Thermochemistry of Oxide Bronzes. Part I. Sodium Vanadium Bronzes $Na_xV_2O_5$ with x between 0·2 and 0·33

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The enthalpies of formation from Na(s) and V_2O_5(s) of five β-phase sodium vanadium bronzes $Na_xV_2O_5$(s) in the range $0{\cdot}20 \leqslant x \leqslant 0{\cdot}33$ have been determined by solution calorimetry. The partial molar enthalpy of solution of Na(s) into V_2O_5(s) is constant over the composition range investigated. The thermodynamic stability of the β-bronze phase towards oxidation and disproportionation is discussed.

An oxide bronze A_xMO_n is, formally, a compound derived by the insertion of an element A into an oxide matrix MO_n of a transition metal M. Bronzes have been prepared where M is one of Ti, V, Nb, Ta, Mo, W, U, or Re. A wide variety of insertion elements has been found, usually metals, but hydrogen and ammonium tungsten bronzes, H_xWO_3 and $(NH_4)_xWO_3$, have also been characterised. These compounds all display to varying degrees intense colour, metallic conduction (or n-type semiconduction), and resistance to attack by non-oxidising acids. Often the proportion x of the inserted element can vary widely across a single phase region. Crystallographic and electronic structures of the oxide bronzes have been studied extensively and have been reviewed;[1,2] however, no primary thermodynamic data have been reported for any bronze system, although Morozova and Ovcharova[3] determined heats of solution of sodium tungsten bronzes Na_xWO_3 in alkaline potassium hexacyanoferrate(III) solution. The present work constitutes the first part of a sytematic investigation by means of solution calorimetry of the enthalpies of formation of the oxide bronzes formed by V, Mo, and W. The well-characterised[4-6] sodium vanadium β-phase bronze was chosen as an initial system for study. Pure V_2O_5 has D^{13}_{2h} (orthohombic) symmetry, which is unchanged by accommodation of small amounts of sodium to give an 'α-phase' bronze $Na_xV_2O_5$ which exists over the composition range $0 < x \leqslant 0{\cdot}02$. In the range $0{\cdot}20 \leqslant x \leqslant 0{\cdot}33$ a β-phase bronze exists in which the parent V_2O_5 structure is distorted and for which the new symmetry is C^3_{2h} (monoclinic).[7] Insertion sites for Na lie in tunnels within the V_2O_5 framework and are of sevenfold co-ordination by oxygen. Such sites occur in pairs and simultaneous occupation of both sites of a pair by sodium does not occur. The maximum sodium content consistent with this constraint is $Na_{0{\cdot}33}V_2O_5$.

EXPERIMENTAL

Samples of $Na_xV_2O_5$ were prepared by heating finely ground mixtures of AnalaR Na_2CO_3 and V_2O_5 to 780 °C in air in a platinum crucible.[8,9] CO_2 was lost and the resulting melt allowed to cool slowly; oxygen was evolved as shiny blue-black needles of the bronze separated. The crystalline products were washed with 6M-ammonia and boiling water. The samples were analysed for total vanadium by the method of Sienko and Sohn[5] and for sodium by atomic absorption spectroscopy. Five samples of $Na_xV_2O_5$ with analysed x values of 0·20, 0·22, 0·25, 0·29, and 0·33 were prepared from melts of original Na : 2V ratios of 0·180, 0·215, 0·250, 0·301, and 0·330 respectively. X-Ray powder photographs were taken with a Guinier camera (with Cu-K_α radiation) and indexed satisfactorily on the unit cell of β-$Na_xV_2O_5$ obtained by Wadsley.[7]

The crystals of $Na_xV_2O_5$ were thoroughly ground to an average particle size of *ca.* 1 μm before dissolution in the calorimetric solvents. The particle size was sufficiently large for surface-energy effects to be negligible.[10] Other solid reagents used in calorimetry were AnalaR. Samples of NaCl and KCl were dried overnight at 100 °C and kept in a vacuum desiccator before use. B.D.H. 100 volume H_2O_2 was analysed before use and shown to be (H_2O_2,6·36H_2O). A solution of hexacyanoferrate(III) reagent for calorimetric use was made by addition of KOH (20 g) and $K_3Fe(CN)_6$ (2 g) to water (100 ml). A corresponding peroxide reagent was prepared by the addition of H_2O_2,6·36H_2O (0·2 ml) to 5M-NaOH solution (100 ml).

Apparatus and Operation.—An LKB 8700 constant-environment solution calorimeter was used. The solvent was contained in a 100 ml Pyrex vessel, which was surrounded by a metal can to provide an insulating air space; the whole assembly was immersed in a thermostat controlled to ±0·01 °C. The solute (solid or liquid) was contained in a sealed 1 ml glass ampoule held between the blades of a gold-plated stirrer. Depression of the stirrer broke away both flat end windows upon a spike, fixed to the bottom of the vessel, and so initiated reaction.

The temperature-sensing device was a thermistor sealed into the vessel and connected to a Wheatstone bridge. The output from a Hewlett-Packard 419A D.C. null voltmeter was led to a potentiometric chart recorder enabling resistance–time plots to be displayed directly.

Electrical calibration was performed by use of an electrical heater also sealed into the vessel. The heater current, I, was measured through the potential drop across a standard resistance in series with the heater, and the heater resistance, R_H, was measured separately by comparison of the potential drops across the heater and another standard resistance in series with it. The heating time, t, was preset electronically (LKB 8705).

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Experiments were performed following the procedure of Wadsö.[11] A thermistor resistance–time plot was obtained for a reaction and an electrical calibration was performed on the resulting solution, to reproduce as far as possible the observed resistance–time characteristics. In both cases Dickinson's method was used to obtain the corrected change in thermistor resistance, ΔR, about its mean value R_m. The main reaction period, or heating period, was less than 5 min in all cases, and the graphical extrapolation was made from fore and after periods of at least 10 minutes' duration.

From the calibration experiment, a calibration constant, ε, was defined by $I^2R_Ht = -\varepsilon(\Delta R/R_m)$ calibration. For the corresponding reaction experiment the measured enthalpy change is given by $\Delta H_{expt} = \varepsilon(\Delta R/R_m)$ reaction. Values for a ' worst case ' situation are given in Table 1.

The overall precision and accuracy obtainable with the calorimeter were tested by Cook, Davies, and Staveley [12] during this work with measurements of the enthalpy of solution of THAM [tris(hydroxymethyl)aminomethane] in 0·1M-HCl at 25 °C (final concentration 6 g l^{-1}). Results were 29·751, 29·756, and 29·747 kJ mol^{-1}, in good agreement with the accepted value of 29·752 ± 0·005 kJ mol^{-1},[13] and within the limits of accuracy of 0·02% claimed by the manufacturer.

TABLE 1

Heat of solution of 0·55 mmol V_2O_5 into 100 ml (vol at 20 °C) of (11·1$K_3Fe(CN)_6$, 647·5KOH, 10,100H_2O) at 25 °C

Wt of V_2O_5/mg	$\Delta R/R_m$	Calibration factor ε/J	ΔH_{expt}/J	ΔH/kJ mol^{-1}
99·7	−0·009552	10,481	−100·11	−182·6
100·0	−0·009600	10,469	−100·50	−182·8
99·9	−0·009627	10,496	−101·04	−184·0

$\Delta H_7 = -183{\cdot}1 \pm 0{\cdot}9$ kJ mol^{-1}

Determinations of Heats of Formation.—Two independent thermochemical reaction schemes were used to determine the enthalpy change of reaction.[1] The first employed aqueous

$$x\mathrm{Na(s)} + \mathrm{V_2O_5(s)} = \mathrm{Na}_x\mathrm{V_2O_5(s)} \tag{1}$$

alkaline potassium hexacyanoferrate(III) solution as calorimetric reagent, the second alkaline hydrogen peroxide solution.

Scheme 1. The enthalpy change of reaction (2) was

$$\mathrm{Na}_x\mathrm{V_2O_5(s)} + x\mathrm{K_3Fe(CN)_6(s)} + \mathrm{3H_2O(l)} + x\mathrm{KCl(s)} = \mathrm{V_2O_5(s)} + x\mathrm{K_4Fe(CN)_6,3H_2O(s)} + \mathrm{NaCl(s)} \tag{2}$$

determined through the reactions shown in Table 2. The symbol (sol) indicates that the designated number of moles of the preceding substance is dissolved in solvent of composition [11·1$K_3Fe(CN)_6$, 647·5KOH, 10,100H_2O). The required enthalpy change is given by equation (10). From equation (2) equation (11) follows. The heats of solution

$$\Delta H_2 = \Delta H_3 + x\Delta H_4 + x\Delta H_5 + x\Delta H_6 - \Delta H_7 - x\Delta H_8 - x\Delta H_9 \tag{10}$$

$$\Delta H_f^\circ\mathrm{Na}_x\mathrm{V_2O_5(s)} - \Delta H_f^\circ\mathrm{V_2O_5(s)} = -\Delta H_2 + x[\Delta H_f^\circ\mathrm{K_4Fe(CN)_6,3H_2O(s)} + \Delta H_f^\circ\mathrm{NaCl(s)} - \Delta H_f^\circ\mathrm{K_3Fe(CN)_6(s)} - 3\Delta H_f^\circ\mathrm{H_2O(l)} - \Delta H_f^\circ\mathrm{KCl(s)}] \tag{11}$$

for reactions (3)—(9) were measured directly. V_2O_5 (100 mg, 0·55 mmol) and equivalent weights of other solutes were dissolved into 100 ml batches of reagent of composition (11·1$K_3Fe(CN)_6$, 647·5KOH, 10,100H_2O). All reactions were carried out at 25 °C. Although the maintenance of strict stoicheiometry requires that reactions (4), (5), and (6) be conducted successively in the same batch of hexacyanoferrate(III) reagent as used for (3), and reactions (8) and (9) be conducted successively in the same batch as (7), for reasons of experimental convenience the solute charges were dissolved into separate batches of reagent of the same initial composition. This procedure is justified by a choice of initial reactant concentrations which ensures that the changes in concentrations of the major reagent species K^+, $Fe(CN)_6^{3-}$, H_2O, and OH^- are very small and where in addition specific chemical interactions are absent between the remaining species Na^+, $Fe(CN)_6^{4-}$, VO_4^{3-} and Cl^-

TABLE 2

Calorimetric reaction scheme 1

Reaction	ΔH (298·15 K)/kJ mol^{-1}
3. $\mathrm{Na}_x\mathrm{V_2O_5(s)} + x\mathrm{Fe(CN)_6^{3-}(sol)} + \mathrm{6OH^-(sol)} = x\mathrm{Na^+(sol)} + \mathrm{2VO_4^{3-}(sol)} + x\mathrm{Fe(CN)_6^{4-}(sol)} + \mathrm{3H_2O(sol)}$	−179·8 ± 0·4(3) $x = 0{\cdot}20$ −180·3 ± 13·(3) $x = 0{\cdot}22$ −179·8 ± 0·2(5) $x = 0{\cdot}25$ −179·9 ± 0·8(3) $x = 0{\cdot}29$ −179·4 ± 0·8(3) $x = 0{\cdot}33$
4. $\mathrm{K_3Fe(CN)_6(s)} = \mathrm{3K^+(sol)} + \mathrm{Fe(CN)_6^{3-}\ (sol)}$	+43·7 ± 0·5(3)
5. $\mathrm{3H_2O(l)} = \mathrm{3H_2O(sol)}$	−0·17 ± 0·1(3)
6. $\mathrm{KCl(s)} = \mathrm{K^+(sol)} + \mathrm{Cl^-(sol)}$	+14·9 ± 0·04(3)
7. $\mathrm{V_2O_5(s)} + \mathrm{6OH^-(sol)} = \mathrm{2VO_4^{3-}(sol)} + \mathrm{3H_2O(sol)}$	−183·1 ± 0·9(3)
8. $\mathrm{K_4Fe(CN)_63H_2O(s)} = \mathrm{4K^+(sol)} + \mathrm{Fe(CN)_6^{4-}(sol)} + \mathrm{3H_2O(sol)}$	+46·2 ± 0·3(3)
9. $\mathrm{NaCl(s)} = \mathrm{Na^+(sol)} + \mathrm{Cl^-(sol)}$	−0·3 ± 0·06(3)

Scheme 2. The enthalpy change of reaction (12) was

$$\mathrm{Na}_x\mathrm{V_2O_5(s)} + \frac{x}{2}\mathrm{(H_2O_2,6{\cdot}4H_2O)(l)} = \mathrm{V_2O_5(s)} + x\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{H_2(g)} + 3{\cdot}2x\mathrm{H_2O(l)} \tag{12}$$

determined through the reaction scheme shown in Table 3. The symbol (sol) in this Table indicates that the designated

TABLE 3

Calorimetric reaction scheme 2

Reaction	ΔH(323·15 K)/kJ mol^{-1}
13. $\mathrm{Na}_x\mathrm{V_2O_5(s)} + \frac{x}{2}\mathrm{H_2O_2(sol)} + \mathrm{6OH^-(sol)} = x\mathrm{Na^+(sol)} + x\mathrm{OH^-(sol)} + \mathrm{2VO_4^{3-}(sol)} + \mathrm{3H_2O(sol)}$	−189·3 ± 0·5(6) $x = 0{\cdot}20$ −189·0 ± 1·0(4) $x = 0{\cdot}22$ −190·9 ± 0·5(6) $x = 0{\cdot}25$ −189·9 ± 0·6(6) $x = 0{\cdot}29$ −191·6 ± 0·5(5) $x = 0{\cdot}33$
14. $\mathrm{(H_2O_2,6{\cdot}4H_2O)(l)} = \mathrm{H_2O_2(sol)}$	−36·9 ± 0·5(3)
15. $\mathrm{V_2O_5(s)} + \mathrm{6OH^-(sol)} = \mathrm{2VO_4^{3-}(sol)} + \mathrm{3H_2O(sol)}$	−195·9 ± 0·4(7)
16. $\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{H_2(g)} = \mathrm{Na^+(sol)} + \mathrm{OH^-(sol)}$	−467·9 ± 1 *
17. $\mathrm{6{\cdot}4H_2O(l)} = \mathrm{6{\cdot}4H_2O(sol)}$	−1·7 ± 0·08(3)

* Value at 25 °C.

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number of moles of the preceding substance is dissolved in reagent of composition ($3{\cdot}15H_2O_2$, 910NaOH, $10{,}100H_2O$). The required enthalpy change is given by equation (18) and

$$\Delta H_{12} = \Delta H_{13} + \frac{x}{2}\Delta H_{14} - \Delta H_{15} - x\Delta H_{16} - \frac{x}{2}\Delta H_{17} \quad (18)$$

the enthalpy of formation of $Na_xV_2O_5$ by equation (19).

$$\Delta H_f^\circ Na_xV_2O_5(s) - \Delta H_f^\circ V_2O_5(s) = -\Delta H_{12} + \frac{x}{2}[6{\cdot}4\Delta H_f^\circ H_2O(l) - \Delta H_f^\circ(H_2O_2,6{\cdot}4H_2O)(l)] \quad (19)$$

The heats of solution for the processes (13), (14), (15), and (16) were measured directly. V_2O_5 (100 mg, 0·55 mmol) and equivalent weights of other solutes were dissolved in 100·2 ml batches of reagent of composition ($3{\cdot}15H_2O_2$, 910NaOH, $10{,}100H_2O$). All measurements were made at 50 °C (since solution of $Na_xV_2O_5$ and V_2O_5 was inconveniently slow at 25 °C). All solutes were dissolved in separate batches of the reagent solution rather than by successive additions to the same batch, a procedure again justified by the choice of high reagent : solute molar ratios and by the absence of specific chemical interactions between the solute species. ΔH_{16} was identified with the differential heat of formation of NaOH in (910NaOH, $10{,}100H_2O$) and obtained from tables.[14]

RESULTS

A complete set of experimental data obtained for a single heat of solution measurement is shown in Table 1. Average measured heats of solution and their uncertainties for the reactions of Schemes 1 and 2 are given in Tables 2 and 3 respectively. The error assigned to each value is twice the standard error of the mean [15] and the number of determinations made is shown in parentheses. Values of standard enthalpies of formation used in the application of equation (11) were NaCl(s) ($-412{\cdot}5 \pm 0{\cdot}8$ kJ mol^{-1}),[16] KCl(s) ($-435{\cdot}9 \pm 0{\cdot}8$ kJ mol^{-1}),[16] H_2O(l) ($-285{\cdot}85 \pm 0{\cdot}04$ kJ mol^{-1}),[14] $K_3Fe(CN)_6$(s) ($-242{\cdot}7 \pm 0{\cdot}5$ kJ mol^{-1}), and $K_4Fe(CN)_6,3H_2O$(s) ($-1458{\cdot}1 \pm 0{\cdot}5$ kJ mol^{-1}). The last two quantities were calculated from values [17] for $\Delta H_f^\circ K^+$(aq), $\Delta H_f^\circ Fe(CN)_6^{3-}$(aq), $\Delta H_f^\circ Fe(CN)_6^{4-}$(aq) and the measured heats of solution of $K_3Fe(CN)_6$(s) and $K_4Fe(CN)_6,3H_2O$(s) at infinite dilution.[18] In the application of equation (19) a value of $\Delta H_f(H_2O_2,6{\cdot}4H_2O)(l) = -191{\cdot}1 \pm 0{\cdot}8$ kJ mol^{-1} was used as the heat of formation from H_2(g), O_2(g), and H_2O(l) [14] at 25 °C. Combination of heat of solution data given in Tables 2 and 3 with the above standard enthalpies of formation enabled the enthalpy change of reaction (1) to be calculated *via* two independent routes using equations (11) and (19) respectively. Final results are shown in Table 4. In the calculation by use of equation (19) the small differences between enthalpies of formation at 25 and 50 °C (<*ca.* 1 kJ mol^{-1}) have been ignored as being comparable with the overall errors of measurement.

TABLE 4

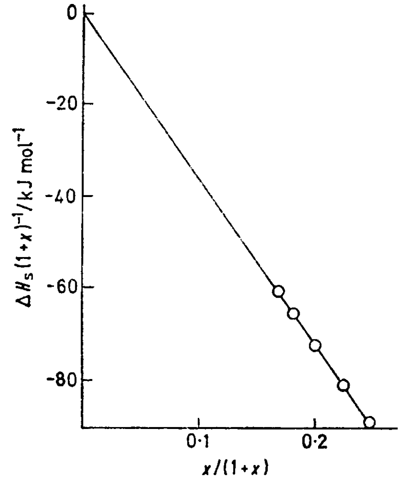
Enthalpies of formation of sodium vanadium bronzes from xNa(s) and V_2O_5(s)

Compound	$\Delta H_f^\circ Na_xV_2O_5(s) - \Delta H_f^\circ V_2O_5(s)$/kJ mol^{-1} (*a*)	(*b*)
$Na_{0{\cdot}20}V_2O_5$	$-72{\cdot}7 \pm 1{\cdot}0$	$-77{\cdot}8 \pm 0{\cdot}7$
$Na_{0{\cdot}22}V_2O_5$	$-79{\cdot}1 \pm 1{\cdot}8$	$-85{\cdot}2 \pm 1{\cdot}1$
$Na_{0{\cdot}25}V_2O_5$	$-90{\cdot}0 \pm 1{\cdot}0$	$-94{\cdot}0 \pm 0{\cdot}7$
$Na_{0{\cdot}29}V_2O_5$	$-104{\cdot}7 \pm 1{\cdot}3$	$-109{\cdot}2 \pm 0{\cdot}7$
$Na_{0{\cdot}33}V_2O_5$	$-119{\cdot}3 \pm 1{\cdot}3$	$-121{\cdot}6 \pm 0{\cdot}7$

(a) Scheme 1, hexacyanoferrate(III) reagent, 25 °C. (b) Scheme 2, peroxide reagent, 50 °C.

DISCUSSION

Comparison of the Peroxide and Hexacyanoferrate(III) *Cycles*.—The values obtained for $\Delta H_f^\circ Na_xV_2O_5(s) - \Delta H_f^\circ V_2O_5(s)$ by the two cycles differ by 2—6 kJ mol^{-1}. The variation with x is similar but in every case values obtained from the peroxide cycle are more negative. This small but systematic discrepancy is probably connected with the slow exothermic decomposition of the peroxide reagent occurring as a side-reaction. Such an effect is automatically allowed for if the rate of heat evolution from this source is constant throughout the whole calorimetric run, but a variation of rate during the reaction period would lead to an uncorrected error. In each cycle the final enthalpy value obtained is the algebraic sum of considerably larger quantities; since the two cycles involve quite independent chemical paths, the overall agreement is thought to be satisfactory. In the following discussion data from the hexacyanoferrate(III) cycle are used, being presumed the more accurate.



Molar heat of solution of Na(s) in V_2O_5(s)

Variation of the Enthalpy of Formation with Composition.—The quantity $\Delta H_f^\circ Na_xV_2O_5(s) - \Delta H_f^\circ V_2O_5(s)$ is the enthalpy change ΔH_s for the solution process (20). In the Figure $\Delta H_s/(1 + x)$ is plotted against

$$x\text{Na(s)} + V_2O_5(s) = Na_xV_2O_5(s) \quad (20)$$

$x/(1 + x)$, the mole fraction of sodium. The intercept of the tangent to the curve on the line $x/(1 + x) = 0$ is $(\bar{H}_{V_2O_5} - H_{V_2O_5})$ and the intercept on the line $x/(1 + x) = 1$ is $(\bar{H}_{Na} - H_{Na})$. Over the range of composition in-

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[18] L. G. Hepler, J. R. Sweet, and R. A. Jesser, *J. Amer. Chem. Soc.*, 1960, **82**, 304.

vestigated Na and V_2O_5 form a solid solution for which $\bar{H}_{Na}$ is constant and $(\bar{H}_{V_2O_5} - H_{V_2O_5}) = 0{\cdot}0 \pm 1{\cdot}4$ kJ mol^{-1}. In this case, since the curve is linear from the origin, the slope of the curve is also equal to $\bar{H}_{Na} - H_{Na}$.

The structural interpretation of this result is that the interactions between sodium atoms in the channels of the V_2O_5 matrix in $Na_xV_2O_5$ are negligible and that the energy of rearrangement of the V_2O_5 matrix in the formation of the β-phase of the bronze is very small and comparable with the errors of measurement of ΔH_s. The relative partial molar enthalpy change $\bar{H}_{Na} - H_{Na}$ is a measure of the interaction between a sodium atom and the V_2O_5 matrix in the bronze. The least-squares value found is $-358{\cdot}5 \pm 7{\cdot}0$ kJ mol^{-1} and this high heat of solution can be compared with values in the range 0 to -80 kJ mol^{-1} typically found for the solution of sodium into other metals in alloy formation.

The high stability of the β-phase bronze can be further demonstrated by an examination of the thermochemistry of its oxidation and disproportionation. For the oxidation process (21) $\Delta H^\circ_{298\,K}$ can be

$$Na_xV_2O_5(s) + \frac{x}{4}O_2(g) = xNaVO_3(s) + \frac{(2-x)}{2}V_2O_5(s) \quad (21)$$

calculated using the measured values of $\Delta H_f^\circ Na_xV_2O_5(s) - \Delta H_f^\circ V_2O_5(s)$ and a recent literature value[19] of $\Delta H_f^\circ NaVO_3(s) - \frac{1}{2}\Delta H_f^\circ V_2O_5(s) = -370{\cdot}7 \pm 1{\cdot}0$ kJ mol^{-1}. Approximate values of $\Delta G^\circ_{298\,K}$ and $\Delta G^\circ_{800\,K}$ can be calculated if the reasonable assumptions are made that the small differences in entropies between solid phases can be ignored in relation to changes involving gaseous species and the temperature variation of ΔH° is small. Calculated values for reaction (21) are given in Table 5.

TABLE 5

x	$\Delta H^\circ_{298\,K}$/ kJ mol^{-1}	$\Delta G^\circ_{298\,K}$/ kJ mol^{-1}	$\Delta G^\circ_{800\,K}$/ kJ mol^{-1}
0·20	$-1{\cdot}4 \pm 1{\cdot}2$	$+2{\cdot}1$	$+8{\cdot}5$
0·22	$-2{\cdot}4 \pm 2{\cdot}0$	$+0{\cdot}9$	$+8{\cdot}0$
0·25	$-2{\cdot}7 \pm 1{\cdot}3$	$+1{\cdot}1$	$+9{\cdot}1$
0·29	$-2{\cdot}8 \pm 1{\cdot}6$	$+1{\cdot}6$	$+10{\cdot}9$
0·33	$-3{\cdot}0 \pm 1{\cdot}7$	$+2{\cdot}3$	$+12{\cdot}9$

For the disproportionation reaction (22) use of Mah and Kelley's data[20] for $\Delta H_f^\circ VO_2(s) - \frac{1}{2}\Delta H_f^\circ V_2O_5(s) = 61{\cdot}5 \pm 2{\cdot}0$ kJ mol^{-1} enabled the corresponding enthalpy

$$Na_xV_2O_5(s) = xNaVO_3(s) + (1-x)V_2O_5(s) + xVO_2(s) \quad (22)$$

changes to be calculated (Table 6); these approximate to changes in free energy since only solid reactants and products are present.

TABLE 6

x	0·20	0·22	0·25	0·29	0·33
$\Delta H^\circ_{298\,K}$/kJ mol^{-1}	$10{\cdot}9 \pm 1{\cdot}6$	$11{\cdot}1 \pm 2{\cdot}4$	$12{\cdot}7 \pm 1{\cdot}7$	$15{\cdot}0 \pm 2{\cdot}1$	$17{\cdot}3 \pm 2{\cdot}2$

Thus the β-phase of $Na_xV_2O_5$ is thermodynamically stable with respect to both oxidation and disproportionation. This statement is consistent with the experimental observations that the reverse of reaction (22) can be used preparatively for the formation of the bronze[6] whilst in the preparation described here cooling of a V_2O_5–$NaVO_3$ melt leads not to solidification of V_2O_5 and $NaVO_3$, but to oxygen evolution and precipitation of the bronze. Thermogravimetry confirmed that no substantial oxidation of the bronze occurs on heating in air below the temperature (*ca.* 660 °C) at which molten products form.

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