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The Thermochemistry of Two Ammonium Vanadium Bronzes: $(NH_4)_{0.5}V_2O_5$ and $(NH_4)_{1.84}V_3O_8$

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The enthalpies of formation of $(NH_4)_{0.5}V_2O_5$ and $(NH_4)_{1.84}V_3O_8$ have been determined by solution calorimetry. The values found were, $\Delta H_f^\circ((NH_4)_{0.5}V_2O_5$, 298.15 K), = −(1677.1 ± 1.6) kJ mole^{-1} and $\Delta H_f^\circ((NH_4)_{1.84}V_3O_8$, 298.15 K), = −(2789.68 ± 2.1) kJ mole^{-1}. The stability of these compounds is discussed. © 1986 Academic Press, Inc.

Introduction

The chemistry of the ammonium ion, NH_4^+, has much in common with that of the alkali metal cations, A^+. The compounds formed by NH_4^+, with $r \sim 1.50$ Å, are often isomorphous with those formed by K^+ (r = 1.38 Å) and Rb^+ (r = 1.52 Å) (*1*). Thus the ammonium bronze $(NH_4)_{0.5}V_2O_5$ (*2*) is isostructural with $K_{0.51}V_2O_5$ (*3*), as is $(NH_4)_{1.84}V_3O_8$ with $K_2V_3O_8$ (*4, 5*). However, the ammonium ion contained in an oxide matrix may also undergo decomposition. Two such decompositions are

$$NH_{4_{NH_4}} + \tfrac{1}{2}O_O = NH_3(g) + \tfrac{1}{2}H_2O(1) \quad (1)$$

(equivalent to NH_4MO_n
$= NH_3 + \tfrac{1}{2}H_2O + MO_{n-1/2}$)

and

$$NH_{4_{NH_4}} + 2\ O_O = \tfrac{1}{2}N_2(g) + 2\ H_2O(g) \quad (2)$$

(e.g., $(NH_4)_2Cr_2O_7 = N_2(g) + 4\ H_2O(g)$).

The existence of such decomposition pathways generally interferes with the high-temperature synthesis of ammonium insertion compounds of transition metal oxides. The thermal decomposition of ammonium vanadium oxides is, however, a useful preparative method. For example, NH_4VO_3 decomposes *in vacuo* at 453 K (*2*):

$$6\ NH_4VO_3(s) = (NH_4)_2V_6O_{16}(s) + 4\ NH_3(g) + 2\ H_2O(g) \quad (3)$$

followed at 500 K by

$$(NH_4)_2V_6O_{16}(s) = 3\ (NH_4)_{0.5}V_2O_5(s) + H_2O(g) + 0.25\ N_2(g) \quad (4)$$

and at 573–623 K by

$$(NH_4)_{0.5}V_2O_5(s) = 2\ VO_2(s) + H_2O(g) + 0.125\ N_2(g). \quad (5)$$

The final reaction can be used to prepare the metastable VO_2 (B) (*6*) which has a structure derived from that of $(NH_4)_{0.5}V_2O_5$ rather than the normal rutile form.

In the present work the standard enthalpies of formation of $(NH_4)_{0.5}V_2O_5$ and

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$(NH_4)_{1.84}V_3O_8$ have been determined in an attempt to rationalize their thermal behavior.

Experimental Materials

NH_4VO_3. A sample of NH_4VO_3 (BDH "AnalaR") was vacuum dried for 2 days. N,H analysis by a conventional chromatographic analyzer (%N = 11.90 (11.97), %H = 3.28 (3.42), theoretical values in brackets) and thermal decomposition in air (MW = 117.0 (116.98)) were used to confirm the composition.

$(NH_4)_{0.5}V_2O_5$. An intimate mixture of NH_4VO_3, V_2O_5 (from NH_4VO_3 oxidized at 500°C) and V_2O_3 (from V_2O_5 reduced in H_2 at 1000°C), of the appropriate stoichiometry, was heated for 10 days at 523 K in a sealed Pyrex tube. The powder X-ray pattern was identical to that of Deschanvres (*2*). The composition of the product was checked using an argentometric method for the determination of the vanadium oxidation state (EW = 378 (382)) and the nitrogen content determined from N,H analysis (%N = 3.63 (3.67), %H = 0.95 (1.05)).

$(NH_4)_{1.84}V_3O_8$. One gram V_2O_5, 30 g NH_4Cl (AnalaR), 150 cm^3 deionized water, and an excess (>2 g) of granulated zinc were refluxed for 3 hr under nitrogen. The black product was filtered off and washed with deionized water until the washings were chloride-free; the product was dried in a vacuum desiccator over silica gel. Powder X-ray data were in agreement with those of Bernard *et al.* (*4*). N,H analysis by a conventional chromatographic analyzer (%N = 8.17 (8.21), %H = 2.26 (2.34)), reducing power measurements using an argentometric method (EW = 373.3 (373.7)) and thermal decomposition in air (MW = 314.0 (313.9) gave the composition as $(NH_4)_{1.84}V_3O_8$.

The reaction medium for calorimetry consisted of 40 g $K_3Fe(CN)_6$ dissolved in 1.99 dm^3 of 3.05 ± 0.05 *M* KOH solution.

Determination of Enthalpies of Formation

Enthalpies of reaction (at 298.15 K) were measured using an LKB 8700 isoperibolic calorimeter. The instrument and mode of operation have been described previously (*7*). Sample charges of 70–110 mg were dissolved in 100-cm^3 batches of the calorimetric reagent. No discernible change in the enthalpies of reaction occurred on varying the sample mass, and previous work has also shown that, for a large excess of reagent, consecutive addition and the maintenance of strict stoichiometry for the components on both sides of the reaction is unnecessary. Fresh aliquots of reaction medium were therefore used for each experiment. At least five enthalpy of reaction measurements were made on each sample, and the uncertainty quoted in the mean is twice the standard error of the mean. Detailed calorimetric data for all the samples have been tabulated (*8*).

All three compounds reacted rapidly (less than 3 min) and the enthalpies of reaction were calculated using the Dickinson method (*9*). Calorimetric reaction schemes for NH_4VO_3, $(NH_4)_{0.5}V_2O_5$, and $(NH_4)_{1.84}V_3O_8$ are shown in Tables I, II, and III respectively. Combining the measured enthalpy of Eq. (11), with $\Delta H_f^\circ(V_2O_5, 298.15\ K) = -(1550.6 \pm 1.7)$ kJ mole^{-1} (*10*), $\Delta H_f^\circ(H_2O(l), 298.15\ K) = -(285.83 \pm 0.04)$ (*11*), $\Delta H_f^\circ(\{HCl, 179.805\ H_2O\}(l), 298.15\ K) = -(166.31 \pm 0.1)$ (*12*), and $\Delta H_f^\circ(NH_4Cl, 298.15\ K) = -(314.4 \pm 0.5)$ (*12*) gives

$$\Delta H_f^\circ(NH_4VO_3, 298.15\ K) = -(1050.4 \pm 1.1)\ \text{kJ mole}^{-1}.$$

Using the above data and $\Delta H_f^\circ(V_2O_3, 298.15\ K), = -(1218.8 \pm 1.6)$ kJ mole^{-1} (*13*) and the measured enthalpy of Eq. (16) gives

$$\Delta H_f^\circ((NH_4)_{0.5}V_2O_5, 298.15\ K) = -(1677.1 \pm 1.6)\ \text{kJ mole}^{-1}.$$

TABLE I

CALORIMETRIC REACTION SCHEME FOR NH_4VO_3

Reaction	$\Delta H_{298.15}$ K (kJ mole^{-1})
(6) $NH_4VO_3(s) + 3OH^-(sol) = [VO_4]^{3-}(sol) + NH_4OH(sol) + H_2O(sol)$	-35.53 ± 0.14
(7) $[HCl{:}179.805H_2O](l) + OH^-(sol) = H_2O(sol) + Cl^-(sol) + 179.805H_2O(sol)$	-78.46 ± 0.20 (*14*)
(8) $0.5V_2O_5(s) + 3OH^-(sol) = [VO_4]^{3-}(sol) + 1.5H_2O(sol)$	-93.28 ± 0.29 (*15*)
(9) $NH_4Cl(s) + OH^-(sol) = NH_4OH(sol) + Cl^-(sol)$	$+ 7.9 \pm 0.1$ (*16*)
(10) $180.305H_2O(l) = 180.305H_2O(sol)$	-12.73 ± 0.29 (*17*)
(11) $NH_4VO_3(s) + [HCl{:}179.805H_2O](l) = NH_4Cl(s) + 0.5V_2O_5(s) + 180.305H_2O(l)$	
$\Delta H_{11} = \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9 - \Delta H_{10}$	
$= -15.55 \pm 0.49$ kJ mole^{-1}	

TABLE II

CALORIMETRIC REACTION SCHEME FOR $(NH_4)_{0.5}V_2O_5$

Reaction	$\Delta H_{298.15}$ K (kJ mole^{-1})
(12) $(NH_4)_{0.5}V_2O_5(s) + 6.5OH^-(sol) + 0.5[Fe(CN)_6]^{3-}(sol)$	
$= 0.5NH_4OH(sol) + 2[VO_4]^{3-}(sol) = 0.5[Fe(CN)_6]^{4-}(sol) + 3H_2O(sol)$	-180.62 ± 0.98
(13) $NH_4VO_3(s) + 3OH^-(sol) = [VO_4]^{3-}(sol) + NH_4OH(sol) + H_2O(sol)$	$- 35.53 \pm 0.14$
(14) $V_2O_5(s) + 6OH^-(sol) = 2[VO_4]^{3-}(sol) + 3H_2O(sol)$	-186.57 ± 0.59 (*15*)
(15) $V_2O_3(s) + 10OH^-(sol) + 4[Fe(CN)_6]^{3-}(sol)$	
$= 2[VO_4]^{3-}(sol) + 4[Fe(CN)_6]^{4-}(sol) + 5H_2O(sol)$	-613.05 ± 1.62 (*15*)
(16) $(NH_4)_{0.5}V_2O_5(s) = 0.5NH_4VO_3(s) + 0.625V_2O_5(s) + 0.125V_2O_3(s)$	
$\Delta H_{16} = \Delta H_{12} - 0.5\Delta H_{13} - 0.625\Delta H_{14} - 0.125\Delta H_{15}$	
$= +30.4 \pm 1.1$ kJ mole^{-1}	

TABLE III

CALORIMETRIC REACTION SCHEME FOR $(NH_4)_{1.84}V_3O_8$

Reaction	$\Delta H_{298.15}$ K (kJ mole^{-1})
(17) $(NH_4)_{1.84}V_3O_8(s) + 10.84OH^-(sol) + 0.84[Fe(CN)_6]^{3-}(sol)$	
$= 1.84NH_4OH(sol) + 3[VO_4]^{3-}(sol) + 0.84[Fe(CN)_6]^{4-}(sol) + 4H_2O(sol)$	-235.92 ± 0.88
(18) $NH_4VO_3(s) + 3OH^-(sol) = [VO_4]^{3-}(sol) + NH_4OH(sol) + H_2O(sol)$	$- 35.53 \pm 0.14$
(19) $V_2O_5(s) + 6OH^-(sol) = 2[VO_4]^{3-}(sol) + 3H_2O(sol)$	-186.57 ± 0.59 (*15*)
(20) $V_2O_3(s) + 10OH^-(sol) + 4[Fe(CN)_6]^{3-}(sol)$	
$= 2[VO_4]^{3-}(sol) + 4[Fe(CN)_6]^{4-}(sol) + 5H_2O(sol)$	-613.05 ± 1.62 (*15*)
(21) $(NH_4)_{1.84}V_3O_8(s) = 1.84NH_4VO_3(s) + 0.37V_2O_5(s) + 0.21V_2O_3(s)$	
$\Delta H_{21} = \Delta H_{17} - 1.84\Delta H_{18} - 0.37\Delta H_{19} - 0.21\Delta H_{20}$	
$= 27.2 \pm 1.0$ kJ mole^{-1}	

Similarly, from reaction Eq. (21)

$$\Delta H_f^\circ((NH_4)_{1.84}V_3O_8,\ 298.15\ \mathrm{K}) = -(2789.68 \pm 2.1)\ \mathrm{kJ\ mole^{-1}}.$$

Discussion

The value $\Delta H_f^\circ(NH_4VO_3$, 298.15 K) = −(1050.4 ± 1.1) kJ mole^{-1} determined in this work is in good agreement with Bertrand and Hepler's value of $\Delta H_f^\circ(NH_4VO_3$, 298.15 K) = −(1053.1 ± 1.5) kJ mole^{-1} (*18*).

Preparation of the Insertion Compounds

The enthalpy changes for the reactions

$$0.5\ NH_4VO_3(s) + 0.625\ V_2O_5(s) + 0.125\ V_2O_3(s) = (NH_4)_{0.5}V_2O_5(s) \quad (22)$$

$$\Delta H_{22}^\circ = -30.4 \pm 1.1\ \mathrm{kJ\ mole^{-1}}$$

$$1.84\ NH_4VO_3(s) + 0.37\ V_2O_5(s) + 0.21\ V_2O_3(s) = (NH_4)_{1.84}V_3O_8(s) \quad (23)$$

$$\Delta H_{23}^\circ = -27.2 \pm 1.0\ \mathrm{kJ\ mole^{-1}}$$

were calculated directly from enthalpy of solution data. The entropy change for a reaction involving only solids is expected to be small, and the enthalpy of reaction should approximate to the free energy change. Equation (22) was used in the preparation of $(NH_4)_{0.5}V_2O_5$. The negative enthalpy change for the reaction in Eq. (23) suggested an additional method of preparation for $(NH_4)_{1.84}V_3O_8$. Consequently the components NH_4VO_3, V_2O_3, and V_2O_5 were heated together in the correct stoichiometry at 523 K in a sealed Pyrex tube for 14 days. The product $(NH_4)_{1.84}V_3O_8$ was identical to that produced by Bernard *et al.* (*4*).

Comparison with $(NH_4)_{0.25}WO_3$

The enthalpy of formation of $(NH_4)_{0.5}V_2O_5$ from $NH_3(g)$, H_2 and V_2O_5 can be calculated (using $\Delta H_f^\circ(NH_3(g)$, 298.15 K) = −(45.94 ± 0.35) kJ mole^{-1} (*11*)) and compared to the corresponding value for the ammonium tungsten bronze (*16*):

$$NH_3(g) + \tfrac{1}{2}H_2(g) + 2\ V_2O_5(s) = 2\ (NH_4)_{0.5}V_2O_5(s) \quad (24)$$

$$\Delta H_{24}^\circ = -207.0 \pm 4.6\ \mathrm{kJ\ mole^{-1}}$$

$$NH_3(g) + \tfrac{1}{2}H_2(g) + 4\ WO_3(s) = 4\ (NH_4)_{0.25}WO_3 \quad (25)$$

$$\Delta H_{25}^\circ = -102.8 \pm 3.2\ \mathrm{kJ\ mole^{-1}}.$$

This shows the greater stability of the vanadium bronze due to the more oxidizing nature of V_2O_5.

Estimation of ΔG_f°

ΔG_f°s for $(NH_4)_{0.5}V_2O_5$ and $(NH_4)_{1.84}V_3O_8$ may be estimated by assuming that, for reactions involving solid phases, $\Delta G^\circ \sim \Delta H^\circ$. ΔG_f°'s are known for all the components other than the ammonium insertion compounds in Eq. (16) and Eq. (21): [$\Delta G_f^\circ(NH_4VO_3$, 298.15 K) = −(888.3) kJ mole^{-1} (*18*), $\Delta G_f^\circ(V_2O_5$, 298.15 K) = −(1419.4) kJ mole^{-1} (*13*), and $\Delta G_f^\circ(V_2O_3$, 298.15 K) = −(1139.1) kJ mole^{-1} (*13*)], whence

$$\Delta G_f^\circ((NH_4)_{0.5}V_2O_5\ 298.15\ \mathrm{K}) = -(1504.1)\ \mathrm{kJ\ mole^{-1}}$$

$$\Delta G_f^\circ((NH_4)_{1.84}V_3O_8\ 298.15\ \mathrm{K}) = -(2426.1)\ \mathrm{kJ\ mole^{-1}}.$$

These values can be used to predict the course of several reactions of interest. A partial phase diagram for the system $\{2NH_3(g), H_2O(1)\} - V_2O_5 - \{2VO_2\}$ is shown in Fig. 1. The stability of the ammonium insertion compounds relative to other compounds shown in the diagram can be estimated, since for the other substances ΔG_f°'s are known [$\Delta G_f^\circ(VO_2$, 298.15 K) = −(659.0) kJ mole^{-1} (*13*), $\Delta G_f^\circ(NH_3(g)$, 298.15 K) = −(16.5) kJ mole^{-1} (*13*), $\Delta G_f^\circ(H_2O(1)$, 298.15 K) = −(237.2) kJ

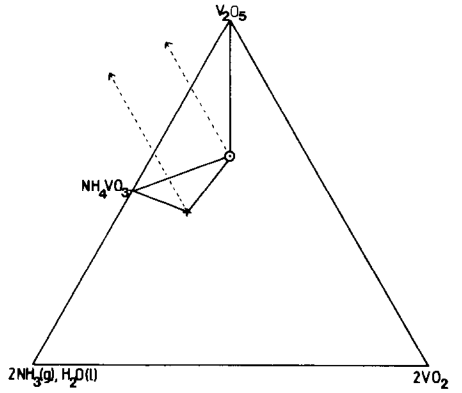

FIG. 1. Partial phase diagram for the $\{2NH_3(g), H_2O(l)\} - V_2O_5 - \{2VO_2\}$ system calculated from measured thermodynamic quantities at 298 K. ⊙ = $(NH_4)_{0.5}V_2O_5$ + = $(NH_4)_{1.84}V_3O_8$, - - → = oxidation pathway.

mole^{-1} (*13*), $\Delta G_f^\circ(VO, 298.15\ K) = -(404.2)$ kJ mole^{-1} (*13*)].

Disproportionation

Both $(NH_4)_{0.5}V_2O_5$ and $(NH_4)_{1.84}V_3O_8$ lie within the triangle formed by NH_4VO_3, V_2O_5 and $\{2VO_2\}$ (Fig. 1); both are stable to decomposition into these components:

$$(NH_4)_{0.5}V_2O_5 = 0.5\ NH_4VO_3 + 0.5\ V_2O_5 + 0.25\ \{2VO_2\} \quad (26)$$

$$\Delta G_{26}^\circ \sim +21\ \text{kJ mole}^{-1}$$

$$(NH_4)_{1.84}V_3O_8 = 1.84\ NH_4VO_3 + 0.16\ V_2O_5 + 0.42\ \{2VO_2\} \quad (27)$$

$$\Delta G_{27}^\circ \sim +11\ \text{kJ mole}^{-1}.$$

$(NH_4)_{0.5}V_2O_5$ lies within the triangle $(NH_4)_{1.84}V_3O_8 - V_2O_5 - \{2VO_2\}$ and is stable to decomposition into these components:

$$(NH_4)_{0.5}V_2O_5 = 0.5/1.84\ (NH_4)_{1.84}V_3O_8 + (1-1/1.84)\ V_2O_5 + 0.25/1.84\ \{2VO_2\} \quad (28)$$

$$\Delta G_{28}^\circ \sim +18\ \text{kJ mole}^{-1}.$$

These results are in good agreement with the formation of the ammonium insertion compounds in sealed Pyrex tubes at 523 K and their stability at room temperature. At higher temperatures reactions forming gaseous products will become important.

Oxidation

From the phase diagram in Fig. 1 the following oxidation reactions should occur. For $(NH_4)_{0.5}V_2O_5$:

$$2\ (NH_4)_{0.5}V_2O_5 + \tfrac{1}{4}O_2 = NH_4VO_3 + \tfrac{3}{2}V_2O_5 \quad (29)$$

$$\Delta G_{29}^\circ \sim -9\ \text{kJ mole}^{-1}$$

and for $(NH_4)_{1.84}V_3O_8$ first

$$0.75/0.34\ (NH_4)_{1.84}V_3O_8 + \tfrac{1}{4}O_2(g) = 0.58/0.34\ (NH_4)_{0.5}V_2O_5 + 1.09/0.34\ NH_4VO_3 \quad (30)$$

$$\Delta G_{30}^\circ \sim -62\ \text{kJ mole}^{-1}$$

followed by oxidation of the $(NH_4)_{0.5}V_2O_5$ according to Eq. (29) if the oxidation is continued.

Although reactions (29) and (30) are thermodynamically favorable they do not occur at 298 K, presumably due to kinetic factors. At higher temperatures oxidation to N_2 becomes the preferred route. The corresponding thermodynamic quantities, at 298.15, are

$$(NH_4)_{0.5}V_2O_5 + \tfrac{1}{4}O_2 = \tfrac{1}{2}V_2O_5 + \tfrac{1}{4}N_2 + \tfrac{1}{2}H_2O(1) \quad (31)$$

$$\Delta G_{31}^\circ \sim -76\ \text{kJ mole}^{-1}$$

$$0.25/1.59\ (NH_4)_{1.84}V_3O_8 + \tfrac{1}{4}O_2 = 0.23/1.59\ N_2 + 0.92/1.59\ H_2O(1) + 0.75/3.18\ V_2O_5 \quad (32)$$

$$\Delta G_{32}^\circ \sim -91\ \text{kJ mole}^{-1}.$$

Decomposition to Give Nitrogen

Oxidation of the ammonium ion by the reaction in Eq. (2) produces nitrogen; the thermodynamic quantities for this reaction are

$$(NH_4)_{0.5}V_2O_5 = \tfrac{1}{4}N_2 + H_2O(1) + \{2VO_2\} \quad (33)$$

$$\Delta G^\circ_{33} \sim -51 \text{ kJ mole}^{-1}$$

$$(NH_4)_{1.84}V_3O_8 = 0.92\ N_2 + 3.68\ H_2O(1) + 0.84\ \{2VO\} + 0.66\ \{2VO_2\} \quad (34)$$

$$\Delta G^\circ_{34} \sim +4 \text{ kJ mole}^{-1}.$$

Thus, the ammonium vanadium bronze $(NH_4)_{0.5}V_2O_5$, is metastable to decomposition though it remains kinetically stable even at 523 K, the temperature at which it is prepared. In practice $(NH_4)_{0.5}V_2O_5$ decomposes to nitrogen and VO_2 as described in the introduction (Eq. (5)) only above 573 K. However, the decomposition of $(NH_4)_{1.84}V_3O_8$ on heating to 623 and 723 K *in vacuo* was found to proceed according to

$$(NH_4)_{1.84}V_3O_8(s) = 1.8\ VO_2(s) + 0.6\ V_2O_5(s) + 1.52\ NH_3(g) + 1.4\ H_2O(g) + 0.16\ N_2(g) \quad (35)$$

both the possible decomposition reactions described in Eq. (1) and Eq. (2) occurring.

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References

1. R. D. Shannon, *Acta Crystallogra. Sect. A* **32,** 751 (1976).
2. A. Deschanvres, G. Nouet, and B. Raveau, *C. R. Acad. Sci. Paris* **261,** 3144 (1965).
3. M. Pouchard, Ph.D Thesis, Bourdeaux, 1967.
4. J. Bernard, F. Theobald, and A. Vidonne, *Bull. Soc. Chim. Fr.*, 2108 (1970).
5. J. C. Vedrine, R. Clad, and J. Renard, *J. Phys. Chem. Solids* **45,** 581 (1984).
6. F. Theobald, R. Cabala, and J. Bernard, *J. Solid State Chem.* **17,** 431 (1976).
7. P. G. Dickens, M. Jewess, D. J. Neild, and J. C. W. Rose, *J. Chem. Soc. Dalton Trans.*, 30 (1973).
8. S. J. Hibble, D. Phil. Thesis, Oxford, 1983.
9. I. Wadsö, *Sci. Tools* **13,** 33 (1966).
10. A. D. Mah and K. K. Kelley, U.S. Bureau of Mines, Report No. 5858, 1961.
11. CODATA, *J. Chem. Thermodynamics* **10,** 903 (1978).
12. U.S. National Bureau of Standards, Circular 500, Washington, 1952, and Technical Notes, 270 (1–6), 1968–1971.
13. O. Kubaschewski and C. B. Alcock, "Metallurgical Thermochemistry," 5th ed., Pergamon, New York, 1979.
14. P. G. Dickens, J. H. Moore, and D. J. Neild, *J. Solid State Chem.* **7,** 241 (1973).
15. P. G. Dickens, S. J. French, A. T. Hight, M. F. Pye, and G. J. Reynolds, *Solid State Ionics* **2,** 27 (1981).
16. P. G. Dickens and D. J. Neild, *J. Solid State Chem.* **7,** 474 (1977).
17. J. J. Birtill and P. G. Dickens, *J. Solid State Chem.* **29,** 367 (1979).
18. G. L. Bertrand and L. G. Hepler, *J. Chem. Eng. Data* **12,** 412 (1967).