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DEPARTMENT OF THE INTERIOR]

High Temperature Heat Contents, Heats of Transition and Heat of Fusion of Anhydrous Sodium Sulfate

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High temperature heat contents were determined for Na_2SO_4 (V) from 298.16 to 450°K., for Na_2SO_4 (III) from 298.16 to 514°K., for Na_2SO_4 (I) from 514 to 1157°K., and for Na_2SO_4 (I) from 1167 to 1850°K. The heat of transition of Na_2SO_4 (III) to Na_2SO_4 (I) at 514°K. and the heat of fusion of Na_2SO_4 (I) at 1157°K. were obtained from the heat content measurements. The heat of transformation of Na_2SO_4 (V) to Na_2SO_4 (III) at 303.16°K. was determined by solution calorimetry. A table of smoothed values of heat content and entropy increments is included, and heat content equations were derived.

Introduction

Kracek and Gibson¹ have shown that five distinct crystalline modifications of anhydrous sodium sulfate occur under various conditions of temperature and thermal history. Two of these forms are known to exist at 298°K.—a stable variety, Na_2SO_4 (V) (thenardite) and a thermodynamically metastable form, Na_2SO_4 (III). No previous high temperature heat content or heat of transition data for any of the forms of sodium sulfate are available from the literature. This paper reports high temperature heat content values for three crystalline modifications (V, III and I) and for the liquid, as well as the heats of transformation (V \rightarrow III) and (III \rightarrow I) and the heat of fusion of crystalline form I. Finally, the entropy of Na_2SO_4 (III) is derived from the above data. The designations of the forms of sodium sulfate are the same as in Kracek and Gibson's¹ paper.

Material

Reagent grade anhydrous sodium sulfate was ignited at 880° for 60 hours, cooled and ground to -60 mesh. The X-ray diffraction pattern agreed with that for Na_2SO_4 (III) in the A.S.T.M. catalog. The water content after the sample bulbs were filled was less than 0.002%.

Na_2SO_4 (V) was prepared by a method similar to that used by Pitzer and Coulter.² Reagent grade sodium sulfate decahydrate was melted and slowly dehydrated at 50–90°. The resulting crystals of Na_2SO_4 (V) were then dried *in vacuo* at 70–80°. The residual water content was 0.105%, equivalent to 0.238% of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The X-ray pattern agreed with those published by Zachariassen and Ziegler³ and Colby.⁴ Individual crystals were estimated by microscopic examination to vary from 2×10^{-3} mm. to 0.1 mm. in size. These materials were prepared by R. E. Lorenson, formerly of this Laboratory.

Measurements and Results

The heat content measurements were made with apparatus and techniques previously described.⁵ Corrections for the heat contents of the 90% platinum–10% rhodium alloy capsules were determined by separate experiments. In every case, the heat content of the container was less than 15% of the total heat measured. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), and the molecular weight of 142.060 conforms with the 1951 International Atomic Weights.⁶ Sample

weights were corrected to vacuum, using the following densities⁷: 2.697 for Na_2SO_4 (III) and 2.664 for Na_2SO_4 (V). During the course of the measurements, the platinum–rhodium furnace thermocouple was calibrated frequently at the melting point of pure gold and occasionally at the melting point of pure palladium. The measurements of Na_2SO_4 (V) were restricted to temperatures below 444°K., to prevent the sample from being transformed, irreversibly, to Na_2SO_4 (III).¹ Na_2SO_4 (III) transforms to Na_2SO_4 (I) at 514°K. with a heat absorption of 1,680 cal./mole, and Na_2SO_4 (I) melts at 1,157°K. with a heat absorption of 5,670 cal./mole. The measured heat content data are limited in Table I.

TABLE I
HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$\frac{H_T - H_{298.16}}{H_{298.16}}$	T, °K.	$\frac{H_T - H_{298.16}}{H_{298.16}}$	T, °K.	$\frac{H_T - H_{298.16}}{H_{298.16}}$
Na_2SO_4 (III, I, 1) (mol. wt. 142.060)					
370.2	2,380	839.4	23,470	1176.7	45,300
407.7	3,750	955.1	28,670	1208.6	46,930
466.0	6,040	1053.2	33,450	1297.7	51,070
495.1	7,180	1127.8	37,530	1399.5	56,050
504.0	8,570 ^a	1142.8	38,010	1503.2	60,860
514.9	9,590	1162.0	42,950 ^b	1605.2	65,580
546.3	10,900	1164.4	43,090 ^b	1707.5	70,340
625.7	14,160	1164.7	44,760	1826.2	75,790
736.7	18,880				
Na_2SO_4 (V) (mol. wt. 142.060)					
328.0	1,040	395.6	3,340	441.3	5,040
345.6	1,620	426.0	4,480	443.4	5,110
370.6	2,400				

^a Shows pretransition effect. ^b Not completely melted.

Table II contains heat content and entropy increments above 298.16°K. at even 100° intervals and at temperatures of phase transformations. The entropy increments have been calculated to match the heat contents by the method of Kelley.⁸ The third set of heat content and entropy increments (columns 6 and 7) is derived using the results of the heat of solution measurements, which permit evaluation of heat contents referred to Na_2SO_4 (V) at 298.16°K. The basis for this derivation is given below.

The heat contents are represented, to within the average deviation indicated in parentheses, by the

(1) F. C. Kracek and R. E. Gibson, *J. Phys. Chem.*, **34**, 188 (1930).
 (2) K. S. Pitzer and L. V. Coulter, *THIS JOURNAL*, **60**, 1310 (1938).
 (3) W. H. Zachariassen and G. E. Ziegler, *Z. Krist.*, **81**, 92 (1932).
 (4) M. Y. Colby, *ibid.*, **77**, 49 (1931).
 (5) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).
 (6) E. Wichers, *THIS JOURNAL*, **74**, 2447 (1952).

(7) F. C. Kracek and R. E. Gibson, *J. Phys. Chem.*, **33**, 1304 (1929).

(8) K. K. Kelley, U. S. Bur. Mines Bull., 476 (1949).

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	Na ₂ SO ₄ (III, I, 1) ^a		Na ₂ SO ₄ (V) ^b		Na ₂ SO ₄ (V, III, I, 1) ^b	
	H _T - H _{298.16}	S _T - S _{298.16}	H _T - H _{298.16}	S _T - S _{298.16}	H _T - H _{298.16}	S _T - S _{298.16}
350	1,680	5.19	1750	5.41	1,750	5.41
400	3,460	9.94	3520	10.13	3,520	10.13
450	5,370	14.43	5370	14.49	5,370(V)	14.49
450	6,110(III)	16.13
500	7,390	18.69	8,130	20.39
514	7,980(III)	19.85	8,720(III)	21.55
514	9,660(I)	23.12	10,400(I)	24.82
600	13,080	29.27	13,820	30.97
700	17,260	35.71	18,000	37.41
800	21,600	41.50	22,340	43.20
900	26,120	46.82	26,860	48.52
1000	30,850	51.80	31,590	53.50
1100	35,830	56.55	36,370	58.25
1157	38,730(I)	59.12	39,470(I)	60.82
1157	44,400(1)	64.02	45,140(1)	65.72
1200	46,430	65.74	47,170	67.44
1300	51,140	69.51	51,880	71.21
1400	55,860	73.01	56,600	74.71
1500	60,580	76.27	61,320	77.97
1600	65,300	79.31	66,040	81.01
1700	70,200	82.17	70,760	83.87
1800	74,730	84.86	75,470	86.56
1850	77,090	86.16	77,830	87.86

^a Base is Na₂SO₄ (III) at 298.16°K. ^b Base is Na₂SO₄ (V) at 298.16°K.

following equations, derived according to the method of Shomate.⁹

Na₂SO₄ (III):

$$H_T - H_{298.16} = 15.54T + 26.40 \times 10^{-3}T^2 - 6980$$

(0.2%; 298-514°K.)

Na₂SO₄ (I):

$$H_T - H_{298.16} = 29.06T + 9.67 \times 10^{-3}T^2 - 7837$$

(0.1%; 514-1157°K.)

Na₂SO₄ (1):

$$H_T - H_{298.16} = 47.18T - 10,190$$

(0.2%; 1157-1850°K.)

Na₂SO₄ (V):

$$H_T - H_{298.16} = 23.50T + 15.87 \times 10^{-3}T^2 - 8418$$

(0.1%; 298-450°K.)

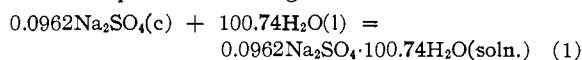
The heat of transition (Na₂SO₄ (V) = Na₂SO₄ (III)) was measured by the heat of solution method in apparatus described by Southard.¹⁰ Some minor improvements were incorporated during the present work. The constant-temperature bath was rebuilt and operated at 30.00°, instead of 25.00° as previously, and a new controller permitting regulation to ±0.002° was installed. A method was devised for correcting individual runs to exactly 30.00°. The calorimeter stirrer was operated at 670 r.p.m. (The heat of stirring was found to be constant at approximately 0.3 cal./min.). The brass-top cover of the calorimeter (labeled "C" in Southard's¹⁰ diagram) was fitted with an oil-tight Tygon gasket, thus permitting the calorimeter to be completely submerged in the constant temperature oil-bath. This resulted in a heat-interchange rate that was virtually independent of room temperature fluctuations.

The heat of solution measurements were made using 1814.9 g. (100.74 moles) of distilled water and an average of 0.0962 mole of sodium sulfate. The energy equivalent of the calorimetric system was determined both before and after each heat of solution measurement. This permitted calculation

(9) C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

(10) J. C. Southard, *Ind. Eng. Chem.*, **32**, 442 (1940).

of the ΔC_p for the average heat of solution reaction



as -6.266 ± 10% cal./deg. or -65.1 ± 6.5 cal./deg. mole for the dissolution 1 mole of sodium sulfate in 1,050 moles of water. Although all the measurements resulted in final temperatures in the range 29.95 to 30.21°, the precision was improved considerably by utilizing this ΔC_p of reaction to correct the measurements to exactly 30.00°. The ΔC_p of reaction may be further utilized for extrapolation of the heat of solution of Na₂SO₄ (V) to 25.00°. This value is -627 + 326 = -301 ± 35 cal./mole at 0.054 molal, compared with Pitzer and Coulter's² average value of -320 cal./mole at 0.050 molal.

The results of the heat of solution measurements are shown in Table III. The calorimeter resistance thermometer and the constant-temperature-bath thermometer were checked by comparison with a thermometer that had been calibrated by the National Bureau of Standards. The resistance thermometer had a measured sensitivity of 1,180 μV./deg. and an absolute reading of 8,890 ± 10 μV. at 30.00°.

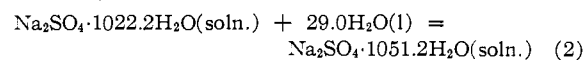
TABLE III

HEATS OF SOLUTION OF Na₂SO₄ (III) AND Na₂SO₄(V) IN 1814.9 G. OF WATER AT 30.00°

Mass, g.	Molal concn. of final soln.	Final temp. of calorimeter, (t, °C.)	Cor. heat of soln. cal./mole
Na ₂ SO ₄ (III)			
14.0152	0.0544	30.054	-1368.0
14.0219	.0544	30.021	-1367.2
14.0631	.0545	30.052	-1358.8
13.5157	.0524	30.073	-1358.9
11.8617	.0460	30.059	-1362.?
12.9158	.0501	30.011	-1364.7
Av.	.0520	Av.	-1363 ± 4
Na ₂ SO ₄ (V)			
14.3860	.0558	29.955	-625.1
14.9333	.0579	29.998	-627.9
13.3525	.0518	30.000	-627.5
13.8541	.0537	30.009	-630.8
13.4207	.0521	30.022	-629.6
Av.	.0543	Av.	-627 ± 3

The results for Na₂SO₄ (V) include a correction of -1.4 cal./mole for the water content of the sample. This involves the assumptions that the water is present as Na₂SO₄·10H₂O and that the +19,080 cal./mole heat of solution measured by Pitzer and Coulter² at 25.00° is valid at 30.00°. The estimated absolute uncertainty in both measurements of Table III is ±10 cal.; the intervals given in the table are precision uncertainties.

Neither set of heat of solution measurements showed dependence on concentration in the range covered, thus verifying the measurements made by Lange and Streeck¹¹ at 25°. As an additional precaution, the heat of the reaction



(11) E. Lange and H. Streeck, *Z. physik. Chem.*, **A157**, 1 (1931).

was determined experimentally. Within the limits of error of measurement, the heat of dilution was zero, *i.e.*, $\Delta H_{303.16} = 0.0 \pm 0.6$ cal./mole, corresponding to a dilution from 0.0543 to 0.0528 molal.

Combination of the two measured heats of solution yields $\Delta H_{303.16} = 735 \pm 15$ cal./mole for the reaction



This result, in conjunction with the heat content values of Table II, leads to $\Delta H_{298.16} = 743 \pm 20$ cal./mole and $\Delta H_{450} = 740 \pm 120$ cal./mole. From

the work of Kracek and Gibson,¹ it is estimated that $\Delta F^\circ = 0$ for this reaction at $450 \pm 5^\circ\text{K}$. Hence, $\Delta S^\circ_{450} = 1.64 \pm 0.30$, from which $\Delta S^\circ_{298} = 1.70$ may be obtained by means of entropy increments in Table II. The latter result and Pitzer and Coulter's value for the entropy of $\text{Na}_2\text{SO}_4(\text{V})$ ($S^\circ_{298.16} = 35.73 \pm 0.10$) yield $S^\circ_{298.16} = 37.4 \pm 0.5$ cal./deg. mole for $\text{Na}_2\text{SO}_4(\text{III})$. Columns 6 and 7 of Table II were obtained by combining the values of ΔH_{450} and ΔS_{450} with the heat content and entropy increments of $\text{Na}_2\text{SO}_4(\text{III}, \text{I}, 1)$ above 450°K .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

X-Ray Crystallography of the Sodium *n*-Alkyl Sulfates¹

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An X-ray crystallographic study has been made of the sodium *n*-alkyl sulfates, for comparison with previous studies of the sodium 1-alkanesulfonates. Six distinct phases are reported, one of which is very similar to the α -phase of the sulfonates. Unit cells and space groups are given for all six phases.

Introduction

As an extension of our previous studies of the sodium 1-alkane sulfonates, RSO_3Na ,³⁻⁷ we have thought it of interest to compare the sodium *n*-alkyl sulfates, RSO_4Na , which may be considered as related to the sulfonates by the replacement of one methylene group by an oxygen atom. The alkyl groups which have been included in the present study are C_6 , C_7 , C_8 , C_9 , C_{10} , C_{11} , C_{12} , C_{14} , C_{16} , C_{18} and C_{20} .

In the work on the sulfonates, six distinct hydrated phases and one anhydrous phase have been recognized and designated α , β , γ , δ , ϵ , ζ , η in the order of their discovery. Because of the extreme similarity in molecular structure between the sulfonates and the sulfates, and therefore the possibility of appearance of identical or similar crystal structures, it was decided to use the same series for the sulfate phases. Thus we shall discuss in this paper the α -phase of the sulfates, which is almost identical with the α -phase of the sulfonates⁸ and the ι , κ , λ , μ and ν phases, which are different from those observed for the sulfonates.

Experimental

With the exception of the *n*-eicosyl alcohol, the normal alcohols used in this work were the purest alcohols obtainable commercially, and no further attempt was made to increase the purity except for the *n*-hexyl and *n*-heptyl alcohols. The *n*-hexyl and *n*-heptyl alcohols were fractionally dis-

tilled under vacuum using a three-foot column having an outside diameter of 18 mm. and packed with small glass helices. The alcohols were obtained from several companies, including the Eastman Kodak Co., Columbia Organic Chemicals Co., Halogen Chemicals, Inc., and the Matheson Co.

The *n*-eicosyl alcohol was made in this Laboratory from *n*-octadecyl bromide (Halogen Chemicals, Inc., Columbia, S. C.) and liquid ethylene oxide (Eastman Kodak Co. white label), using the Grignard reaction. The purity of the *n*-eicosyl alcohol (m.p. 65-65.5°) was checked by comparing the powder pattern with those of known alcohols, namely, the *n*-hexadecyl and *n*-octadecyl alcohols.

All sodium *n*-alkyl sulfates were prepared by the method of Lottermoser and Stoll⁹ with the exception of the sodium *n*-hexyl sulfate and sodium *n*-eicosyl sulfate which were prepared following the procedure outlined by Dreger.¹⁰

The crystals were grown from mixed solvents, primarily ethanol and water, by slow evaporation of the solvent from saturated solutions at constant temperature ($\pm 1^\circ$). The best crystals were grown from solutions which contained no solvents other than ethanol and water. With the sulfonates, improved crystal formation can often be attained by the addition of such solvents as carbon tetrachloride, 1,4-dioxane and glycerol. In the case of the sodium *n*-alkyl sulfates these additions were usually more detrimental than beneficial.

The data in Table I show the most favorable conditions for growing each of the phases. It should be mentioned that the crystals of the ι and λ phases are very unstable at room temperature and effloresce to form the more stable α phase almost immediately. The μ -phase is also unstable at room temperature and changes to the α -phase by absorption of water vapor. The compounds having a chain of less than eleven carbon atoms form only gels if the percentage of water is raised above 5% in ethanol-water mixtures. The crystals, with the exception of the α -phase in the region of C_{10} to C_{12} and the κ -phase for C_{18} and C_{20} , were very small and poorly formed. All the crystals are extremely thin and show a considerable tendency to bend and warp.

An anhydrous phase, which we have designated the ξ phase, is known to exist from powder patterns but single crystal growth has not been attempted up to the present time due to the elaborate precautions which must be taken to grow anhydrous crystals.

The hydrate determinations were made in the apparatus

(1) This work was supported in part under contract DA-04-200-ORD-236 with the Office of Ordnance Research.

(2) Taken from a thesis submitted by F. F. Rawlings, Jr., in partial fulfillment of the requirements for the Ph.D. degree. Procter and Gamble Fellow, 1949-1950.

(3) L. H. Jensen and E. C. Lingafelter, *THIS JOURNAL*, **66**, 1946 (1944).

(4) L. H. Jensen and E. C. Lingafelter, *ibid.*, **68**, 1729 (1946).

(5) E. C. Lingafelter and L. H. Jensen, *Acta Cryst.*, **3**, 257 (1950).

(6) J. E. Minor and E. C. Lingafelter, *ibid.*, **4**, 183 (1951).

(7) L. A. Wilcox and E. C. Lingafelter, *THIS JOURNAL*, **75**, 5761 (1953).

(8) F. F. Rawlings, Jr. and E. C. Lingafelter, *ibid.*, **72**, 1852 (1950).

(9) A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).

(10) E. E. Dreger, G. I. Keim, G. D. Miles, Leo Shedlovsky and John Ross, *Ind. Eng. Chem.*, **36**, 610 (1944).