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The relative enthalpy to 573 K and standard enthalpy of formation of sodium tetrachloroaluminate, $NaAlCl_4$

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The relative enthalpy of $NaAlCl_4$ has been determined by drop calorimetry in the temperature interval 298 to 573 K to be:

$$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}} = 143.16(T/\mathrm{K})-42804, \quad (298\ \text{to}\ 414\ \mathrm{K}),$$

$$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}} = 175.75(T/\mathrm{K})-37285, \quad (433\ \text{to}\ 573\ \mathrm{K}).$$

The molar enthalpy of fusion is $(19431 \pm 377)\ \mathrm{J\ mol^{-1}}$. By measurement of the enthalpies of solution of $NaAlCl_4$(c), NaCl(c), and $AlCl_3$(c) in 0.05 mol kg^{-1} HCl the standard enthalpy of formation of $NaAlCl_4$ has been determined to be $\Delta H_f^\circ(NaAlCl_4, c, 298.15\ \mathrm{K}) = -(1139.45 \pm 1.20)\ \mathrm{kJ\ mol^{-1}}$.

1. Introduction

The heat capacities of $NaAlCl_4$ reported in JANAF Thermochemical Tables(1) were estimated by comparison with $KAlCl_4$, which values in turn were estimated from the experimental values for $KMgCl_3$; the enthalpy of fusion of $NaAlCl_4$ was reported as unknown.

The enthalpy of formation of $NaAlCl_4$(c) from NaCl(c) and $AlCl_3$(c) was determined by Baud(2) to be 22.80 kJ mol^{-1}, using the method of solution calorimetry, but the reference temperature chosen (288 K) was low by modern standards and the effects of ion association and hydrolysis in water were apparently not accounted for. Combining this result with literature values for the standard enthalpy of formation of NaCl and $AlCl_3$, Stull and Prophet(1) calculated the standard enthalpy of formation: $\Delta H_f^\circ(NaAlCl_4, c, 298.15\ \mathrm{K}) = -(1143.23 \pm 4.18)\ \mathrm{kJ\ mol^{-1}}$. The enthalpy of formation of $NaAlCl_4$(c), was also determined by Boxall, Jones, and Osteryoung(3) incidentally to a study of the electrochemistry of molten $NaAlCl_4$, but the authors themselves drew attention to a discrepancy between their value and that based on Baud's work.(2)

In view of the paucity of reliable thermodynamic quantities for $NaAlCl_4$, further experimental determinations were desirable.

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2. Experimental

Sodium tetrachloroaluminate was prepared by fusing together stoichiometric quantities of analytical-reagent grade NaCl (previously fused at 1023 K) and pure $AlCl_3$ in a sealed pyrex tube filled with argon gas. The $AlCl_3$ was prepared by direct chlorination of Al metal (99.99 mass per cent purity) and subsequently purified by passing it over pure Al at 875 K. The aluminium content of the tetrachloroaluminate, estimated by titration with disodium EDTA, was (14.65 ± 0.03) mass per cent (theoretical 14.68). Total chlorine estimated argentimetrically was (73.96 ± 0.03) mass per cent (theoretical, 73.94).

The calorimeter vessel consisted of a 1 dm^3 silvered Dewar vessel closed by a PVC cap fitted with a glass stirrer, sample crusher, non-inductively wound electrical heater, and either a chromel-to-alumel thermocouple or a platinum resistance thermometer. The vessel was held in a 12 dm^3 capacity Haake water bath maintained at (298.65 ± 0.01) K. An aluminium block furnace controlled to ± 0.1 K was mounted above the calorimeter and a stainless-steel drop tube connected the two assemblies.

The signal from the chromel-to-alumel thermocouple in the calorimeter was amplified by a 9835B Leeds and Northrup microvolt amplifier and the output displayed on a Hewlett Packard 7045A $X-Y$ recorder. Similarly, the signal from the platinum resistance thermometer, after amplification by a Leeds and Northrup model 8078 precision bridge, was displayed on the same recorder. The platinum resistance thermometer was calibrated by the CSIRO National Measurement Laboratory, and a certificate issued in accordance with the IPTS–68.

The energy equivalent of the calorimeter was determined by electrical calibrations. The enthalpy of copper and α-alumina determined using this energy equivalent was consistent with published values(1) within ±0.27 per cent.

DROP-CALORIMETRIC METHOD

Sodium tetrachloroaluminate was loaded into pyrex ampoules (55 mm length, 12 mm diameter, 0.75 wall thickness) in a dry box and sealed off under argon gas at atmospheric pressure. The glass and sample masses were approximately 4.5 and 5 g respectively. The relative enthalpy contribution due to the pyrex glass and sample were 52 and 48 per cent respectively for the solid phase; for the liquid phase the respective contributions were 41 and 59 per cent.

The relative enthalpy of the pyrex glass was determined over the temperature interval 298 to 573 K. The following equation, obtained by a least-squares fit of the above results was used to correct for the enthalpy contribution due to the pyrex ampoule:

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ g^{-1}} = 0.879(T/\mathrm{K}) - 263.8.$$

The pressure of vapours above $NaAlCl_4$ is negligible in the temperature interval investigated here,(4, 5) so that no corrections are required for condensation of vapour.

SOLUTION-CALORIMETRIC METHOD

The samples of NaCl, $AlCl_3$, and $NaAlCl_4$ were weighed into dry pyrex capsules (25 mm length, 12.5 mm diameter) which were then sealed with microscope cover slips held in place by paraffin wax. These were broken into 500 g of 0.05 mol kg^{-1} HCl according to the scheme:

$$AlCl_3(c)+(xHCl+yH_2O) = (AlCl_3+xHCl+yH_2O), \tag{1}$$

$$NaCl(c)+(AlCl_3+xHCl+yH_2O) = (AlCl_3+NaCl+xHCl+yH_2O), \tag{2}$$

$$NaAlCl_4(c)+(xHCl+yH_2O) = (AlCl_3+NaCl+xHCl+yH_2O), \tag{3}$$

where $x = 370.4$ and $y = 10271.0$.

The effect of ion association on the enthalpy of solution of $NaAlCl_4$ was compensated in the overall scheme by determining the enthalpy of solution of NaCl in the product solution of reaction (1). The quantities of $AlCl_3$ and $NaAlCl_4$ were adjusted to yield approximately 800 J. For NaCl, the low positive enthalpy of solution required extrapolation from experimental enthalpies of solution using 0.5, 1.0, 1.5, and 2.0 g of NaCl against the square root of the molality to give $(4322 \pm 21)\ \mathrm{J\ mol^{-1}}$ at 0.0054 mol kg^{-1} of NaCl. The solution enthalpies were corrected for the contribution due to vaporization of water by the gas enclosed in the capsules.

3. Results

The experimental enthalpies are given in table 1. Reported in this table are the average values of three drops at each temperature within the interval 313 to 573 K.

TABLE 1. Relative enthalpies of $NaAlCl_4$ obtained in the drop calorimeter in the temperature interval 298 to 573 K. $\delta = 100\{\Delta H(\text{calc.})-\Delta H(\text{obs.})\}/\Delta H(\text{calc.})$

	$\{H^\circ(T)-H^\circ(298.15\ K\}/\mathrm{J\ mol^{-1}}$				$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}}$		
T/K	observed	equations (1), (2)	δ	T/K	observed	equations (1), (2)	δ
313.2	2170	2026	−7.1	426.2	—	37638	—
323.2	3579	3457	−3.5	433.2	38586	38868	+0.7
333.2	4703	4889	+3.8	443.2	40825	40626	−0.5
343.2	6270	6321	+0.8	453.2	42592	42384	−0.5
353.2	7712	7752	+0.5	463.2	44156	44141	−0.03
363.2	8882	9184	+3.3	473.2	45761	45899	+0.3
373.2	10686	10615	−0.6	483.2	47372	47656	+0.6
383.2	11838	12047	+1.7	493.2	49344	49414	+0.1
393.2	13375	13478	+0.8	503.2	51090	51171	+0.2
403.2	15141	14910	−1.5	513.2	53191	52929	−0.5
413.2	16363	16341	−0.1	523.2	55189	54686	−0.9
414.2	16667	16485	−1.1	533.2	56717	56443	−0.5
426.2	—	18203	—	543.2	58140	58201	+0.1
				553.2	59521	59959	+0.7
				563.2	61365	61716	+0.6
				573.2	63719	63474	−0.4

The results can be expressed by the equations (determined by the method of least squares):

$$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}} = 143.16(T/\mathrm{K})-42805, \quad (298\ \text{to}\ 414\ \mathrm{K}), \quad (4)$$

$$\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}} = 175.75(T/\mathrm{K})-37285, \quad (433\ \text{to}\ 573\ \mathrm{K}). \quad (5)$$

Equation (4) was obtained by use of the constraint that $\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\} = 0$ at 298.15 K and the standard deviation of the residuals is 172 $\mathrm{J\ mol^{-1}}$. The standard deviation of the residuals for equation (5) is 284 $\mathrm{J\ mol^{-1}}$.

The enthalpy of fusion is obtained by extrapolation of the results in the form of equations (4) and (5) to the reported melting temperature, (426.0 ± 0.5) K;(6) the value is $(19431 \pm 377)\ \mathrm{J\ mol^{-1}}$.

The experimental solution enthalpies for $AlCl_3$, $NaAlCl_4$, and NaCl are shown in tables 2, 3, and 4. The enthalpy of reaction for the formation of $NaAlCl_4(c)$:

$$NaCl(c)+AlCl_3(c) = NaAlCl_4(c), \quad (6)$$

was calculated to be $\Delta H_r(298.15\ \mathrm{K}) = -(22.70 \pm 0.79)\ \mathrm{kJ\ mol^{-1}}$ by summing the respective enthalpies of solution obtained for reactions (1), (2), and (3). This value of ΔH_r agrees with the earlier value of Baud(2) but has a considerably lower estimated error. Combining ΔH_r with data(1) for the standard enthalpy of formation for $AlCl_3$, $\Delta H_f^\circ = -(705.63 \pm 0.84)\ \mathrm{kJ\ mol^{-1}}$, and for NaCl, $\Delta H_f^\circ = -(411.12 \pm 0.33)\ \mathrm{kJ\ mol^{-1}}$, the standard enthalpy of formation of $NaAlCl_4$, is obtained: $\Delta H_f^\circ = -(1139.45 \pm 1.20)\ \mathrm{kJ\ mol^{-1}}$.

A summary of the thermodynamic properties of $NaAlCl_4$ in the temperature interval 298 to 600 K calculated on the basis of this work is shown in table 5.

TABLE 2. Calorimetric results for solution of $AlCl_3(c)$ in 500 g of 0.05 $\mathrm{mol\ kg^{-1}}$ of HCl

Run	$m(AlCl_3)/\mathrm{g}$	$\Delta H_{sol}/\mathrm{J\ mol^{-1}}$
1	0.3498	−327381
2	0.3507	−326975
3	0.3759	−327607
4	0.3697	−328373
5	0.3632	−327875
6	0.3437	−327235
Mean		−327574 ± 498

TABLE 3. Calorimetric results for solution of $NaAlCl_4(c)$ in 500 g of 0.05 $\mathrm{mol\ kg^{-1}}$ of HCl

Run	$m(NaAlCl_4)/\mathrm{g}$	$\Delta H_{sol}/\mathrm{J\ mol^{-1}}$
1	0.5822	−301047
2	0.5604	−301102
3	0.5480	−300963
4	0.5504	−300637
5	0.5487	−299800
6	0.5615	−299788
Mean		−300566 ± 612

TABLE 4. Calorimetric results for solution of NaCl in 500 g of 0.05 mol kg^{-1} of HCl and 0.36 g of aluminium chloride

m(NaCl)/g	m/mol kg^{-1}	ΔH_{sol}/J mol^{-1} [a]
0.5	0.01711	4307
1.0	0.03422	4289
1.5	0.05133	4277
2.0	0.06844	4248

[a] Average value of 3 runs.

TABLE 5. Derived thermodynamic quantities for $NaAlCl_4$; $T^{\dagger} = 298.15$ K

T/K	$C_p(T)$/J K^{-1} mol^{-1}	$S^{\circ}(T)$/J K^{-1} mol^{-1}	$\{G^{\circ}-H^{\circ}(T^{\dagger})\}/T$/J K^{-1} mol^{-1}	$H^{\circ}(T)-H^{\circ}(T^{\dagger})$/J mol^{-1}	$\Delta H^{\circ}(T)$/J mol^{-1}	$\Delta G^{\circ}(T)$/J mol^{-1}
298.15	143.16	184.10 [a]	−184.10	0	−1139454	−1037686
300.00	143.16	184.98	−184.10	264	−1139412	−1037055
350.00	143.16	207.05	−185.84	7422	−1138402	−1020078
371.00	143.16	215.39	−187.28	10431	−1138046	−1012990
371.00	143.16	215.39	−187.28	10431	−1140645	−1012990
400.00	143.16	226.17	−189.71	14581	−1140194	−1003029
426.00	143.16	235.18	−192.22	18305	−1139804	−994125
426.00	175.75	280.79	−192.22	37736	−1120373	−994125
450.00	175.75	290.43	−197.20	41953	−1119240	−987044
500.00	175.75	308.94	−207.47	50739	−1116907	−972481
550.00	175.75	325.69	−217.46	59526	−1114607	−958150
600.00	175.75	340.99	−227.13	68312	−1112341	−944027

[a] Entropy estimated using revised Latimer entropy contributions.(11)

4. Discussion

The heat capacity $C_p = 143$ J K^{-1} mol^{-1} from the slope of equation (4) for $NaAlCl_4$(c), is equal to the sum of the heat capacities for NaCl(c) and $AlCl_3$(c) and is less than the value estimated by comparison with $KMgCl_3$.(1)

The entropy of fusion is 2.58 J K^{-1} mol^{-1} which is low for an ionic substance (compare Kubaschewski, Evans, and Alcock),(7) but in agreement with the 50 per cent covalent character of the Al–Cl bonds estimated from lattice-energy calculations (compare Wood and D'Orazio).(8) The values of the heat capacity, enthalpy of fusion, and entropy of fusion are similar to those of sodium tetrachloroferrate.(9) This is to be expected from the similarities of charge and size of Fe^{3+} and Al^{3+} ions. The enthalpy of mixing has been computed(10) using results from table 5 for $NaAlCl_4$(l) and data(1) for NaCl(l) and $AlCl_3$(l) for the process: NaCl(l)+$AlCl_3$(l) = $NaAlCl_4$(l). The value −63.73 kJ mol^{-1} at 450 K, shows that there is significant non-ideality arising from the predominance of the $AlCl_4^-$ ion in the melt.

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REFERENCES

1. Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*, 2nd Ed. NSRDS–NBS 37, **1971.**
2. Baud, M. E. *Ann. chim. Phys.* **1904,** 1, 8.
3. Boxall, L. G.; Jones, H. L.; Osteryoung, R. A. *J. Electrochem. Soc.* **1973,** 120, 223.
4. Dewing, E. W. *J. Am. Chem. Soc.* **1955,** 77, 2639.
5. Rogers, L. J., unpublished work cited by Davey, T. R. A., Floyd, J. M., Marcantonio, P. J.; "The $AlCl_3$–NaCl System Vapour Pressures and Liquidus", presented before the Meeting of American Institute of Metallurgical Engineers, New York, N.Y., March **1971**.
6. Levin, E. M.; Kinney, J. F.; Wells, R. D.; Benedict, J. T. *J. Res. Nat. Bur. Stand.* **1974,** 78, 505.
7. Kubaschewski, O.; Evans, E. L.; Alcock, C. B. *Metallurgical Thermochemistry*. 4th Ed. Pergamon Press: London. **1967**.
8. Wood, R. H.; D'Orazio, L. A. *Inorg. Chem.* **1966,** 5, 682.
9. Cook, C. M.; Dunn, W. E. *J. Phys. Chem.* **1961,** 65, 1505.
10. Turnbull, A. G. *Chemistry in Australia* **1977,** 44, 334.
11. Mills, K. C. *Nat. Phys. Lab. (U.K.) DCS Note* 20, **1974**.