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Surface Depletion During Effusion

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SURFACE depletion can be a significant source of error in the use of the effusion method for determining the thermodynamic properties of alloys, particularly in the case of solid alloys.[1] However, as yet this problem has not been treated quantitatively by experimentalists in the field.[1-3]

The method necessitates diffusive transport of material out of the source alloy to obtain a relevant measurement. The general character of the system is shown in Fig. 1. The diffusive flux ($\dot{n}_D$) at the alloy surface is equal to the effusive flux ($\dot{n}_E$):

$$\dot{n}_D = -\rho D A_S \left[\frac{\partial C}{\partial X}\right]_{X=0} = -\alpha C_S = \dot{n}_E \qquad [1]$$

where D is the diffusion coefficient of the diffusing substance, C is its concentration, X is the distance from the surface into the source alloy, ρ is the density of the alloy, and A_S is the actual available surface of the alloy. The concentration of the diffusing substance at the surface is C_S, and

$$\alpha = 0.05835\, f_E A_E \gamma P^\circ \sqrt{M/T} \qquad [2]$$

Here f_E is the Clausing factor, A_E is the area (sq cm) of the orifice, γ is the activity coefficient of the substance in the alloy, P° is the vapor pressure (Torr) of the pure substance, M is the molecular weight of the effusing species, and T is the absolute temperature.

The differential equation for diffusive transport in the source alloy is Fick's second law. Its solution is dependent on the geometry of the source alloy. Two boundary conditions must be established to obtain the proper solution, the first being Eq. [1], or its equivalent. The solutions for several important forms of the source alloy are considered below.

a) A semi-infinite body with a planar surface, $X = 0$ at surface. The differential equation is

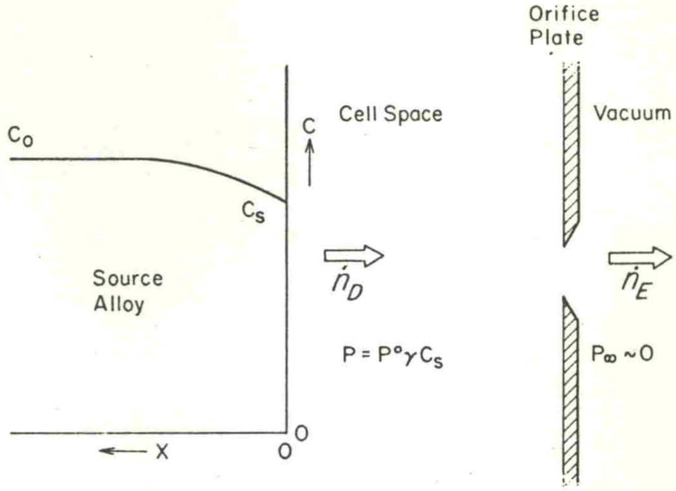

Fig. 1—Transport necessary to effusion measurement.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \qquad [3]$$

The initial and boundary conditions are

$$C(X,0) = C_0;\ [\partial C/\partial X\,(X = 0, t)] = LC_S$$
$$C(X=\infty, t) = C_0 \qquad [3a]$$

where $L = \alpha/DA_S\rho$. The solution[4] is:

$$\frac{C_S}{C_0} = \exp[L^2Dt]\cdot erfc[L(Dt)^{1/2}] \qquad [3b]$$

b) A planar sheet of thickness $2l$, $X = 0$ at central plane. The differential equation is Eq. [3]. The initial and boundary conditions are

$$C(X,0) = C_0;\ [\partial C/\partial X\,(X = l, t)] = LC_S;$$
$$\partial C/\partial X\ (X = 0, t) = 0 \qquad [4a]$$

The solution of Eq. [3] for this case[4] is

$$\frac{C_S}{C_0} = 2lL\sum_{n=1}^{\infty}\frac{\exp - (\beta_n^2 Dt/l^2)}{[(Ll)^2 + Ll + \beta_n^2 l]} \qquad [4b]$$

where β_n is the positive nth root of the relationship

$$\beta \tan\beta = Ll$$

c) A cylinder (wire) of radius l, $r = 0$ at center line. The differential equation for this case is

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right] \qquad [5]$$

and the initial and boundary conditions are

$$C(r,0) = C_0;\ [\partial C/\partial r\ (r = l, t)] = LC_S;$$
$$\partial C/\partial r\ (r = 0, t) = 0 \qquad [5a]$$

The solution of Eq. [5][4] is

$$\frac{C_S}{C_0} = \frac{2L}{l}\sum_{n=1}^{\infty}\frac{\exp - (\phi_n^2 Dt)}{[L^2 + \phi_n^2]} \qquad [5b]$$

The terms ϕ_n are the roots of the equation

$$\phi J_0'(l\phi) + LJ_0(l\phi) = 0 \qquad [5c]$$

in which J_0 is the zero-order Bessel function and J_0' is its first derivative.

d) Many small spheres, each with a radius l, $r = 0$ at center. The differential equation is

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