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Title	CHEMICAL POTENTIAL VARIATIONS IN TUNGSTEN BRONZES
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 28(3), 163-168
Issue Date	1981-06
Doc URL	https://hdl.handle.net/2115/25084
Type	departmental bulletin paper
File Information	28(3)_P163-168.pdf

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J. Res. Inst. Catalysis. Hokkaido Univ., Vol. 28, No. 3, pp. 163 to 168 (1980)

CHEMICAL POTENTIAL VARIATIONS IN TUNGSTEN BRONZES

By

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(Received August 18, 1980)

Abstract

A theoretical relation between guest atom concentration and chemical potential in the tungsten bronzes $M_x WO_3$ is presented. Some consequences of the model are discussed and compared with experiment.

1. Introduction

The determination and understanding of the behaviour of the non-stoichiometric inorganic compounds called the tungsten bronzes — M_xWO_3 — is interesting and important for a number of technical reasons. These tungesten bronzes are a small but significant part of the larger class of *insertion compounds* which include the oxide bronzes (the host being the transition metal oxide in its highest oxidation state), the chalcogenide bronzes, and the graphite intercalation compounds. In this paper, we report, and offer an explanation for, the variation in chemical potential of guest metal atom M as a function of mole fraction, x, in the host solid WO_3. The significance of the model arrived at for such non-equilibrium phenomena as guest atom diffusion is outlined.

2. Guest Atom Chemical Potential as a Function of x

The variation in the chemical potential of Na in Na_xWO_3 (as a function of x) has been measured by an electrochemical method and is reported in a brief publication.[1] The experimental data are summarised in Fig. 1. A simple theory for the variation in $\overline{\Delta G}$ with x up to about 0.25 has been put forward[1] and is summarised here because of its significance in the interpretation of guest atom diffusion, which is the topic of the last section.

Guest atoms of WO_3 are treated as an expanded lattice of ions embedded

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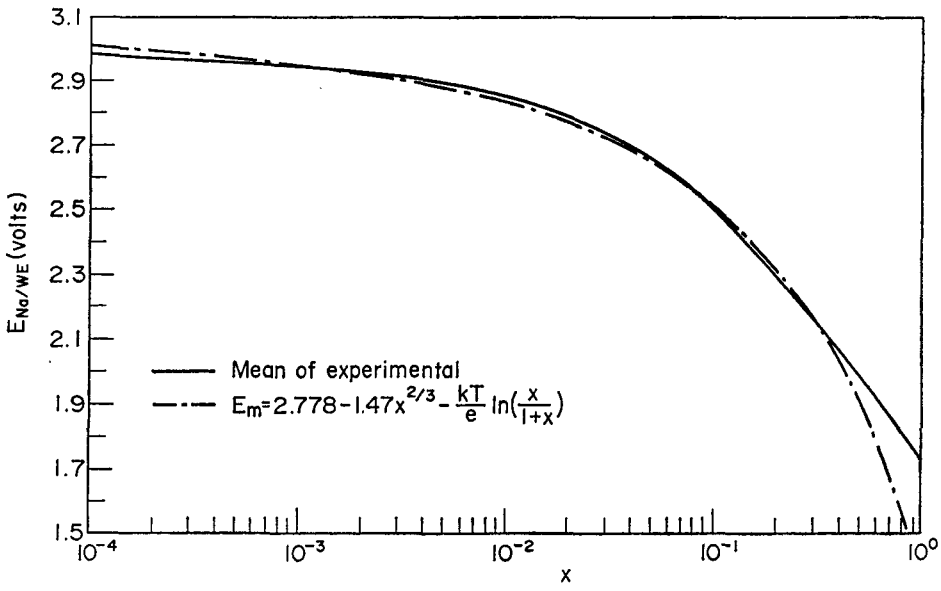

Fig. 1. The cell e. m. f. (Na|Na-β-alumina|Na_xWO_3) for five thin film Na_xWO_3 electrodes of varying sodium content (at 25±2°C). All data are corrected for grain boundary volume. The dashed line is the theoretical curve.

in a dielectric (the WO_3) and the electrons are treated as a free electron gas. The enthalpy contribution to the free energy now comes from the binding energy of the ion to the lattice and is taken to be highly local and independent of x up to $x \approx 1/4$, plus the average kinetic energy of the free electron gas which, of course, is a function of x.

The entropy contribution is obtained from the arrangement of the ions over the sites of the host (here we abandon the lattice of ions and treat the purely random case: the inconsistency is not serious.) The final expression for the variation in chemical potential, or the EMF of the cell, Na|Na-β-alumina|Na_xWO_3, is:

$$-\overline{\Delta G} = eE_m = L_0 - 1.47x^{2/3} - kT\ln\left[x/(1+x)\right] \qquad (1)$$

(electron-volts)

In this expression, L_0 is the local ion-lattice interaction energy term, its value is determined from experiment by fitting the data at low x values ($\lesssim 10^{-3}$). Clearly L_0 will vary from one ionic species to the next. The constant 1.47 is obtained from the expression for the average kinetic energy, K, of a free electron Fermi gas, namely,

$$K = 0.3\frac{\hbar^2}{m_e}(3\pi^2 nx)^{2/3} \qquad (2)$$

$\hbar$ and m_e are Planck's constant and the rest mass of the electron respectively, while n is the electron concentration for $x=1$, *i.e.* $n=a_0^{-3}$ where a_0 is the lattice constant for cubic WO_3 ($=3.85\times10^{-10}$ m). The solid line in Fig. 1 is the fit of the theoretical expression with L_0 for sodium equal to 2.78 eV. Divergence between theory and experiment occurs at $x\gtrsim0.25$ which is where it should occur since we then start to get a significant number of nearest neighbour sodium ion pairs.

3. Galvani Potential Difference as a Function of x

In reading this section it is worth while to recall that the electrochemical potential of a species i of charge z in a homogeneous phase α of relative activity a_i is written as

$$\bar{\mu}_i^\alpha = \mu_i^{o\alpha} + kT\ln a_i^\alpha + ze\phi^\alpha \qquad (3)$$

where $\mu_i^{o\alpha}$ is the standard chemical potential of i in α and ϕ^α is the inner potential of phase α, (see *e.g.* ref. 3). The Nernst equation for the cell potential can be written as

$$eE = eE^0 - kT\ln a_{Na} \qquad (4)$$

or

$$eE = eE^{o'} - kT\ln a_{Na} + a_e \qquad (5)$$

where we refer to the relative activity in the Na_xWO_3 phase. Comparison of eqn. (5) with eqn. (1), taking a_{Na} equal to $x/(1+x)$, gives

$$kT\ln a_e = \text{Const.} + 1.47\ x^{2/3} \qquad (6)$$

If there is a gradient in x in the tungsten bronze but no electric current flowing it will nevertheless be true that the electrochemical potential of electrons will be the same everywhere so that with eqns. (3) and (6) we obtain

$$e\phi = -\bar{\mu}_e(r) + \text{Const.} + 1.47\ x^{2/3} \qquad (7)$$

and $\bar{\mu}_e(r)$ is the electron electrochemical potential which is independent of the spatial coordinate, r. Thus,

$$d\phi/dx = (2/3)\ 1.47\ x^{-1/3} \qquad (8)$$

It follows from eqn. (8) that a local guest atom concentration gradient will have an associated local electric field, namely,

$$d\phi/dr = 0.98\, x^{-1/3}\, dx/dr \qquad (9)$$

That a change of "doping" concentration is accompanied by a change in electrostatic potential is to be expected, it is highly familiar to those whose work is with the physics of semiconductors. The important physical constraint for eqn. (9) to be valid is that the screening length for the Fermi gas should be sufficiently short compared with a characteristic length associated with the local concentration and the local concentration gradient.

4. Guest Atom Diffusion Coefficient

The internal electric field which we can now associate with a guest atom concentration gradient can have a considerable effect upon the diffusion coefficient, D, of the guest atom. Mott and Gurney showed that the activation energy for interstitial diffusion is modified by any external electric field according to the relation

$$D = D^{\circ} \exp\left(e\lambda F/2kT\right) \qquad (10)$$

where D° is the zero field diffusion coefficient, and λ is the distance between adjacent interstitial sites ($=a_0$). There is no difference in kind between the internal and the external electric field, thus eqn. (10) with eqn. (9) gives

$$D = D^{\circ} \exp\left[e\lambda(0.98\, x^{-1/3}\, dx/dr)/2kT\right], \qquad (11)$$

where the influence of a concentration gradient is apparent.

We[5] have carried out galvanostatic studies on Na_xWO_3/Na-β-alumina electrodes under conditions in which the sodium concentration gradient at the surface of the Na_xWO_3 is given by

$$dx/dr\Big|_s = I_0/ND^0 \qquad (12)$$

where I_0 is the flux of sodium particles to the surface of the Na_xWO_3 and N is the concentration of sodium atoms corresponding to $x=1$. In this way we have determined that at 25°C, D^0 is 6×10^{-20} cm^2/sec. We have also carried out galvanostatic studies as a function of current density and calculated the apparent D, using the relation[6]

$$\left[x(t)-x(t=0)\right]_s = \frac{2I_0 t^{\frac{1}{2}}}{\sqrt{\pi}\, ND^{\frac{1}{2}}} \qquad (13)$$

Some of these data are plotted in Fig. 2.

In order to obtain a tractible relation for something like x_s up to 1/4 the approximation (I think it is a highly valid one) is made that D at any particular current density is a constant independent of position. Under these

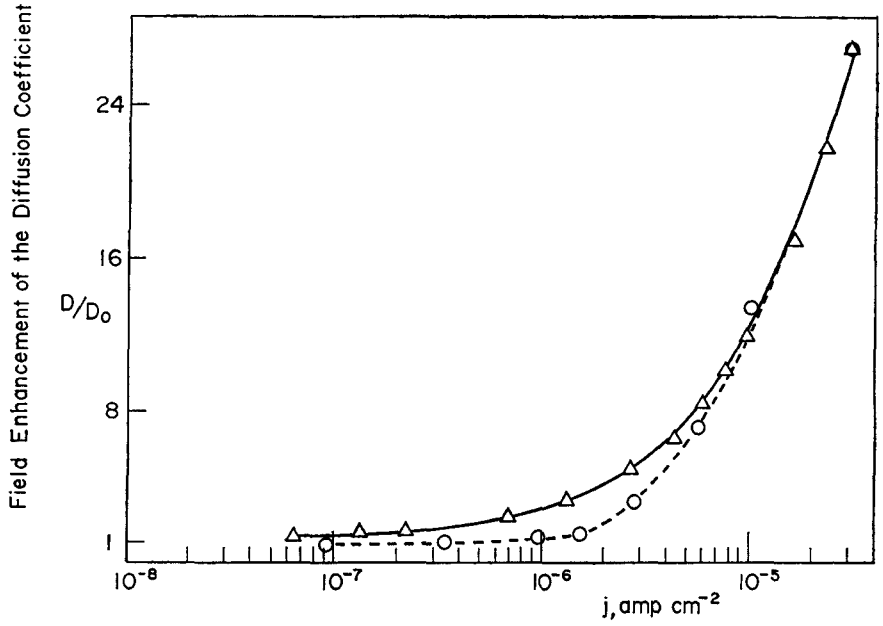

Fig. 2. Variation of sodium diffusion coefficient in $Na_{0.1}WO_3$ as a function of insertion current density. The solid line is the theoretical curve.

conditions eqn. (12) (dropping the superscript on the D) is inserted into eqn. (11) whereupon

$$D = D^0 \exp(\beta I_0/D) \tag{14}$$

where

$$\beta = \left(\frac{e\lambda\, 0.98\, x^{-1/3}}{2kT\,N}\right) \tag{15}$$

For the experimental conditions used $x^{-1/3}$ could be replaced by $\langle x\rangle^{-1/3}$ without serious loss of precision (fortunately for the approximation this is a slowly varying quantity). The solid line in Fig. 2 is the solution to eqn. (14) for $\lambda = 3.85$ Å, $N = 1/a_0^3$ and $\langle x\rangle^{-1/3} = 2$, D^0 having been previously determined. The fit seems good and furthermore seems to be well obeyed up to very much higher current densities.

References

1) Mino Green and Karam S. Kang, Thin Solid Films, **62**, 385 (1979).
2) B. T. Matthias, Phys. Rev., **76**, 430 (1949).
3) Mino Green, J. Chem. Phys., **31**, 200, (1959).
4) N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals*, Oxford Univ. Press, 2nd Ed., 1948, p. 42.
5) Mino Green and K. S. Kang, to be published, also; K. S. Kang, Ph.D. Thesis, University of London, 1979.
6) Mino Green, Thin Solid Films, **50**, 145 (1978).