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Note

Thermodynamic functions for Na_2CrO_4 and Na_2WO_4

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Together with measures of specific heat at low temperature[1,2] a calorimetric study of Na_2CrO_4 and Na_2WO_4 from ordinary temperature to 1500 K (ref. 3) has allowed the calculation of enthalpy, entropy and Gibbs free energy of these salts. The value of entropy at melting point is compared with the value assessed by an acoustical method[4].

TABLE 1

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Na_2CrO_4

$\Delta H/T = \frac{H^\circ - H_0^\circ}{T}$, $\Delta S = S^\circ - S_0^\circ$, $\Delta G/T = \frac{G^\circ - G_0^\circ}{T}$.

T (K)	*ΔH/T (cal mol⁻¹ K⁻¹)*	*ΔS (cal mol⁻¹ K⁻¹)*	*−ΔG/T (cal mol⁻¹ K⁻¹)*
274	20.1	39.4	19.2
340	22.9	46.7	23.9
450	26.5	57.3	30.8
560	29.3	66.2	36.9
692	32.5	75.9	43.4
Transition temperature: (694 ± 3) K			
Transition enthalpy: (2290 ± 100) cal mol^{-1}			
Transition entropy: (3.3 ± 0.1) cal mol^{-1} K^{-1}			
695	35.8	79.4	43.5
790	36.9	85.1	48.2
885	37.9	90.4	52.5
980	38.8	95.2	56.4
1056	39.5	98.8	59.3
Melting temperature: (1070 ± 2) K			
Melting enthalpy: (5790 ± 100) cal mol^{-1}			
Melting entropy: (5.4 ± 0.1) cal mol^{-1} K^{-1}			
1071	45.1	104.9	59.9
1155	45.3	108.6	63.3
1260	45.6	112.9	67.2
1344	45.8	116.0	70.9
1428	46.0	119.0	73.0

TABLE 2

VALUES OF ENTHALPY, ENTROPY AND GIBBS FREE ENERGY FOR Na_2WO_4

$\Delta H/T = \frac{H^\circ - H_0^\circ}{T}$, $\Delta S = S^\circ - S_0^\circ$, $\Delta G/T = \frac{G^\circ - G_0^\circ}{T}$.

T (K)	$\Delta H/T$ (cal mol^{-1} K^{-1})	ΔS (cal mol^{-1} K^{-1})	$-\Delta G/T$ (cal mol^{-1} K^{-1})
299	23.1	38.6	15.5
444	29.6	55.7	26.2
589	31.8	66.6	34.8
676	33.1	72.4	39.3
850	35.1	82.2	47.1
Transition temperature: (859 ± 3) K			
Transition enthalpy: (7530 ± 120) cal mol^{-1}			
Transition entropy: (8.8 ± 0.1) cal mol^{-1} K^{-1}			
860	43.9	91.4	47.5
890	44.0	93.0	49.0
914	44.1	94.3	50.2
938	44.2	95.6	51.4
962	44.4	96.9	52.5
Melting temperature: (967 ± 2) K			
Melting enthalpy: (6660 ± 140) cal mol^{-1}			
Melting entropy: (6.9 ± 0.1) cal mol^{-1} K^{-1}			
967	51.3	104.0	52.7
1045	51.3	108.0	56.7
1201	51.3	115.2	63.8
1305	51.4	119.5	68.1
1409	51.4	123.5	72.1

In the acoustical method, the entropy is assumed to be the sum of internal movements contributions in the ions ($S_{vib.} + S_{rot.}$) on the one hand together with the entropy of the quasi-lattice liquid (S_r) on the other.

TABLE 3

VALUES OF THE VARIOUS ENTROPIES AND THE TOTAL ENTROPY CALCULATED FOR Na_2CrO_4 AND Na_2WO_4 AT THEIR MELTING POINT

Salt	Melting temp., T_F (K)	Speed of sound, u_F (ms^{-1}) (ref. 6)	Entropy (cal mol^{-1} K^{-1})				
			$S_{vib.}$	$S_{rot.}$	S_r	S_{total}	$S_{exp.}$
Na_2CrO_4	1070	1926	24.4	24.5	57.0	105.9	104.9
Na_2WO_4	967	1487	23.4	24.8	60.0	108.2	104.0

The acoustical method appears to be able to produce only an order of magnitude as has been shown in the case of alkali sulphates[4].

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