gen double bond and a single bond, then each bond would possess 50% double bond character. The interatomic distance found by application of the usual resonance curve is 1.69 Å. The discrepancy between this value and that observed is probably due to the importance of electronic structures in which the oxygen is bonded to the selenium atom by a triple bond. A bond of this type is possible because selenium is not restricted rigorously by the octet rule.

The observed sulfur-oxygen distance in sulfur dioxide bears about the same relation to the radii as that found for selenium dioxide, and the two molecules are probably closely similar in electronic structure.

The selenium dioxide crystal[4] does not contain discrete SeO_2 molecules, but instead consists of infinite chains. The observed Se–O distances in the crystal, 1.78 Å. and 1.73 Å., have been discussed by McCullough.

We are indebted to Dr. James D. McCullough for furnishing us with the sample of selenium dioxide, and to Professor Linus Pauling for his aid and criticism during the course of this investigation.

Summary

Electron diffraction photographs of selenium dioxide vapor have been interpreted to lead to the value 1.61 ± 0.03 Å. for the Se–O distance. The value of the angle O–Se–O could not be determined.

PASADENA, CALIF. RECEIVED MARCH 10, 1938

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[4] James D. McCullough, THIS JOURNAL, **59**, 789 (1937).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities, Entropies, and Heats of Solution of Anhydrous Sodium Sulfate and of Sodium Sulfate Decahydrate. The Application of the Third Law of Thermodynamics to Hydrated Crystals

BY KENNETH S. PITZER AND LOWELL V. COULTER

It is known that true equilibrium is not attained when ice is cooled to very low temperatures, and that consequently the entropy of ice as calculated from low temperature heat capacity data in the usual manner is incorrect.[1] The reason for this behavior has been ascribed to a randomness in the position of the protons which form hydrogen bonds between the oxygen atoms.[2] The question then arises as to whether a similar situation may not exist in hydrated crystals, particularly those containing a relatively large number of loosely held molecules of water. In order to investigate this possibility, and in addition to obtain an accurate value for the entropy of sulfate ion, we have measured the heat capacity of both anhydrous sodium sulfate and its decahydrate from 14 to 300°K., and have determined the heat of solution in water for both substances.

Materials.—Samples of sodium sulfate decahydrate were prepared by recrystallization of the "C. P." salt, and were dried in a vacuum desiccator over anhydrous sodium sulfate. A slight "premelting" effect observed below the 32.38° "transition" can be explained on the basis of less than 0.1% of impurity which is soluble in the solution present above 32.38°. The sample of decahydrate used in the heat capacity measurements (wt. 58.715 g. *in vacuo*) contained a very small excess (0.02 g.) of water which was determined both by analysis and by the high heat capacity value obtained at the ice-point, the two results being concordant. Correction was made for its presence as ice below 0°C. and as water above. The samples of decahydrate used in heat of solution measurements were the same except that no appreciable excess of water was present.

The anhydrous sodium sulfate was prepared by dehydration of the decahydrate under vacuum at temperatures below 80°C. A sample of 115.52 g. (wt. *in vacuo*) was used in the heat capacity measurements. A high heat capacity measurement near 32.38°C. indicated the presence of a trace (less than 0.1%) of the decahydrate, for which suitable correction was made.

Apparatus.—The cryostat and block assembly which have been used for some time and have been described previously[3] were retained for this investigation. However, a new calorimeter containing a strain-free platinum resistance thermometer was constructed. The platinum thermometer serves the purposes of both the copper-constantan thermocouple and the gold resistance thermometer (non-strain-free) which were used previously, thus considerably simplifying both the measurements and calculations. Also it is hoped that a somewhat improved temperature scale may result, although to date only the initial steps have been taken in this direction. As yet the platinum

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[1] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933); Giauque and Stout, THIS JOURNAL, **58**, 1144 (1936).

[2] Pauling, *ibid.*, **57**, 2680 (1935).

[3] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928); Brown Smith and Latimer, *ibid.*, **58**, 1758 (1936).

resistance thermometer has been calibrated above 22°K. only by comparison with a standard copper–constantan thermocouple, and consequently the accuracy in this region is that of the thermocouple, about 0.05°. Below 22°K. comparison was made with the vapor pressure and triple point of hydrogen,[4] and a subsequent calibration, made after all heat capacities had been measured, checked the original within 0.01° throughout this region.

The calculations were made in the usual manner except that corrections arising from an external resistance thermometer were of course avoided. Since a detailed description of a calorimeter of this type is already available[5] no further details will be given here.

Heat Capacity Measurements.—The results of the heat capacity measurements are presented in Tables I and II and are shown graphically in Fig. 1. Smoothed values of the heat capacities for both substances at even temperatures are given in Table III. The approximate temperature differences of the individual heat capacity determinations can be judged from the spacing of the reported results. The absolute temperature of the ice point was assumed to be 273.10°K., and one calorie was taken as 4.1833 int. joules.

TABLE I

THE MOLAL HEAT CAPACITY OF ANHYDROUS SODIUM SULFATE, Na_2SO_4

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
13.74	0.171	57.22	8.108	163.43	22.56
16.25	.286	62.37	9.278	179.41	23.79
18.30	.426	68.15	10.48	195.80	24.88
20.43	.626	75.28	11.89	211.35	26.00
23.04	.939	82.96	13.28	220.40	26.63
25.48	1.288	87.55	14.05	229.90	27.06
27.73	1.615	95.71	15.33	240.09	27.63
30.52	2.076	104.51	16.56	250.48	28.31
33.64	2.678	114.59	17.83	259.96	28.74
37.00	3.428	125.07	18.99	270.37	29.29
41.11	4.346	136.41	20.17	281.19	29.85
44.87	5.194	149.18	21.34	292.14	30.22
48.68	6.086			299.87	30.53
52.72	7.032			313.44	31.03

TABLE II

THE MOLAL HEAT CAPACITY OF SODIUM SULFATE DECAHYDRATE, $Na_2SO_4 \cdot 10H_2O$

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
14.28	1.70	52.95	27.18	173.01	88.82
16.15	2.35	59.27	31.82	187.67	94.25
18.11	3.21	66.15	36.73	201.77	100.5
20.08	4.26	72.77	41.00	215.55	105.0
22.31	5.62	79.42	45.10	228.56	110.2
24.46	6.95	86.95	49.43	239.83	114.6
26.79	8.40	96.36	54.19	249.98	119.0
29.30	10.00	107.29	60.03	259.33	123.0
34.41	13.41	120.45	66.13	266.87	128.3
39.79	17.53	133.91	72.29	281.21	131.9
44.10	20.69	145.99	77.81	289.83	137.3
48.31	23.70	158.58	83.06	298.37	145.9

TABLE III

SMOOTHED VALUES OF THE HEAT CAPACITY OF Na_2SO_4 AND $Na_2SO_4 \cdot 10H_2O$

	C_p, cal./deg.			C_p, cal./deg.	
T, °K.	Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$	T, °K.	Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$
15	0.222	1.94	100	15.93	56.19
20	.581	4.20	120	18.45	65.93
25	1.213	7.30	140	20.50	75.10
30	1.990	10.53	160	22.25	83.68
35	2.980	13.96	180	23.82	91.54
40	4.077	17.51	200	25.23	99.18
45	5.222	21.18	220	26.51	106.8
50	6.423	24.95	240	27.67	114.7
60	8.743	32.38	260	28.73	122.9
70	10.85	39.25	280	29.67	131.4
80	12.76	45.43	300	30.51	140.5
90	14.44	50.97			

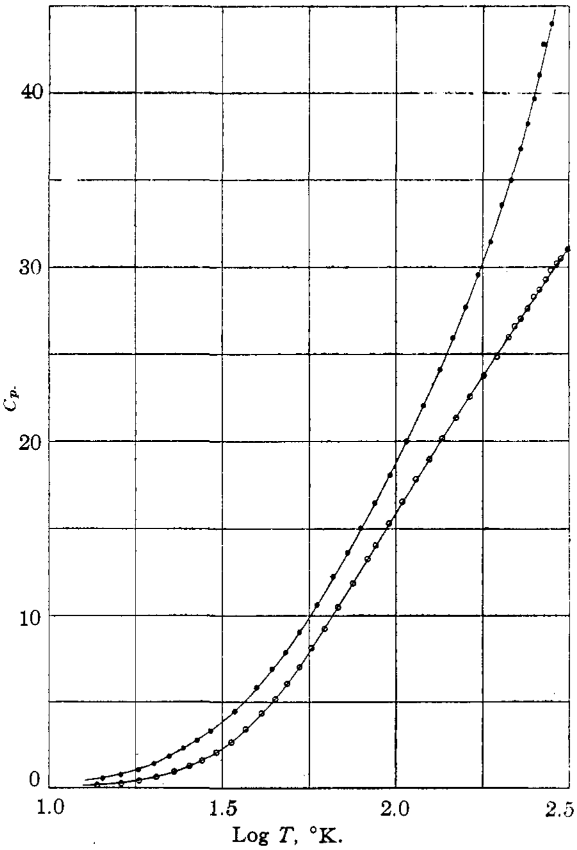

Fig. 1.—Heat capacity in cal. per deg.: open circles for one mole of anhydrous sodium sulfate; solid circles, one-third mole of sodium sulfate decahydrate.

Heat of Solution Measurements.—The calorimeter employed in these measurements has been described in an earlier publication.[6] The results

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[4] Henning and Otto, *Physik. Z.*, **37**, 635 (1936).

[5] Southard and Brickwedde, THIS JOURNAL, **55**, 4378 (1933).

[6] Pitzer, *ibid.*, **59**, 2365 (1937).

of the measurements are presented in Table IV, together with the heats of dilution of the resulting solutions, which were taken from data of Lange and Streeck.[7]

TABLE IV

THE HEATS OF SOLUTION OF Na_2SO_4 AND $Na_2SO_4 \cdot 10H_2O$ IN WATER AT 25°C.

Subst.	Wt., g.	Molal concn. of final soln.	Heat absorbed cal. per mole	ΔH of diln.	ΔH° cal. per mole
Na_2SO_4	6.3701	0.0510	−323	−241	−564
Na_2SO_4	6.1390	.0492	−316	−240	−556
					−560 ± 10
$Na_2SO_4 \cdot 10H_2O$	24.800	.0882	19,075	−234	18,841
$Na_2SO_4 \cdot 10H_2O$	17.421	.0617	19,085	−242	18,843
$Na_2SO_4 \cdot 10H_2O$	12.376	.0438	19,076	−238	18,838
					18,840 ± 20

Entropies.—The entropies were calculated by graphical integrations above 14°K. combined with extrapolations below that point based on the T^3 law. The results are presented in Table V.

TABLE V

ENTROPIES OF Na_2SO_4 AND $Na_2SO_4 \cdot 10H_2O$

		Na_2SO_4	$Na_2SO_4 \cdot 10H_2O$
0–14°K.	T^3 extrapolation	0.06	0.5
14–298.1°K.	graphical from data	35.67	140.0
	$S^\circ_{298.1} - S^\circ_0$	35.73 ± 0.1	140.5 ± 0.3

There would seem to be no reason to doubt the correctness of the value for the anhydrous salt. The possibility of false equilibrium in the decahydrate may now be checked. Consider the reaction

$$Na_2SO_{4(solid)} + 10H_2O_{(gas)} = Na_2SO_4 \cdot 10H_2O_{(solid)} \quad (1)$$

The free energy change for this reaction is given by $\Delta F = +RT \ln P^{10}$, where P is the dissociation pressure of the decahydrate. Table VI summarizes the values of the dissociation pressure at 25°C. obtained by various observers.

TABLE VI

DISSOCIATION PRESSURE OF SODIUM SULFATE DECAHYDRATE

Observer	P, mm.
Lescoeur[8]	19.00
Foote and Scholes[9]	18.20
Wuite[10]	18.10
Norton and Johnston[11]	18.55
Matsui, *et al.*[12]	18.10
Wilson[13]	19.22 ± 0.02
Schumb[14]	19.16
Baxter and Lansing[15]	19.20
Perman and Urry[16]	19.17
Rode[17]	19.20
(Average of last 5)	19.19 = 0.02525 atm.

As can be seen easily from Table VI the results of the last five observers listed are in good agreement, and the average of their results will be used. This gives for the free energy change in equation (1), $\Delta F = -21{,}795$ cal.

The change in heat content for equation (1) is obtained from the heats of the following reactions

$$Na_2SO_{4(solid)} = 2Na^+_{(aq.)} + SO_4^{=}{}_{(aq.)} \quad (2)$$

$$Na_2SO_4 \cdot 10H_2O_{(solid)} = 2Na^+_{(aq.)} + SO_4^{=}{}_{(aq.)} + 10H_2O_{(liq.)} \quad (3)$$

$$H_2O_{(liq.)} = H_2O_{(gas)} \quad (4)$$

(2) − (3) − 10(4) gives

$$Na_2SO_{4(solid)} + 10H_2O_{(gas)} = Na_2SO_4 \cdot 10H_2O_{(solid)} \quad (1)$$

The heats of reactions (2) and (3) are, of course, the heats of solution of the anhydrous salt and its decahydrate, respectively. The value of $\Delta H^\circ_{(2)} - \Delta H^\circ_{(3)}$ as obtained from the heats of solution in Table IV is −19,400 ± 30 cal. per mole. For this quantity Pickering[18] obtained −19,470 cal. and Thomsen[19] obtained −19,260 cal., both values being reduced to 25°C. by means of the heat capacity data given above for the two solids. In interpreting Thomsen's data, values for the heat of solution of almost completely dehydrated sodium sulfate were employed rather than the values for the completely dehydrated samples since the latter had been heated to very high temperatures and had likely remained in a higher temperature crystalline form.

The heat of vaporization of water, equation (4), was taken from Keenan and Keyes,[20] the value for 25°C. being 10,518 cal. per mole. This gives for equation (1), $\Delta H^\circ = -124{,}580 \pm 100$ cal. and $\Delta S^\circ = (\Delta H - \Delta F^\circ)/T = -344.8 \pm 0.4$ cal. per deg. The entropy of sodium sulfate decahydrate may now be obtained from the entropy of the anhydrous salt, the entropy of water vapor,[21] and the entropy change for equation (1) as fol-

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[7] Lange and Streeck, *Z. physik. Chem.*, **A157**, 1 (1931).

[8] Lescoeur, *Ann. chim. phys.*, [6] **21**, 529 (1890).

[9] Foote and Scholes, THIS JOURNAL, **33**, 1309 (1911).

[10] Wuite, *Z. physik. Chem.*, **86**, 349 (1914).

[11] Norton and Johnston, *Am. J. Sci.*, **12**, 467 (1926).

[12] Matsui, *et al.*, *J. Soc. Chem. Ind. Japan*, **32**, 172B (1929).

[13] Wilson, THIS JOURNAL, **43**, 704 (1921).

[14] Schumb, *ibid.*, **45**, 342 (1923).

[15] Baxter and Lansing, *ibid.*, **42**, 419 (1920).

[16] Perman and Urry, *Trans. Faraday Soc.*, **24**, 337 (1928).

[17] Rode, *Ann. inst. anal. phys.-chim. (Leningrad)*, **6**, 97 (1933).

[18] Pickering, *J. Chem. Soc.*, **49**, 260 (1886).

[19] Thomsen, "Thermochemische Untersuchungen," Vol. III, Barth, Leipzig, 1882, p. 123.

[20] Keenan and Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.

[21] Gordon, *J. Chem. Phys.*, **2**, 65 (1934); Wilson, *ibid.*, **4**, 526 (1936).

lows: $S^\circ = 10S_{H_2O} + S^\circ_{Na_2SO_4} + \Delta S^\circ = 451.3 + 35.7 - 344.8 = 142.2 \pm 0.5$ cal. per deg. This value is 1.7 units higher than that obtained by the integral of (C_p d ln T) as given in Table V. Although this entropy difference might conceivably be due to experimental error, this seems highly improbable and we are therefore led to the conclusion that false equilibrium does exist at low temperatures in sodium sulfate decahydrate. It should be mentioned that the use of a lower dissociation pressure for the decahydrate only makes the discrepancy larger. At no temperature was the attainment of apparent thermal equilibrium abnormally slow.

The cause of this entropy discrepancy presumably lies in some randomness in the position of the protons which are forming hydrogen bonds in the crystal. Since the detailed crystal structure of the decahydrate is not known, little more can be said at present concerning this randomness. A knowledge of the structure of this crystal would, of course, be very desirable. It should be noted that, per molecule of water, the discrepancy here is but 0.17 cal. per deg. as compared to 0.81 in the case of ice, as is to be expected.

Since this is the first case of this kind for which complete and precise data are available, it is impossible to state whether this effect is likely to be present in many hydrates or not. However, at least until additional data are obtained, the entropies of hydrated crystals obtained by the application of the third law of thermodynamics must be regarded as uncertain by a few tenths of a cal. per deg. for each molecule of water present. The third law entropies are of course minimum values, since any lack of equilibrium will leave a positive entropy at the absolute zero.

Entropy of Sulfate Ion.—Latimer, Hicks and Schutz[22] have determined the entropy of sulfate ion by several methods. However, a value can be calculated from the above data which would seem at least as accurate as those previously obtained. Various observers[23] agree on a value near 1.972 *M* for the solubility of sodium sulfate decahydrate at 25°C. Three methods were employed to obtain the free energy of solution, equation (3). The first method involved the use of the e. m. f. data of Åkerlöf[24]; while the second made use of the vapor pressure data of Gibson and Adams and of Pearce and Eckstrom.[25] In the third method the free energy of solution was calculated first for 0°C. using the solubility at that point (0.342 *M*) and the activity coefficient which is well known at this much smaller concentration. Then using the heat of solution given above and the heat capacities of the various substances involved[26] the result was converted to 25°C. Account was taken of the activity of water in the saturated solution in each calculation. The values obtained are, respectively: 1645, 1670, and 1620 cal. per mole. Combining the average of these with the heat of solution from Table IV, one obtains for the entropy of solution 57.7 cal. per deg. The entropy of sulfate ion is then given by the expression: $S^\circ_{SO_4^{-}} = S^\circ_{Na_2SO_4\cdot 10H_2O} + \Delta S^\circ - 10\ S^\circ_{H_2O} - 2S^\circ_{Na^+} = 142.2 + 57.7 - 167.5 - 28.0 = 4.4 \pm 1$ cal. per deg. Since some of the data involved in the other calculations of the entropy of sulfate ion should now be revised, comparison with these values will be postponed until a general revision is made. The above value for the entropy of sodium ion is a slightly revised one, the source of which also will be explained later.

Summary

The heat capacities of anhydrous sodium sulfate and its decahydrate were determined from 14 to 300°K. and their entropies calculated by the usual methods. The heat of solution was measured for each salt. The entropy of the decahydrate was also calculated by use of the known entropy of water vapor and dissociation pressure of the hydrate together with the heats of solution and the entropy of the anhydrous salt. The value thus obtained is 1.7 cal. per degree higher than that calculated from the low temperature heat capacities, thus suggesting the presence of false thermal equilibrium at low temperatures. The cause of this effect is presumably analogous to that in the case of ice, *i. e.*, a randomness in the position of protons forming hydrogen bonds. A value was also obtained for the entropy of sulfate ion.

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(22) Latimer, Hicks and Schutz, *J. Chem. Phys.*, **1**, 424, 620 (1933).

(23) "International Critical Tables" and Landolt-Börnstein, "Tabellen," give numerous references.

(24) Åkerlöf, THIS JOURNAL, **48**, 1160 (1926).

(25) Gibson and Adams, *ibid.*, **55**, 2679 (1933); Pearce and Eckstrom, *ibid.*, **59**, 2689 (1937).

(26) Randall and Rossini, *ibid.*, **51**, 323 (1929).