Sodium (Na) REFERENCE STATE $A_r = 22.98977$ Sodium (Na) $Na_1(ref)$

0 to 370.98 K crystal
370.98 to 1170.525 K liquid
above 117.525 K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	C_p HUMP MAXIMUM		
55.120	18.791	11.738	121.072	−6.027	TRANSITION		
100	22.451	23.814	74.885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	CRYSTAL <--> LIQUID		
370.980	31.827	64.915	52.098	4.755	TRANSITION		
400	31.510	67.301	53.116	5.674	0.	0.	0.
500	30.552	74.225	56.675	8.775	0.	0.	0.
600	29.807	79.726	60.074	11.791	0.	0.	0.
700	29.271	84.278	63.216	14.743	0.	0.	0.
800	28.945	88.163	66.097	17.652	0.	0.	0.
900	28.836	91.564	68.742	20.540	0.	0.	0.
1000	28.945	94.606	71.179	23.427	0.	0.	0.
1100	29.259	97.377	73.436	26.335	0.	0.	0.
1170.525	29.613	99.206	74.934	28.411	LIQUID <--> IDEAL GAS		
1170.525	20.786	182.094	74.934	125.433	FUGACITY = 1 bar		
1200	20.786	182.611	77.573	126.046	0.	0.	0.
1300	20.786	184.275	85.717	128.124	0.	0.	0.
1400	20.786	185.815	92.813	130.203	0.	0.	0.
1500	20.787	187.249	99.061	132.282	0.	0.	0.
1600	20.787	188.591	104.616	134.360	0.	0.	0.
1700	20.789	189.851	109.593	136.439	0.	0.	0.
1800	20.792	191.039	114.085	138.518	0.	0.	0.
1900	20.797	192.164	118.165	140.598	0.	0.	0.
2000	20.805	193.231	121.892	142.678	0.	0.	0.
2100	20.816	194.246	125.313	144.759	0.	0.	0.
2200	20.833	195.215	128.469	146.841	0.	0.	0.
2300	20.856	196.141	131.391	148.925	0.	0.	0.
2400	20.886	197.029	134.108	151.012	0.	0.	0.
2500	20.924	197.883	136.642	153.103	0.	0.	0.
2600	20.973	198.704	139.013	155.198	0.	0.	0.
2700	21.032	199.497	141.238	157.298	0.	0.	0.
2800	21.104	200.263	143.333	159.405	0.	0.	0.
2900	21.189	201.005	145.309	161.519	0.	0.	0.
3000	21.289	201.725	147.177	163.643	0.	0.	0.
3100	21.403	202.425	148.948	165.777	0.	0.	0.
3200	21.535	203.106	150.630	167.924	0.	0.	0.
3300	21.680	203.771	152.230	170.084	0.	0.	0.
3400	21.845	204 421	153.756	172.260	0.	0.	0.
3500	22.030	205.057	155.213	174.454	0.	0.	0.
3600	22.234	205.680	156.606	176.667	0.	0.	0.
3700	22.460	206.292	157.941	178.901	0.	0.	0.
3800	22.709	206.894	159.221	181.160	0.	0.	0.
3900	22.981	207.488	160.451	183.444	0.	0.	0.
4000	23.278	208.073	161.634	185.757	0.	0.	0.
4100	23.602	208.652	162.774	188.100	0.	0.	0.
4200	23.945	209.224	163.873	190.475	0.	0.	0.
4300	24.324	209.792	164.934	192.889	0.	0.	0.
4400	24.611	210.345	165.959	195.298	0.	0.	0.
4500	24.992	210.901	166.952	197.769	0.	0.	0.
4600	25.421	211.454	167.913	200.289	0.	0.	0.
4700	25.876	212.006	168.846	202.854	0.	0.	0.
4800	26.359	212.556	169.750	205.466	0.	0.	0.
4900	26.868	213.104	170.630	208.127	0.	0.	0.
5000	27.388	213.651	171.484	210.832	0.	0.	0.
5200	28.537	214.747	173.127	216.423	0.	0.	0.
5400	29.789	215.847	174.689	222.254	0.	0.	0.
5600	31 141	216.955	176.179	228.346	0.	0.	0.
5800	32.583	218.073	177.604	234.717	0.	0.	0.
6000	33.880	219.173	178.969	241.226	0.	0.	0.

PREVIOUS June 1962 (1 atm) CURRENT: June 1962 (1 bar)

Sodium (Na) CRYSTAL $A_r = 22.98977$ Sodium (Na) $Na_1(cr)$

$S°(298.15\ K) = 51.455\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 370.98 \pm 0.02\ K$

$\Delta_f H°(0\ K) = 0\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 2.602\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Martin[1] reports that the low temperature heat capacity of sodium depends on the thermal history of the sample and ascribes this to a martensitic transformation. The effect is most pronounced in the range 40–80 K, where the graph of C_p against T increases continuously for some samples and rises to a peak at 55 K for others. Martin[1] lists heat capacities obtained in several runs on "high purity" sodium at 21 to 300 K and the higher values, those defining the peak at 55 K, have been selected here The heat capacities reported by Dauphinee *et al.*,[2] have not been used, since one of the authors in a later publication, Martin[1] questions the accuracy of the measurements above 100 K, and at lower temperatures there is no rise to a peak at 55 K. In the range 1.5 to 20 K, Roberts[3] and Parkinson and Quarrington[4] have measured the heat capacity of very high purity sodium. The values of Parkinson and Quarrington[4] are somewhat higher than those of Roberts[3] and have been given greater weight, since they show better continuity with Martin's[1] results The results of Pickard and Simon[5] have been rejected below 10 K, since they show a peak between 5 and 8 K, a feature not verified by other workers; between 10 and 25 K they agree exactly with the results of Parkinson and Quarrington.[4] Rayne[6] states that the graph of C_p against T has a small peak at about 0.9 K. This peak has not been observed in the work of Lien and Phillips[7] from 0.15 to 1 K, Gaumer and Heer from 0.4 to 2 K and Martin[9] from 0.4 to 1.5 K.

Douglas *et al.*[10] report heat capacities in the range 273 to 1173 K on a sample of not less than 99.9% purity. These values agree to within 1% with those of Martin[1] in the range 273 to 300 K, and the two sets of dates have been smoothly joined.

Fusion Data

Douglas *et al.*[10] have determined the triple point to be 97.82 ± 0.02°C, from which the melting point is calculated to be 97.83 ± 0.02°C, and have measured the enthalpy of fusion.

Sublimation Data

At the boiling point and higher temperatures sodium vapor contains an appreciable proportion of diatomic moleculses. Thompson and Garelis[11] have made a careful analysis of the available vapor pressure data. Their results are consistent with the Gibbs energy functions calculated in the present work and have been adopted.

References

[1] D. L. Martin, Proc. Roy. Soc. A254, 433 (1960).
[2] T. M. Dauphinee, D. L. Martin, and H. Preston–Thomas, Proc. Roy. Soc. A233, 214 (1955).
[3] L. M. Roberts, Proc. Phys. Soc. B70, 744 (1957).
[4] D. H. Parkinson and J. E. Quarrington Proc. Phys. Soc. A68, 762 (1955).
[5] G. L. Pickard and F. E. Simon, Proc. Phys. Soc. 61, 1 (1948).
[6] J. Rayne, Phys. Rev. 95, 1428 (1954).
[7] W. H. Lien and N. E. Phillips, Phys. Rev. 118, 958 (1960).
[8] R. E. Gaumer and C. V. Heer, Phys. Rev. 118, 955 (1960).
[9] D. L. Martin, Phys. Rev. 124, 438 (1961).
[10] T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952).
[11] G. W. Thompson and E. Garelis "Sodium–its Manufacture, Properties and Uses," Ed. M. Sittig, Chapter 3, Reinhold Publishing Corporation, Inc., New York (1956).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	C_p HUMP MAXIMUM TRANSITION		
55.120	18.791	11.738	121.072	−6.027			
100	22.451	23.814	74 885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
350	30.142	56.104	51.805	1.505	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	--- CRYSTAL <--> LIQUID ---		
400	32.489	60.315	52.608	3.083	−2.591	0.203	−0.027
450	33.103	64.180	53.683	4.724	−2.513	0.548	−0.064
500	33.472	67.689	54.910	6.389	−2.386	0.882	−0.092
600	33.472	73.792	57.564	9.736	−2.055	1.506	−0.131
700	33.472	78.951	60.260	13.084	−1.660	2.069	−0.154
800	33.472	83.421	62.882	16.431	−1.222	2.572	−0.168
900	33.472	87.363	65.388	19.778	−0.762	3.019	−0.175
1000	33.472	90.890	67.765	23.125	−0.302	3.414	−0.178

PREVIOUS: CURRENT· June 1962

Sodium (Na) LIQUID $A_r = 22.98977$ Sodium (Na) $Na_1(l)$

$S°(298.15 K) = [57.862] J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15 K) = [2.406] kJ·mol^{-1}$

$T_{fus} = 370.98 \pm 0.02 K$ $\Delta_{fus}H° = 2.602 kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Na, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(370.98 K)-H°(298.15 K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity values are derived from the enthalpy measurements of Douglas *et al.*[1] The heat capacity curve was extrapolated to 298 15 K and 2000 K in a reasonable manner.

The entropy is calculated in a manner anologous to that used for the enthalpy of formation.

Fusion Data

The enthalpy of fusion and the melting point were measured by Douglas *et al.*[1]

Vaporization Data

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm at 1156 K. The vapor pressure of the monatomic gas reaches 1 atm at 1176.9 K and the enthalpy of vaporization to monatomic gas is 23.285 kcal·mol^{-1}.

Reference

[1] T. B. Douglas, A. F. Ball, D. C. Ginnmgs and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	32.706	57.862	57.862	0.	2.406	0.495	−0.087
300	32.685	58.064	57.863	0.060	2.414	0.483	−0.084
350	32.068	63.056	58.258	1.679	2.580	0.147	−0.022
370.9180	31.827	64.915	58.583	2.349	--- CRYSTAL <--> LIQUID ---		
400	31.510	67.301	59.130	3.268	0.	0.	0.
450	31.004	70.982	60.247	4.831	0.	0.	0.
500	30.552	74.225	61.486	6.370	0.	0.	0.
600	29.807	79.726	64.083	9.386	0.	0.	0.
700	29.271	84.278	66.652	12.338	0.	0.	0.
800	28.945	88.163	69.104	15.247	0.	0.	0.
900	28.836	91.564	71.415	18.134	0.	0.	0.
1000	28.945	94.606	73.584	21.021	0.	0.	0.
1100	29.259	97.377	75.623	23.930	0.	0.	0.
1170.525	29.613	99.206	76.989	26.005	----- FUGACITY = 1 bar -----		
1200	29.790	99.945	77.544	26.881	−96.760	2.440	−0.106
1300	30.514	102.357	79.361	29.895	−95.824	10.669	−0.429
1400	31.351	104.649	81.086	32.988	−94.809	18.823	−0.702
1500	32.188	106.840	82.730	36.165	−93.711	26.902	−0.937
1600	33.024	108.944	84.303	39.426	−92.529	34.905	−1.140

PREVIOUS: CURRENT. June 1962

Sodium (Na)

CRYSTAL-LIQUID

0 to 370.98 K crystal
above 370.98 K liquid

Refer to the individual tables for details.

$A_r = 22.98977$ Sodium (Na) Na (cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	C_p HUMP MAXIMUM TRANSITION		
55.120	18.791	11.738	121.072	−6.027			
100	22.451	23.814	74.885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
350	30.142	56.104	51.805	1.505	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	CRYSTAL <--> LIQUID TRANSITION		
370.980	31.827	64.915	52.098	4.755			
400	31.510	67.301	53.116	5.674	0.	0.	0.
450	31.004	70.982	54.901	7.236	0.	0.	0.
500	30.552	74.225	56.675	8.775	0.	0.	0.
600	29.807	79.726	60.074	11.791	0.	0.	0.
700	29.271	84.278	63.216	14.743	0.	0.	0.
800	28.945	88.163	66.097	17.652	0.	0.	0.
900	28.836	91.564	68.742	20.540	0.	0.	0.
1000	28.945	94.606	71.179	23.427	0.	0.	0.
1100	29.259	97.377	73.436	26.335	0.	0.	0.
1170.525	29.613	99.206	74.934	28.411	----- FUGACITY = 1 bar -----		
1200	29.790	99.945	75.539	29.286	−96.760	2.440	−0.106
1300	30.514	102.357	77.510	32.300	−95.824	10.669	−0.429
1400	31.351	104.649	79.368	35.394	−94.809	18.823	−0.702
1500	32.188	106.840	81.127	38.571	−93.711	26.902	−0.937
1600	33.024	108.944	82.800	41.831	−92.529	34.905	−1.140

PREVIOUS: CURRENT. June 1962

Sodium (Na) Na_1(cr,l)

Sodium (Na) **IDEAL GAS** $A_r = 22.98977$ **Sodium (Na)** **$Na_1(g)$**

IP(Na, g) = 41449.44 ± 0.03 cm^{-1}
$S°$(298.15 K) = 153.667 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_fH°$(0 K) = 107.5 ± 0.7 $kJ·mol^{-1}$
$\Delta_fH°$(298.15 K) = 107.3 ± 0.7 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2
$^2P_{1/2}$	16956.172	2
$^2P_{3/2}$	16973.368	4
$^2S_{1/2}$	25739.991	2
.	.	.
.	.	.
.	.	.
$^2P_{3/2}$	41404.006	4
IP	41449.44	

Enthalpy of Formation

The enthalpy of formation of sodium gas, $\Delta_fH°$(298.15 K) = 107.5 ± 0.7 $kJ·mol^{-1}$, is chosen to be the value recommended by CODATA.[1] This value was obtained from 2nd and 3rd law treatment of vapor pressure data. The reported vapor pressures were corrected for the effects of $Na_2(g)$, using D_0° = 70.63 $kJ·mol^{-1}$. At higher pressures, an alternate virial treatment was employed.

As stated by CODATA,[1] the selected value is the weighted average of the 3rd law values of $\Delta_{sub}H°$(298.15 K) calculated from the following:

Source	$\Delta_{sub}H°$(298.15 K), $kJ·mol^{-1}$
Haycock and Lamplough[2]	107.52 ± 0.68
Rodebush and Devries[3]	107.37 ± 0.60
Thiele[4]	107.99 ± 0.60
Kis Tiakowsky[5]	107.38 ± 0.70
Makansi *et al.*[6]	107.18 ± 0.95
Shpil'rain and Belova[7]	107.26 ± 0.78
Sowa[8]	107.60 ± 1.35
Stone *et al.*[9]	107.68 ± 1.33
Achener and Jouthas[10]	107.85 ± 0.80
Vinogradov and Volyak[11]	107.44 ± 0.60
Bohdansky and Schins[12]	107.47 ± 1.00
Schins *et al.*[13]	107.36 ± 1.22

The 2nd law calculations from the above sources led to somewhat more positive values.[1]

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[15]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[15]

The atomic energy levels have been taken from the compilation of Martin and Zalubas.[14] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	-6.197	107.549	107.549	INFINITE
100	20.786	130.960	172.147	-4.119	108.288	97.574	-50.967
200	20.786	145.367	155.568	-2.040	107.911	86.977	-22.716
250	20.786	150.006	154.009	-1.001	107.626	81.776	-17.086
298.15	20.786	153.667	153.667	0.	107.300	76.825	-13.460
300	20.786	153.795	153.667	0.038	107.286	76.636	-13.344
350	20.786	157.000	153.920	1.078	106.873	71.560	-10.680
400	20.786	159.775	154.482	2.117	103.743	66.753	-8.717
450	20.786	162.223	155.209	3.156	103.220	62.161	-7.216
500	20.786	164.413	156.022	4.196	102.721	57.626	-6.020
600	20.786	168.203	157.746	6.274	101.783	48.697	-4.239
700	20.786	171.407	159.475	8.353	100.909	39.919	-2.979
800	20.786	174.183	161.144	10.431	100.079	31.263	-2.041
900	20.786	176.631	162.731	12.510	99.270	22.710	-1.318
1000	20.786	178.821	164.232	14.589	98.462	14.246	-0.744
1100	20.786	180.802	165.650	16.667	97.632	5.865	-0.278
1170.525	20.786	182.094	166.602	18.133	----- FUGACITY = 1 bar -----		
1200	20.786	182.611	166.989	18.746	0.	0.	0.
1300	20.786	184.275	168.256	20.824	0.	0.	0.
1400	20.786	185.815	169.456	22.903	0.	0.	0.
1500	20.787	187.249	170.595	24.982	0.	0.	0.
1600	20.787	188.591	171.678	27.060	0.	0.	0.
1700	20.789	189.851	172.710	29.139	0.	0.	0.
1800	20.792	191.039	173.696	31.218	0.	0.	0.
1900	20.797	192.164	174.639	33.298	0.	0.	0.
2000	20.805	193.231	175.542	35.378	0.	0.	0.
2100	20.816	194.246	176.408	37.459	0.	0.	0.
2200	20.833	195.215	177.241	39.541	0.	0.	0.
2300	20.856	196.141	178.043	41.626	0.	0.	0.
2400	20.886	197.029	178.816	43.713	0.	0.	0.
2500	20.924	197.883	179.562	45.803	0.	0.	0.
2600	20.973	198.704	180.282	47.898	0.	0.	0.
2700	21.032	199.497	180.979	49.998	0.	0.	0.
2800	21.104	200.263	181.654	52.105	0.	0.	0.
2900	21.189	201.005	182.309	54.219	0.	0.	0.
3000	21.289	201.725	182.944	56.343	0.	0.	0.
3100	21.403	202.425	183.561	58.477	0.	0.	0.
3200	21.535	203.106	184.161	60.624	0.	0.	0.
3300	21.680	203.771	184.746	62.784	0.	0.	0.
3400	21.845	204.421	185.315	64.960	0.	0.	0.
3500	22.030	205.057	185.870	67.154	0.	0.	0.
3600	22.234	205.680	186.411	69.367	0.	0.	0.
3700	22.460	206.292	186.941	71.601	0.	0.	0.
3800	22.709	206.894	187.458	73.860	0.	0.	0.
3900	22.981	207.488	187.964	76.144	0.	0.	0.
4000	23.278	208.073	188.459	78.457	0.	0.	0.
4100	23.602	208.652	188.945	80.800	0.	0.	0.
4200	23.945	209.224	189.421	83.175	0.	0.	0.
4300	24.324	209.792	189.888	85.589	0.	0.	0.
4400	24.611	210.345	190.346	87.998	0.	0.	0.
4500	24.992	210.901	190.796	90.469	0.	0.	0.
4600	25.421	211.454	191.239	92.990	0.	0.	0.
4700	25.876	212.006	191.675	95.554	0.	0.	0.
4800	26.359	212.556	192.105	98.166	0.	0.	0.
4900	26.868	213.104	192.528	100.827	0.	0.	0.
5000	27.388	213.651	192.944	103.533	0.	0.	0.
5100	27.949	214.199	193.356	106.299	0.	0.	0.
5200	28.537	214.747	193.762	109.123	0.	0.	0.
5300	29.150	215.297	194.163	112.007	0.	0.	0.
5400	29.789	215.847	194.560	114.954	0.	0.	0.
5500	30.453	216.400	194.952	117.966	0.	0.	0.
5600	31.141	216.955	195.340	121.046	0.	0.	0.
5700	31.851	217.512	195.724	124.195	0.	0.	0.
5800	32.583	218.073	196.104	127.417	0.	0.	0.
5900	33.334	218.636	196.481	130.712	0.	0.	0.
6000	33.880	219.173	196.852	133.926	0.	0.	0.

PREVIOUS: June 1962 (1 atm) — CURRENT December 1983 (1 bar)

Sodium (Na) **$Na_1(g)$**

Sodium, Ion (Na^+) IDEAL GAS $M_r = 22.98922$ Sodium, Ion (Na^+) $Na_1^+(g)$

IP(Na^+, g) = 381390 ± 50 eV
$S°(298.15\ K) = 147.953 \pm 0.025\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 603.4 \pm 0.7\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [609.343]\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(Na^+, g, 0\ K)$ is calculated from $\Delta_f H°(Na, g, 0\ K)$[1] using the spectroscopic value of IP(Na) = 41449.44 ± 0.03 cm^{-1}(495.846 ± 0.0000 $kJ{\cdot}mol^{-1}$) from Martin and Zolubas.[2] The ionization limit is converted from cm^{-1} to $kJ{\cdot}mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ{\cdot}mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Na^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Na, g, 0\ K)$ by using IP(Na) with JANAF[1] enthalpies, $H°(0\ K)–H°(298.15\ K)$, for Na(g), Na^+(g), and e^-(ref). $\Delta_r H°(Na \rightarrow Na^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ{\cdot}mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zolubas,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 264924 cm^{-1} above the ground state Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1] JANAF Thermochemical Tables: Na(g), 12–31–83; e^-(ref), 3–31–82.
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[3] E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4] H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
[5] R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS–NBS–71, (1982).
[6] J R. Downey, The Dow Chemical Company, AFOSR–TR–78–960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	603.395		
100	20.786	125.246	166.434	−4.119			
200	20.786	139.654	149.855	−2.040			
250	20.786	144.292	148.296	−1.001			
298.15	20.786	147.953	147.953	0.	609.343	574.317	−100.618
300	20.786	148.082	147.954	0.038	609.368	574.100	−99.960
350	20.786	151.286	148.207	1.078	609.994	568.171	−84.795
400	20.786	154.062	148.769	2.117	607.903	562.364	−73.437
450	20.786	156.510	149.496	3.156	608.419	556.641	−64.613
500	20.786	158.700	150.309	4.196	608.959	550.859	−57.548
600	20.786	162.490	152.033	6.274	610 100	539.133	−46.936
700	20.786	165.694	153.761	8.353	611.305	527.211	−39.341
800	20.786	168.470	155.430	10.431	612.553	515.112	−33.633
900	20.786	170.918	157.018	12.510	613.823	502.856	−29.185
1000	20.786	173.108	158.519	14.589	615.093	490.458	−25.619
1100	20.786	175.089	159.937	16.667	616.342	477.934	−22.695
1200	20.786	176.898	161.276	18.746	520.789	467.738	−20.360
1300	20.786	178.561	162.542	20.824	522.867	463.232	−18.613
1400	20.786	180.102	163.742	22.903	524.946	458.567	−17.109
1500	20.786	181.536	164.881	24.982	527.025	453.753	−15.801
1600	20.786	182.877	165.965	27.060	529.103	448.801	−14.652
1700	20.786	184.137	166.997	29.139	531.181	443.718	−13.634
1800	20.786	185.326	167.982	31.217	533.260	438.513	−12.725
1900	20.786	186.449	168.925	33.296	535.337	433.193	−11.909
2000	20.786	187.516	169.828	35.375	537.415	427.763	−11.172
2100	20.786	188.530	170.695	37.453	539.491	422.229	−10.502
2200	20.786	189.497	171.528	39.532	541.566	416.597	−9.891
2300	20.786	190.421	172.329	41.610	543.638	410.870	−9.331
2400	20.786	191.305	173.102	43.689	545.709	405.053	−8.816
2500	20.786	192.154	173.847	45.768	547.775	399.150	−8.340
2600	20.786	192.969	174.567	47.846	549.838	393.164	−7.899
2700	20.786	193.754	175.263	49.925	551.895	387.099	−7.489
2800	20.786	194.509	175.937	52.004	553.945	380.958	−7.107
2900	20.786	195.239	176.590	54.082	555.988	374.744	−6.750
3000	20.786	195.944	177.223	56.161	558.021	368.460	−6.415
3100	20.786	196.625	177.838	58.239	560.044	362.107	−6.101
3200	20.786	197.285	178.436	60.318	562.055	355.690	−5.806
3300	20.786	197.925	179.017	62.397	564.052	349.210	−5.528
3400	20.786	198.545	179.582	64.475	566.033	342.670	−5.264
3500	20.786	199.148	180.132	66.554	567.997	336.072	−5.016
3600	20.786	199.733	180.669	68.632	569.941	329.418	−4.780
3700	20.786	200.303	181.192	70.711	571.863	322.710	−4.556
3800	20.786	200.857	181.702	72.790	573.762	315.951	−4.343
3900	20.786	201.397	182.200	74.868	575.635	309.142	−4.140
4000	20.786	201.923	182.687	76.947	577.480	302.285	−3.947
4100	20.786	202.437	183.162	79.025	579.293	295.383	−3.763
4200	20.786	202.937	183.627	81.104	581.075	288.437	−3.587
4300	20.786	203.427	184.082	83.183	582.819	281.448	−3.419
4400	20.786	203.904	184.527	85.261	584.567	274.417	−3.258
4500	20.786	204.372	184.963	87.340	586.253	267.348	−3.103
4600	20.786	204.828	185.390	89.418	587.890	260.243	−2.955
4700	20.786	205.275	185.808	91.497	589.483	253.103	−2.813
4800	20.786	205.713	186.218	93.576	591.028	245.929	−2.676
4900	20.786	206.142	186.620	95.654	592.524	238.724	−2.545
5000	20.786	206.562	187.015	97.733	593.976	231.488	−2.418
5100	20.786	206.973	187.402	99.811	595.366	224.225	−2.297
5200	20.786	207.377	187.783	101.890	596.700	216.934	−2.179
5300	20.786	207.773	188.156	103.969	597.973	209.619	−2.066
5400	20.786	208.161	188.523	106.047	599.183	202.280	−1.957
5500	20.786	208.543	188.883	108.126	600.328	194.919	−1.851
5600	20.786	208.917	189.238	110.204	601.406	187.539	−1.749
5700	20.786	209.285	189.586	112.283	602.414	180.139	−1.651
5800	20.786	209.647	189.929	114.362	603.349	172.722	−1.556
5900	20.786	210.002	190.266	116.440	604.211	165.290	−1.463
6000	20.786	210.351	190.598	118.519	605.155	157.826	−1.374

PREVIOUS: March 1965 (1 atm)   CURRENT. December 1983 (1 bar)

Sodium, Ion (Na^-) IDEAL GAS $M_r = 22.99032$ Sodium, Ion (Na^-) $Na_1^-g)$

EA(Na, g) = 0.547930 ± 0.000025 eV
$S°(298.15\text{ K}) = 147.954 \pm 0.005\ \text{J·K}^{-1}\text{·mol}^{-1}$

$\Delta_fH°(0\text{ K}) = 54.68 \pm 0.1\ \text{kJ·mol}^{-1}$
$\Delta_fH°(298.15\text{ K}) = [48.236]\ \text{kJ·mol}^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for Na^-(g) is calculated from the adopted electron affinity, EA(Na, g) = 0.547930 ± 0 000025 eV (52.867 ± 0.002 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[6] was measured by a tunable laser detachment threshold technique.[2] Additional discussion on Na^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[1 6] Rosenstock *et al.*,[3] and Massey.[4]

$\Delta_fH°(Na^-, g, 298.15\text{ K})$ is obtained from $\Delta_fH°(Na, g, 0\text{ K})$ by using EA(Na, g) with JANAF[5] enthalpies, $H°(0\text{ K})–H°(298.15\text{ K})$, for Na^-(g), Na(g), and e^-(ref). $\Delta_rH°(Na^- \rightarrow Na + e^-, 298.15\text{ K})$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_fH°(298.15\text{ K})$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Na^-(g) is given by Hotop and Lineberger[1 6] and Rosenstock *et al.*[3] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

[1] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).
[2] P. A. Schulz, R. D. Mead, and W. C. Lineberger, Phys. Rev. A, in preparation.
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[5] JANAF Thermochemical Tables: Na(g), 3–31–82; e^-(ref), 3–31–82.
[6] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, 14, 731 (1985).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−6.197	54.683		
100	20.786	125.247	166.434	−4.119			
200	20.786	139.655	149.855	−2.040			
250	20.786	144.293	148.296	−1.001			
298.15	20.786	147.954	147.954	0.	48.236	25.719	−4.506
300	20.786	148.083	147.954	0.038	48.184	25.580	−4.454
350	20.786	151.287	148.207	1.078	46.731	21.926	−3.272
400	20.786	154.062	148.770	2.117	42.562	18.692	−2.441
450	20.786	156.511	149.496	3.156	40.999	15.803	−1.834
500	20.786	158.701	150.309	4.196	39.461	13.086	−1.367
600	20.786	162.490	152.033	6.274	36.445	8.095	−0.705
700	20.786	165.695	153.762	8.353	33.492	3.604	−0.269
800	20.786	168.470	155.431	10.431	30.583	−0.467	0.030
900	20.786	170.918	157.018	12.510	27.696	−4.174	0.242
1000	20.786	173.108	158.520	14.589	24.809	−7.561	0.395
1100	20.786	175.090	159.937	16.667	21.900	−10.657	0.506
1200	20.786	176.898	161.277	18.746	−77.810	−11.047	0.481
1300	20.786	178.562	162.543	20.824	−79.889	−5.400	0.217
1400	20.786	180.102	163.743	22.903	−81.967	0.408	−0.015
1500	20.786	181.536	164.882	24.982	−84.046	6.365	−0.222
1600	20.786	182.878	165.965	27.060	−86.125	12.460	−0.407
1700	20.786	184.138	166.998	29.139	−88.203	18.685	−0.574
1800	20.786	185.326	167.983	31.217	−90.282	25.033	−0.726
1900	20 786	186.450	168.926	33.296	−92.362	31.496	−0.866
2000	20.786	187.516	169.829	35.375	−94.442	38.069	−0.994
2100	20.786	188.530	170.695	37.453	−96.523	44.745	−1.113
2200	20.786	189.497	171.528	39.532	−98.605	51.521	−1.223
2300	20.786	190.421	172.330	41.610	−100.690	58.392	−1.326
2400	20.786	191.306	173.102	43.689	−102.777	65.353	−1.422
2500	20.786	192.154	173.847	45.768	−104.867	72.401	−1.513
2600	20.786	192.970	174.567	47.846	−106.962	79.533	−1.598
2700	20.786	193.754	175.263	49.925	−109.062	86.746	−1.678
2800	20.786	194.510	175.937	52.004	−111.169	94.037	−1.754
2900	20.786	195.239	176.590	54.082	−113.283	101.403	−1.826
3000	20.786	195.944	177.224	56.161	−115.407	108.842	−1.895
3100	20.786	196.626	177.839	58.239	−117.541	116.352	−1.961
3200	20.786	197.286	178.436	60.318	−119.688	123.931	−2.023
3300	20.786	197.925	179.017	62.397	−121.848	131.578	−2.083
3400	20.786	198.546	179.583	64.475	−124.024	139.290	−2.140
3500	20.786	199.148	180.133	66.554	−126.218	147.066	−2.195
3600	20.786	199.734	180.669	68.632	−128.431	154.906	−2.248
3700	20.786	200.303	181.192	70.711	−130.665	162.807	−2.298
3800	20.786	200.858	181.703	72.790	−132.924	170.769	−2.347
3900	20.786	201.398	182.201	74.868	−135.208	178.790	−2.395
4000	20.786	201.924	182.687	76.947	−137.521	186.871	−2.440
4100	20.786	202.437	183.163	79.025	−139.865	195.010	−2.484
4200	20.786	202.938	183.628	81.104	−142.239	203.206	−2.527
4300	20.786	203.427	184.082	83.183	−144.653	211.459	−2.569
4400	20.786	203.905	184.528	85.261	−147.062	219.766	−2.609
4500	20.786	204.372	184.963	87.340	−149.533	228.130	−2.648
4600	20.786	204.829	185.390	89.418	−152.054	236.550	−2.686
4700	20.786	205.276	185.809	91.497	−154.618	245.026	−2.723
4800	20.786	205.714	186.219	93.576	−157.230	253.556	−2.759
4900	20.786	206.142	186.621	95.654	−159.891	262.142	−2.794
5000	20.786	206.562	187.016	97.733	−162.597	270.781	−2.829
5100	20.786	206.974	187.403	99.811	−165.363	279.476	−2.862
5200	20.786	207.377	187.783	101.890	−168.187	288.226	−2.895
5300	20.786	207.773	188.157	103.969	−171.071	297.031	−2.927
5400	20.786	208.162	188.524	106.047	−174 018	305.890	−2.959
5500	20.786	208.543	188.884	108.126	−177.030	314.805	−2.990
5600	20.786	208.918	189.239	110.204	−180.110	323.775	−3.020
5700	20.786	209.286	189.587	112.283	−183.259	332.801	−3.050
5800	20.786	209.647	189.930	114.362	−186.481	341.883	−3.079
5900	20.786	210.003	190.267	116.440	−189.776	351.020	−3.108
6000	20.786	210.352	190.599	118.519	−192.990	360.197	−3.136

PREVIOUS: CURRENT: December 1983 (1 bar)

Sodium Oxide (NaO) IDEAL GAS $M_r = 38.98917$

$S°(298.15\ K) = [229.13 \pm 2.1]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [85.04 \pm 41.8]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [83.68 \pm 41.8]\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$[^2\Pi]$	0	[4]

$\omega_e = [440]\ cm^{-1}$ $\quad \omega_e x_e = [3.0]\ cm^{-1}$ $\quad \sigma = 1$
$B_e = [0.4467]\ cm^{-1}$ $\quad \alpha_e = [0.0043]\ cm^{-1}$ $\quad r_e = [2.0]$ Å

Enthalpy of Formation

Bawn and Evans[1] studied the reaction rate of sodium vapor with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite, using the diffusion flame method. On the evidence of reaction rate measurements they estimated the value, $\Delta_r H°(298.15\ K) < 0$, for the reaction $Na(g) + NO_2(g) = NaO(g) + NO(g)$. Based on this result, we calculate $\Delta_f H°(NaO,\ g,\ 298.15\ K) > 12\ kcal{\cdot}mol^{-1}$, using $\Delta_f H°(298.15\ K) = 25.8$, 7.9 and 21.6 kcal·mol^{-1} for Na(g), $NO_2(g)$ and NO(g), respectively.

Assuming that $D_0°(NaO) = 1/2\ [D_0°(Na_2) + D_0°(O_2)]$, or $\Delta_r H°(0\ K) = 68.1\ kcal{\cdot}mol^{-1}$ for the reaction $NaO(g) = Na(g) + O(g)$, we derive $\Delta_f H° = 16.7$ and $\Delta_f H°(298\ 15\ K) = 16.4\ kcal{\cdot}mol^{-1}$, using $\Delta_f H°(0\ K) = 25.8$ and 59.0 kcal·mol^{-1} for Na(g) and O(g), respectively.

Somayajulu[2] found that in a sequence of similar diatomic molecules the force constant (k_e), dissociation energy ($D_0°$ and equilibrium bond distance (r_e) are related by the expression $k_e r_e(D_0° = $ constant. Using $r_e = 1.62$ Å,$D_0° = 77.9\ kcal{\cdot}mol^{-1}$ for LiO(g), $r_e = 2.0$ Å for NaO(g) and $k_e(NaO)/k_e(LiO) = 0.4827$, we evaluate $D_0° = 65.4\ kcal{\cdot}mol^{-1}$ for NaO(g), yielding $\Delta_f H°(NaO,\ g,\ 298.15\ K) = 19.4\ kcal{\cdot}mol^{-1}$. The value k_e is calculated from the relation $k_e = 4\ ^2\mu^2$where is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta_f H°(NaO,\ g,\ 298.15\ K)$ is tentatively adopted as 20 ± 10 kcal·mol^{-1}. The corresponding $D_0°(NaO)$ is 65 ± 10 kcal·mol^{-1}.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for OH(g) which has the same number of valence electrons as NaO(g). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiO(g), LiF(g) and NaF(g). The value of r_e is estimated from those for OH(g), HF(g) and NaF(g). B_e and α_e are derived from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg.[3]

References

[1] C. E. H. Bawn and A. G Evans, Trans. Faraday Soc. 33, 1571 (1937).
[2] G. R. Somayajulu, J. Chem. Phys. 33, 1541 (1960).
[3] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

Sodium Oxide (NaO) $Na_1O_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.427	85.042	85.042	INFINITE
100	29.760	193.820	258.890	−6.507	85.169	76.834	−40.134
200	33.116	215.486	232.293	−3.361	84.404	68.794	−17.967
250	34.324	223.013	229.708	−1.674	84.038	64.935	−13.567
298.15	35.147	229.133	229.133	0.	83.680	61.287	−10.737
300	35.173	229.351	229.134	0.065	83.666	61.149	−10.647
350	35.777	234.821	229.565	1.840	83.249	57.428	−8.571
400	36.218	239.628	230.528	3.640	80.133	53.977	−7.049
450	36.550	243.914	231.782	5.460	79.632	50.738	−5.889
500	36.809	247.779	233.191	7.294	79.157	47.553	−4.968
600	37.189	254.526	236.201	10.995	78.262	41.317	−3.597
700	37.457	260.280	239.240	14.728	77.415	35.227	−2.629
800	37.664	265.295	242.190	18.484	76.594	29.256	−1.910
900	37.833	269.742	245.009	22.259	75.779	23.388	−1.357
1000	37.979	273.736	247.685	26.050	74.952	17.611	−0.920
1100	38.109	277.362	250.221	29.855	74.093	11.918	−0.566
1200	38.228	280.683	252.623	33.672	−23.575	8.745	−0.381
1300	38.339	283.747	254.901	37.500	−23.616	11.440	−0.460
1400	38.445	286.592	257.064	41.339	−23.662	14.139	−0.528
1500	38.546	289.248	259.122	45.189	−23.712	16.840	−0.586
1600	38.645	291.739	261.084	49.049	−23.765	19.546	−0.638
1700	38.740	294.085	262.956	52.918	−23.820	22.254	−0.684
1800	38.834	296.302	264.748	56.797	−23.878	24.966	−0.724
1900	38.926	298.404	266.464	60.685	−23.940	27.681	−0.761
2000	39.017	300.403	268.112	64.582	−24.004	30.400	−0.794
2100	39.107	302.309	269.695	68.488	−24.071	33.122	−0.824
2200	39.196	304.130	271.219	72.403	−24.142	35.847	−0.851
2300	39.285	305.874	272.688	76.327	−24.218	38.575	−0.876
2400	39.373	307.548	274.106	80.260	−24.299	41.307	−0.899
2500	39.460	309.157	275.476	84.202	−24.385	44.043	−0.920
2600	39.547	310.706	276.802	88.152	−24.477	46.781	−0.940
2700	39.633	312.201	278.085	92.111	−24.577	49.524	−0.958
2800	39.720	313.643	279.330	96.079	−24.685	52.271	−0.975
2900	39.806	315.039	280.537	100.055	−24.802	55.021	−0.991
3000	39.891	316.390	281.710	104.040	−24.930	57.776	−1.006
3100	39.977	317.699	282.850	108.033	−25.068	60.535	−1.020
3200	40.062	318.970	283.959	112.035	−25.220	63.298	−1.033
3300	40.147	320.204	285.038	116.046	−25.385	66.067	−1.046
3400	40.233	321.404	286.090	120.065	−25.566	68.841	−1.058
3500	40.317	322.571	287.116	124.092	−25.764	71.621	−1.069
3600	40.402	323.708	288.117	128.128	−25.981	74.406	−1.080
3700	40.487	324.816	289.094	132.173	−26.218	77.198	−1.090
3800	40.572	325.897	290.048	136.226	−26.478	79.996	−1.100
3900	40.656	326.952	290.981	140.287	−26.761	82.802	−1.109
4000	40.741	327.982	291.893	144.357	−27.072	85.615	−1.118
4100	40.825	328.989	292.786	148.435	−27.412	88.436	−1.127
4200	40.909	329.974	293.659	152.522	−27.781	91.266	−1.135
4300	40.994	330.938	294.515	156.617	−28.186	94.106	−1.143
4400	41.078	331.881	295.354	160.721	−28.585	96.951	−1.151
4500	41.162	332.805	296.176	164.833	−29.043	99.808	−1.159
4600	41.246	333.711	296.982	168.953	−29.548	102.677	−1.166
4700	41.330	334.599	297.773	173.082	−30.095	105.557	−1.173
4800	41.415	335.470	298.549	177.219	−30.687	108.450	−1.180
4900	41.499	336.325	299.311	181.365	−31.326	111.355	−1.187
5000	41.583	337.164	300.060	185.519	−32.008	114.273	−1.194
5100	41.667	337.988	300.796	189.681	−32.749	117.206	−1.200
5200	41.751	338.798	301.519	193.852	−33.547	120.154	−1.207
5300	41.835	339.594	302.230	198.032	−34.403	123.118	−1.213
5400	41.918	340.377	302.929	202.219	−35.321	126.098	−1.220
5500	42.002	341.147	303.617	206.415	−36.304	129 096	−1.226
5600	42.086	341.904	304.294	210.620	−37.355	132.114	−1.232
5700	42.170	342.650	304.960	214.832	−38.476	135.149	−1.239
5800	42.254	343.384	305.616	219.054	−39.670	138.206	−1.245
5900	42.338	344.107	306.263	223.283	−40.940	141.283	−1.251
6000	42.422	344.819	306.899	227.521	−42.130	144.365	−1.257

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

Sodium Oxide (NaO) $Na_1O_1(g)$

Sodium Oxide, Ion (NaO^-) IDEAL GAS $M_r = 38.98972$ Sodium Oxide, Ion (NaO^-) $Na_1O_1^-(g)$

$S°(298.15\ K) = [217.49 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_fH°(0\ K) = [-113.76 \pm 83.7]\ kJ\cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = [-121.34 \pm 83.7]\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma]$	0	[1]

$\omega_e = [450]\ cm^{-1}$ $\omega_ex_e = [3.2]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.4467]\ cm^{-1}$ $\alpha_e = [0.00495]\ cm^{-1}$ $r_e = [2.0]$ Å

Enthalpy of Formation

The electron affinity of $NaO^-(g)$ is unavailable, therefore the value of $\Delta_fH°(NaO^-, g, 298.15\ K)$ is estimated. We first assume that the enthalpy change $\Delta_rH°(0\ K)$ of the reaction (1) $NaO^{-1}(g) = Na(g) + O^-(g)$ is close to the average of the $\Delta_rH°(0\ K)$uccircl values for the reactions (2) $NaO(g) = Na(g) + O(g)$ and (3) $NaF(g) = Na(g) + F(g)$. The atom F(g) is isoelectronic with $O^-(g)$. In other words, the $\Delta_rH°(0\ K)$ for reaction (1) is approximately 1/2 (64.8 + 113.9) = 89.3 $kcal\cdot mol^{-1}$. Then we compare the $\Delta_rH°(0\ K)$ values for the reactions (4) $HO(g) = H(g) + O(g)$, (5) $HO^-(g) = H(g) + O^-(g)$, and (6) $HF(g) = H(g) + F(g)$, and find that $\Delta_rH°(0\ K)$ for reaction (5) is experimentally determined as 109.7 $kcal\cdot mol^{-1}$ which is about 8 $kcal\cdot mol^{-1}$ more negative than the average of $\Delta_rH°(0\ K)$ values for reactions (4) and (6). Based on this fact we estimate $\Delta_rH°(0\ K) = 80\ kcal\cdot mol^{-1}$ for reaction (1), yielding $\Delta_fH°(NaO^-, g, 298.15\ K) = -29\ kcal\cdot mol^{-1}$ which is tenatively adopted. The uncertainty of this value may be $\pm 20\ kcal\cdot mol^{-1}$. Based on this $\Delta_fH°(298.15\ K)$ value we calculate E. A. = 2.1 ± 0.9 eV for NaO(g). The corresponding value for HO(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of NaF(g) which is isoelectronic with $NaO^-(g)$. The values of ω_e, ω_ex_e and r_e are estimated by comparison with the observed data for NaF(g). The values of B_e and α_e are calculated from r_e, ω_e and ω_ex_e using the method recommended by Herzberg.[1]

Reference

[1] G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	-9.405	-113.755		
100	29.702	182.286	247.150	-6.486			
200	32.996	203.881	220.638	-3.351			
250	34.222	211.383	218.060	-1.669			
298.15	35.064	217.487	217.487	0.	-121.336	-134.001	23.476
300	35.091	217.704	217.488	0.065	-121.389	-134.080	23.345
350	35.712	223.163	217.917	1.836	-122.848	-136.081	20.309
400	36.168	227.963	218.879	3.633	-127.006	-137.662	17.977
450	36.513	232.243	220.131	5.451	-128.549	-138.901	16.123
500	36.781	236.105	221.538	7.283	-130.066	-139.970	14.623
600	37.175	242.848	224.544	10.982	-133.041	-141.670	12.333
700	37.455	248.601	227.580	14.715	-135.967	-142.876	10.662
800	37.670	253.617	230.527	18.471	-138.866	-143.665	9.380
900	37.846	258.064	233.345	22.247	-141.759	-144.091	8.363
1000	37.997	262.059	236.020	26.040	-144.663	-144.195	7.532
1100	38.132	265.687	238.554	29.846	-147.598	-144.006	6.838
1200	38.256	269.011	240.956	33.666	-247.342	-141.109	6.142
1300	38.371	272.077	243.233	37.497	-249.460	-132.170	5.311
1400	38.481	274.925	245.397	41.340	-251.581	-123.068	4.592
1500	38.586	277.584	247.455	45.193	-253.705	-113.815	3.963
1600	38.688	280.077	249.417	49.057	-255.833	-104.419	3.409
1700	38.788	282.426	251.290	52.931	-257.962	-94.891	2.916
1800	38.885	284.645	253.082	56.814	-260.094	-85.237	2.474
1900	38.981	286.750	254.799	60.708	-262.228	-75.465	2.075
2000	39.075	288.752	256.447	64.611	-264.366	-65.580	1.713
2100	39.168	290.661	258.031	68.523	-266.506	-55.588	1.383
2200	39.261	292.485	259.556	72.444	-268.649	-45.493	1.080
2300	39.352	294.232	261.026	76.375	-270.797	-35.302	0.802
2400	39.443	295.909	262.445	80.315	-272.949	-25.017	0.544
2500	39.534	297.521	263.816	84.264	-275.107	-14.642	0.306
2600	39.624	299.074	265.142	88.221	-277.270	-4.181	0.084
2700	39.714	300.571	266.427	92.188	-279.441	6.364	-0.123
2800	39.803	302.017	267.672	96.164	-281.619	16.989	-0.317
2900	39.892	303.415	268.881	100.149	-283.806	27.692	-0.499
3000	39.981	304.769	270.055	104.143	-286.004	38.471	-0.670
3100	40.070	306.081	271.196	108.145	-288.212	49.323	-0.831
3200	40.158	307.355	272.306	112.157	-290.433	60.246	-0.983
3300	40.247	308.592	273.387	116.177	-292.667	71.239	-1.128
3400	40.335	309.795	274.440	120.206	-294.916	82.301	-1.264
3500	40.423	310.965	275.467	124.244	-297.182	93.428	-1.394
3600	40.511	312.105	276.469	128.290	-299.467	104.621	-1.518
3700	40.598	313.216	277.447	132.346	-301.772	115.877	-1.636
3800	40.686	314.300	278.403	136.410	-304.099	127.196	-1.748
3900	40.774	315.358	279.337	140.483	-306.450	138.577	-1.856
4000	40.861	316.391	280.250	144.565	-308.827	150.018	-1.959
4100	40.949	317.402	281.144	148.655	-311.233	161.519	-2.058
4200	41.036	318.389	282.019	152.755	-313.668	173.079	-2.153
4300	41.124	319.356	282.876	156.863	-316.139	184.697	-2.244
4400	41.211	320.302	283.716	160.979	-318.603	196.370	-2.331
4500	41.298	321.229	284.539	165.105	-321.126	208.101	-2.416
4600	41.385	322.138	285.347	169.239	-323.696	219.890	-2.497
4700	41.473	323.029	286.139	173.382	-326.308	231.735	-2.575
4800	41.560	323.903	286.917	177.534	-328.964	243.636	-2.651
4900	41.647	324.761	287.681	181.694	-331.667	255.594	-2.725
5000	41.734	325.603	288.431	185.863	-334.413	267.606	-2.796
5100	41.821	326.431	289.168	190.041	-337.217	279.674	-2.864
5200	41.908	327.243	289.892	194.227	-340.078	291.797	-2.931
5300	41.995	328.043	290.604	198.422	-342.997	303.977	-2.996
5400	42.082	328.828	291.305	202.626	-345.978	316.211	-3.059
5500	42.169	329.601	291.994	206.839	-349.023	328.502	-3.120
5600	42.256	330.362	292.673	211.060	-352.135	340.849	-3.179
5700	42.343	331.111	293.340	215.290	-355.318	353.252	-3.237
5800	42.430	331.848	293.998	219.529	-358.573	365.711	-3.294
5900	42.517	332.574	294.646	223.776	-361.903	378.227	-3.349
6000	42.604	333.289	295.284	228.032	-365.154	390.782	-3.402

PREVIOUS December 1967 (1 atm) CURRENT· December 1967 (1 bar)

Sodium Superoxide (NaO_2) CRYSTAL M_r = 54.98857 Sodium Superoxide (NaO_2) $Na_1O_2(cr)$

$S°(298.15\ K) = 115.90 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 196.5\ K$
$T_{trs2} = 223.3\ K$
$T_{fus} = 825 \pm 10\ K$

$\Delta_f H°(0\ K) = -263.88 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -260.66\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 1464.400\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 1548.080\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was obtained from Wagman.[1] Giles and Margrave[2] measured the enthalpy of decomposition of $NaO_2(cr)$ in H_2O, yielding $\Delta_f H°(298.15\ K) = -62.1 \pm 0.7\ kcal \cdot mol^{-1}$. From the original experimental data by de Forcrand,[3] the value of $\Delta_f H°(298\ 15\ K)$ was recalculated to be $-65.0\ kcal \cdot mol^{-1}$ by Gilles and Margrave.[2]

Heat Capacity and Entropy

The low temperature heat capacities, 52.13–296.46 K, were measured by Todd.[4] The heat capacities above 298 15 K were estimated by comparison with those for $Na_2O(cr)$. $S°(298.15\ K)$ was given by Todd[4] using $S°(51\ K) = 2.23\ cal \cdot K^{-1} \cdot mol^{-1}$(extrap.).

Transition Data

T_{trs1}, T_{trs2}, $\Delta_{trs1} H°$ and $\Delta_{trs2} H°$ were calculated from the data reported by Todd.[4]

Fusion Data

The melting temperature was obtained from Margrave.[5]

References

[1] D. D. Wagman, U. S. Nat. Bur. Stand. Report 7437, ch. B4 (1962).
[2] P. W Giles and J. L. Margrave, J. Phys. Chem. 60, 1333 (1956).
[3] R. de Forcrand, Compt. Rend. 127, 514 (1898); 158, 843, 991 (1914).
[4] S. S. Todd, J. Amer. Chem. Soc. 75, 1229 (1953).
[5] J. L. Margrave, University of Wisconsin, personal communication, (May 21, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.351	−263.884	−263 884	INFINITE
100	45.564	30.585	194.891	−16.431	−266.208	−249.554	130.354
200	78.450	78.241	118.679	−8.088	−263.232	−232.044	60.604
298.15	72.141	115.897	115.897	0.	−260.663	−218.712	38.317
300	72.216	116.343	115.898	0.134	−260.636	−218.452	38.036
400	76.274	137.673	118.779	7.558	−261.805	−204.405	26.693
500	80.375	155.134	124.354	15.390	−260.133	−190.240	19.874
600	84.475	170.151	130.763	23.633	−258.066	−176.450	15.361
700	88.502	183.474	137.358	32.281	−255.625	−163.035	12.166
800	92.634	195.560	143.889	41.337	−252.814	−149.996	9.794
900	96.962	206.721	150.258	50.817	−249.627	−137.331	7.970
1000	101.211	217.158	156.431	60.726	−246.067	−125.041	6.531
1100	105.186	226.991	162.403	71.046	−242.164	−113.124	5.372
1200	109.177	236.314	168.177	81.764	−334.706	−99.137	4.315
1300	113.186	245.211	173.763	92.882	−329.249	−79.725	3.203
1400	117.211	253.746	179.173	104.402	−323.422	−60.747	2.267
1500	121.252	261.971	184.421	116.325	−317.219	−42.199	1.470
1600	125.311	269.925	189.517	128.653	−310.637	−24.077	0.786
1700	129.386	277.645	194 475	141.388	−303.672	−6.378	0.196
1800	133.478	285.156	199.305	154.531	−296.324	10.899	−0.316
1900	137.587	292.483	204.017	168.084	−288.590	27.758	−0.763
2000	141.712	299.645	208.620	182.048	−280.468	44.200	−1.154

PREVIOUS: CURRENT June 1963

Sodium (Na_2) IDEAL GAS $M_r = 45.975$ Sodium (Na_2) $Na_2(g)$

$D_0^\circ = 71.113 \pm 0.072$ kJ·mol^{-1}
$S^\circ(298.15\ K) = 230.243 \pm 0.030$ J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 144.56 ± 1.20 kJ·mol^{-1}
$\Delta_f H^\circ(298.15\ K) = 142.07 \pm 1.20$ kJ·mol^{-1}

Spectroscopic Data for Na_2 in cm^{-1}

State	T_e	D_0°	ω_e	$\omega_e x_e$	B_e	$10^3\ \alpha_e$	10^6 D$_e$	r_e Å	Reference
$^1\Sigma_g^+$	0	6024	159.11	0.72142[a]	0.15474	0.86827[b]	0.58972[c]	3.07857	d[2], e[6]
$^1\Sigma_u^+$	14681	22900[f]	117.32	0.35758[g]	0.11078	0.54884[h]	0.38816	3.6384	[5]

(a) $-1.5354 \times 10^{-3}(v+1/2)^3 - 2.3576 \times 10^{-5}(v+1/2)^4$
(b) $-4.2855 \times 10^{-6}(v+1/2)^2 - 1.4784 \times 10^{-7}(v+1/2)^3$
(c) $-3.9068 \times 10^{-9}(v+1/2) + 9.1188 \times 10^{-11}(v+1/2)^2$
(d) Reference for D_0°
(e) Reference for constants
(f) This value was estimated based on the estimate of Konowalow, et al[4], $D_e = 8275$ cm^{-1}
(g) $+5.1671 \times 10^{-5}(v+1/2)^3 + 9.2770 \times 10^{-6}(v+1/2)^4$
(h) $+1.6252 \times 10^{-8}(v+1/2)^2 + 3.1645 \times 10^{-8}(v+1/2)^3$

Enthalpy of Formation

Using the adopted value of the dissociation energy for $Na_2(g)$, $D_0^\circ = 71\ 113$ kJ·mol^{-1},[2] and the recommended $\Delta_f H^\circ$(Na, g, 0 K) = 107.32 kJ·mol^{-1} from NBS,[7] we calculate $\Delta_f H^\circ$(Na_2, g, 0 K) = 143.51 kJ·mol^{-1}. Since this value is only 1.05 kJ·mol^{-1}smaller than the NBS recommended value of 144.56 kJ·mol^{-1}[7] we adopt the NBS result. Correcting this value to 298.15 K using the current value of $H^\circ(298.15\ K) - H^\circ(0\ K) = 10403.27$ J·K^{-1}·mol^{-1} for Na_2 and the NBS value of $H^\circ(298.15\ K) - H^\circ(0\ K)$ for Na(cr)[1] we obtain $\Delta_f H^\circ$(Na_2, g, 298.15 K) = 142.05 kJ·mol^{-1}.

Heat Capacity and Entropy

The heat capacity and entropy were calculated using a direct summation technique similar to the $Li_2(g)$ calculation (refer to $Li_2(g)$ table) using data recommended by Stwalley[1] [2] for the ground state. Reliable spectroscopic data for the lower lying excited states of Na_2 is sparse. Only the $^1\Sigma_u^+$ state at $T_e = 14680.6$ cm^{-1} has been experimentally characterized with any degree of confidence.[3] [6] Theoretical calculations by Konowalow, Rosenkrantz and Olson[4] show that the relative ordering of states is equivalent to that of $Li_2(g)$ (see $Li_2(g)$ table). Since the excited state contribution to all thermodynamic functions (except for the heat capacity) for $Li_2(g)$ was small (~0.2% at 6000 K) we decided to treat the excited states for $Na_2(g)$ in an approximate way as follows. First, the $^3\Sigma_u^+$ state was neglected entirely due to the extremely shallow potential well (The $^3\Sigma_u^+$ state of $Li_2(g)$ contributes insignificantly to the thermodynamic functions.) Second, the $^3\Pi_u$, $^1\Sigma_u^+$, and $^3\Sigma_g^+$ states were combined as a single $^1\Sigma_u^+$ state using the spectroscopic constants of Kamimsky[5] and an artifical degeneracy of 10 (6 for the $^3\Pi_u$, 1 for the $^1\Sigma_u^+$, and 3 for the $^3\Sigma_g^+$ state). This procedure certainly overestimates the $^3\Sigma_g^+$ contribution (which lies above the $^1\Sigma_u^+$ state by ca. 3300 cm^{-1}) but at the same time underestimates the $^3\Pi_u$ contribution (which lies below the $^1\Sigma_u^+$ state by ca 1100 cm^{-1}).[4] In any case the contribution to the Gibbs energy function is very small (< 0.01 J·K^{-1}·mol^{-1}) at temperatures below 2500 K and only contributes ca. 3 J·mol^{-1} K^{-1} at 6000 K. Note also that the Dunham coefficients for the ground state are reported to higher order in[6] than used in the calculation. The neglect of these higher order terms results in uncertainties similar to the $Li_2(g)$ calculation (the Gibbs energy function at 6000 K is probably only 0.3 J·K^{-1}·mol^{-1} smaller than the truncated rovib expression method). The rotational levels of the ground state were weighted in accordance with the nuclear spin of 3/2 (even J weight = 0.625, odd J weight = 0.375). The adopted value of $S^\circ(298.15\ K)$ is only 0.1 J·K^{-1}·mol^{-1} lower than that adopted by NBS.[7]

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−10.403	144.560	144.560	INFINITE
100	34.747	190.419	263.127	−7.271	145.013	130.734	−68.288
200	36.922	215.363	233.663	−3.660	143.713	116.919	−30.536
250	37.315	223.647	230.860	−1.803	142.920	110.310	−23.048
298.15	37.577	230.243	230.243	0.	142.070	104.105	−18.239
300	37.585	230.476	230.244	0.070	142.035	103.870	−18.085
350	37.799	236.286	230.702	1.954	141.014	97.587	−14.564
400	37.984	241.346	231.723	3.849	134.571	91.873	−11.997
450	38.157	245.830	233.046	5.752	133.349	86.610	−10.053
500	38.327	249.859	234.529	7.665	132.184	81.480	−8.512
600	38.667	256.876	237.686	11.514	130.002	71.547	−6.229
700	38.998	262.862	240.865	15.398	127.981	61.966	−4.624
800	39.269	268.088	243.949	19.312	126.077	52.667	−3.439
900	39.411	272.723	246.893	23.247	124.238	43.601	−2.531
1000	39.369	276.875	249.687	27.188	122.404	34.740	−1.815
1100	39.123	280.618	252.332	31 114	120.513	26.064	−1.238
1200	38.680	284.004	254.833	35.006	−75.016	22.445	−0.977
1300	38.074	287.077	257.197	38.845	−75.334	30.579	−1.229
1400	37.347	289.873	259.432	42.617	−75.720	38.741	−1.445
1500	36.546	292.423	261.548	46.312	−76.182	46.932	−1.634
1600	35.714	294.755	263.552	49.925	−76.726	55.157	−1.801
1700	34.891	296.895	265 451	53.455	−77.354	63 418	−1.949
1800	34.110	298.867	267.253	56.904	−78.062	71.719	−2.081
1900	33.399	300.692	268.966	60.279	−78.846	80.061	−2.201
2000	32.782	302.389	270.595	63.587	−79.698	88.447	−2.310
2100	32.280	303.976	272.147	66.840	−80.608	96.876	−2.410
2200	31.908	305.468	273.628	70.048	−81.565	105.350	−2.501
2300	31.681	306.881	275.044	73.226	−82.555	113.868	−2.586
2400	31.610	308.227	276.398	76.389	−83.566	122.430	−2.665
2500	31.700	309.519	277.698	79.553	−84.583	131.034	−2.738
2600	31.957	310.767	278.946	82.735	−85.591	139.678	−2.806
2700	32.381	311.980	280.147	85.950	−86.575	148.361	−2.870
2800	32.968	313.168	281.305	89.217	−87.523	157.080	−2.930
2900	33.712	314.337	282.424	92.549	−88.419	165.832	−2.987
3000	34.601	315.495	283.507	95.964	−89.252	174 614	−3.040
3100	35.624	316.646	284.557	99.474	−90.011	183.422	−3.091
3200	36.761	317.794	285.578	103.092	−90.686	192.253	−3.138
3300	37.996	318.944	286.572	106.830	−91.269	201.105	−3.183
3400	39.305	320.098	287.541	110.694	−91.756	209.972	−3.226
3500	40.666	321.257	288.488	114.692	−92.145	218.852	−3.266
3600	42.055	322.422	289.414	118.828	−92.435	227.742	−3.304
3700	43.449	323.593	290.322	123.103	−92.629	236.639	−3.341
3800	44.823	324.770	291.213	127.517	−92.732	245.540	−3.375
3900	46.156	325.952	292.088	132.067	−92.751	254.442	−3.408
4000	47.426	327.136	292.950	136.746	−92.697	263.344	−3.439
4100	48.616	328.322	293.798	141.549	−92.582	272.243	−3.468
4200	49.710	329.507	294.634	146.466	−92.414	281.139	−3.496
4300	50.695	330.689	295.459	151.488	−92.220	290.031	−3.523
4400	51.560	331.864	296.273	156.601	−91.925	298.911	−3.549
4500	52.299	333.032	297.077	161.795	−91.673	307.789	−3.573
4600	52.908	334.188	297.871	167.057	−91.452	316.664	−3.596
4700	53.386	335.331	298.656	172.373	−91.266	325.534	−3.618
4800	53.733	336.459	299.432	177.730	−91.132	334.401	−3.639
4900	53.952	337.569	300.199	183.115	−91.069	343.265	−3.659
5000	54.050	338.660	300.957	188.516	−91.079	352.128	−3.679
5100	54.032	339.731	301.707	193.921	−91.207	360.993	−3.697
5200	53.906	340.779	302.448	199.319	−91.458	369.862	−3.715
5300	53.681	341.804	303.181	204.699	−91.846	378.737	−3.733
5400	53.366	342.804	303.906	210.052	−92.386	387.620	−3.749
5500	52.971	343.780	304.622	215.370	−93.093	396.516	−3.766
5600	52.504	344.731	305.330	220.644	−93.977	405.425	−3.782
5700	51.976	345.655	306.029	225.868	−95.052	414.353	−3.797
5800	51.395	346.554	306.720	231.037	−96.326	423.300	−3.812
5900	50.769	347.428	307.403	236.146	−97.809	432.272	−3.827
6000	50.107	348.275	308.077	241 190	−99.192	441.234	−3.841

PREVIOUS: June 1962 (1 atm) CURRENT. December 1983 (1 bar)

Sodium Oxide (Na_2O) CRYSTAL (γ–β–α) $M_r = 61.97894$ Sodium Oxide (Na_2O) $Na_2O_1(cr)$

$S°(298.15\ K) = 75.042\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs}(\gamma \rightarrow \beta) = 1023.2\ K$
$T_{trs}(\beta \rightarrow \alpha] = 1243.2\ K$
$T_{fus} = 1405.2\ K$

$\Delta_fH°(0\ K) = -413.15 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_fH°(298.15\ K) = -417.98 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H°(\gamma \rightarrow \beta) = 1.757\ kJ{\cdot}mol^{-1}$
$\Delta_{trs}H°(\beta \rightarrow \alpha) = 11.924\ kJ{\cdot}mol^{-1}$
$\Delta_{fus}H° = 47.698\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpy change of the reaction $Na_2O(cr) + H_2O(l) = 2\ NaOH(aq)$ has been determined by Matsui and Oka[1,2] Roth and Kaule[3],[4] and Rengade.[5] Based on their reported $\Delta_rH°$ values, the corresponding $\Delta_fH°(298.15\ K)$ for $Na_2O(cr)$ are calculated, using $\Delta_fH°(H_2O,\ l,\ 298.15\ K) = -68.315\ kcal{\cdot}mol^{-1}$ obtained from.[6] and $\Delta_fH°(NaOH,\ nH_2O,\ 298.15\ K)$ derived from JANAF $\Delta_fH°(NaOH,\ cr,\ 298.15\ K)$ and $\Delta_{sln}H°$ and $\Delta_{dil}H°$ reported by Parker.[7] The sample employed by Matsui and Oka was prepared by the method of Rengade[9] and contains $Na_2O(cr)$ and $Na(cr)$ as impurities. The sample used by Roth also contains 3.96% (by weight) $Na_2O_2(cr)$. Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaciton $2\ Na(cr) + H_2O(l) = Na_2O(cr) + H_2(g)$ was calculated by Rengade[5] from his measurements incorporating with $\Delta_rH° = -85.2\ kcal{\cdot}mol^{-1}$ for the reaction $2\ Na(cr) + 2\ H_2O(l) = 2\ NaOH(aq) + H_2(g)$ determined by Joannis.[10] The value $\Delta_fH°(298.15\ K) = -94.9\ kcal{\cdot}mol^{-1}$ is derived from the data of Forcrand[8] using $\Delta_fH°(Na_2O_2,\ cr,\ 298.15\ K) = -122.66\ kcal{\cdot}mol^{-1}$. The results are presented in the table below.

Brewer and Margrave[13] determined the equilibrium constants, 918 1467 K, for the vaporization of $Na_2O(cr)$, using an effusion method. The Na_2O vapor consists predominately of $Na(g)$ and $O_2(g)$ molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na_2O. Based on the reported data, we derive the equilibrium constants for the reaction $Na_2O(cr) = 2\ Na(g) + 1/2\ O_2(g)$ and evaluate the 3rd law $\Delta_rH°(298.15\ K)$ as $117.1 \pm 10\ kcal{\cdot}mol^{-1}$.From this $\Delta_rH°(298.15\ K)$ value, we obtain $\Delta_fH°(Na_2O,\ cr,\ 298.15\ K) = -65.6 \pm 10\ kcal{\cdot}mol^{-1}$, employing $\Delta_fH°(298.15\ K)$ for Na(g). The value $-\ 65.6\ kcal{\cdot}mol^{-1}$ is not consistent with the other values described above. This may be caused by an invalid assumption used in the calculation.

The enthalpy of formation at 298.15 K for $Na_2O(cr)$ is tentatively selected as $-\ 99.90 \pm 1.0\ kcal{\cdot}mol^{-1}$.

Source	Reaction	$\Delta_rH°(298.15\ K)$ $kcal{\cdot}mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal{\cdot}mol^{-1}$
1	$Na_2O(cr) + H_2O(l) = 2\ NaOH(7890\ H_2O)$	-56.61 ± 0.16	-100.08
2	$Na_2O(cr) + H_2O(l) = 2\ NaOH(4600\ H_2O)$	-56.70 ± 0.07	-99.89
3	$Na_2O(cr) + H_2O(l) = 2\ NaOH(825\ \ H_2O)$	-56.03 ± 0.13	-100.55
4	$Na_2O(cr) + H_2O(l) = 2\ NaOH(825\ \ H_2O)$	-55.98 ± 0.13	-100.60
5	$Na_2O(cr) + H_2O(l) = 2\ NaOH(aq)$	-56.50	-100.09
	$2\ Na(cr) + H_2O(l) = Na_2O(cr) + H_2(g)$	-28.70	-97.02
8	$Na_2O(cr) + 1/2\ O_2(g) = Na_2O_2(cr)$	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15–380 K, were obtained from Furukawa.[11] We make the corrections in the reported $C_p°$ values for impurity $Na_2CO_3(cr)$ 2.33% (by weight), analyzed by Grimley and Margrave.[12] The effect on heat capacity due to the presence of Na_2O_2(0.91%) impurity is insignificant. Using the smoothed low temperature $C_p°$ data, the $S°(298.15\ K)$ is calculated, based on $S°(15\ K) = 0.0122\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Grimley and Margrave[12] measured the high temperature enthalpies, 380.1–1174.6 K, with a copper block drop type calorimeter. The enthalpies for the γ phase, 380.1–980.4 K, are joined smoothly with the low temperature data and extrapolated to 1023.2 K (the γ → β transition temperature. The enthalpies above 1023.2 K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6 K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz *et al.*[14] who used a very pure sample. The adopted $\Delta_{trs}H° = 0.42$ and $2.85\ kcal{\cdot}mol^{-1}$, are averages of the derived values, 0.36–0 48 and 2.7–3.0 $kcal{\cdot}mol^{-1}$, respectively.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were obtained from Bouaziz *et al.*[14] The adopted $\Delta_{fus}H°$ is an average of the reported 10.8–12.0 $kcal{\cdot}mol^{-1}$. T_{fus} has been reported as 1193 and 1190 ± 10 K by Bunzel and Kohlmeyer[15] and Brewer and Margrave,[13] respectively, which are not adopted.

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−12.399	−413.146	−413.146	INFINITE
100	32.752	16.649	128.981	−11.233	−416.111	−404.348	211.210
200	59.551	49.209	81.114	−6.381	−417.626	−391.841	102.338
298.15	69.103	75.042	75.042	0.	−417.982	−379.090	66.415
300	69.245	75.470	75.043	0.128	−417.985	−378.849	65.964
400	75.776	96.304	77.840	7.386	−423.456	−365.363	47.712
500	81.496	113.855	83.332	15.262	−423.312	−350.842	36.652
600	85.709	129.103	89.717	23.631	−422.555	−336.410	29.287
700	88.851	142.560	96.324	32.365	−421.353	−322.142	24.039
800	91.291	154.589	102.869	41.376	−419.828	−308.070	20.115
900	93.266	165.458	109.229	50.607	−418.075	−294.204	17.075
1000	94.918	175.373	115.355	60.018	−416.169	−280.541	14.654
1023.150	95.264	177.549	116.737	62.219	——— GAMMA <−−> BETA ———		
1023.150	95.265	179.266	116.737	63.977	TRANSITION		
1100	96.353	186.205	121.351	71.340	−412.418	−267.206	12.689
1200	97.629	194.645	127.111	81.040	−603.913	−249.215	10.848
1243.150	98.140	198.103	129.516	85.264	——— BETA <−−> ALPHA ———		
1243 150	98.142	207.695	129.516	97.188	TRANSITION		
1300	98.788	212.098	133.031	102.786	−588.116	−220.358	8.854
1400	99.860	219.459	138.945	112.719	−584.147	−192.218	7.172
1405.200	99.913	219.829	139.243	113.239	−−−− ALPHA <−−> LIQUID −−−−		
1500	100.868	226.383	144.545	122.756	−580.088	−164.364	5.724
1600	101.822	232.923	149.866	132.891	−575.944	−136.784	4.466
1700	102.734	239.124	154.936	143.119	−571.720	−109.465	3.363
1800	103.617	245.021	159.778	153.437	−567.418	−82.398	2.391
1900	104.470	250.646	164.414	163.841	−563.042	−55.571	1.528
2000	105.307	256.026	168.861	174.330	−558.594	−28.977	0.757

PREVIOUS: June 1962 CURRENT: June 1968

Sodium Oxide (Na_2O) LIQUID $M_r = 61.97894$ Sodium Oxide (Na_2O) $Na_2O_1(l)$

$S°(298.15\ K) = [91.607]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = [-372.843]\ kJ{\cdot}mol^{-1}$

$T_{fus} = 1405.2\ K$ $\Delta_{fus}H° = 47.698\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_2O, l, 298.15\ K)$ is calculated from $\Delta_f H°(Na_2O, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1405.2\ K)-H°(298.15\ K)$, between $Na_2O(cr)$ and $Na_2O(l)$.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $Na_2SiO_3(l)$ and $SiO_2(l)$. $S°(l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

$T_{dcm} = 2223\ K$ is the temperature at $\Delta_f G° = 0$ for the decomposition reaction $Na_2O(l) = 2\ Na(g) + 1/2\ O_2(g)$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.600	91.607	91.607	0.	−372.843	−338.890	59.372
300	104.600	92.254	91.609	0.194	−372.780	−338.680	58.969
400	104.600	122.346	95.712	10.654	−375.049	−327.373	42.751
500	104.600	145.687	103.460	21.114	−372.321	−315.766	32.988
600	104.600	164.757	112.135	31.574	−369.474	−304.721	26.528
700	104.600	180.882	120.834	42.034	−366.545	−294.160	21.950
800	104.600	194.849	129.232	52.494	−363.572	−284.022	18.545
900	104.600	207.169	137.221	62.954	−360.589	−274.257	15.917
1000	104.600	218.190	144.776	73.414	−357.635	−264.824	13.833
1100	104.600	228.159	151.911	83.874	−354.746	−255.683	12.141
1200	104.600	237.261	158.649	94.334	−545.481	−241.922	10.531
1300	104.600	245.633	165.023	104.794	−540.970	−216.808	8.711
1400	104.600	253.385	171.061	115.254	−536.474	−192.041	7.165
1405.200	104.600	253.773	171.366	115.797	---- ALPHA <--> LIQUID ----		
1500	104.600	260.601	176.792	125.714	−531.992	−167.596	5.836
1600	104.600	267.352	182.244	136.174	−527.523	−143.448	4.683
1700	104.600	273.693	187.438	146.634	−523.066	−119.580	3.674
1800	104.600	279.672	192.398	157.094	−518.622	−95.974	2.785
1900	104.600	285.328	197.142	167.554	−514.191	−72.614	1.996
2000	104.600	290.693	201.686	178.014	−509.772	−49.488	1.292
2100	104.600	295.796	206.047	188.474	−505.367	−26.582	0.661
2200	104.600	300.662	210.238	198.934	−500.976	−3.886	0.092
2300	104.600	305.312	214.271	209.394	−496.600	18.611	−0.423
2400	104.600	309.764	218.158	219.854	−492.240	40.918	−0.891
2500	104.600	314.034	221.908	230.314	−487.899	63.044	−1.317
2600	104.600	318.136	225.531	240.774	−483.576	84.996	−1.708
2700	104.600	322.084	229.034	251.234	−479.275	106.783	−2.066
2800	104.600	325.888	232.426	261.694	−474.998	128.410	−2.396
2900	104.600	329.559	235.712	272.154	−470.745	149.885	−2.700
3000	104.600	333.105	238.900	282.614	−466.522	171.214	−2.981

PREVIOUS June 1962 CURRENT June 1968

Sodium Oxide (Na_2O)

CRYSTAL(γ–β–α–)–LIQUID

0 to	1023.2	K	crystal, gamma
1023.2 to	1243.2	K	crystal, beta
1243.2 to	1405.2	K	crystal, alpha
above	1405.2	K	liquid

Refer to the individual tables for details.

M_r = 61.67894 Sodium Oxide (Na_2O) Na_2O_1(cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.399	−413.146	−413.146	INFINITE
100	32.752	16.649	128.981	−11.233	−416.111	−404.348	211.210
200	59.551	49.209	81.114	−6.381	−417.626	−391.841	102.338
298.15	69.103	75.042	75.042	0.	−417.982	−379.090	66.415
300	69.245	75.470	75.043	0.128	−417.985	−378.849	65.964
400	75.776	96.304	77.840	7.386	−423.456	−365.363	47.712
500	81.496	113.855	83.332	15.262	−423.312	−350.842	36.652
600	85.709	129.103	89.717	23.631	−422.555	−336.410	29.287
700	88.851	142.560	96.324	32.365	−421.353	−322.142	24.039
800	91.291	154.589	102.869	41.376	−419.828	−308.070	20.115
900	93.266	165.458	109.229	50.607	−418.075	−294.204	17.075
1000	94.918	175.373	115.355	60.018	−416.169	−280.541	14.654
1023.150	95.264	177.549	116.737	62.219	GAMMA <––> BETA TRANSITION		
1023.150	95.265	179.266	116.737	63.977			
1100	96.353	186.205	121.351	71.340	−412.418	−267.206	12.689
1200	97.629	194.645	127.111	81.040	−603.913	−249.215	10.848
1243.150	98.140	198.103	129.516	85.264	BETA <––> ALPHA TRANSITION		
1243.150	98.142	207.695	129.516	97.188			
1300	98.788	212.098	133.031	102.786	−588.116	−220.358	8.854
1400	99.860	219.459	138.945	112.719	−584.147	−192.218	7.172
1405.200	99.913	219.829	139.243	113.239	ALPHA <––> LIQUID TRANSITION		
1405.200	104.600	253.773	139.243	160.936			
1500	104.600	260.601	146.700	170.853	−531.992	−167.596	5.836
1600	104.600	267.352	154.032	181.313	−527.523	−143.448	4.683
1700	104.600	273.693	160.886	191.773	−523.066	−119.580	3.674
1800	104.600	279.672	167.321	202.233	−518.622	−95.974	2.785
1900	104.600	285.328	173.384	212.693	−514.191	−72.614	1.996
2000	104.600	290.693	179.117	223.153	−509.772	−49.488	1.292
2100	104.600	295.796	184.552	233.613	−505.367	−26.582	0.661
2200	104.600	300.662	189.720	244.073	−500.976	−3.886	0.092
2300	104.600	305.312	194.646	254.533	−496.600	18.611	−0.423
2400	104.600	309.764	199.350	264.993	−492.240	40.918	−0.891
2500	104.600	314.034	203.853	275.453	−487.899	63.044	−1.317
2600	104.600	318.136	208.170	285.913	−483.576	84.996	−1.708
2700	104.600	322.084	212.316	296.373	−479.275	106.783	−2.066
2800	104.600	325.888	216.305	306.833	−474.998	128.410	−2.396
2900	104.600	329.559	220.147	317.293	−470.745	149.885	−2.700
3000	104.600	333.105	223.854	327.753	−466.522	171.214	−2.981

PREVIOUS: CURRENT: June 1968

Sodium Oxide (Na_2O_2) CRYSTAL (α–β) $M_r = 77.97834$ Sodium Peroxide (Na_2O_2) $Na_2O_2(cr)$

$S°(298.15 K) = 94.80 \pm 1.3$ J·K^{-1}·mol^{-1}
$T_{trs} = 785 \pm 1$ K
$T_{fus} = 948$ K

$\Delta_f H°(0 K) = -507.34 \pm 5.0$ kJ·mol^{-1}
$\Delta_f H°(298.15 K) = -513.21 \pm 5.0$ kJ·mol^{-1}
$\Delta_{trs} H° = 5.732$ kJ·mol^{-1}
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy change of the reaction $Na_2O_2(cr) + H_2O(l) = 2 NaOH(aq, 1200 H_2O) + 1/2 O_2(g)$ was measured at 18.5°C by Roth and Kaule.[1] He employed a sample with composition 96.81% Na_2O_2 and 3.4% Na_2O by weight. Using $\Delta_{sln}H°(Na_2O_2, cr) = -56.02$ kcal·mol^{-1}, Roth derived the value $\Delta_{sln}H°(Na_2O_2, cr) = -34.85$ kcal·mol^{-1}. This value was later corrected to be -35.75 kcal·mol^{-1} by Roth.[2] From these data we calculate the enthalpy of formation (298.15 K) of $Na_2O_2(cr)$ as -121.0 kcal·mol^{-1}. Forcrand obtained $\Delta_{sln}H° = -36.65$ kcal·mol^{-1} for the same reaction, quoted by Roth and Kaule,[1] yielding $\Delta_f H°(Na_2O_2, cr, 298.15 K) = -120.0$ kcal·mol^{-1}. The auxiliary data $\Delta_f H°(H_2O, l, 298.15 K)^3 = -68.315$ kcal·mol^{-1}; and $\Delta_f H°(NaOH·aq, 1200 H_2O, 298.15 K) = 112.458$ kcal·mol^{-1} is derived based on $\Delta_f H°(NaOH, cr, 298.15 K) = -101.90$ kcal·mol^{-1} from JANAF Table and $\Delta_{sol}H°(aq, \infty) = -10.637$ kcal·mol^{-1} and $\Delta_{dil}H°(aq, 1200 H_2O \rightarrow aq, \infty) = -0.079$ kcal·mol^{-1} from Parker.[4]

Gilles and Margrave[5] determined the enthalpy change of the reaction $Na_2O_2(cr) + H_2O(l) = 2 NaOH(aq, 3800 H_2O) + 1/2 O_2(g)$, using a purer sample ($Na_2O_2$, 99.2%; Na_2O, 0.8%). Based on the reported value $\Delta_r H°(298.15 K) = -34.0 \pm 0.3$ kcal·mol^{-1} and derived $\Delta_f H°(NaOH·aq, 3800 H_2O, 298.15 K) = -112.487$ kcal·mol^{-1}, we calculate $\Delta_f H°(298.15 K) = -122.66 \pm 1.2$ kcal·mol^{-1} for $Na_2O_2(cr)$.

Leffler and Wiederhorn[6] studied the oxygen pressure melt composition for the liquid sodium oxygen system between 780 and 980 °C. These results, together with the thermodynamic data for Na_2O_2, were used to calculate the enthalpies and Gibbs energies of formation of melt compositions between $NaO_{1.0}$ and $NaO_{0.5}$. However, there are no numerical results reported. Therefore these data are not used for evaluation.

The enthalpy of formation at 298.15 K is adopted as -122.66 ± 1.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The low temperature heat capacities, 52.31 296.22 K, were measured by Todd.[7] His sample contains (percent) 94 $Na_2O_2(cr)$, 3.6 $Na_2O(cr)$ and 2.4 Na_2CO_3. Corrections in the reported results have been made for Na_2CO_3 content, but not for Na_2O content which was estimated to be small. The $C_p°$ values below 52.31 K are calculated using the equation $C_p° = D(252/T) + 3E(399/T)$ reported by Todd. $S°(298.15 K)$ is derived from the adopted $C_p°$, based on $S°(50 K) = 1.012$ cal·K^{-1}·mol^{-1}.

The high temperature enthalpies, 375.4–869.2 K, were determined by Chandrasekharaiah *et al.*,[8] using drop calorimetry. Corrections were made for the contributions from impurities (Na_2CO_3, 1.5 and Na_2O, 0.2%). A discontinuity was observed in the enthalpies between 773 and 793 K, indicating some kind of transition (see Transition Data). The $C_p°$ for $Na_2O_2(\alpha)$ at temperatures 298–769.5 K are derived from the enthalpy measurements, 375.4–769.5 K, and joined smoothly with the low temperature data at 298.15 K, and extrapolated to 785 K(T_{trs}). The $C_p°$ for $Na_2O_2(\beta)$ is derived from the enthalpy data, 794–869.2 K, as constant, 27.15 cal·K^{-1}·mol^{-1}, and extrapolated to 2500 K.

Vedeneev and Skuratov[9] measured the high temperature specific heat of $Na_2O_2(cr)$ in the temperature interval 292–373 K using adiabatic calorimetry. The reported average value, 21.46 cal·K^{-1}·mol^{-1}, is in fair agreement with the adopted ones.

Transition Data

T_{trs} was reported by Tallman and Margrave,[10] who measured the X-ray power diffraction pattern by a Geiger counter diffractometer and found that at about 510°C the pattern changes entirely and a new set of peaks indicates a new phase. Separate thermal analysis measurements[10] confirm the transition temperature ($\alpha \rightarrow \beta$) is 512 ± 1°C or 785 ± 1 K, which is adopted here. Foppl[11] found a thermal anomaly at 485°C in both heating and cooling curves. $\Delta_{trs}H°$ is derived from the adopted enthalpy and $C_p°$ data on $Na_2O_2(\alpha)$ and $Na_2O_2(\beta)$.

Fusion Data

T_{fus} is obtained from Bunzel and Kohlmeyer.[12] $T_{fus} = 733$ and 783 K were reported by Blumenthal[13] and Rode and Gol'der,[14] respectively, which are not adopted.

References

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.707	−507.339	−507.339	INFINITE
100	40.689	20.882	163.515	−14.263	−511.480	−491.475	256.720
200	75.479	61.785	102.600	−8.163	−513.202	−470.583	122.904
298.15	89.266	94.801	94.801	0.	−513.209	−449.627	78.773
300	89.408	95.354	94.803	0.165	−513.203	−449.233	78.218
400	97.721	122.268	98.416	9.541	−518.042	−427.560	55.834
500	103.767	144.748	105.495	19.626	−517.218	−405.020	42.312
600	108.445	164.093	113.687	30.244	−515.792	−382.706	33.318
700	112.332	181.108	122.127	41.287	−513.908	−360.668	26.913
785.000	115.253	194.149	129.230	50.961	ALPHA <--> BETA		
785 000	113.596	201.451	129.230	56.694	TRANSITION		
800	113.596	203.601	130.604	58.397	−505.952	−339.036	22.137
900	113.596	216.981	139.473	69.757	−503.773	−318.303	18.474
1000	113.596	228.949	147.833	81.117	−501.650	−297.810	15.556
1100	113.596	239.776	155.707	92.476	−499.616	−277.525	13.179
1200	113.596	249.660	163.130	103.836	−691.226	−252.540	10.993
1300	113.596	258.753	170.141	115.195	−687.607	−216.130	8.684
1400	113.596	267.171	176.775	126.555	−684.018	−179.997	6.716
1500	113.596	275.008	183.065	137.914	−680.457	−144.121	5.019
1600	113.596	282.340	189.043	149.274	−676.922	−108.480	3.542
1700	113.596	289.226	194.736	160.634	−673.412	−73.060	2.245
1800	113.596	295.719	200.168	171.993	−669.926	−37.846	1.098
1900	113.596	301.861	205.360	183.353	−666.465	−2.825	0.078
2000	113.596	307.688	210.332	194 712	−663.028	32.014	−0.836
2100	113.596	313.230	215.101	206.072	−659.616	66.682	−1.659
2200	113.596	318.515	219.682	217.431	−656.229	101.189	−2.403
2300	113.596	323.564	224.090	228.791	−652.869	135.542	−3.078
2400	113.596	328.399	228.336	240.150	−649.537	169.748	−3.694
2500	113.596	333.036	232.432	251.510	−646.233	203.817	−4.259

PREVIOUS. June 1963   CURRENT June 1968

Sodium Silicate (Na_2SiO_3) CRYSTAL M_r = 122.06324 Sodium Silicate (Na_2SiO_3) $Na_2O_3Si_1(cr)$

$S°(298.15\ K) = 113.847 \pm 1.3\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{fus} = 1362 \pm 0.5\ K$

$\Delta_f H°(0\ K) = -1551.20 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298\ 15\ K) = -1561\ 43 \pm 4.2\ kJ{\cdot}mol^{-1}$
$\Delta_{fus} H° = 51.798\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr), SiO_2(quartz), Na_2SiO_3(cr), HCl(aq) and H_2SO_4(aq) in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] The author derived two values of $\Delta_{sln} H°$ of Na_2O(cr) from those of NaCl(cr), Na_2SO_4(cr), HCl(aq) and H_2SO_4(aq) presumably employing auxiliary data from.[2] We recalculate $\Delta_{sln} H°$ of Na_2O(cr) in the calorimetric solution as −87.50 (chloride scheme, originally −87.66) and −88.74 kcal·mol⁻¹ (sulfate scheme, originally −89.19), using recent $\Delta_f H°$(298.15 K) values for NaCl(cr), Na_2SO_4(cr), HCl(aq), H_2SO_4(aq), and Na_2O(cr). The corresponding enthalpy changes, $\Delta_r H°$(298.15 K), for the reaction $Na_2O(cr) + SiO_2(quartz) = Na_2SiO_3(cr)$ are derived as −55.20 and −56.38 kcal·mol⁻¹. Adopting the weighted average $\Delta_r H°$(298.15 K) = −55.59 kcal·mol⁻¹ with $\Delta_f H°$(Na_2O, cr, 298.15 K) = −99.9 kcal·mol⁻¹ and $\Delta_f H°$(SiO_2, quartz, 298.15 K) = −217.7 kcal·mol⁻¹, we obtain $\Delta_f H°$(298.15 K) = −373.19 kcal·mol⁻¹ for Na_2SiO_3(cr). This $\Delta_f H°$(Na_2SiO_3, cr, 298 15 K) value is independent of future changes in $\Delta_f H°$(298.15 K) of Na_2O(cr) but the values of $\Delta_{sln} H°$ and $\Delta_r H°$ are not independent. The adopted value of $\Delta_f H°$(Na_2, cr, 298.15 K) is the average of −100.1 and −99.7 kcal·mol⁻¹ reported by Roth and Kaule[3] and Matsui and Oka,[4] respectively.

Roth and Troitzsch[5] have measured the enthalpies of solution of SiO_2(quartz), Na_2SiO_3(cr) and Na_2O(cr) in 10.3% HF at 22°C to be −32.85, −67.96 and −89.9 kcal·mol⁻¹, respectively Using these results, we calculate the enthalpy change of the reaction $Na_2O(cr) + SiO_2(quartz) = Na_2SiO_3(cr)$ as −53.79 kcal·mol⁻¹ and $\Delta_f H°$(Na_2SiO_3, cr, 298 15 K) = −371.39 kcal mol⁻¹.

By use of high temperature reaction calorimetry, Kroger and Janetzko[6] have determined the enthalpy change of the reaction $Na_2C_3(cr) + Na_2Si_2O_5(g,\ l) = 2\ Na_2SiO_3(cr) + CO_2(g)$ as 17.99 kcal·mol⁻¹. Based on $\Delta_f H°$(298.15 K) = −270.26, −582.92 and −94.05 kcal·mol⁻¹ for Na_2SiO_3(cr).

The enthalpies of solution of Na_2CO_3(cr), SiO_2(quartz) and Na_2SiO_3(cr) in 39% HF at 26.5°C were measured to be −244.1, −564.5 and −673.6 cal·g⁻¹ by Hummel and Schwiete.[7] From these results we calculate the enthalpy change to be 22.43 kcal·mol⁻¹ for the reaction $Na_2CO_3(cr) + SiO_2(quartz) = Na_2SiO_3(cr) + CO_2(g)$, yielding $\Delta_f H°$(Na_2SiO_3, cr, 298.15 K) = −371.48 kcal·mol⁻¹.

Many other older calorimetric measurements have been made in order to derive the enthalpies of formation for Na_2SiO_2(cr), but most of these are of questionable accuracy and in some cases the products of the reaction are uncertain. For further details, refer to the review by McCready.[8]

Heat Capacity and Entropy

The low temperature heat capacities, 53.6–294.5 K, were measured by Kelley,[9] and high temperature enthalpies, 360.5–1747 K were determined by Naylor.[10] The high temperature heat capacities are derived from the measured enthalpy data and joined smoothly with the low temperature $C_p°$ values. The entropy at 298.15 K is calculated using the adopted low temperature heat capacities, based on $S°(50\ K) = 1.195$ cal K⁻¹·mol⁻¹.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.913	−1551.203	−1551.203	INFINITE
100	48.308	25.568	196.995	−17.143	−1556.736	−1528.150	798.224
200	89.743	73.542	123.451	−9.982	−1560.031	−1498.083	391.259
298.15	111.880	113.847	113.847	0.	−1561.427	−1467.330	257.070
300	112.395	114.540	113.849	0.207	−1561.442	−1466.746	255.383
400	127.779	149.118	118.459	12.264	−1567.208	−1434.679	187.350
500	138.716	178.865	127.635	25.615	−1566.925	−1401.558	146.420
600	147.114	204.926	138.390	39.922	−1565.766	−1368.581	119.146
700	153.946	228.133	149.583	54.985	−1563.937	−1335.853	99.683
800	159.749	249.078	160.732	70.677	−1561.578	−1303.425	85.105
900	164.841	268.193	171.625	86.911	−1558.788	−1271.319	73.785
1000	169.423	285.801	182.174	103.628	−1555.650	−1239.544	64.747
1100	173.628	302.149	192.346	120.783	−1552.231	−1208.096	57.368
1200	177.540	317.425	202.140	138.343	−1742.114	−1172.091	51.020
1300	181.230	331.783	211.566	156.283	−1736.446	−1124.817	45.196
1362.000	183.407	340.278	217.233	167.587	--- CRYSTAL <--> LIQUID ---		
1400	184.736	345.343	220.641	174.582	−1730.507	−1077.989	40.220
1500	188.100	358.203	229.387	193.224	−1724.308	−1031.596	35.923
1600	191.347	370.441	237.824	212.187	−1717.869	−985.624	32.177
1700	195.748	382.186	245.972	231.564	−1761.273	−939 617	28.871
1800	197.560	393.420	253.854	251.219	−1754.069	−891.492	25.870
1900	200.556	404.182	261.485	271.125	−1746.650	−843.772	23 197
2000	203.489	414.544	268.880	291.328	−1738.971	−796.449	20.801
2100	206.376	424.543	276.056	311.822	−1731.037	−749.517	18.643
2200	209.213	434.209	283.026	332.601	−1722.854	−702.968	16.691
2300	212.016	443.571	289.804	353.663	−1714.427	−656.798	14.916
2400	214.781	452.653	296.401	375.003	−1705.760	−611.000	13.298
2500	217.518	461.476	302.829	396.618	−1696.857	−565.567	11.817

PREVIOUS: June 1965 CURRENT: September 1967

Sodium Silicate (Na_2SiO_3) $Na_2O_3Si_1(cr)$

Sodium Silicate (Na_2SiO_3) LIQUID M_r = 122.06324 Sodium Silicate (Na_2SiO_3) $Na_2O_3Si_1(l)$

$S°(298.15\ K)$ = [150.496] J·K⁻¹·mol⁻¹
T_{fus} = 1362 ± 0.5 K

$\Delta_f H°(298.15\ K)$ = [−1510.875] kJ·mol⁻¹
$\Delta_{fus}H°$ = 51.798 kJ·mol⁻¹

Enthalpy of Formation

$\Delta_f H°(Na_2SiO_3$, *l*, 298.15 K) is calculated from $\Delta_f H°(Na_2SiO_3$, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1362\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity above 900 K is derived as constant from the high temperature enthalpy data, 1414–1747 K, measured by Naylor.[1] A glass transition temperature is assumed at 900 K, i.e., the heat capacities below 900 K are taken to be those for Na_2SiO_3(cr).

$S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation. The low temperature heat capacities, 63.74–162.48 K, have been measured by Tarasov and Savitskaya;[2] however, these are not adequate to be used to evaluate $S°(298.15\ K)$.

Fusion Data

The adopted T_{fus} = 1362 K, determined by Kracek,[3] is in good agreement with the value 1261 K reported by Jaeger[4] and later confirmed by Morey and Bowen.[5]

Other reported T_{fus} values are 1280, 1291, and 1329 K by Kultascheff,[6] Wallace[7] and van Klooster,[8] respectively. These values are all lower than the adopted T_{fus} value, probably because the sample compositions were not the exact composition of metasilicate.

The value of $\Delta_{fus}H°$ is evaluated from the adopted heat capacities for Na_2SiO_3(cr) and Na_2SiO_3(l), and the enthalpy data reported by Naylor,[1] assuming the final state of the calorimetric sample to be Na_2SiO_3(cr). From the phase diagrams of Na_2SiO_3 with other compounds, Kelley[9] derived the values of $\Delta_{fus}H°$ of 9.8–10.5 kcal·mol⁻¹

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	111.880	150.496	150.496	0.	−1510.875	−1427.704	250.128
300	112.395	151.189	150.498	0.207	−1510.890	−1427.188	248.496
400	127 779	185.767	155.108	12.264	−1516.655	−1398.786	182.663
500	138.716	215.514	164.284	25.615	−1516.373	−1369.330	143.053
600	147.114	241.575	175.039	39.922	−1515.214	−1340.018	116.659
700	153.946	264.782	186.232	54.985	−1513.385	−1310.955	97.825
800	159.749	285.727	197.381	70.677	−1511.025	−1282.192	83.719
900	164.842	304.843	208.274	86.912	−1508.235	−1253.751	72.766
900.000	164.842	304.843	208.274	86.912	GLASS <−−> LIQUID		
900.000	177.318	304.843	208.274	86.912	TRANSITION		
1000	177.318	323.525	218.882	104.644	−1504.081	−1225.699	64.024
1100	177.318	340.425	229.175	122.375	−1500.086	−1198.055	56.891
1200	177.318	355.854	239 098	140.107	−1689.797	−1165.888	50.750
1300	177.318	370.047	248.632	157.839	−1684.338	−1122.451	45.101
1362.000	177.318	378.308	254.349	168.833	−−− CRYSTAL <−−> LIQUID −−−		
1400	177.318	383.188	257.780	175.571	−1678.966	−1079.431	40.274
1500	177.318	395.421	266.553	193.303	−1673.677	−1036.792	36.104
1600	177.318	406.865	274.969	211.034	−1668.470	−994.504	32.467
1700	177.318	417.615	283.047	228.766	−1713.518	−952.091	29.254
1800	177.318	427.750	290.807	246.498	−1708.238	−907.454	26.334
1900	177.318	437.337	298.269	264.230	−1702.994	−863.110	23.729
2000	177.318	446.433	305.452	281.962	−1697.785	−819.040	21.391
2100	177.318	455.084	312.373	299.693	−1692.613	−775.230	19.283
2200	177.318	463.333	319.049	317.425	−1687.478	−731.665	17.372
2300	177.318	471.215	325.495	335.157	−1682.381	−688.333	15.633
2400	177.318	478.762	331.725	352.889	−1677.322	−645.223	14.043
2500	177.318	486.000	337.752	370.621	−1672.303	−602.322	12.585

PREVIOUS: June 1965 — CURRENT: September 1967

Sodium Silicate (Na_2SiO_3) CRYSTAL-LIQUID

0 to 1362 K crystal
above 1362 K liquid

Refer to the individual tables for details.

M_r = 122.06324 Sodium Silicate (Na_2SiO_3) $Na_2O_3Si_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° (J·K⁻¹mol⁻¹)	S° (J·K⁻¹mol⁻¹)	$-[G^\circ-H^\circ(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H^\circ-H^\circ(T_r)$ (kJ·mol⁻¹)	Δ_fH° (kJ·mol⁻¹)	Δ_fG° (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−18.913	−1551.203	−1551.203	INFINITE
100	48.308	25.568	196.995	−17.143	−1556.736	−1528.150	798.224
200	89.743	73.542	123.451	−9.982	−1560.031	−1498.083	391.259
298.15	111.880	113.847	113.847	0.	−1561.427	−1467.330	257.070
300	112.395	114.540	113.849	0.207	−1561.442	−1466.746	255.383
400	127.779	149.118	118.459	12.264	−1567.208	−1434.679	187.350
500	138.716	178.865	127.635	25.615	−1566.925	−1401.558	146.420
600	147.114	204.926	138.390	39.922	−1565.766	−1368.581	119.146
700	153.946	228.133	149.583	54 985	−1563.937	−1335.853	99.683
800	159.749	249.078	160.732	70.677	−1561.578	−1303.425	85.105
900	164.841	268.193	171.625	86.911	−1558.788	−1271.319	73.785
1000	169.423	285.801	182.174	103.628	−1555.650	−1239.544	64.747
1100	173.628	302.149	192.346	120.783	−1552.231	−1208.096	57.368
1200	177.540	317.425	202.140	138.343	−1742.114	−1172.091	51.020
1300	181.230	331 783	211.566	156.283	−1736.446	−1124.817	45.196
1362.000	183.407	340.278	217.233	167.587	CRYSTAL <--> LIQUID		
1362.000	177.318	378.308	217.233	219.385		TRANSITION	
1400	177.318	383 188	221.671	226.123	−1678.966	−1079.431	40.274
1500	177.318	395.421	232.851	243.855	−1673.677	−1036 792	36.104
1600	177.318	406.865	243.374	261.587	−1668.470	−994.504	32.467
1700	177.318	417.615	253.310	279.319	−1713.518	−952.091	29.254
1800	177.318	427.750	262.722	297.050	−1708.238	−907.454	26.334
1900	177.318	437.337	271.663	314.782	−1702.994	−863.110	23.729
2000	177.318	446.433	280.176	332.514	−1697.785	−819.040	21.391
2100	177.318	455.084	288.300	350.246	−1692.613	−775.230	19.283
2200	177.318	463.333	296.070	367.978	−1687.478	−731.665	17.372
2300	177.318	471.215	303.515	385.709	−1682.381	−688.334	15.633
2400	177.318	478.762	310.661	403.441	−1677.322	−645.223	14.043
2500	177.318	486.000	317.531	421.173	−1672.303	−602.322	12.585

PREVIOUS: CURRENT. September 1967

Sodium Sulfate, delta (Na_2SO_4) CRYSTAL(δ) M_r = 142.03714 Sodium Sulfate, Delta (Na_2SO_4) $Na_2O_4S_1$(cr)

$S°$(298.15 K) = [163.212] J·K^{-1}·mol^{-1}
T_{tr}(I → δ) = [986] K
T_{fus}(δ → l) = [1170] K

$\Delta_f H°$(298.15 K) = [−1379.294] kJ·mol^{-1}
$\Delta_{trs} H°$(I → δ) = [0.502] kJ·mol^{-1}
$\Delta_{fus} H°$(δ → l) = [21.338] kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation adopted in this tabulation is obtained from $\Delta_f H°$(298.15 K) for Na_2SO_4(cr, I) by adding $\Delta_{trs} H°$(I → δ) and the difference between $H°$(986 K) $H°$(298.15 K) for Na_2SO_4(cr, I) and Na_2SO_4(cr, δ).[2]

Heat Capacity and Entropy

Heat capacities in the range 900–1010 K were measured by Shmidt and Sokolov[1] in an adiabatic calorimeter. We have graphically extrapolated these data down to 298.15 K, paralleling the $C_p°$ data of Na_2SO_4(cr, I), and extended the data smoothly to 1500 K. Our calculated enthalpies are biased by some 300 cal·K^{-1}·mol^{-1} above the experimental results (for the I phase) of Denielou *et al.*[3] and Coughlin.[4] See the discussion in the Na_2SO_4(cr, I) table.[2]

Transition Data

The existence of Na_2SO_4(cr, δ) is based on the work of Shmidt and Sokolov[1] who found an anomolous region in the heat capacity curve of Na_2SO_4(cr, I) between 963–993 K. Popov and Ginzburg[5] also observed a sharp change in the heat capacity above 837.6 K. Simanov and Kirkina[6] have observed an orthorhombic modification of Na_2SO_4 at 993 K by X-ray diffraction. As noted above, our calculated enthalpies do not agree with measured enthalpies above 980 K. The evidence for the existence of the δ phase is not conclusive. We have deleted the δ phase from our combined phase table for Na_2SO_4. The heat of transition $\Delta_{trs} H°$(I → δ, 986 K) = 120 ± 10 cal·mol^{-1} is obtained by graphical integration of the area between the measured $C_p°$ curve from[1] and the adopted $C_p°$ curve for Na_2SO_4(cr, I).[2] The temperature of the transition is assumed to be 986 K.

Fusion Data

Based on our selected $C_p°$ values for Na_2SO_4(cr, δ) and Na_2SO_4(l), we derive $\Delta_{fus} H°$(δ → l) = 5.10 ± 0.10 kcal·mol^{-1} using the experimental liquid enthalpies from Denielou *et al.*[3] and Coughlin.[4] T_{fus}(δ → l) = 1170 K is the calculated temperature at which $\Delta_r G°$ = 0 for Na_2SO_4(cr, δ) → Na_2SO_4(l).

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[6] Y. P. Simanov and D. R. Kirkina, Russ. J. Inorg. Chem. 2, 364 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.812	163.212	163.212	0.	−1379.294	−1265.387	221.690
300	155.896	164.176	163.215	0.288	−1379.261	−1264.680	220.200
400	163.050	210.099	169.427	16.269	−1385.063	−1226.248	160.132
500	166.251	246.782	181.355	32.714	−1384.866	−1186.573	123.960
600	171.816	277.574	194.889	49.611	−1383.905	−1146.990	99.854
700	178.113	304.516	208.664	67.097	−1382.180	−1107.631	82.652
800	185.707	328.766	222.184	85.266	−1379.714	−1068.569	69.770
900	195.979	351.212	235.287	104.333	−1429.489	−1028.786	59.709
1000	208.112	372.490	247.951	124.539	−1423.838	−984.557	51.428
1100	220.413	392.907	260.207	145.970	−1417.113	−940.945	44.682
1200	232.086	412.592	272.090	168.602	−1602.887	−893.112	38.876
1300	242.881	431.600	283.633	192.357	−1592.358	−834.384	33.526
1400	252.923	449.977	294.862	217.160	−1580.856	−776.504	28.972
1500	261.333	467.723	305.798	242.887	−1568.503	−719.477	25.054

PREVIOUS: December 1966   CURRENT: June 1978

Sodium Sulfate, I (Na_2SO_4) CRYSTAL $M_r = 142.03714$ Sodium Sulfate, I (Na_2SO_4) $Na_2O_4S_1(cr)$

$S°(298.15\ K) = [160.132 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(III \rightarrow I) = 509 \pm 1\ K$
$T_{trs}(IV \rightarrow I) = 514 \pm 1\ K$
$T_{fus}(I \rightarrow l) = 1157 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1380.899 \pm 0.8]\ kJ\ mol^{-1}$
$\Delta_{trs} H°(III \rightarrow I) = 6.887 \pm 0.084\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(IV \rightarrow I) = 10.908 \pm 0.084\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(I \rightarrow l) = 23.849 \pm 0.42\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation adopted in this tabulation is obtained from $\Delta_f H°(Na_2SO_4$, cr, III, 298 15 K) by adding $\Delta_{trs} H°$(III → I, 509 K) = 1646 $cal \cdot K^{-1} \cdot mol^{-1}$ [1,2] and the difference between $H°$(509 K) $H°$(298 15 K) for Na_2SO_4(cr, III) and Na_2SO_4(cr, I).[2]

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(cr, I) have been measured by Shmidt and Sokolov[3] in an adiabatic calorimeter over the temperature range 538.65–1021.75 K. The direct heating measurements of Popov and Galchenko[4] using a heat flow calorimeter are in substantial agreement. Enthalpy measurements by drop calorimetry have been carried out by Coughlin,[5] 515–1143 K, Popov and Ginzburg,[6] 1173–1290 K, May,[7] (520–1157 K), and by Denielou *et. al.*,[8] 516–1154 K.

The data of May[7] are not in agreement with the other enthalpy results. The enthalpy data of references[5, 6, 8] are in general agreement but our derived $C_p°$ values are lower than the calorimetric $C_p°$[3] results below 800 K but show the proper slope Derived $C_p°$ values from Denielou *et. al.*[8] are in agreement with the calorimetric results above 930 K. All of the experiments seem to show a change in the slope of the $C_p°$ curve near 900 K. We adopt $C_p°$ from 530–880 K from[3] and extrapolate smoothly to 1500 K. $C_p°$ values below 530 K are obtained by graphical extrapolation. The entropy, $S°$(298.15 K), is calculated in a manner analogous to that of the heat of formation.

Transition Data

Na_2SO_4(cr, I) is the hexagonal modification (space group D^3_{3d} or C3ml)[9, 10] of anhydrous sodium sulfate stable from 514–1157 K. All the low temperature modifications (III, IV, V) are converted to the high temperature form between 500–530 K;[2] $\Delta_{trs} H°$(IV → I, 514 K) = 2607 $cal \cdot mol^{-1}$,[1, 2] $\Delta_{trs} H°$(V → I, 512 K) = 2663 $cal \cdot mol^{-1}$,[1, 2] and $\Delta_{trs} H°$(III → I, 509 K) = 1646 $cal \cdot mol^{-1}$.[1, 2]

A small anomalous region between 963.15–993.15 K on the $C_p°$ curve for Na_2SO_4(cr, I) was reported by Shmidt and Sokolov,[3] who attributed the anomaly to a transition to another phase of Na_2SO_4 which they referred to as the δ phase. There is not sufficient evidence to warrant our inclusion of the δ phase.

Fusion Data

The enthalpy of melting of Na2SO4(cr, I) → Na2SO4 (l) has been derived from drop calorimetry data by Denielou *et. al.*,[8] 5.58 ± 0.13 $kcal \cdot mol^{-1}$, Coughlin,[5] 5.67 ± 0.1 $kcal \cdot mol^{-1}$, Popov and Ginzburg,[6] 5.77 ± 0.2 $kcal \cdot mol^{-1}$, and May,[7] 5.8 ± 0.2 $kcal \cdot mol^{-1}$. No mention was made of the δ phase. Based on our selected $C_p°$ values for Na_2SO_4(cr, I) and Na_2SO_4(l), we derive $\Delta_{fus} H°(I \rightarrow l) = 5.70 \pm 0.10\ kcal \cdot mol^{-1}$, using the enthalpy data of Coughlin.[5] There is good agreement on the melting temperature which we take as $T_{fus}(I \rightarrow l) = 1157 \pm 1$ K.

References

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[2] JANAF Thermochemical Tables: Na_2SO_4(cr, V), Na_2SO_4(cr, IV), Na_2SO_4(cr, III), 6–30–78.
[3] N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 6, 1321 (1961).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298 15	159.620	160.132	160.132	0.	−1380.899	−1266.074	221.811
300	159.724	161.120	160.135	0.295	−1380.859	−1265.361	220.319
400	164.758	207.754	166.460	16.518	−1386.419	−1226.666	160.186
500	170.017	245.088	178.571	33.258	−1385.927	−1186.787	123.983
514 000	170.732	249.793	180.447	35.644	------- IV <--> I -------		
600	175.331	276.549	192.345	50.522	−1384.599	−1147.069	99.861
700	181.042	303.999	206.375	68.337	−1382.545	−1107.634	82.653
800	187.276	328.577	220.140	86.750	−1379.835	−1068.539	69.768
900	193.845	351.015	233.452	105.807	−1429.621	−1028 740	59.707
1000	200.309	371.773	246.259	125.515	−1424.467	−984.470	51.423
1100	206.731	391.167	258.560	145.867	−1418.821	−940.739	44.672
1157.000	210.367	401.702	265.354	157.755	----- I <--> LIQUID ------		
1200	213.133	409.428	270.379	166.860	−1606.234	−892.663	38.857
1300	219.447	426.739	281.746	188.490	−1597.830	−833.536	33.492
1400	225.598	443.227	292.696	210.744	−1588.878	−775.076	28.918
1500	231.584	458.997	303.261	233.604	−1579.391	−717.276	24.978

PREVIOUS: December 1966 CURRENT: June 1978

Sodium Sulfate, I (Na_2SO_4) $Na_2O_4S_1(cr)$

Sodium Sulfate, III (Na_2SO_4) CRYSTAL(III) $M_r = 142.03714$ Sodium Sulfate, III (Na_2SO_4) $Na_2O_4S_1(cr)$

$S°(298.15\ K) = 154.908 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(III \rightarrow I) = 509 \pm 1\ K$

$\Delta_f H°(0\ K) = -1373.71 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1384.85 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(III \rightarrow I) = 6.887 \pm 0.084\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Brodale and Giauque[1] determined the enthalpy of solution at infinite dilution $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1273 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}$ for the process $Na_2SO_4(cr, III) \rightarrow Na_2SO_4(aq, \infty)$. When this result is combined with the enthalpies of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4, aq, \infty, 298.15\ K) = -332.266 \pm 0.13\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.993 \pm 0.15\ kcal \cdot mol^{-1}$. Coughlin[3] also measured the enthalpy of solution, $\Delta_{sln}H°(Na_2SO_4, cr, III, 303\ K) = -1363 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}$ for the process $Na_2SO_4(cr, III) \rightarrow Na_2SO_4(aq, 1068\ H_2O)$. Using $\Delta C_p°$ as determined by Coughlin to extrapolate the heat of solution to 298 K gives $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1037 \pm 20\ cal \cdot K^{-1} \cdot mol^{-1}$. Extrapolating to infinite dilution using the data of Lange and Streeck[4] and Wallace and Robinson[5] gives $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1282 \pm 20\ cal \cdot K^{-1} \cdot mol^{-1}$. Using the same auxiliary data as above[2] $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.984 \pm 0.15\ kcal \cdot mol^{-1}$. The enthalpy of solution data of Coughlin[3] as corrected by Brodale and Giauque[1] leads to $\Delta_r H°(V \rightarrow III, 298.15\ K) = 716 \pm 8\ cal \cdot K^{-1} \cdot mol^{-1}$. When this is combined with auxiliary data for $Na_2SO_4(cr, V)$,[6] we obtain $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.980 \pm 0.2\ kcal \cdot mol^{-1}$. We adopt an intermediate value $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.988 \pm 0.15\ kcal \cdot mol^{-1}$ for this tabulation.

Heat Capacity and Entropy

Heat capacities of $Na_2SO_4(cr, III)$ have been measured by Brodale and Giauque[1] over the ragne 13.16–297.71 K and by Shmidt and Sokolov[7] in an adiabatic calorimeter over the temperature range 319.03–520.56 K. Paukov and Lavrent'eva[8] also measured the low temperature heat capacity of $Na_2SO_4(cr, III)$ but their results are intermediate between $Na_2SO_4(cr, V)$ and $Na_2SO_4(cr, III)$ indicating that their sample may have been converted to as much as two–thirds of the V modification. Coughlin[3] measured enthalpies of $Na_2SO_4(cr, III)$ from 370.2–514.9 K by drop calorimetry, but his data appear high by 2% at 450 K. Enthalpy measurements of Denielou *et al.*[9] are in very good agreement with the $C_p°$ measurements of Shmidt and Sokolov.[7] We combine the three sets of experimental data[1, 7, 9] by graphical smoothing and by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. $C_p°$ is smoothly extrapolated to 1000 K. $S°(298.15\ K)$ is derived from our combined smooth fit based on $S°(14\ K) = 0.100\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(14\ K) - H°(0\ K) = 1.051\ cal \cdot K^{-1} \cdot mol^{-1}$ derived from a Debye T^3–law extrapolation.

Transition Data

$Na_2SO_4(cr, III)$ is the meltable low–temperature orthorhombic modification of anhydrous sodium sulfate which is obtained on cooling, in the absence of moisture, the high–temperature hexagonal form $Na_2SO_4(cr, I)$. $Na_2SO_4(cr, III)$ is metastable with respect to the two other low–temperature orthorhombic forms $Na_2SO_4(cr, V)$ and $Na_2SO_4(cr, IV)$. The space group of $Na_2SO_4(cr, III)$ has been given as Cmcm.[10]

The second–order transformation from $Na_2SO_4(cr, III)$ to $Na_2SO_4(cr, I)$ in which both phases are metastable, has been observed by Shmidt and Sokolov[7] at 521.5 K, $\Delta_{trs}H°(III \rightarrow I) = 1642 \pm 20\ cal \cdot mol^{-1}$; by Coughlin[3] at 514 K, $\Delta_{trs}H°(III \rightarrow I) = 1680\ cal \cdot mol^{-1}$, by Denielou *et al.*[9] at 515 ± 1 K, $\Delta_{trs}H°(III \rightarrow I) = 1650 \pm 90\ cal \cdot mol^{-1}$; and by May[11] at 520 ± 5 K, $\Delta_{trs}H°(III \rightarrow I) = 1150\ cal \cdot mol^{-1}$. We adopt the transition temperature from the analysis of Brodale and Giauque.[1] This is consistent with our analysis which yields $\Delta_{trs}H°(III \rightarrow I, 298.15\ K) = 1646 \pm 20\ cal \cdot mol^{-1}$. The heat of transition from metastable $Na_2SO_4(cr, V)$ to metastable $Na_2SO_4(cr, III)$ has been measured by heat of solution measurements on the separate crystalline forms by Coughlin,[3] Brodale and Giauque[1] and Pickering.[12] $\Delta_r H°(V \rightarrow III, 298.15\ K) = 716 \pm 8\ cal\ mol\ l^{-1}$,[1, 3] $699 \pm 10\ cal \cdot mol^{-1}$,[1] $709 \pm 10\ cal \cdot mol^{-1}$[1, 13] and $\Delta_r H°(V \rightarrow III, 294\ K) = 708 \pm 20\ cal \cdot mol^{-1}$.[12] Using the heat of transition value from[1] and the difference between $H°(517\ K) - H°(298.15\ K)$ for $Na_2SO_4(cr, III)$ and $Na_2SO_4(cr, V)$,[6] we obtain $\Delta_{trs}H°(V \rightarrow III, 517\ K) = 1041 \pm 20\ cal \cdot mol^{-1}$. The heat of transition from metastable $Na_2SO_4(cr, IV)$ to metastable $Na_2SO_4(cr, III)$ is discussed on the table for $Na_2SO_4(cr, IV)$. Our analysis yields $\Delta_{trs}H°(IV \rightarrow III, 519\ K) = 988 \pm 20\ cal \cdot mol^{-1}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.527	−1373.708	−1373.708	INFINITE
100	68.216	47.861	252.668	−20.481	−1379.841	−1343.950	702.008
200	105.621	108.169	165.992	−11.565	−1383.300	−1306.534	341.232
298.15	129.168	154.908	154.908	0.	−1384.854	−1268.471	222.231
300	129.570	155.709	154.911	0.239	−1384.870	−1267.748	220.735
400	150.143	195.743	160.231	14.205	−1392.687	−1228.129	160.377
500	173.167	231.587	170.966	30.311	−1392.829	−1186.938	123.999
600	200.091	265.539	183.916	48.973	−1390.103	−1145.967	99.765
700	227.011	298.405	197.935	70.329	−1384.508	−1105.681	82.507
800	253.935	330.475	212.505	94.376	−1376.164	−1066.386	69.628
900	280.859	361.939	227.366	121.116	−1418.266	−1027.217	59.618
1000	307.779	392.924	242.376	150.548	−1403.389	−984.542	51.427

PREVIOUS: December 1966 CURRENT: June 1978

Sodium Sulfate, IV (Na_2SO_4)　CRYSTAL(IV)　$M_r = 142.03714$

$S°(298.15\ K) = [150.157 \pm 0.4]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs}(V \rightarrow IV) = 458 \pm 1\ K$
$T_{trs}(IV \rightarrow I) = 514 \pm 1\ K$

$\Delta_f H°(0\ K) = [-1380.09]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1387.559 \pm 0.63\ kJ\cdot mol^{-1}$
$\Delta_{trs} H°(V \rightarrow IV) = 0.255 \pm 0.063\ kJ\cdot mol^{-1}$
$\Delta_{trs} H°(IV \rightarrow I) = 10.908 \pm 0.084\ kJ\cdot mol^{-1}$

Enthalpy of Formation

Brodale and Giauque[1] determined the enthalpy of solution at infinite dilution $\Delta_{sln} H°(Na_2SO_4$, cr, IV, 298.15 K) = 635 ± 1 kcal·mol^{-1} for the process Na_2SO_4(cr, IV) → Na_2SO_4(aq, ∞). When this result is combined with the enthalpies of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4$, aq, ∞, 298.15 K) = 332.266 ± 0.13 kcal·mol^{-1}and $\Delta_f H°(Na_2SO_4$, cr, IV, 298.15 K) = −331.631 ± 0.15 kcal·mol^{-1}. Brodale and Giauque[1] have also determined the difference in $\Delta_f H°$(298.15 K) between Na_2SO_4(cr, IV) and Na_2SO_4(cr, V) by direct heat of solution experiments. We prefer to give complete weight to these results using the same calorimeter. $\Delta_{sln} H°(Na_2SO_4$, cr, V, 298.15 K) = −574 cal·K^{-1}·mol^{-1} [1] which leads to $\Delta_r H°$(V → IV, 298.15 K) = 61 ± 15 cal·K^{-1}·mol^{-1}. When this is combined with auxiliary data for Na_2SO_4(cr, V),[3] we obtain $\Delta_f H°(Na_2SO_4$, cr, IV, 298.15 K) = −331.635 ± 0.15 kcal·mol^{-1}. This value of $\Delta_f H°$(298.15 K) is adopted in this tabulation.

Heat Capacity and Entropy

The heat capacity of Na_2SO_4(cr, IV) has been taken equal to the heat capacity of the V form from 298–514 K.[1 3] The heat of transition (V → IV) adopted here leads to a calculated entropy of transition of 0.133 cal·K^{-1}·mol^{-1} and $S°(Na_2SO_4$, cr, IV, 458 K) = 50.304 cal·K^{-1}·mol^{-1}. Brodale and Giauque[1] state that the small difference in entropy (between IV and V) means that on the average the heat capacity of Na_2SO_4(cr, IV) should exceed the heat capacity of Na_2SO_4(cr, V) by only about 0.3% over the range 298–514 K. We calculate $S°(Na_2SO_4$, cr, IV, 298.15 K) = 35.887 cal·K^{-1}·mol^{-1}.

Transition Data

Na_2SO_4(cr, IV) is the orthorhombic modification of anhydrous sodium sulfate stable from 458 514 K.[1 4] This form can persist down to low temperatures. The presence of moisture enhances the achievement of equilibrium. A recent Raman and DSC study has failed to observe the IV modification.[8] The (V → IV) transition at 458 K has been discussed previously (see [3] and above), $\Delta_r H°$(V → IV, 298.15 K) = 61 ± 15 cal·mol^{-1}. Since $\Delta C_p° = 0$,[1, 3] $\Delta_{trs} H°$(V → IV, 458 K) = 61 ± 15 cal·mol^{-1}. The temperature of 458 K for the transition is taken from Kracek[4] and Brodale and Giauque.[1]

The transition from Na_2SO_4(cr, IV) to Na_2SO_4(cr, I) has been found to occur at 514 K.[1 4] The heat of the transition has not been directly measured although Shmidt and Sokolov[5] obtained $\Delta_{trs} H°$(516 K) = 2584 ± 15 cal·mol^{-1} for a sample of ground Na_2SO_4 which could have been Na_2SO_4(cr, IV) (see [1]). We adopt the value of the heat of transition $\Delta_{trs} H°$(IV → I, 514 K) = 2607 ± 20 cal·mol^{-1}. This is obtained by summation of $\Delta_{trs} H°$(IV → III)[1, 3] and $\Delta_{trs} H°$(III → I),[1, 3] all reduced to 514 K. Other measurements include that of Kreidl and Simon[6] who found $\Delta_{trs} H°$(IV → I, 511 K) = 2300 cal·mol^{-1} and Popov and Galchenko[7] who found $\Delta_{trs} H°$(518 K) = 2586 ± 64 cal·mol^{-1} on first heating. Later heating apparently converted some sample over to the III modification. Brodale and Giauque[1] give $\Delta_{trs} H°$(IV → I, 514 K) = 2611 cal·mol^{-1}.

The heat of transition from metastable Na_2SO_4(cr, IV) to metastable Na_2SO_4(cr, III) is obtained from heat of solution measurements on the separate crystalline forms. Brodale and Giauque[1] obtained $\Delta_{sln} H°(Na_2SO_4$, cr, IV, 298.15 K) = −635 ± 1 cal·mol^{-1} and $\Delta_{sln} H°(Na_2SO_4$, cr, III, 298.15 K) = −1273 ± 4 cal·mol^{-1} from which $\Delta_r H°$(IV → III, 298.15 K) = 638 ± 10 cal·mol^{-1}. Combining this result with the difference between $H°$(519 K)–$H°$(298.15 K) for Na_2SO_4(cr, IV) and Na_2SO_4(cr, III) we obtain $\Delta_{trs} H°$(IV → III, 519 K) = 988 ± 20 cal·mol^{-1}. Shmidt and Sokolov[5] have measured the heats of transformation of Na_2SO_4(thenardite) → Na_2SO_4,cr, I) and Na_2SO_4(cr, III) → Na_2SO_4(cr, I) calorimetrically from which we obtain $\Delta_{trs} H°$(thenardite → III, 516 K) = 954 ± 20 cal·mol^{-1}. Brodale and Giauque[1] have speculated that the "ground thenardite" of Shmidt and Sokolov[5] was actually the IV modification of Na_2SO_4.

References

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Sodium Sulfate, IV (Na_2SO_4)　$Na_2O_4S_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K　　Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	128.143	150.157	150.157	0.	−1387.559	−1269.759	222.456
300	128.495	150.950	150.159	0.237	−1387.577	−1269.028	220.957
400	145.101	190.263	155.407	13.943	−1395.654	−1228.904	160.478
458.000	153.331	210.462	161.117	22.600	-------- V <--> IV --------		
500	158.908	224.159	165.842	29.158	−1396.687	−1187.082	124.014
514.000	160.712	228.572	167.491	31.396	-------- IV <--> I --------		
600	171.322	254.242	178.113	45.677	−1396.104	−1145.190	99.698
700	182.933	281.530	190.967	63.394	−1394.148	−1103.508	82.345
800	194.046	306.686	203.879	82.246	−1390.999	−1062.190	69.354
900	204.828	330 166	216.620	102.191	−1439.895	−1020.251	59.214
1000	215.371	352.295	229.091	123.203	−1433.438	−973.962	50.875

PREVIOUS:　　CURRENT June 1978

Sodium Sulfate, IV (Na_2SO_4)　$Na_2O_4S_1(cr)$

Sodium Sulfate, V (Na_2SO_4) CRYSTAL(V) $M_r = 142.03714$ Sodium Sulfate, V (Na_2SO_4) $Na_2O_4S_1(cr)$

$S°(298.15\ K) = 149.595 \pm 0.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs}(V \rightarrow IV) = 458 \pm 1\ K$

$\Delta_f H°(0\ K) = -1376.361 \pm 0.63\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -1387.816 \pm 0.63\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H°(V \rightarrow IV) = 0.255 \pm 0.063\ kJ{\cdot}mol^{-1}$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	$\log K_f$
0	0.	0.	INFINITE	−23.217	−1376.361	−1376.361	INFINITE
100	66.542	43.120	247.007	−20.389	−1382.711	−1346.347	703.259
200	105.667	103.010	160.624	−11.523	−1386.221	−1308.422	341.725
298.15	128.143	149.595	149.595	0.	−1387.816	−1269.849	222.472
300	128.495	150.388	149.597	0.237	−1387.834	−1269.117	220.973
400	145.101	189.702	154.845	13.943	−1395.911	−1228.937	160.483
458.000	153.331	209.905	160.555	22.602	-------- V <---> IV --------		
500	158.908	223.596	165.280	29.158	−1396.944	−1187.058	124.011
600	171.322	253.678	177.551	45.676	−1396.362	−1145.110	99.691
700	182.933	280.966	190.404	63.393	−1394.406	−1103.372	82.335
800	194.046	306.122	203.316	82.245	−1391.257	−1061.997	69.341
900	204.828	329.602	216.057	102.190	−1440.154	−1020.002	59.199
1000	215.371	351.731	228.529	123.202	−1433.696	−973.656	50.859

PREVIOUS: December 1966 CURRENT: June 1978

Enthalpy of Formation

Shibata *et. al.*[1] measured the emf of the cell: Na(amalgam, 0.2077%)|Na_2SO_4(sat. soln), Hg_2SO_4|Hg at 306–310 K. Extrapolating their results to 298 K, correcting the observed voltage for the formation of the Na amalgam, and converting to absolute volts, we have $E_{cell} = 3.33404$ volts for the reaction at 298 K, $2\ Na(cr) + Hg_2SO_4(cr) = 2\ Hg(l) + Na_2SO_4(cr,\ V)$. From this voltage we calculate $\Delta_r G°(298.15\ K) = -153.77\ kcal{\cdot}mol^{-1}$. Taking $\Delta_f G°(Hg_2SO_4,\ cr,\ 298.15\ K) = -149.66\ kcal{\cdot}mol^{-1}$ [2] and reference entropies from,[3] we calculate $\Delta_f G°(Na_2SO_4,\ cr,\ V,\ 298.15\ K) = -303.43\ kcal{\cdot}mol^{-1}$ and $\Delta_f H°(Na_2SO_4,\ cr,\ V,\ 298.15\ K) = -331.60 \pm 0.2\ kcal{\cdot}mol^{-1}$.

The enthalpy of solution at infinite dilution, $\Delta_{sln} H°(Na_2SO_4,\ cr,\ V,\ 298.15\ K) = -570 \pm 10\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ adopted in this tabulation is based on our reanalysis of the enthalpy of solution measurements of Gardner *et al.*,[4] Brodale and Giauque,[5] Pitzer and Coulter,[6] Coughlin[7] as corrected in,[5] and Readnour and Cobble.[8] When this result is combined with heats of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4,\ aq,\ \infty,\ 298.15\ K) = -332.266 \pm 0.13\ kcal{\cdot}mol^{-1}$ and $\Delta_f H°(Na_2SO_4,\ cr,\ V,\ 298.15\ K) = -331.696 \pm 0.15\ kcal{\cdot}mol^{-1}$. The experimental $\Delta_{sln} H°$ values and the number of determinations are $-582 \pm 5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, 6,[4] $-574\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, 1;[5] $-564 \pm 10\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, 2,[6] $-565 \pm 30\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, 5,[7,5] and $-567 \pm 12\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$, 9.[8]

We adopt $\Delta_f H°(Na_2SO_4,\ cr,\ V,\ 298.15\ K) = -331.696 \pm 0.5\ kcal{\cdot}mol^{-1}$ from the heat of solution results for consistency with the other modifications of Na_2SO_4(cr).[3]

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(cr, V) have been measured by Pitzer and Coulter[6] over the range 13.74–313.44 K and by Shmidt and Sokolov[9] in an adiabatic calorimeter over the temperature range 324.62–503.06 K. Shmidt[10] later carried out additional measurements which he combined with the earlier measurements of Shmidt and Sokolov[9] and reported $C_p°$ values extending from 298.5–503.1 K. We have smoothed the experimental data[6, 9, 10] by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. The data have been smoothly extrapolated to 1000 K. We have given no weight to the calorimetry enthalpy differences measured by Coughlin,[7] May,[11] and Denielou *et. al.*[12] These measured enthalpies are higher than our calculated enthalpies by 6%, 9% and 2%, respectively at 400 K. The $C_p°$ measurements of Popov and Galchenko[13] from 373–468 K appear to be biased, being too low at 373 K and too high at 468 K. $S°(298.15\ K)$ is derived from our combined smooth fit based on $S°(14\ K) = 0.059\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $H°(14\ K) - H°(0\ K) = 0.620\ cal{\cdot}mol^{-1}$ derived from a T^3 law extrapolation.

Transition Data

Na_2SO_4(cr, V) is the stable low temperature modification of anhydrous sodium sulfate which is obtained by crystallization from aqueous solution above 305.65 K under ordinary pressure. The mineral is known as thenardite and exists in the form of orthorhombic crystals (space group Fddd).[15]

Polymorphism studies by Kracek[14] indicated five distinct modifications of anhydrous sodium sulfate, i.e., V, IV, III, II, I. Calorimetric studies by Shmidt and Sokolov[9] as well as the X-ray work of Simanov and Kirkina[15] suggested another form, stable at high temperatures which is labeled as δ. Brodale and Giauque[5] have recently reviewed the relationships among the various crystalline forms of Na_2SO_4(cr). Their analysis shows that Na_2SO_4(cr, V) is the stable form from 0 to 458 K; Na_2SO_4(cr, IV) rather than Na_2SO_4 (cr, III) is the stable form from 458 to 514 K; Na_2SO_4(cr, I) is the form stable from 514 K to the melting point. Na_2SO_4(cr, III) is metastable at all temperatures from 0 to 517 K. Na_2SO_4(cr, II) is a meta stable phase intermediate between forms III and I. The phase transitions are sluggish and subject to hysteresis. Forms V, IV and III can all persist far beyond their stable regions.

The heat of transition $\Delta_{trs} H°(V \rightarrow IV,\ 458\ K) = 61 \pm 15\ cal{\cdot}mol^{-1}$ is discussed on the table for Na_2SO_4(cr, IV).[3] The temperature of the transition is taken from the work of Kracek[14] and Brodale and Giauque.[5] The heat of transition from metastable Na_2SO_4(cr, V) to metastable Na_2SO_4(cr, III) $\Delta_{trs} H°(V \rightarrow III,\ 517\ K) = 1041 \pm 20\ cal{\cdot}mol^{-1}$ has been discussed on the table for Na_2SO_4(cr, III).[3] This compares to $\Delta_{trs} H°(V \rightarrow III,\ 521\ K) = 1030 \pm 25\ cal{\cdot}mol^{-1}$ from Shmidt and Sokolov[9] and $\Delta_{trs} H°(V \rightarrow III,\ 514\ K) = 1040 \pm 20\ cal{\cdot}mol^{-1}$ from.[5] The heat of transition from metastable Na_2SO_4(cr, V) to metastable Na_2SO_4(cr, I) at 512 ± 1 K is obtained by summation of $\Delta_{trs} H°(V \rightarrow III) = 1021\ cal{\cdot}mol^{-1}$ and $\Delta_{trs} H°(III \rightarrow I) = 1642\ cal{\cdot}mol^{-1}$ [5] to yield $\Delta_{trs} H°(V \rightarrow I,\ 512\ K) = 2663 \pm 25\ cal{\cdot}mol^{-1}$, in good agreement with the value measured by Shmidt and Sokolov,[9] $\Delta_{trs} H°(V \rightarrow I,\ 521\ K) = 2673 \pm 5\ cal{\cdot}mol^{-1}$. Brodale and Giauque[5] give $\Delta_{trs} H°(V \rightarrow I,\ 512\ K) = 2681 \pm 20\ cal{\cdot}mol^{-1}$.

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Sodium Sulfate (Na_2SO_4) LIQUID M_r = 142.03714

$S°$(298.15 K) = [181.172] $J \cdot K^{-1} \cdot mol^{-1}$
T_{fus}(I → l) = 1157 ± 1 K
T_{dcm} = 2500 K

$\Delta_f H°$(298.15 K) = [−1356.385] $kJ \cdot mol^{-1}$
$\Delta_{fus} H°$(I → l) = 238.49 ± 0.42 $kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(Na_2SO_4, cr, I, 298.15 K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(1157 K)–$H°$(298.15 K), between Na_2SO_4(cr, I) and Na_2SO_4(l).[5]

Heat Capacity and Entropy

The enthalpies for Na_2SO_4(l) have been measured by drop calorimetry in the temperature range 1164.7–1826.2 K by Coughlin[1], 1173.3–1502.6 K by Denielou,[2] 1157–1500 K by May[3] and 1173.4–1290.2 K by Popov and Ginzburg.[4] The more recent studies[1, 2, 4] are in very good agreement. The study of May[4] appears biased, being 1% low at 1200 K and 2% high at 1500 K. We have adopted heat capacities derived from the enthalpy data of Coughlin[1] over the range 1157–1800 K. The data have been extended to 800 K and 3000 K. Below an assumed glass transition temperature of 800 K, the heat capacities are taken to be identical to those of the I phase. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The enthalpy of melting of Na_2SO_4(cr, I) → Na_2SO_4(l) has been discussed in the Na_2SO_4(cr, I) table.[5] Kelley[6] had previously reported $\Delta_{fus} H°$(1157 K) = 5.83 $kcal \cdot mol^{-1}$ from data on binary systems. We prefer the results from direct calorimetric measurements.

Vaporization and Decomposition Data

Vaporization data on Na_2SO_4(l) is discordant due primarily to the extent to which the vapor is dissociated. Na_2SO_4(l) can decompose according to various mechanisms, the most significant of which is the reaction $Na_2SO_4(l) = 2\ Na(g) + SO_2(g) + O_2(g)$. Recent experimental data[7,8,9] are in good agreement with dissociation pressures and the heat of reaction calculated from the JANAF Thermochemical Tables.[5] Decomposition to the oxides of sodium produces lower decomposition pressures than decomposition to the metal. In the presence of water vapor, significant decomposition can occur according to $Na_2SO_4(l) + H_2O(g) = 2\ NaOH(g) + SO_2(g) + 1/2\ O_2(g)$.[10] Molecular vaporization data are discussed in the Na_2SO_4(g) table.[5] T_{dec} = 2500 K is the calculated temperature at which the Gibbs energy difference is zero for the reaction $Na_2SO_4(l) = 2\ Na(g) + SO_2(g) + O_2(g)$.

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Sodium Sulfate (Na_2SO_4) $Na_2O_4S_1$(l)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	159.620	181.172	181.172	0.	−1356.385	−1247.832	218.615
300	159 724	182.160	181.175	0.295	−1356.345	−1247.159	217.150
400	164.758	228.794	187.500	16.518	−1361.905	−1210.568	158.084
500	170.017	266.128	199.611	33.258	−1361 412	−1172.792	122.521
600	175.331	297.589	213.385	50.522	−1360.085	−1135.179	98.826
700	181.042	325.038	227.415	68.337	−1358.031	−1097.848	81.922
800	187.276	349.614	241.179	86.748	−1355.323	−1060.856	69.267
800.000	187.276	349.614	241.179	86 748	GLASS <- -> LIQUID TRANSITION		
800.000	197.033	349.614	241 179	86.748			
900	197.033	372.822	254.542	106.451	−1404.461	−1023.207	59.385
1000	197.033	393.581	267.426	126.155	−1399.313	−981.123	51.249
1100	197.033	412.360	279.762	145.858	−1394.316	−939.547	44.615
1157 000	197.033	422.314	286.541	157.089	------ I <- -> LIQUID ------		
1200	197.033	429.504	291.537	165.561	−1583.018	−893.538	38.895
1300	197.033	445.275	302.764	185.265	−1576.541	−836.345	33.605
1400	197 033	459.877	313 471	204 968	−1570.140	−779.647	29.089
1500	197.033	473.471	323 690	224.671	−1563.809	−723.405	25.191
1600	197 033	486.187	333.453	244.374	−1557.546	−667.583	21 794
1700	197.033	498.132	342.792	264 078	−1551.347	−612.150	18.809
1800	197.033	509.394	351.738	283.781	−1545.210	−557.082	16.166
1900	197.033	520.047	360.319	303.484	−1539.134	−502.351	13.811
2000	197.033	530.154	368.560	323 188	−1533.117	−447.939	11.699
2100	197.033	539.767	376.486	342.891	−1527.159	−393.827	9.796
2200	197.033	548.933	384.118	362.594	−1521.259	−339.997	8 073
2300	197.033	557.692	391 475	382.298	−1515.418	−286.435	6.505
2400	197.033	566.077	398.577	402.001	−1509.635	−233.125	5.074
2500	197.033	574 120	405.439	421.704	−1503.912	−180.055	3.762
2600	197.033	581.848	412.076	441 407	−1498.246	−127.213	2.556
2700	197.033	589.284	418.503	461.111	−1492.640	−74.587	1.443
2800	197.033	596 450	424.731	480.814	−1487.093	−22.168	0.414
2900	197.033	603.364	430.772	500.517	−1481.607	30.053	−0.541
3000	197.033	610.044	436.637	520.221	−1476.185	82.087	−1.429

PREVIOUS December 1966   CURRENT June 1978

Sodium Sulfate (Na_2SO_4) $Na_2O_4S_1$(l)

Sodium Sulfate (Na_2SO_4) CRYSTAL(V-IV-I)-LIQUID

0	to	458	K crystal, V
458	to	514	K crystal, IV
514	to	1157	K crystal, I
above		1157	K liquid

Refer to the individual tables for details.

M_r = 142.03714 Sodium Sulfate (Na_2SO_4) $Na_2O_4S_1(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−23.217	−1376.361	−1376.361	INFINITE
100	66.542	43.120	247.007	−20.389	−1382.711	−1346.347	703.259
200	105.667	103.010	160.624	−11.523	−1386.221	−1308.422	341.725
298.15	128.143	149.595	149.595	0.	−1387.816	−1269.849	222.472
300	128.495	150.388	149.597	0.237	−1387.834	−1269.117	220.973
400	145.101	189.702	154.845	13.943	−1395.911	−1228.937	160.483
458.000	153.331	209.905	160.555	22.602		V <--> IV	
458.000	153.331	210.462	160.555	22.857		TRANSITION	
500	158.908	224.159	165.328	29.415	−1396.687	−1187.082	124.014
514.000	160.712	228.572	166.990	31.653		IV <--> I	
514.000	170.732	249.793	166.990	42.560		TRANSITION	
600	175.331	276.549	180.817	57.439	−1384.599	−1147.069	99.861
700	181.042	303.999	196.494	75.253	−1382.545	−1107.634	82.653
800	187.276	328.577	211.494	93.666	−1379.835	−1068.539	69.768
900	193.845	351.015	225.767	112.723	−1429.621	−1028.740	59.707
1000	200.309	371.773	239.342	132.431	−1424.467	−984.470	51.423
1100	206.731	391.166	252.272	152.784	−1418.821	−940.739	44.672
1157.000	210.367	401.702	259.376	164.671		I <--> LIQUID	
1157.000	197.033	422.314	259.376	188.520		TRANSITION	
1200	197.033	429.504	265.344	196.992	−1583.018	−893.538	38.895
1300	197.033	445.275	278.586	216.696	−1576.541	−836.345	33.605
1400	197.033	459.877	291.021	236.399	−1570.140	−779.647	29.089
1500	197.033	473.471	302.736	256.102	−1563.809	−723.405	25.191
1600	197.033	486.187	313.809	275.806	−1557.546	−667.583	21.794
1700	197.033	498.132	324.303	295.509	−1551.347	−612.150	18.809
1800	197.033	509.394	334.276	315.212	−1545.210	−557.081	16.166
1900	197.033	520.047	343.776	334.916	−1539.134	−502.351	13.811
2000	197.033	530.154	352.844	354.619	−1533.117	−447.939	11.699
2100	197.033	539.767	361.518	374.322	−1527.159	−393.827	9.796
2200	197.033	548.933	369.831	394.025	−1521.259	−339.997	8.073
2300	197.033	557.692	377.809	413.729	−1515.418	−286.435	6.505
2400	197.033	566.077	385.480	433.432	−1509.635	−233.125	5.074
2500	197.033	574.120	392.866	453.135	−1503.912	−180.055	3.762
2600	197.033	581.848	399.987	472.839	−1498.246	−127.213	2.556
2700	197.033	589.284	406.861	492.542	−1492.640	−74.587	1.443
2800	197.033	596.450	413.505	512.245	−1487.093	−22.168	0.414
2900	197.033	603.364	419.934	531.948	−1481.607	30.053	−0.541
3000	197.033	610.044	426.160	551.652	−1476.185	82.087	−1.429

PREVIOUS: CURRENT: June 1978

Sodium Sulfate (Na_2SO_4) $Na_2O_4S_1(cr,l)$

Sodium Sulfate (Na_2SO_4) IDEAL GAS $M_r = 142.03714$ Sodium Sulfate (Na_2SO_4) $Na_2O_4S_1(g)$

$S°(298.15\ K) = [346.854 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1020.106 \pm 25.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1033.615 \pm 25.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Symmetries and Degeneracies

ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
A_1 961 (1)	B_1[460] (1)	E 1101 (2)
[510](1)	$B_2$1131 (1)	610 (2)
[160](1)	640 (1)	[333](2)
[391](1)	[81](2)	

Ground State Quantum Weight: [1] $\sigma = [4]$
Point Group: [D_{2d}]
Bond Distances: S–O = [1.48] Å Na–O = [2.21] Å
Bond Angles: O–S–O = [109.47]° O–Na–O = [66.205]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.9153 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of the enthalpy of formation, $\Delta_f H°(Na_2SO_4, g, 298.15\ K) = -247.04 \pm 6.0\ kcal \cdot mol^{-1}$, is based on JANAF analyses of the vaporization data given below. Early studies of the vaporization of sodium sulfate failed to take dissociation into account. The many of the effusion and transpiration results in the literature are in error. The dissociation is retarded in the presence of SO_2, O_2 mixtures as in the study of Cubicciotti and Kenesha[1] or in the presence of air (O_2) as in the study of Fryxell *et al.*[4] We have "corrected" some of the original data by subtracting the calculated dissociation pressures[15] from the total pressure to give molecular vaporization pressures. These "corrected data sets" are explicitly noted. Mass spectrometric experiments[2, 3, 5, and 14] can lead to direct molecular vaporization data provided the $Na_2SO_4^+$ ion is directly measured. Results from the Knudsen effusion experiments[5, 14] are in reasonable agreement with the most reliable transpiration experiments.[1, 4] The calculated 3rd law $\Delta_f H°(298.15\ K)$ may have an uncertainty of 4 $kcal \cdot mol^{-1}$ since the JANAF free energy functions are partially based on the estimated molecular constants of $Na_2SO_4(g)$. Vapor pressures from[1, 4 and 5] are in general agreement. Our adopted heat of formation is based on a weighted average of the 2nd or 3rd law results from.[1, 4, 5, 14]

Source	Method	Reaction[a]	T/K	Points	δS^b cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1b	Transpiration (N_2)	A	1400–1624	8	9.24 ± 2.8	90.36 ± 4.2	76.31 ± 2.0	−247.86 ± 6
1	Transpiration ($SO_2 + O_2$)	A	1305–1663	12	4.69 ± 1.2	84.26 ± 1.8	77.06 ± 1.1	−247.11 ± 4
4b	Transpiration (air)	A	1283–1477	20	0.23 ± 1.1	78.51 ± 1.5	78.20 ± 0.6	−245.97 ± 4
4	Transpiration (air)	A	1339–1477	16	3.70 ± 1.1	83.18 ± 1.5	78.05 ± 0.6	−246.12 ± 3
13	Transpiration ($SO_2 + O_2$)	A	1289–1412	6	5.60 ± 1.4	81.39 ± 1.8	73.81 ± 0.6	−250.36 ± 6
13b	Transpiration (N_2)	A	1301–1426	4	17.3 ± 2.5	98.78 ± 3.5	75.05 ± 2.0	−249.12 ± 6
5	Knudsen mass spec	A	1180–1370	2	—	75.76 ± 4.0	—	−248.41 ± 4
5	Knudsen mass spec	A	1196–1349	19	−1.89 ± 0.9	78.36 ± 0.9	78.76 ± 0.4	−245.41 ± 2
14	Knudsen mass spec	A,B	1069–1281	?	—	74.93 ± 2.5	—	−249.24 ± 4
14	Knudsen mass spec	A	1440–1540	?	—	77.41 ± 4.0	—	−246.76 ± 4

[a] A) $Na_2SO_4(l) = Na_2SO_4(g)$ B) $Na_2SO_4(cr) = Na_2SO_4(g)$
[b] data corrected for dissociation.

Heat Capacity and Entropy

The adopted structure (D_{2d} symmetry) is based on the similar symmetry assigned to $Cs_2SO_4(g)$ and to $K_2SO_4(g)$ in the high temperature electron diffraction studies of Ugarov *et al.*[6] and Spiridonov and Lutoshkin.[7] This symmetry is supported by the IR and Raman study of Atkins and Gingerich[9] on Na_2SO_4 and K_2SO_4. The molecule can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging sodium atoms between two pairs of oxygens. The internuclear distance of 1 48 Å for S–O is taken from data on other sulphates[6, 7, 8] while Na–O = 2.21 Å is an estimate from.[7] The principal moments of inertia are $I_A = 15.518 \times 10^{-39}$ and $I_B = I_C = 71.418 \times 10^{-39}\ g \cdot cm^2$.

Atkins and Gingerich[9] have observed the infrared and Raman spectra of Na_2SO_4 and K_2SO_4 isolated in oxygen and nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. The two other sulphate–ion group fundamentals are estimates taken from Gurvich *et al.*[10] The four fundamentals involving the metal atoms are based on the Raman single–crystal study of Montero[11] and comparisons involving K_2SO_4, Cs_2SO_4,[10] LiO_2 and NaO_2.[12] Uncertainties in the estimates of the gas phase frequencies may contribute an uncertainty of 4 $cal \cdot K^{-1} \cdot mol^{-1}$ to $S°(298.15\ K)$.

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.163	−1020.106	−1020.106	INFINITE
100	58.797	259.777	426.257	−16.648	−1024.770	−1010.071	527.607
200	85.280	308.790	355.907	−9.423	−1029.920	−993.278	259.418
250	96.480	329.057	348.544	−4.872	−1031.953	−983.875	205.569
298.15	105.619	346.854	346.854	0.	−1033.615	−974.461	170.721
300	105.940	347.509	346.856	0.196	−1033.675	−974.094	169.605
350	113.834	364 451	348.176	5.696	−1035.199	−964.041	143.875
400	120.370	380.092	351.201	11.556	−1044.097	−953.279	124.485
450	125.760	394.591	355.226	17 714	−1046.024	−941.817	109.323
500	130.203	408.078	359.845	24.117	−1047.785	−930.140	97.171
600	136.924	432.449	369.960	37.494	−1050.344	−906.354	78.905
700	141.606	453.929	380.452	51.434	−1052.164	−882.204	65.831
800	144.949	473.068	390.854	65.771	−1053.531	−857.827	56 010
900	147.397	490.289	400.962	80.394	−1107.749	−832.215	48.301
1000	149.234	505.918	410.688	95.230	−1107.468	−801.615	41.872
1100	150.641	520.211	420.005	110.227	−1107.178	−771.044	36.614
1200	151.741	533.367	428.911	125.348	−1300.462	−735.618	32.021
1300	152.614	545.549	437.420	140.567	−1298.469	−688.628	27.669
1400	153.319	556.885	445.553	155.865	−1296.473	−641.792	23.946
1500	153.895	567 483	453.332	171.227	−1294.484	−595.099	20.723
1600	154.371	577.431	460.781	186.641	−1292.511	−548.538	17.908
1700	154.769	586.802	467.921	202.098	−1290.557	−502.099	15.428
1800	155.106	595.658	474.774	217.592	−1288.629	−455.776	13.226
1900	155.392	604.052	481.359	233.118	−1286.731	−409.558	11.260
2000	155.638	612.029	487.695	248.670	−1284.865	−363.439	9.492
2100	155.851	619.628	493.798	264.244	−1283.036	−317.413	7.895
2200	156.036	626.883	499.683	279.839	−1281.245	−271.472	6.446
2300	156.198	633.822	505.366	295.451	−1279.496	−225.613	5.124
2400	156.340	640.473	510.858	311.078	−1277.789	−179.830	3.914
2500	156.467	646.858	516.171	326.718	−1276.128	−134.116	2.802
2600	156.579	652.997	521.316	342.371	−1274.513	−88.467	1.777
2700	156.679	658.908	526.303	358.034	−1272.947	−42.879	0.830
2800	156.769	664.608	531.141	373.706	−1271.431	2.652	−0.049
2900	156.849	670.111	535.839	389.387	−1269.968	48.127	−0.867
3000	156.922	675.429	540.404	405.076	−1268.560	93.555	−1.629
3100	156.988	680.576	544.843	420.771	−1267.208	138.938	−2.341
3200	157.049	685.561	549.163	436.473	−1265.915	184.275	−3.008
3300	157.103	690.394	553.370	452.181	−1264.681	229.573	−3.634
3400	157.153	695.085	557.469	467.894	−1263.512	274.837	−4.222
3500	157.199	699.641	561.467	483.611	−1262.410	320.066	−4.777
3600	157.241	704.070	565.367	499.333	−1261.377	365.265	−5.300
3700	157.280	708.379	569.174	515.059	−1260 416	410.435	−5.794
3800	157.316	712.574	572.893	530.789	−1259.533	455.583	−6.262
3900	157.349	716.661	576.527	546.523	−1258.729	500.708	−6.706
4000	157.380	720.645	580.080	562.259	−1258.011	545.811	−7.128
4100	157.408	724.531	583.556	577.998	−1257.383	590.899	−7.528
4200	157.435	728.325	586.958	593.741	−1256.844	635.972	−7.909
4300	157.459	732.030	590.289	609.485	−1256.410	681.034	−8.273
4400	157.482	735.650	593.552	625.232	−1255.996	726.079	−8.620
4500	157.504	739.189	596.749	640.982	−1255.731	771.121	−8.951
4600	157.524	742.651	599.883	656.733	−1255.594	816.159	−9.268
4700	157.543	746.039	602.957	672.486	−1255.573	861.198	−9.571
4800	157.560	749.356	605.972	688.242	−1255.676	906.236	−9.862
4900	157.577	752.605	608.932	703.999	−1255 908	951.280	−10.141
5000	157.593	755.789	611.837	719 757	−1256.261	996.327	−10.409
5100	157.608	758.910	614.691	735.517	−1256.767	1041.384	−10.666
5200	157.621	761.970	617.494	751.278	−1257.422	1086.450	−10.914
5300	157.635	764.973	620.248	767.041	−1258.231	1131.533	−11.152
5400	157.647	767.919	622.955	782.805	−1259.203	1176.631	−11.382
5500	157.659	770.812	625.618	798.571	−1260.343	1221.748	−11.603
5600	157.670	773.653	628.236	814.337	−1261.658	1266.891	−11.817
5700	157 680	776.444	630.811	830.105	−1263.155	1312.055	−12.024
5800	157.690	779.186	633.346	845.873	−1264.839	1357.250	−12.223
5900	157.700	781.882	635.841	861.643	−1266.717	1402.471	−12.417
6000	157 709	784.533	638.297	877.413	−1268.480	1447.695	−12.603

PREVIOUS: June 1978 (1 atm)   CURRENT: June 1978 (1 bar)

Sodium Tungten Oxide (Na_2WO_4) CRYSTAL $M_r = 293.82714$ Sodium Tungsten Oxide (Na_2WO_4) $Na_2O_4W_1(cr)$

$S°(298.15\ K) = 160.331 \pm 2.1\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs1} = 862.0\ K$
$T_{trs2} = 860.8\ K$
$T_{fus} = 968.7\ K$

$\Delta_f H°(0\ K) = -1534.79 \pm 8.4\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1544.73 \pm 8.4\ kJ\cdot mol^{-1}$
$\Delta_{trs1}H° = 4.113\ kJ\cdot mol^{-1}$
$\Delta_{trs2}H° = 30.849\ kJ\cdot mol^{-1}$
$\Delta_{fus}H° = 23.799\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -369.2\ kcal\cdot mol^{-1}$, is calculated from $\Delta_r H°(303.15\ K) = 19.44 \pm 0.08\ kcal\cdot mol^{-1}$ for the reaction of $H_2WO_4(cr) + 2\ NaCl(cr) = Na_2WO_4(cr) + 2\ HCl(aq, 12.731\ H_2O)$, using the JANAF value of $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -270.5\ kcal\cdot mol^{-1}$ and $\Delta_f H°(NaCl, cr, 298.15\ K) = -98.26\ kcal\cdot mol^{-1}$, and auxiliary data for HCl(aq).[11] The value of $\Delta_r H°(303.15\ K)$ was determined by solution calorimetry by Koehler *et al.*[1]

Sherfey and Brenner[2] measured by electrochemical calorimetry the enthalpy of reaction $\Delta_r H°(298.15\ K) = -7 \pm 1.5\ kcal\cdot mol^{-1}$ for $W(cr) + 2\ NaOH(aq, 55.55\ H_2O) + 2\ H_2O(l) = Na_2WO_4(aq, \infty) + 3\ H_2(g)$. This value, combined with the heat of solution,[1,3,9] $\Delta_{sln}H° = 1.7 \pm 0.1\ kcal\cdot mol^{-1}$ for $Na_2WO_4(cr) = Na_2WO_4\ (aq, \infty)$, gives $\Delta_f H°(298.15\ K)\ (Na_2WO_4, cr) = -368.4\ kcal\cdot mol^{-1}$, which is in good agreement with the value adopted.

The previously accepted value,[1,3] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -379 \pm 0.5\ kcal\cdot mol^{-1}$, was based on the unreliable $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -280.2 \pm 0.4\ kcal\cdot mol^{-1}$. (See JANAF H_2WO_4, cr, table of March 31, 1967.) The other quoted value,[4] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -395\ kcal\cdot mol^{-1}$, was obtained from Mixter's[5] measurement of the heat of reaction of tungsten powder with excess Na_2O_2. This value was probably in error because the complex tungstate and peroxytungstates were formed in the reaction.

Heat Capacity and Entropy

Low temperature heat capacities (52–299.87 K) were measured calorimetrically by King and Weller.[6] The heat capacities above 300 K are estimated by extrapolation of the low temperature heat capacity curve to $C_p°(860\ K) = 49.0\ cal\cdot K^{-1}\cdot mol^{-1}$. The latter is obtained from an estimate of $C_p°$ equal to $7\ cal\cdot K^{-1}$ g–atom at the first transition temperature.

The entropy, $S°(298.15\ K) = 38.32 \pm 0.5\ cal\cdot K^{-1}\cdot mol^{-1}$, is calculated from low temperature heat capacity data of King and Weller,[6] based on an extrapolation of $S°(51\ K) = 2.77 \pm 0.5\ cal\cdot K^{-1}\cdot mol^{-1}$.

Transition Data

Transition temperatures and heats were obtained from differential heating and cooling curves both at atmospheric and higher pressures by Goranson and Kracek.[7] Existence of three phases is confirmed by the earlier birefringence studies of Boeke.[8]

Riccardi and Sinistri[10] found only one transition at 864 K with $\Delta_{trs}H° = 8.23\ kcal\cdot mol^{-1}$ by differential thermal analysis. This heat is apparently the sum of the two adopted heats of transition.

Fusion Data

The adopted melting data were measured by the differential heating and cooling curve method by Goranson and Kracek.[7] Riccardi and Sinistri[10] found the melting point at 971 K with $\Delta_{fus}H° = 7.52\ kcal\cdot mol^{-1}$ by differential thermal analysis.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.286	−1534.786	−1534.786	INFINITE
100	69.860	43.482	267.673	−22.419	−1541.060	−1505.022	786.143
200	117.244	108.962	172.462	−12.700	−1544.082	−1467.547	383.284
298.15	139.775	160.331	160.331	0.	−1544.733	−1429.786	250.493
300	140.122	161.197	160.334	0.259	−1544.732	−1429.073	248.824
400	155.335	203.750	166.032	15.087	−1549.553	−1390.158	181.536
500	167.360	239.748	177.264	31.242	−1548.233	−1350.438	141.079
600	178.238	271.237	190.355	48.529	−1545.854	−1311.086	114.140
700	188.698	299.500	203.961	66.877	−1542.521	−1272.209	94.933
800	198.740	325.351	217.541	86.248	−1538.287	−1233.871	80.564
860.800	205.101	340.137	225.682	98.524		I <--> II	
860.800	205.099	375.975	225.682	129.372		TRANSITION	
862.000	205.226	376.260	225.891	129.618		II <--> III	
862.000	205.224	381.032	225.891	133.731		TRANSITION	
900	209.200	389.971	232.631	141.606	−1498.203	−1197.704	69.513
1000	219.242	412.530	249.504	163.026	−1492.216	−1164.628	60.834
1100	229.492	433.907	265.304	185.463	−1485.393	−1132.192	53.763
1200	239.743	454.314	280.211	208.923	−1671.275	−1095.535	47.687
1300	250.120	473.913	294.362	233.417	−1660.975	−1047.968	42.108
1400	260.454	492.828	307.866	258.946	−1649.746	−1001.228	37.356
1500	270.705	511.147	320.811	285.505	−1637.590	−955.325	33.267

PREVIOUS: CURRENT: June 1967

Sodium Silicate ($Na_2Si_2O_5$) CRYSTAL(B–Aβ–Aα) $M_r = 182.14754$ Sodium Silicate ($Na_2Si_2O_5$) $Na_2O_5Si_2(cr)$

$S°(298.15\ K) = 164.055 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(B \rightarrow A\beta) = 951\ K$
$T_{trs}(A\beta \rightarrow A\alpha) = 980\ K$
$T_{fus} = 1147\ K$

$\Delta_f H°(0\ K) = -2455.46 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2470.07 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.418\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.628\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 35.564\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr) SiO_2(quartz), $Na_2Si_2O_5$(cr), HCl(aq) and H_2SO_4(aq), in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] The author derived two values of $\Delta_{sln}H°$ of Na_2O(cr) from those of NaCl(cr), Na_2SO_4(cr), HCl(aq) and H_2SO_4(aq), presumably employing auxiliary data from.[2] We recalculate $\Delta_{sln}H°$ of Na_2O(cr) in the calorimetric solution as −87.50 (chlorine scheme, originally −87.66) and −88.74 kcal·mol⁻¹ (sulfate scheme, originally −89 19), using recent $\Delta_f H°(298.15\ K)$ values[16,17,18] for NaCl(cr), HCl(aq), H_2SO_4(aq), Na_2SO_4(cr), and Na_2O(cr). The corresponding enthalpy changes, $\Delta_r H°(298.15\ K)$, for the reaction $Na_2O(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(cr)$ are derived as −54.65 and −55.89 kcal·mol⁻¹. Adopting the weighted average $\Delta_r H°(298.15\ K) = -55.06$ kcal·mol⁻¹ with $\Delta_f H°(Na_2O,\ cr,\ 298.15\ K) = -99.9$ kcal·mol⁻¹ and $\Delta_f H°(SiO_2,\ quartz,\ 298.15\ K) = -217.7$ kcal·mol⁻¹, we obtain $\Delta_f H°(298.15\ K) = -590.36$ kcal·mol⁻¹ for $Na_2Si_2O_5$(cr). This $\Delta_f H°(Na_2Si_2O_5,\ cr,\ 298\ 15\ K)$ value is independent of future changes in $\Delta_f H°(298.15\ K)$ of Na_2O(cr), but the values of $\Delta_{sln}H°$ and $\Delta_r H°$ are not independent.

Stevens *et al.*[3] measured the enthalpies of solution of $Na_2Si_2O_5$(cr), Na_2O(cr) and SiO_2(quartz) in HF(aq) at 25°C. Based on the reported results, the enthalpy change for the reaction $Na_2O(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(cr)$ is calculated as −53 25 ± 0.32 kcal·mol⁻¹, yielding $\Delta_f H°(Na_2Si_2O_5,\ cr,\ 298.15\ K) = -588.55$ kcal·mol⁻¹.

Hummel[4] determined the enthalpies of solution of $Na_2Si_2O_5$(cr), SiO_2(quartz) and Na_2CO_3(cr) in 39% HF at 26.5°C. From the data reported we derive the enthalpy change to be 20.88 kcal·mol⁻¹ for the reaction $Na_2CO_3(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(cr) + CO_2(g)$. Employing $\Delta_f H°(298.15\ K) = -270.26$, −217.7 and −94.05 kcal·mol⁻¹ for Na_2CO_3(cr), SiO_2(quartz) and CO_2(g), respectively, we obtain $\Delta_f H°(298.15\ K) = -590.78$ kcal·mol⁻¹ for $Na_2Si_2O_5$(cr) which is in good agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, 54.3–294.7 K, have been measured by Kelley[5] and the high temperature enthalpies, 376.8–1100.2 K, by Naylor.[6] The derived high temperature heat capacities are joined smoothly with the low temperature ones at 298.15 K. An approximate $C_p°$ of 70 cal·K⁻¹·mol⁻¹ is derived from the enthalpies above 980 K; this value is extrapolated to 2000 K. The value of $S°(298.15\ K)$ is calculated from the adopted low temperature heat capacities based on $S°(50\ K) = 2.945$ cal·K⁻¹mol⁻¹. The entropy extrapolation derives from the Debye–Einstein extrapolation of Kelley[5] which yields a $C_p°$ curve with an extra inflection in the region from 15 to 50 K. A more normal extrapolation would lead to a value of $S°(50\ K)$ which is lower by 0.5 cal·K⁻¹·mol⁻¹.

Transition Data

There are six slowly inverting polymorphous phases,[1,7-9] namely A, B, C, D, E and F, of which only the first two phases are stable. Two rapid transitions have been reported at 951 and 980 K.[1,10] Phase A, which has two subphases, Aα and Aβ, is stable above 951 K. The stable phase below 951 K is known as phase B, previously called β–$Na_2Si_2O_5$. The $\Delta_{trs}H°$ values are derived from the enthalpy data of Naylor[6] using the adopted $C_p°$ values. Three more rapid transitions have been reported at 822, 846 and 866 K[1,10] in E, previously called γ–$Na_2Si_2O_5$. Willgallis and Range[10] have examined these transitions.

Fusion Data

T_{fus} is obtained from Morey.[11] The selected value of $\Delta_{fus}H°$ is based on the following $\Delta_{fus}H°$ values derived from four different kinds of measurements.

	$\Delta_{fus}H°$, kcal·mol⁻¹*		
Source	298.15 K	1147 K	Method**
12	(7.51)	8.46	I
1	5.25	(6.20)	II
13	8.81	(9.76)	III
14	8.83	(9.78)	II
15	(7.50)	8.45	IV
4	8.09	(9.04)	II

* The numbers in parentheses are derived from the measured ones at the other listed temperatures.
**I = phase diagram, II = solution calorimetry; III = high temperature reaction calorimetry; and IV = dynamic–differential calorimetric method.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.430	−2455 459	−2455 459	INFINITE
100	66.906	42.058	279.416	−23.736	−2463.238	−2418.587	1263.340
200	124.081	107 976	177.452	−13.895	−2467.943	−2371.851	619 464
298.15	156.984	164.055	164.055	0.	−2470.066	−2324.163	407.184
300	157.494	165.027	164 058	0.291	−2470.090	−2323.258	404.515
400	183.401	214.007	170.560	17.379	−2475.916	−2273.781	296.925
500	203.246	257.178	183.653	36 762	−2474.938	−2223.325	232.269
600	217.576	295.572	199.168	57.843	−2472.541	−2173.208	189.195
700	227.840	329.925	215.438	80.141	−2469 179	−2123.575	158 463
800	235.162	360.855	231.715	103.312	−2465 186	−2074.470	135.449
900	240.325	388.869	247.645	127.102	−2460.809	−2025.890	117.580
951.000	242.313	402.170	255.578	139.409	I <--> II		
951.000	242.316	402.610	255.578	139.828	TRANSITION		
980 000	243.275	409.903	260.037	146.869	II <--> III		
980 000	292.880	410.544	260.037	147 497	TRANSITION		
1000	292.880	416.461	263.107	153.354	−2454.208	−1977.854	103.312
1100	292.880	444.375	278.337	182.642	−2444.821	−1930.674	91.680
1147.000	292.880	456.629	285.393	196.408	----- III <--> LIQUID -----		
1200	292.880	469.859	293.251	211 930	−2629.223	−1879 459	81.811
1300	292.880	493.302	307.750	241.218	−2618.531	−1817.413	73.025
1400	292.880	515.007	321.788	270.506	−2607.999	−1756.184	65.524
1500	292.880	535.213	335.351	299.794	−2597.620	−1695.704	59.050
1600	292.880	554.115	348.439	329.082	−2587.389	−1635.911	53.407
1700	292.880	571.871	361.065	358.370	−2677.658	−1575.859	48.420
1800	292.880	588.612	373.246	387.658	−2667.257	−1511.349	43 858
1900	292.880	604.447	385.002	416.946	−2656.916	−1447.414	39.792
2000	292.880	619.470	396.353	446.234	−2646.633	−1384.022	36.147

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Continued on page 1673

Sodium Silicate ($Na_2Si_2O_5$) LIQUID $M_r = 182.14754$ Sodium Silicate ($Na_2Si_2O_5$) $Na_2O_5Si_2(l)$

$S°(298.15\ K) = [188.705]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_fH°(298.15\ K) = [-2438.485]\ kJ{\cdot}mol^{-1}$
$T_{fus} = 1147\ K$ $\Delta_{fus}H° = 35.564\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(l,\ 298.15\ K)$ is calculated from $\Delta_fH°(cr,\ 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1147\ K)-H°(298.15\ K)$, between the crystal and liquid.

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr), HCl(aq), H_2SO_4(aq), SiO_2(quartz) and $Na_2Si_2O_5$(g, l) in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] Following the same procedure as described in the $Na_2Si_2O_5$(cr) table, we derive the enthalpy changes, $\Delta_rH°(298.15\ K)$, for the reaction $Na_2O(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(g,\ l)$ as −49.40 and −50.64 kcal·mol⁻¹ using the heats of solution of Na_2O(cr) as −87.50 (chloride scheme) and −88.74 kcal·mol⁻¹ (sulfate scheme), respectively. Adopting the weighted average $\Delta_rH°(298.15\ K) = -49.81$ kcal·mol⁻¹ with $\Delta_fH°(Na_2O,\ cr,\ 298.15\ K) = -99.9$ kcal·mol⁻¹ and $\Delta_fH°(SiO_2,\ quartz,\ 298.15\ K) = -217.7$ kcal·mol⁻¹, we obtain $\Delta_fH°(298.15\ K) = -585.113$ kcal·mol⁻¹ for $Na_2Si_2O_5$(g, l).

Using high temperature reaction calorimetry, Kroger[2] determined the enthalpy changes as 25.28 ± 0.22 and −18.58 ± 0.36 kcal·mol⁻¹ for the reactions $Na_2CO_3(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(g,\ l) + CO_2(g)$ and $2\ NaOH(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(g,\ l) + H_2O(l)$, respectively. From the given results, we calculate the corresponding values of $\Delta_fH°(Na_2Si_2O_5,\ g,\ l,\ 298.15\ K)$ to be −586.32 and −589.46 kcal·mol⁻¹, using $\Delta_fH°(298.15\ K) = -270.26, -217.70, -94.05, -101.90$ and -68.32 kcal·mol⁻¹ for Na_2CO_3(cr), SiO_2(quartz, CO_2(g), NaOH(cr) and H_2O(l), respectively. These two $\Delta_fH°(Na_2Si_2O_5,\ l,\ 298.15\ K)$ values, as well as the value −585.113 kcal·mol⁻¹ based on Kracek's data, are not adopted, because incorporating these $\Delta_fH°(g,\ l,\ 298.15\ K)$ values with the value of $\Delta_fH°(cr,\ 298.15\ K)$, gives values of the enthalpy of melting at 298.15 K which are too low in comparison with the other values (see the $Na_2Si_2O_5$, cr, table).

Hummel[3] measured the enthalpies of solution of Na_2CO_3(cr), SiO_2(quartz) and $Na_2Si_2O_5$(g, l) in 39% hydrofluoric acid at 26.5°C, as −244.1, −564.5 and −673.7 cal·g⁻¹, respectively. Based on these results, we derive the enthalpy change for the reaction $Na_2CO_3(cr) + 2\ SiO_2(quartz) = Na_2Si_2O_5(g,\ l) + CO_2(g)$ to be 29.01 kcal·mol⁻¹, yielding $\Delta_fH°(Na_2Si_2O_5,\ g,\ l,\ 298.15\ K) = -582.6$ kcal·mol⁻¹ which is in good agreement with the adopted value.

Heat Capacity and Entropy

Using drop calorimetry, Naylor[4] has measured the enthalpies of $Na_2Si_2O_5$(g, l), 445.5–1120.7 K, and $Na_2Si_2O_5$(l), 1173.2–1744 K. Based on the liquid enthalpy data, we evaluate the heat capacity of $Na_2Si_2O_5$(l) to be 62.43 cal·K⁻¹·mol⁻¹. The $C_p°$ values below 1147 K are derived from the enthalpies measured at 445.5–1120.7 K by Naylor.[4] Below 600 K, $C_p°$ is identical with that of the crystal. The adopted curve rises rapidly to a maximum in the glass transition region, 650–950 K, then smoothly approaches the value of the real liquid near T_{fus}. The heat capacity of $Na_2Si_2O_5$(l) is assumed to be constant in the temperature range 1147 to 2500 K.

$S°(l,\ 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_fH°$ (kJ·mol⁻¹)	$\Delta_fG°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	156.984	188.705	188.705	0.	−2438.485	−2299.931	402.938
300	157.494	189.678	188.708	0.291	−2438.508	−2299.071	400.304
400	183.401	238.657	195.210	17.379	−2444.334	−2252.060	294.089
500	203.246	281.828	208.304	36.762	−2443.356	−2204.069	230.258
600	217.576	320.191	223.817	57.825	−2440.978	−2156.416	187.733
700	245.810	355.525	240.121	80.783	−2436.956	−2109.271	157.396
800	272.169	390.353	256.734	106.895	−2430.022	−2062.904	134.694
900	276.228	422.809	273.415	134.455	−2421.874	−2017.501	117.093
1000	267.776	451.569	289.825	161.744	−2414.237	−1972.990	103.058
1100	261.207	476.706	305.694	188.113	−2407.769	−1929.186	91.609
1147.000	261.207	487.635	312.927	200.390	----- III <--> LIQUID -----		
1200	261.207	499.434	320.906	214.234	−2595.338	−1881.064	81.881
1300	261.207	520.342	335.454	240.355	−2587.813	−1821.847	73.203
1400	261.207	539.700	349.360	266.475	−2580.448	−1763.204	65.786
1500	261.207	557.721	362.657	292.596	−2573.236	−1705.082	59.376
1600	261.207	574.579	375.381	318.717	−2566.173	−1647.437	53.783
1700	261.207	590.415	387.569	344.838	−2659.609	−1589.334	48.834
1800	261.207	605.345	399.257	370.958	−2652.376	−1526.587	44.300
1900	261.207	619.468	410.479	397.079	−2645.202	−1464.239	40.255
2000	261.207	632.866	421.266	423.200	−2638.086	−1402.267	36.623
2100	261.207	645.610	431.648	449.320	−2631.031	−1340.650	33.347
2200	261.207	657.761	441.652	475.441	−2624.034	−1279.366	30.376
2300	261.207	669.373	451.302	501.562	−2617.098	−1218.401	27.671
2400	261.207	680.489	460.622	527.683	−2610.223	−1157.736	25.197
2500	261.207	691.152	469.631	553.803	−2603.410	−1097.356	22.928

PREVIOUS: June 1965 CURRENT: September 1967

Sodium Silicate ($Na_2Si_2O_5$) CRYSTAL(B–Aβ–Aα)-LIQUID

0 to 951 K crystal, B
951 to 980 K crystal, Aβ
980 to 1147 K crystal, Aα
above 1147 K liquid

Refer to the individual tables for details.

M_r = 182.14754 Sodium Silicate ($Na_2Si_2O_5$) $Na_2O_5Si_2(cr,l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	Δ_fH°	Δ_fG°	log K_f
0	0.	0.	INFINITE	−26.430	−2455.459	−2455.459	INFINITE
100	66.906	42.058	279.416	−23.736	−2463.238	−2418.587	1263.340
200	124.081	107.976	177.452	−13.895	−2467.943	−2371.851	619 464
298.15	156.984	164.055	164.055	0.	−2470.066	−2324.163	407.184
300	157.494	165.027	164.058	0.291	−2470.090	−2323.258	404.515
400	183.401	214.007	170.560	17.379	−2475.916	−2273.781	296.925
500	203.246	257.178	183.653	36.762	−2474.938	−2223.325	232.269
600	217.576	295.572	199.168	57.843	−2472.541	−2173.208	189.195
700	227.840	329.925	215.438	80.141	−2469.179	−2123.575	158.463
800	235.162	360.855	231.715	103.312	−2465.186	−2074.470	135.449
900	240.325	388.869	247.645	127.102	−2460.809	−2025.890	117.580
951.000	242.313	402.170	255.578	139.409		I <--> II	
951.000	242.316	402.610	255.578	139.828		TRANSITION	
980.000	243 .275	409.903	260.037	146.869		II <--> III	
980.000	292 .880	410.544	260.037	147.497		TRANSITION	
1000	292.880	416.461	263.107	153.354	−2454.208	−1977.854	103.312
1100	292.880	444.375	278.337	182.642	−2444.821	−1930.674	91.680
1147.000	292.880	456.629	285.393	196.408		III <--> LIQUID	
1147.000	261.207	487.635	285.393	231.972		TRANSITION	
1200	261.207	499.434	294.588	245.816	−2595.338	−1881.064	81.881
1300	261.207	520.342	311.160	271.936	−2587.813	−1821.847	73.203
1400	261.207	539.700	326.802	298 057	−2580.448	−1763.204	65.786
1500	261.207	557.721	341.603	324.178	−2573.236	−1705.082	59.376
1600	261.207	574.579	355.643	350.298	−2566.173	−1647.437	53.783
1700	261.207	590.415	368.992	376.419	−2659.609	−1589.334	48.834
1800	261.207	605.345	381.712	402.540	−2652.376	−1526.587	44.300
1900	261.207	619.468	393.857	428.661	−2645.202	−1464.239	40.255
2000	261.207	632.866	405.475	454.781	−2638.086	−1402.267	36.623
2100	261.207	645.610	416.609	480.902	−2631.031	−1340.650	33.347
2200	261.207	657.761	427.297	507.023	−2624.035	−1279.366	30.376
2300	261.207	669.373	437.571	533.143	−2617.098	−1218.401	27.671
2400	261.207	680.489	447.463	559.264	−2610.223	−1157.736	25 197
2500	261.207	691.152	456.999	585.385	−2603.410	−1097.356	22.928

PREVIOUS. CURRENT· September 1967

Sodium Sulfide (Na_2S) CRYSTAL $M_r = 78.03954$ Sodium Sulfide (Na_2S) $Na_2S_1(cr)$

$\Delta_f H°(0\ K)$ = Unknown
$S°(298.15\ K) = 96.232 \pm 16.7\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ $\Delta_f H°(298.15\ K) = -366.10 \pm 12.6\ kJ{\cdot}mol^{-1}$
$T_{trs} = [1276 \pm 20\ K]$ (lambda transition) $\Delta_{trs}H° = 0$
$T_{fus} = 1445 \pm 10\ K$ $\Delta_{fus}H° = [19.246 \pm 4.2]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

We adopt the average value, $\Delta_f H°(298.15\ K) = -87.5\ kcal{\cdot}mol^{-1}$, derived from the experimental results summarized below.

Source	Reaction	$\Delta_f H°(298.15\ K)$, $kcal{\cdot}mol^{-1}$
[1]	$\Delta_{sln}H°$ $Na_2S(cr)$ and $Na(cr)$, $\Delta_a H°$ $NaOH(aq) + H_2S(aq)$	−88.2
[2]		−89.7
[3]	$Na\ (in\ NH_3) + S(cr) = Na_2S(cr)$	−87.0
[4]	$H_2SO_4(aq,\ 1100\ H_2O) + Na_2S(cr) = Na_2SO_4(soln.) + H_2S(g)$	−85.1*

* The author's value of $-84.35 \pm 0\ 9\ kcal{\cdot}mol^{-1}$ is corrected for newer values for $\Delta_f H°(298\ 15\ K)$ of $Na_2SO_4(c,\ V)$ and $H_2S(g)$.[5,11]

The adopted value is reasonably consistent with $-86.6 \pm 1\ kcal{\cdot}mol^{-1}$ calculated from the 2nd law analysis of Uusitalo's equilibrium data[10] described in the following section.

Heat Capacity and Entropy

The heat capacity is based on the drop calorimetry of May[6] (400–1500 K). The pre-melt S–shaped enthalpy curve is reinterpreted as incorporating a lambda transition in view of the enthalpy measurements on K_2S by Dworkin and Bredig[7] and the occurrence of lambda transitions in other materials having the fluorite or anti flourite type of structure.[8] The adopted heat capacity shows the maximum of the lambda transition at $50.65\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and 1276 K. The heat capacity then falls to a constant value of $32\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ at 1420 K. This interpretation along with the adopted melting point, heat of melting, and liquid heat capacity ($22\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$,[9] leads to an enthalpy of the liquid consistent with May's measurement.

May,[6] (648–656 K) and Uusitalo,[10] (462–763 K) have measured equilibrium pressures for the reaction $Na_2SO_4(cr) + 2\ C(solid) = Na_2S(cr) + 2\ CO_2(g)$ and have derived $S°(Na_2S,\ cr,\ 298.15\ K) = 18.6$ and $18.5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. These derivations are open to question because of the uncertainty of the crystalline form of Na_2SO_4 used in the reaction (forward direction) or resulting from the reaction (reverse direction). Five crystalline forms of Na_2SO_4 have been identified.[11] [12] $S°(298.15\ K)$ for form V, stable at room temperature, has erroneously been used to derive $S°(Na_2S,\ cr,\ 298.15\ K)$ rather than $S°(298.15\ K)$ for form I which is the form stable at the equilibrium measurement temperature. Furthermore, Uusitalo[10] used charcoal which probably deviates from graphite, the standard reference state. Our 2nd law treatment of Uusitalo's data[10] with auxiliary data for $Na_2SO_4(cr,\ I)$ and C(graphite),[11] which is still questionable, leads to $S°(Na_2S,\ cr,\ 298.15\ K) = 23.2\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. The agreement of this derivation with the estimate below is almost surely fortuitous.

Kubaschewski *et. al.*[13] have estimated the entropy as $23.5 \pm 2.5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. Voronin's[14] estimate is $21.6\ cal{\cdot}K^{-1}mol^{-1}$. The summation of Kelley's additive entropy constants[15] gives $23.0\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. We adopt $S°(Na_2S,\ cr,\ 298.15\ K) = 23.0 \pm 4\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Fusion Data

Tegman[16] indicated that many of the early measurements of the melting point of Na_2S were made on impure brown material. Several measurements on white or light pink material are in reasonable agreement: in °C, 1200,[17] 1180 ± 10,[18] 1180,[19] 1160 ± 5,[20,21] 1175 ± 10,[22] and 1168 ± 10.[23] We adopt a melting point of 1445 ± 10 K (1172 ± 10°C). This is consistent with May's[6] enthalpy measurements.

In an examination of May's enthalpy data, Wagman[24] has used an entropy of fusion of $3.21\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ —the entropy of fusion of K_2S is $3.16\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ —which leads to an entahlpy of fusion of $4.8\ kcal{\cdot}mol^{-1}$ at the adopted melting point of 1445 K. From the Na_2S–S phase diagram work of Rosen and Tegman,[23] Wagman[24] calculates an average enthalpy of fusion of $5.7\ kcal{\cdot}mol^{-1}$ and recommends $\Delta_{fus}H° = 5 \pm 1\ kcal{\cdot}mol^{-1}$. We adopt $\Delta_{fus}H° = 4.8\ kcal{\cdot}mol^{-1}$ to remain consistent with our incorporation of a lambda transition in the evaluation of May's[6] enthalpy measurements.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	82.801	96.232	96.232	0.	−366.100	−354.552	62.116
300	82.843	96.744	96.234	0.153	−366.093	−354.480	61.720
400	84.308	120.780	99.501	8.512	−373.575	−350.129	45.722
500	85.772	139.753	105.719	17.017	−375.200	−344.086	35.946
600	87.236	155.522	112.742	25.668	−376.166	−337.761	29.405
700	88.701	169.081	119.844	34.466	−376.619	−331.319	24.723
800	90 165	181.023	126.760	43.411	−376.704	−324.838	21.210
900	91.337	191.717	133.394	52.491	−429.655	−317.282	18.415
1000	92.843	201.418	139.718	61.700	−428.077	−304.880	15.925
1100	110.458	210.823	145.749	71.581	−425.884	−292.653	13.897
1200	159.494	222.269	151.627	84.771	−614.002	−275.864	12.008
1276.000	211 921	233.718	156.162	98.962	C_p LAMBDA MAXIMUM TRANSITION		
1276.000	211.939	233.718	156.162	98.962			
1300	187.652	237.411	157.629	103 718	−601.115	−248.179	9.972
1400	137.152	249.134	163.773	119.505	−591.403	−221.426	8.262
1445.000	133.888	253.390	166.498	125.559	--- CRYSTAL <--> LIQUID ---		
1500	133.888	258.392	169.777	132.923	−584.076	−195.256	6.799
1600	133.888	267.033	175.588	146.312	−576.793	−169.572	5.536
1700	133.888	275.150	181.208	159.700	−569.524	−144.343	4.435
1800	133.888	282.802	186.642	173.089	−562.270	−119.542	3.469
1900	133.888	290.041	191.895	186.478	−555.029	−95.144	2.616
2000	133.888	296.909	196.976	199.867	−547.802	−71.126	1.858

PREVIOUS: December 1960 CURRENT: March 1978

Sodium Sulfide (Na_2S) **LIQUID** $M_r = 78.03954$ **Sodium Sulfide (Na_2S)** **$Na_2S_1(l)$**

$S°(298.15\ K) = [127.656]\ J\ K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-323.940]\ kJ\cdot mol^{-1}$
$T_{fus} = 1445 \pm 10\ K$ $\Delta_{fus}H° = [19.246 \pm 4.2]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_2S,\ l,\ 298.15\ K)$ is calculated from $\Delta_f H°(Na_2S,\ cr,\ 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1445\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of 22 cal $K^{-1}\cdot mol^{-1}$ is from the estimated value of Barin *et al.*[1] and is assumed to be constant above the assumed glass transition at 970 K. Below the glass transition, the heat capacity is that of the crystal.

The entropy at 298.15 K is calculated in a manner similar to that used for the enthalpy of formation.

Reference

[1] I. Barin, D. Knacke, and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances," Supplement, Springer Verlag, Berlin, (1977).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
250							
298.15	82.801	127.656	127.656	0.	−323.940	−321.761	56.371
300	82.843	128.169	127.658	0.153	−323.933	−321.747	56.021
400	84.308	152.205	130.925	8.512	−331.415	−320.539	41.858
500	85.772	171.177	137.143	17.017	−333.040	−317.638	33.183
600	87.236	186.947	144.166	25.668	−334.006	−314.455	27.376
700	88.701	200.506	151.268	34.466	−334.459	−311.156	23.219
800	90.165	212.447	158.184	43.411	−334.544	−307.817	20.098
900	91.337	223.141	164.818	52.491	−387.495	−303.404	17.609
970.010	92.425	230.023	169.278	58.923	——— GLASS <−−> LIQUID ———		
970.010	92.048	230.023	169.278	58.923	TRANSITION		
1000	92.048	232.826	171.142	61.684	−385.933	−294.144	15.365
1100	92.048	241.599	177.155	70.888	−384.416	−285.039	13.535
1200	92.048	249.608	182.864	80.093	−576.519	−271.189	11.805
1300	92.048	256.976	188.285	89.298	−573.374	−245.872	9.879
1400	92.048	263.798	193.438	98.503	−570.245	−220.797	8.238
1445.000	92.048	266.710	195.675	102.645	−−− CRYSTAL <−−> LIQUID −−−		
1500	92.048	270.148	198.343	107.708	−567.131	−195.945	6.823
1600	92.048	276.089	203.019	116.912	−564.031	−171.301	5.592
1700	92.048	281.669	207.483	126.117	−560.947	−146.849	4.512
1800	92.048	286.930	211.752	135.322	−557.877	−122.579	3.557
1900	92.048	291.907	215.841	144.527	−554.820	−98.480	2.707
2000	92.048	296.629	219.763	153.732	−551.777	−74.541	1.947
2100	92.048	301.120	223.531	162.936	−548.747	−50.753	1.262
2200	92.048	305.402	227.156	172.141	−545.729	−27.110	0.644
2300	92.048	309.494	230.647	181.346	−542.725	−3.604	0.082
2400	92.048	313.411	234.015	190.551	−539.735	19.772	−0.430
2500	92.048	317.169	237.266	199.756	−536.760	43.024	−0.899
2600	92.048	320.779	240.409	208.960	−533.800	66.157	−1.329
2700	92.048	324.253	243.451	218.165	−530.858	89.176	−1.725
2800	92.048	327.600	246.397	227.370	−527.934	112.087	−2.091
2900	92.048	330.830	249.253	236.575	−525.032	134.893	−2.430
3000	92.048	333.951	252.024	245.780	−522.153	157.600	−2.744

PREVIOUS: December 1960 CURRENT: March 1978

Disodium Monosulfide (Na_2S) CRYSTAL-LIQUID

M_r = 78.03954 Sodium Sulfide (Na_2S) $Na_2S_1(cr,l)$

0 to 1276* K crystal
1276 to 1445 K crystal
above 1445 K liquid

*There is a lambda transition at 1276 K.

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1}mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	82.801	96.232	96.232	0.	−366.100	−354.552	62.116
300	82.843	96.744	96.234	0.153	−366.093	−354.480	61.720
400	84.308	120.780	99.501	8.512	−373.575	−350.129	45.722
500	85.772	139.753	105.719	17.017	−375.200	−344.086	35.946
600	87.236	155.522	112.742	25.668	−376.166	−337.761	29.405
700	88.701	169.081	119.844	34.466	−376.619	−331.319	24.723
800	90.165	181.023	126.760	43.411	−376.704	−324.838	21.210
900	91.337	191.717	133.394	52.491	−429.655	−317.282	18.415
1000	92.843	201.418	139.718	61.700	−428.077	−304.880	15.925
1100	110.458	210.823	145.749	71.581	−425.884	−292.653	13.897
1200	159.494	222.269	151.627	84.771	−614.002	−275.864	12.008
1276.000	211.921	233.718	156.162	98.962	C_p LAMBDA MAXIMUM		
1276.000	211.939	233.718	156.162	98.962	TRANSITION		
1300	187.652	237.411	157.629	103.718	−601.115	−248.179	9.972
1400	137.152	249.134	163.773	119.505	−591.403	−221.426	8.262
1445.000	133.888	253.390	166.498	125.559	CRYSTAL <− −> LIQUID		
1445.000	92.048	266.710	166.498	144.805	TRANSITION		
1500	92.048	270.148	170.236	149.868	−567.131	−195.945	6.823
1600	92.048	276.089	176.668	159.073	−564.031	−171.301	5.592
1700	92.048	281.669	182.682	168.278	−560.947	−146.849	4.512
1800	92.048	286.931	188.329	177.482	−557.877	−122.579	3.557
1900	92.048	291.907	193.651	186.687	−554.820	−98.480	2.707
2000	92.048	296.629	198.683	195.892	−551.777	−74.541	1.947
2100	92.048	301.120	203.455	205.097	−548.747	−50.753	1.262
2200	92.048	305.402	207.992	214.302	−545.729	−27.110	0.644
2300	92.048	309.494	212.317	223.506	−542.725	−3.604	0.082
2400	92.048	313.411	216.448	232.711	−539.735	19.772	−0.430
2500	92.048	317.169	220.402	241.916	−536.760	43.024	−0.899
2600	92.048	320.779	224.194	251.121	−533.800	66.157	−1.329
2700	92.048	324.253	227.836	260.326	−530.858	89.176	−1.725
2800	92.048	327.600	231.339	269.530	−527 934	112.087	−2.091
2900	92.048	330.830	234.715	278.735	−525.032	134.893	−2.430
3000	92.048	333.951	237.971	287.940	−522.153	157.600	−2.744

PREVIOUS: CURRENT: March 1978

Sodium Sulfide (Na_2S) $Na_2S_1(cr,l)$

Sodium Sulfide, Beta (β–Na_2S_2) CRYSTAL(β) $M_r = 110.09954$

$S°(298.15\ K) = 150.6 \pm 24\ J{\cdot}K^{-1}{\cdot}mol^{-1}$
$T_{trs} = 423 - 523\ K$
$T_{fus} = 753 \pm 5\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -397.1 \pm 8\ kJ{\cdot}mol^{-1}$
$\Delta_{trs} H°$ = Unknown
$\Delta_{fus} H° = [18.91 \pm 1.7]\ kJ{\cdot}mol^{-1}$

Enthalpy of Formation

Kraus and Ridderhof[1] determined $\Delta_f H°(Na_2S_2,\ cr,\ 298.15\ K) = -96.2\ kcal{\cdot}mol^{-1}$ from the enthalpy of reaction of Na(in NH_3) and S(cr) to form Na_2S_2(cr) in liquid ammonia. Letoffe *et al.*[2] derived $\Delta_f H°(Na_2S_2,\ cr,\ 298.15\ K) = -92.7\ kcal{\cdot}mol^{-1}$ from the enthalpy of reaction of Na_2S_2(cr) and H_2SO_4(1100 H_2O) to form Na_2SO_4(acid solution), H_2S(g), and S(cr). With newer values for the enthalpies of formation of H_2SO_4(1100 H_2O),[3] Na_2SO_4(cr),[4] and H_2S(g),[4] the value of Letoffe *et al.* corrects to $-93.6\ kcal{\cdot}mol^{-1}$. We adopt the average of $\Delta_f H°(Na_2S_2,\ cr,\ 298.15\ K) = -94.9 \pm 2\ kcal{\cdot}mol^{-1}$.

Heat Capacity and Entropy

The heat capacities are those estimated by Barin *et al.*[5]

Mills[6] gives $S°(298.15\ K) = 21.4 \pm 5\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ derived from the dissociation pressure measurements of Teder and Tiberg;[7] the path of the derivation is not clear. Tegman[8] has measured the vapor pressure of sulfur over sodium polysulfide melts which he has supplemented with other measurements from the literature to form an extensive data set covering a composition range of $Na_2S_{1.3}$–$Na_2S_{6.0}$ and a temperature range of 523–1273 K. His analysis of this data set via computer modeling gave, among other things, the entropy changes for the reactions: $Na_2S(l) + 1/2\ S_2(g) = Na_2S_2(l)$; $\Delta S° = -9.00\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ and $Na_2S_2(cr) = Na_2S_2(l)$; $\Delta S° = 4.43\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. It had been assumed these values are independent of temperature, but for our calculation of $S°(Na_2S_2,\ cr,\ 298.15\ K)$ we have used a temperature of 900 K, near the mid-point of the experimental range. With auxiliary data for Na_2S(l) and S_2(g)[4] and $S°(900\ K)$–$S°(298.15\ K)$ for Na_2S_2(cr) from a preliminary table, we derive $S°(Na_2S_2,\ cr,\ 298.15\ K) = 42.1\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

A graphical comparison of the standard entropies of K_2S(cr),[5] K_2S_3(cr),[19] K_2S_5(cr),[19] and Na_2S(cr)[5] indicates that $21.4\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is probably too low and $42.1\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$ is probably too high for $S°(Na_2S_2,\ cr,\ 298.15\ K)$. We adopt $S°(Na_2S_2,\ cr,\ 298.15\ K) = 36 \pm 6\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$.

Transition and Fusion Data

The existence of two forms of Na_2S_2 is well established,[9-13] but the α–β transition is sluggish. Some indicate the transition is irreversible[9-12] while others find it reversible.[13] On heating the α–form, it changes to the β–form in the 150–250° range[9, 12,13] (423–523 K).

The melting point of the β–form has been determined as 473.9,[14] ~490,[9] 482 ± 2,[15] 478 ± 5,[16] 475,[17] 475,[12] 455,[13] and 484°C.[18] We adopt 480 ± 5°C (753 ± 5 K).

The adopted $\Delta_{fus} H° = 4.52\ kcal{\cdot}mol^{-1}$ is taken from the tabulation of Barin *et al.*,[5] referenced to private communications from Mills.[6] It is not known if this is a measured or an estimated value. Tegman[8] derived a $\Delta_{fus} H° = 4.62\ kcal{\cdot}mol^{-1}$ from liquid–vapor and solid–liquid equilibria data via complex computer modeling. This indirectly calculated figure apparently corresponds to an average temperature of approximately 1000 K so that $\Delta_{fus} H°(753\ K) \sim 4.8\ kcal{\cdot}mol^{-1}$; this value tends to confirm the adopted value and is used in estimating an uncertainty of $\pm 0.4\ kcal{\cdot}mol^{-1}$.

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Sodium Sulfide, Beta (Na_2S_2) Na_2S_2(cr)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.625	150.624	150.624	0.	−397.062	−392.173	68.707
300	98.726	151.234	150.626	0.183	−397.067	−392.142	68.278
400	104.299	180.399	154.565	10.334	−407.354	−389.839	50.908
500	109.872	204.272	162.187	21.042	−410.704	−385.082	40.229
600	115.445	224.796	170.949	32.308	−412.640	−379.752	33.060
700	121.018	243.011	179.966	44.131	−413.415	−374.196	27.923
753.000	123.972	251.950	184.720	50.624	---- BETA <--> LIQUID ----		
800	126.591	259.534	188.894	56.512	−413.275	−368.593	24.067
900	132.164	274.766	197.600	69.450	−518.625	−360.893	20.946
1000	137.737	288.979	206.035	82.945	−514.617	−343.578	17.947

PREVIOUS: CURRENT: December 1983

Sodium Sulfide (Na_2S_2) LIQUID M_r = 110.09954 Sodium Sulfide (Na_2S_2) $Na_2S_2(l)$

$S°$(298.15 K) = [172.365] J·K^{-1}·mol^{-1}
T_{fus} = 753 ± 5 K

$\Delta_f H°$(298.15 K) = [−380.114] kJ·mol^{-1}
$\Delta_{fus}H°$ = [18.91 ± 1.7] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(Na_2S_2, l, 298 15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(753 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of 29.8 cal·K^{-1}·mol^{-1} is from the estimated value of Barin *et al.*[1] and is assumed to be constant above an assumed glass transition at 500 K. Below the glass transition, the heat capacity is that of the crystal.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the β–crystal table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.625	172.365	172.365	0	−380.114	−381 707	66.873
300	98.726	172.975	172.367	0 183	−380.119	−381 717	66.463
400	104.299	202.140	176.305	10.334	−390.405	−381.587	49.830
500	109.872	226.012	183.928	21.042	−393 756	−379.005	39.594
500.000	109.872	226.012	183.928	21.042	——— GLASS <--> LIQUID ———		
500.000	124.683	226.012	183.928	21 042	TRANSITION		
600	124.683	248.745	192.894	33.511	−394.489	−375.971	32.731
700	124.683	267.965	202.280	45.979	−394.619	−372.868	27.824
753.000	124.683	277.065	207.228	52.587	---- BETA <--> LIQUID ----		
800	124.683	284.614	211.555	58.447	−394.391	−369.773	24.144
900	124.683	299.299	220.504	70.916	−500.211	−364.559	21.158
1000	124.683	312.436	229.052	83.384	−497.229	−349.647	18.264
1100	124.683	324.320	237.181	95.852	−494.321	−335.030	15.909
1200	124.683	335.168	244.901	108.321	−685.047	−315 794	13.746
1300	124.683	345.148	252.234	120.789	−680.541	−285.206	11.460
1400	124.683	354.388	259.205	133.257	−676.066	−254.963	9.513
1500	124.683	362.991	265.840	145.726	−671.622	−225.040	7.837

PREVIOUS: CURRENT December 1983

Sodium Sulfide (Na_2S_2) $Na_2S_2(l)$

Sodium Sulfide (Na_2S_2) CRYSTAL(β)-LIQUID

298 to 753 K crystal, beta
above 753 K liquid

Refer to the individual tables for details.

M_r = 110.09954 Sodium Sulfide (Na_2S_2) Na_2S_2(cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K   Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.625	150.624	150.624	0.	−397.062	−392.173	68.707
300	98.726	151.234	150.626	0.183	−397.067	−392.142	68.278
400	104.299	180.399	154.565	10.334	−407.354	−389.839	50.908
500	109.872	204.272	162.187	21.042	−410.704	−385.082	40.229
600	115.445	224.796	170.949	32.308	−412.640	−379.752	33.060
700	121.018	243.011	179.966	44.131	−413.415	−374.196	27.923
753.000	123.972	251.950	184.720	50.624	BETA <−−> LIQUID		
753.000	124.683	277.065	184.720	69.535	TRANSITION		
800	124.683	284.614	190.370	75.395	−394.391	−369.773	24.144
900	124.683	299.299	201.673	87.864	−500.211	−364.559	21.158
1000	124.683	312.436	212.104	100.332	−497.229	−349.647	18.264
1100	124.683	324.320	221.774	112.800	−494.321	−335.030	15.909
1200	124.683	335.168	230.778	125.269	−685.047	−315.794	13.746
1300	124.683	345.148	239.197	137.737	−680.541	−285.206	11.460
1400	124 683	354.388	247.099	150.205	−676.066	−254.963	9.513
1500	124.683	362.991	254.542	162.674	−671.622	−225.040	7.837

PREVIOUS: CURRENT: December 1983

Continued from page 1641

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