated electron E^- at unit activity. Unit activity of E^- is that prevailing in the molal hydrogen half cell; the corresponding thermodynamic constants are: $\Delta F = 0$, $\Delta H = 0$, and $S_{298.1} = 15.6$ cal./deg., just those necessary to fulfill the requirements $\Delta F = 0$, $\Delta H = 0$, and $\Delta S = 0$ for equation (4). Recognition of these values permits one to balance thermodynamically half-cell reactions like equation (3) (treating E^- as any other chemical reactant) without first having chemically to balance the couple against the hydrogen couple to make a complete reaction.