

Free Energy of Formation of Sodium Tungsten Bronzes, Na_xWO_3

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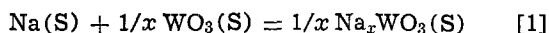
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The sodium tungsten bronzes, Na_xWO_3 , are highly nonstoichiometric compounds which are metallic conductors (1) and have therefore been used as electrodes for both fuel cells (2) and conductivity cells (3); yet until recently nothing quantitative was known about their thermodynamic properties. This paper reports some electrochemical studies of the sodium activity in these materials for $0.3 < x < 0.8$ at ambient temperatures.

Single crystal samples were prepared by the electrolytic decomposition of sodium polytungstates (4) and powder samples by the solid-state reaction of Na_2WO_4 , WO_3 , and W in the appropriate proportions (5). Analysis of phase and composition was performed by x-ray diffractometry, the lattice constant of the cubic perovskite phase being a linear function of composition (6). The partial molar free energy of sodium was measured using an electrochemical cell comprising a sodium electrode and a tungsten bronze electrode, and as electrolyte a solution of sodium iodide in propylene carbonate. The use of sodium hexafluorophosphate as the electrolyte salt gave consistently high emf's (e.g., 2.78V at $x = 0.4$) presumably due to reaction with the oxide matrix giving an oxyfluoride salt. The tungsten bronze crystal was held in the end of a glass tube by epoxy cement, electrical contact being made through a mercury pool (7). Powders were packed into a capillary tube around a platinum wire.

The emf results are shown in Table I; these were stable over several weeks to within ± 5 mV. The variation between different compositions was confirmed by measuring the potential difference between two bronzes immersed in the above electrolyte and in an aqueous sodium chloride solution. The sodium partial molar free energy, ΔG_{Na} , and the free energy of reaction [1], ΔG , calculated using the graphical technique (8), are also listed in Table I



In Fig. 1 the free energy of formation per mole of sodium tungsten bronze obtained here is compared with the enthalpy of formation measured by Dickens

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Table I. Thermodynamic properties of Na_xWO_3

x	E , volts	$-\Delta G_{\text{Na}}$, kJ/mole	$-\Delta G$, kJ/mole	$-\log [\text{O}_2]$ atmos.
0.273 p	2.600	250.9	250.9	12.0
0.400 c	2.598	250.7	250.8	13.7
0.597 c	2.570	248.0	250.6	17.9
0.695 p	2.500	241.2	249.8	19.0
0.755 p	2.470	238.4	249.2	20.9
0.790 c	2.430	234.5	248.4	22.8

c = single crystal; p = powder sample.

and Nield (9) using solution calorimetry. The error introduced by using the enthalpy rather than the free energy in this comparison is about 5 kJ/mole, assuming a partial molar entropy change of 23.0 J/K mole as calculated (9) from the data of Gerstein, Klein, and Shanks (10) for $x = 0.68$. These data compare well with the emf's obtained by Steele (11) using beta-alumina as the electrolyte. It should be noted, however, that the sodium activity will be a function of the oxygen activity, and may therefore vary from sample to sample; the oxygen activities of the specimens used here have been determined (4, 12), and are given in Table I.

At all but the highest sodium concentrations the integral molar free energy of solution, ΔG , of sodium into the WO_3 matrix is almost independent of sodium content indicating that interactions between the sodium ions only become significant at high x values. In addition ΔG is independent of the phase, the 0.4 sample being a pure single crystal of the complex tetragonal II tunnel structure (1), all higher x values having the perovskite structure, and the $x = 0.3$ speci-

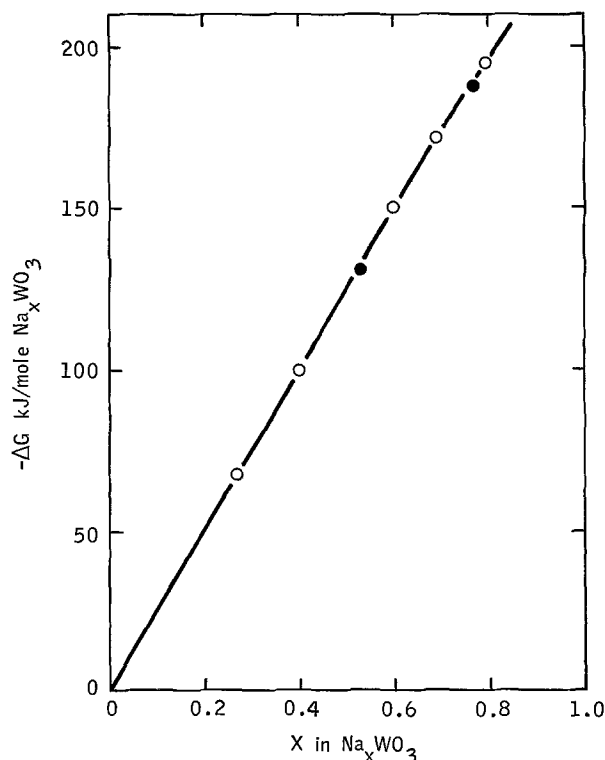


Fig. 1. Free energy of formation per mole of sodium tungsten bronze. ○, This work; ●, calorimetric enthalpies of formation of Ref. (9).

men is a mixture of the two. This is in agreement with the measurements of oxygen activity (12) which, although they showed a marked composition dependence, exhibited no measurable phase dependence. This explains why it has been easy to obtain the cubic phase at very low sodium concentrations (13) in the domain of the tetragonal phases.

Diffusion of the sodium ions in the cubic structure is very low (14), $\sim 10^{-15}$ cm²/sec for the cubic perovskite phase, $\sim 10^{-9}$ cm²/sec for the ammonium ion in the hexagonal tunnel structure, and intermediate for the tetragonal tunnel structure. Although these values in the tungsten bronzes are insufficient for their use as cathodes in battery systems at ambient temperatures, such is not the case for the layer-like compounds of V₂O₅ and MoO₃ which have been successfully used (15, 16). The potentials, measured as above, are shown in Fig. 2; they compare well with previous data (15-17). As expected from the increase in stability of the highest oxidation states in going down the periodic table the emf is higher for V₂O₅ than for either MoO₃ or WO₃. In these cases alkali metal ions, in particular lithium, can be readily intercalated within the oxide matrices without any appreciable change in their structures forming a ternary phase, Li_xV₂O₅ or

Li_xMoO₃. It is this ternary phase formation that is responsible for the voltage found being higher than that expected for the simple disproportionation reaction, i.e., to Li₂O and VO₂ or MoO₂. The importance of this insertion-type reaction in determining the cathodic properties of materials will be discussed in detail in a future paper. For contrast the emf characteristics of the potassium intercalation compounds of graphite (18) are also shown in Fig. 2; these are much more akin to metallic alloys than to the salt-like oxide phases discussed above and could conceivably be used as the anode of a battery system.

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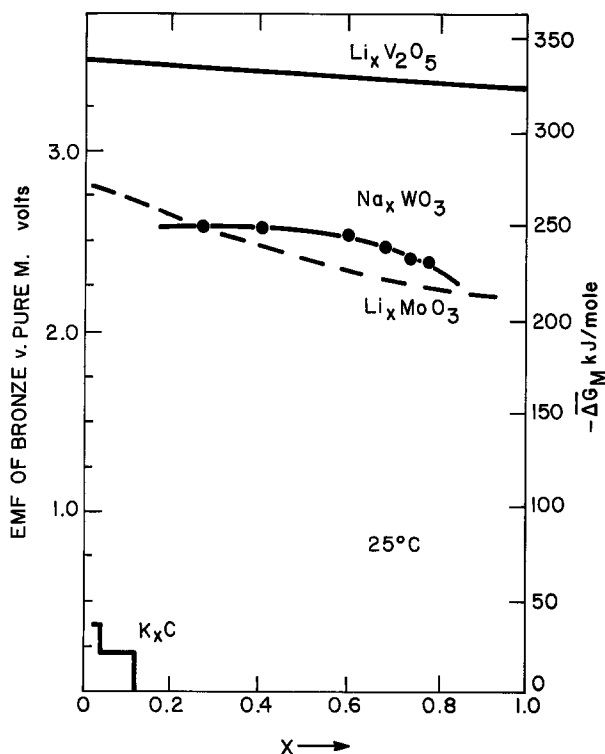


Fig. 2. Thermodynamics of sodium tungsten bronze compared with the ternary phases Li_xV₂O₅ and Li_xMoO₃ and the graphite intercalation compound C_xK (18).