Thermochemistry of Oxide Bronzes. Part II.[1] Sodium Tungsten Bronzes Na_xWO_3 ($x = 0{\cdot}53$ and $0{\cdot}77$)

By **P. G. Dickens** * and **D. J. Neild**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The enthalpies of formation from Na(s) and WO_3(s) of two cubic phase sodium tungsten bronzes, $Na_{0{\cdot}53}WO_3$(s) and $Na_{0{\cdot}77}WO_3$(s), have been determined by solution calorimetry. The thermodynamic stability of the cubic phase towards oxidation and disproportionation is discussed.

THE sodium tungsten bronzes, Na_xWO_3 ($0 < x \leqslant 1$), constitute a series of non-stoicheiometric solid phases whose principal structural and electronic properties have been reviewed.[2,3] Thermodynamically they can be regarded as solid solutions of sodium in WO_3. The detailed crystal structure adopted by a phase is dependent on the value of x but in all cases sodium atoms are located interstitially in a WO_3 matrix formed by WO_6 octahedra linked together through corner sharing. The largest range of homogeneity is shown by the cubic phase which extends from $0{\cdot}3 \leqslant x \leqslant 1$. The perovskite ABO_3 structure is adopted with a fraction x of the A sites occupied by sodium nuclei.[4] The lattice parameter varies linearly with x across the phase.[5] The sodium tungsten bronzes are inert chemically at room temperature except in the presence of oxidizing agents in alkaline media. Morozova and Ovcharova [6] measured enthalpies of solution of the cubic tungsten bronzes in alkaline hexacyanoferrate(III) solution and established that this quantity also varied linearly with x. In the present work a thermochemical cycle has been employed, based on the reaction of Na_xWO_3 with alkaline hexacyanoferrate(III) solution, which has enabled the enthalpies of formation of the cubic sodium tungsten bronzes to be determined.

EXPERIMENTAL

Two sodium tungsten bronze samples in the cubic range were prepared by heating together AnalaR sodium tungstate, tungsten trioxide, and tungsten metal according to the equation: $3xNa_2WO_4 + (6 - 4x)WO_3 + xW = 6Na_xWO_3$. The reactants were finely ground and heated *in vacuo* at 850 °C for 8 h. The product was reground and the heating process repeated. The final product was washed successively in warm dilute NaOH, hot concentrated HCl, and water before drying *in vacuo*. Pure cubic phases of $Na_{0{\cdot}53}WO_3$ and $Na_{0{\cdot}77}WO_3$ were identified by powder X-ray diffraction; the x values ($\pm 0{\cdot}01$) were obtained by use of Brown and Banks' equation relating lattice parameters to composition [5] and corresponded closely to those expected from the preparative equation. The reaction medium, identical to that used in Part I,[1] was prepared by addition of KOH (20 g) and $K_3Fe(CN)_6$ (2 g) to water (100 cm³).

Determination of Enthalpies of Formation.—Enthalpies of reaction were measured with an LKB 8700 solution calorimeter operated at 298·15 K. A detailed description of the apparatus and its mode of operation was given in Part I;[1] the same procedures were adopted in the present work. The solute charges taken were approximately stoicheiometric with 0·100 g (0·43 mmol) of WO_3. 100 cm³ Batches of the calorimetric reagent were used in all measurements. Reaction periods were of less than 10 min duration. The calorimetric reactions used to obtain the enthalpies of formation of Na_xWO_3 are given in skeleton form in Table 1, together with average measured enthalpy changes and their uncertainties. The number of determinations made of each calorimetric heat of solution is given in parentheses. The uncertainties given for individual values are twice the standard error of the mean and the overall uncertainty given for a thermochemical cycle is the root of the sum of the squares of the individual uncertainties. The symbols (s) and (l) designate solid and liquid substances respectively and the symbol (sol) indicates that the number of mols of substance designated in Table 1 was dissolved in reagent of molar composition [$14{\cdot}1K_3Fe(CN)_6$, 826KOH, 12 870H_2O].

TABLE 1

Calorometric reaction scheme

Reaction	$\Delta H_{298{\cdot}15\ K}$/kJ mol⁻¹
1. $Na_xWO_3(s) + xFe(CN)_6^{3-}(sol) + 2OH^-(sol) = xNa^+(sol) + WO_4^{2-}(sol) + H_2O(sol) + xFe(CN)_6^{4-}(sol)$	$-115{\cdot}8 \pm 0{\cdot}13$ (3) $x = 0{\cdot}53$ $-143{\cdot}2 \pm 1{\cdot}3$ (3) $x = 0{\cdot}77$
2. $K_3Fe(CN)_6(s) = 3K^+(sol) + Fe(CN)_6^{3-}(sol)$	$+43{\cdot}7 \pm 0{\cdot}5$ (3)
3. $KCl(s) = K^+(sol) + Cl^-(sol)$	$+14{\cdot}9 \pm 0{\cdot}04$ (3)
4. $3H_2O(l) = 3H_2O(sol)$	$-0{\cdot}17 \pm 0{\cdot}01$ (3)
5. $WO_3(s) + 2OH^-(sol) = WO_4^{2-}(sol) + H_2O(sol)$	$-61{\cdot}9 \pm 0{\cdot}5$ (3)
6. $K_4Fe(CN)_6,3H_2O(s) = 4K^+(sol) + Fe(CN)_6^{4-}(sol) + 3H_2O(sol)$	$+46{\cdot}2 \pm 0{\cdot}3$ (3)
7. $NaCl(s) = Na^+(sol) + Cl^-(sol)$	$-0{\cdot}30 \pm 0{\cdot}06$ (3)
8. $Na_xWO_3(s) + xK_3Fe(CN)_6(s) + xKCl(s) + 3xH_2O(l) = WO_3(s) + xK_4Fe(CN)_6,3H_2O(s) + xNaCl(s)$	
$\Delta H_8 = \Delta H_1 + x(\Delta H_2 + \Delta H_3 + \Delta H_4) - \Delta H_5 - x(\Delta H_6 + \Delta H_7)$	$-47{\cdot}3 \pm 0{\cdot}6$ $x = 0{\cdot}53$ $-71{\cdot}6 \pm 1{\cdot}5$ $x = 0{\cdot}77$

RESULTS

The results of three measurements at each composition of the enthalpy change of reaction (1) were $-115{\cdot}9$, $-115{\cdot}9$, and $-115{\cdot}7$ kJ mol⁻¹ for $x = 0{\cdot}53$ and $-143{\cdot}4$, $-144{\cdot}2$, and $-142{\cdot}0$ kJ mol⁻¹ for $x = 0{\cdot}77$. The enthalpy changes for reactions (2)—(7) had been determined previously [1,7] by

---

[1] Part I, P. G. Dickens, M. Jewess, D. J. Neild, and J. C. W. Rose, *J.C.S. Dalton*, 1973, 30.

[2] P. G. Dickens and M. S. Whittingham, *Quart. Rev.*, 1968, **22**, 30.

[3] P. Hagenmuller, *Progr. Solid State Chem.*, 1971, **5**, 71.

[4] M. Atoji and R. E. Rundle, *J. Chem. Phys.*, 1960, **32**, 627.

[5] B. W. Brown and E. Banks, *J. Amer. Chem. Soc.*, 1954, **76**, 963.

[6] M. P. Morozova and G. P. Ovcharova, *Russ. J. Phys. Chem.*, 1969, **43**, 1966.

[7] P. G. Dickens, J. H. Moore, and D. J. Neild, *J. Solid State Chem.*, 1973, **6**, in the press.

the authors using the identical calorimetric reagent at 25 °C and with solute : solvent ratios sufficiently close to those required by strict stoicheiometry to avoid the introduction of significant error.[1]

Reaction (8) represents the overall calorimetric reaction determined. From (8) equation (9) follows. Combination

$$\Delta H_f^\circ \mathrm{Na}_x\mathrm{WO}_3(\mathrm{s}) - \Delta H_f^\circ \mathrm{WO}_3(\mathrm{s}) = -\Delta H_8 + x[\Delta H_f^\circ \mathrm{K}_4\mathrm{Fe(CN)}_6,3\mathrm{H}_2\mathrm{O}(\mathrm{s}) + \Delta H_f^\circ \mathrm{NaCl}(\mathrm{s}) - \Delta H_f^\circ \mathrm{K}_3\mathrm{Fe(CN)}_6(\mathrm{s}) - 3\Delta H_f^\circ \mathrm{H}_2\mathrm{O}(\mathrm{l}) - \Delta H_f^\circ \mathrm{KCl}(\mathrm{s})] \qquad (9)$$

of the measured values of ΔH_8 with the standard enthalpies of formation previously listed[1] gave the final results in equations (10) and (11).

$$0{\cdot}53\mathrm{Na}(\mathrm{s}) + \mathrm{WO}_3(\mathrm{s}) = \mathrm{Na}_{0\cdot53}\mathrm{WO}_3(\mathrm{s}), \quad \Delta H_{298\cdot15\ \mathrm{K}} = -129{\cdot}9 \pm 0{\cdot}9\ \mathrm{kJ} \qquad (10)$$

$$0{\cdot}77\mathrm{Na}(\mathrm{s}) + \mathrm{WO}_3(\mathrm{s}) = \mathrm{Na}_{0\cdot77}\mathrm{WO}_3(\mathrm{s}), \quad \Delta H_{298\cdot15\ \mathrm{K}} = -185{\cdot}8 \pm 1{\cdot}8\ \mathrm{kJ} \qquad (11)$$

DISCUSSION

The values obtained by Morozova and Ovcharova[6] for the enthalpies of solution of $\mathrm{Na}_x\mathrm{WO}_3(\mathrm{s})$ into alkaline hexacyanoferrate(III) were linear in x in the range $0{\cdot}4 \leqslant x \leqslant 0{\cdot}8$. Interpolation of their data at $x = 0{\cdot}53$ and $0{\cdot}77$ gave values of ΔH_1 of $-112{\cdot}9 \pm 3$ and $-141{\cdot}2 \pm 3$ kJ mol^{-1} respectively (a contribution of ±1 kJ mol^{-1} to the estimated error arises from the experimental uncertainty in x of $\pm0{\cdot}01$). The corresponding values found in the present work are $-115{\cdot}8 \pm 1$ and $-143{\cdot}2 \pm 2$ kJ mol^{-1} (Table 1). A small systematic discrepancy between the two sets of values is understandable since the compositions of the calorimetric solvents and the solute : solvent ratios used differed somewhat. Nevertheless the two sets of data agree within the estimated limits of experimental error. It follows from equation (9) and the present confirmation of Morozova and Ovcharova's work that the enthalpies of formation of cubic phase $\mathrm{Na}_x\mathrm{WO}_3$ from Na(s) and WO_3(s) are also approximately linear in x over the experimental range studied. A similar result was obtained for the enthalpies of formation of β-phase $\mathrm{Na}_x\mathrm{V}_2\mathrm{O}_5$ and the same inference may again be drawn, namely that the interactions between sodium ions in the parent oxide matrices of the bronze phase are too small to be detected calorimetrically.

Formation, Oxidation, and Disproportionation of $\mathrm{Na}_x\mathrm{WO}_3$.—From the experimentally determined values of the enthalpies of formation at $x = 0{\cdot}53$ and $0{\cdot}77$ a mean value of $-243{\cdot}2 \pm 3$ kJ is found for the enthalpy change of reaction (12). This quantity is the integral

$$\mathrm{Na}(\mathrm{s}) + \frac{1}{x}\mathrm{WO}_3(\mathrm{s}) = \frac{1}{x}\mathrm{Na}_x\mathrm{WO}_3(\mathrm{s}) \qquad (12)$$

molar heat of solution of sodium into the WO_3 matrix in the cubic phase. The corresponding molar value found[1] for the solution of sodium into the matrix of $\mathrm{V}_2\mathrm{O}_5$ to form β-phase $\mathrm{Na}_x\mathrm{V}_2\mathrm{O}_5$ was $-358{\cdot}5 \pm 7$ kJ mol^{-1}. Both processes are highly exothermic. The difference in exothermicity reflects the greater stability of high oxidation states relative to low found generally for tungsten compounds compared with those of vanadium. Thus the related reaction (13) is also strongly exothermic.[8]

$$\mathrm{WO}_2(\mathrm{s}) + \mathrm{V}_2\mathrm{O}_5(\mathrm{s}) = \mathrm{WO}_3(\mathrm{s}) + 2\mathrm{VO}_2(\mathrm{s}), \quad \Delta H = -130\ \mathrm{kJ} \qquad (13)$$

Gerstein, Klein, and Shanks[9] obtained a value for the entropy at 298·15 K of cubic $\mathrm{Na}_{0\cdot679}\mathrm{WO}_3(\mathrm{s})$ of 95·25 J K^{-1} mol^{-1}. Corresponding values for WO_3(s) and Na(s) are 75·9 and 51·5 J K^{-1} mol^{-1} respectively.[8] An interpolation of the present experimental enthalpy data gives a value for the enthalpy of formation of $\mathrm{Na}_{0\cdot679}\mathrm{WO}_3(\mathrm{s})$ from Na(s) and WO_3(s) of $-0{\cdot}679 \times 243{\cdot}2$ kJ mol^{-1}. Combination of these data provides the following values (at 298·15 K) of thermodynamic functions associated with equation (14).

$$0{\cdot}679\mathrm{Na}(\mathrm{s}) + \mathrm{WO}_3(\mathrm{s}) = \mathrm{Na}_{0\cdot679}\mathrm{WO}_3(\mathrm{s}) \quad \Delta H^\circ = -165{\cdot}0\ \mathrm{kJ},\ \Delta S^\circ = -15{\cdot}6\ \mathrm{J\ K^{-1}},\ \Delta G^\circ = -160{\cdot}4\ \mathrm{kJ} \qquad (14)$$

Combination of the measured enthalpies of formation of $\mathrm{Na}_x\mathrm{WO}_3$(s) with standard enthalpies of formation (at 298·15 K) of WO_3(s) ($-842{\cdot}7$ kJ mol^{-1}),[8] WO_2(s) ($-589{\cdot}5$ kJ mol^{-1}),[8] and $\mathrm{Na}_2\mathrm{WO}_4$(s) ($-1546{\cdot}1$ kJ mol^{-1})[10,11] enables enthalpy changes and estimated free energy changes for the processes of oxidation (15) and disproportionation (16) and (17) to be evaluated as shown in Table 2.

TABLE 2

$$\mathrm{Na}_x\mathrm{WO}_3(\mathrm{s}) + \frac{x}{4}\mathrm{O}_2(\mathrm{g}) = \frac{x}{2}\mathrm{Na}_2\mathrm{WO}_4(\mathrm{s}) + \left(1 - \frac{x}{2}\right)\mathrm{WO}_3(\mathrm{s}) \qquad (15)$$

$$x = 0{\cdot}53,\ \Delta H = -56{\cdot}5\ \mathrm{kJ},\ \Delta G^\circ \sim -48{\cdot}4\ \mathrm{kJ}$$
$$x = 0{\cdot}77,\ \Delta H = -85{\cdot}0\ \mathrm{kJ},\ \Delta G^\circ \sim -73{\cdot}2\ \mathrm{kJ}$$

$$\mathrm{Na}_x\mathrm{WO}_3(\mathrm{s}) = \frac{x}{2}\mathrm{Na}_2\mathrm{WO}_4(\mathrm{s}) + \left(1 - \frac{2x}{3}\right)\mathrm{WO}_3(\mathrm{s}) + \frac{x}{6}\mathrm{W}(\mathrm{s}) \qquad (16)$$

$$x = 0{\cdot}53,\ \Delta H = +17{\cdot}9\ \mathrm{kJ},\ x = 0{\cdot}77,\ \Delta H + 23{\cdot}3\ \mathrm{kJ}$$

$$\mathrm{Na}_x\mathrm{WO}_3(\mathrm{s}) = (1 - x)\mathrm{WO}_3(\mathrm{s}) + \frac{x}{2}\mathrm{WO}_2(\mathrm{s}) + \frac{x}{2}\mathrm{Na}_2\mathrm{WO}_4(\mathrm{s}) \qquad (17)$$

$$x = 0{\cdot}53,\ \Delta H = +10{\cdot}6\ \mathrm{kJ},\ x = 0{\cdot}77,\ \Delta H = +12{\cdot}5\ \mathrm{kJ}$$

An experimental value for the entropy of $\mathrm{Na}_2\mathrm{WO}_4$(s) was not available and consequently free energy changes have been estimated for reaction (15) by the neglect of entropy differences between solid phases in comparison with those of gaseous species. For the disproportionation reactions (16) and (17), which involve only solid phases, calculated enthalpy changes are assumed to approximate to free energy changes.

Cubic $\mathrm{Na}_x\mathrm{WO}_3$ is thermodynamically unstable with

---

[8] Circular 500, U.S. Nat. Bur. Stand., Washington, 1952.

[9] B. C. Gerstein, A. H. Klein, and H. R. Shanks, *J. Phys. Chem. Solids*, 1964, **25**, 177.

[10] M. F. Koehler, L. B. Pankratz, and R. Barany, *Bur. Mines Rept. of Inv.*, 1962, 5973.

[11] V. I. Spitsyn and N. N. Patsuokova, *Russ. J. Inorg. Chem.*, 1965, **10**, 1304.

respect to oxidation at room temperature. This contrasts with the predicted and observed stability of β-$Na_xV_2O_5$ [1] a feature which again emphasizes the relative instability of the V^V state. Bulk oxidation of cubic Na_xWO_3 is slow below *ca.* 600 °C; such kinetic control of the reaction can be accounted for by the extremely low mobility which has been observed for the Na ion in Na_xWO_3.[12] Cubic Na_xWO_3, like β-$Na_xV_2O_5$, is stable towards disproportionation and the reverse of reactions (16) and (17) may be used for its preparation.

We thank the S.R.C. for an equipment grant and for a Studentship (to D. J. N.).

[2/2607 *Received, 17th November,* 1972]

---

[12] J. E. Smith and C. G. Danielson, *J. Chem. Phys.*, 1954, **22**, 266.