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MET 731 **Effect of gravity on chemical equilibrium of solution components** Oct 10, 1990

The First Law may be written to include the effect of gravity

$$dU + d\phi = \delta q - \delta w \quad (1)$$

where $d\phi$ is the energy to change the potential energy in a gravitational field g .

The Criterion of Equilibrium at $dT = dV = 0$ may be obtained from the 3rd Fundamental Equation

$$dA = dU - TdS \quad (2)$$

If the only work is PdV work

$$dA + d\phi = \delta q - TdS \quad (3)$$

Therefore,

$$dA + d\phi \leq 0 \quad \text{Rev/Irrev} \quad (4)$$

The change in potential energy $d\phi$ as component i goes from elevation α to β in a gravitational field g is

$$d\phi_i = M_i g (h_\beta - h_\alpha) dn_i \quad (5)$$

$$d\phi_i = M_i g h_\beta dn_i - M_i g h_\alpha dn_i \quad (6)$$

The change in A for dn_i moles going from state α to β

$$\alpha = \beta \quad (7)$$

is

$$dA = \mu_{i,\alpha} dn_i - \mu_{i,\beta} dn_i^1 \quad (8)$$

Subtracting Eq. (8) from Eq. (4) for the equilibrium condition ($dA + d\phi = 0$), substituting Eq. (6), and dividing by dn_i gives

$$\mu_{i,\alpha} + M_i g h_\alpha = M_i g h_\beta + \mu_{i,\beta} \quad (9)$$

1. Note: $\mu_i \equiv \left(\frac{\partial G_T}{\partial n_i} \right)_{T,P,n_{\text{other}}} = \left(\frac{\partial A_T}{\partial n_i} \right)_{T,V,n_{\text{other}}}$

Equation (9) shows that $\mu_i + M_i gh$ must remain constant for each component in a varying gravitational field, or

$$d\mu_i + M_i d(gh) = 0 \quad (10)$$

The chemical potential may be replaced using the total differential for $G_i(x_i, P)$ at constant T

$$dG_i \equiv \left(\frac{\partial G_i}{\partial x_i} \right)_{P,T} dx_i + \left(\frac{\partial G_i}{\partial P} \right)_{x_i,T} dP \quad (11)$$

to give

$$\left(\frac{\partial G_i}{\partial x_i} \right)_{P,T} dx_i + V_i dP + M_i d(gh) = 0 \quad (12)$$

This may be further simplified by multiplying by x_i and summing over all components.

$$\sum_{i=1}^j x_i \left(\frac{\partial G_i}{\partial x_i} \right)_{P,T} dx_i + \sum_{i=1}^j x_i V_i dP + \sum_{i=1}^j x_i M_i d(gh) = 0 \quad (13)$$

The first term is zero according to the Gibb's-Duhem Equation. Therefore,

$$\sum_{i=1}^j x_i V_i dP + \sum_{i=1}^j x_i M_i d(gh) = 0 \quad (14)$$

Example

A Cr fan blade at 1000 K is located 50 to 56 cm from the axis of rotation is rotating at 40,000 rpm. If the fan blade contains an average of 0.05 wt % C, what is the expected maximum percent C in the blade? The carbon may be assumed to be interstitial.

Eq. (14) becomes

$$\left(\frac{\partial (RT \ln a_i)}{\partial x_i} \right)_{P,T} dx_i + V_i \rho \omega^2 dr - M_i \omega^2 r dr = 0 \quad (15)$$

where $\partial RT \ln a_i$ has been substituted for ∂G_i , $\rho \omega^2 r^2$ for P, and $-\omega^2 r^2$ for the gravitational force. Differentiating assuming constant ρ and dividing by dr and rearranging gives

$$2 \left(\frac{\partial (RT \ln a_i)}{\partial x_i} \right)_{P,T} \frac{dx_i}{dr^2} = M_i \omega^2 - V_i \rho \omega^2 \quad (16)$$

Since $a_i = \gamma_i x_i$

$$\left(\frac{\partial(\ln \gamma_i)}{\partial x_i} + \frac{\partial(\ln x_i)}{\partial x_i} \right)_{P,T} \frac{dx_i}{dr^2} = \frac{M_i \omega^2 - V_i \rho \omega^2}{2RT} \quad (17)$$

$$\left(\frac{\partial(\ln \gamma_i) \partial(\ln x_i)}{\partial x_i \partial(\ln x_i)} + \frac{\partial(\ln x_i)}{\partial x_i} \right)_{P,T} \frac{dx_i}{dr^2} = \frac{\omega^2 (M_i - V_i \rho)}{2RT} \quad (18)$$

$$\left(\frac{\partial(\ln \gamma_i)}{\partial(\ln x_i)} + 1 \right)_{P,T} \frac{\partial(\ln x_i)}{dr^2} = \frac{\omega^2 (M_i - V_i \rho)}{2RT} \quad (19)$$

$$\frac{\partial(\ln x_i)}{dr^2} = \frac{\omega^2 (M_i - V_i \rho)}{2RT \left[\left(1 + \frac{\partial(\ln \gamma_i)}{\partial(\ln x_i)} \right) \right]} \quad (20)$$

The density at low concentrations of I in a binary i-j solution is approximately M_j/V_j ; therefore,

$$\frac{\partial(\ln x_i)}{dr^2} = \frac{\omega^2 \left(M_i - M_i \frac{V_i}{V_j} \right)}{2RT \left[\left(1 + \frac{\partial(\ln \gamma_i)}{\partial(\ln x_i)} \right) \right]} \quad (21)$$

If Darken's Quadratic formula holds for a binary i-j alloy, the following is true at low mole fraction of i.

$$\ln \gamma_i = a + b(1 - x_i)^2 \quad (22)$$

$$\lim_{x_i \rightarrow 0} \frac{\partial(\ln \gamma_i)}{\partial(\ln x_i)} \rightarrow 0 \quad (23)$$

Also, the ratio $\frac{V_i}{V_j}$ is approximately zero for interstitial components such as for C in Cr and unity

for substitutional components. Solving for mole fraction at selected r gives

$$\ln x_i = (r^2 - b)a \quad (24)$$

where

$$a = \frac{\omega^2 M_C}{2RT} \quad (25)$$

The total carbon in the blade remains constant and is found by integrating over the blade length to get

$$n_C = \int_{r=r_1}^{r_2} x_C^o \theta r dr = x_C^o \theta \left[\frac{r_2^2 - r_1^2}{2} \right] \quad (26)$$

The total carbon in the blade at equilibrium is found by integrating over the blade length using the mole fraction of C set by Eq. (21) to get

$$n_C = \int_{r=r_1}^{r_2} x_C \theta r dr = \int_{r=r_1}^{r_2} \frac{e^{(r^2-b)a} \theta dr^2}{2} = \frac{\theta}{2a} \left[e^{(r_2^2-b)a} - e^{(r_1^2-b)a} \right] \quad (27)$$

The constant of integration, b, can be determined by equating Eqs. (26) and (27)

$$2ax_C^o \left[\frac{r_2^2 - r_1^2}{2} \right] = e^{(r_2^2-b)a} - e^{(r_1^2-b)a} = \frac{e^{ar_2^2} - e^{ar_1^2}}{e^{ab}} \quad (28)$$

The value of b is

$$b = \frac{1}{a} \ln \left[\frac{e^{ar_2^2} - e^{ar_1^2}}{ax_C^o (r_2^2 - r_1^2)} \right] \quad (29)$$

The values shown in Table 1 for this problem, the value of b is, as shown. The value of includes 10^7 in the denominator to rectify the use of Joules ($\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$) in the gas constant and radius in cm. Once the value of b is known, Eq. (24) is used to generate the values shown in Table 2 and plotted in Figure 1. Integrating the final c distribution for total c gives the same value as for the initial moles of carbon. This value is for a unit thickness blade. The maximum and minimum mole fraction for an interstitial is then

$$x_i^{\max} = \frac{e^{ar_2^2}}{e^{ab}} \quad (30)$$

$$x_i^{\min} = \frac{e^{ar_1^2}}{e^{ab}} \quad (31)$$

Table 1 Variables and computed parameters for Cr Blade

Parameter	Value	Units
θ	0.03	radians
C initial	0.050%	wt %
xo	0.002163	
$_r1$	50	cm
$_r2$	56	cm
RPM	40000	Rev per minute
ω	4188.8	radians*s ⁻¹
$_R$	8.31	J*gmole ⁻¹ K ⁻¹
T	1000	K
a	2.53E-03	m ⁻²
b	5281.6	m ²
Mc	12	g/gmole
RHS Eq. (28)	0.6879	see Eq. (28)
RHS Eq. (29)	0.6879	see Eq. (29)
Δ (Eq. (28)- Eq. (29))	0.0000	

Table 2 Wt% C at equilibrium

radius	wt % C
50	0.0201%
51	0.0259%
52	0.0337%
53	0.0440%
54	0.0577%
55	0.0761%
56	0.1008%

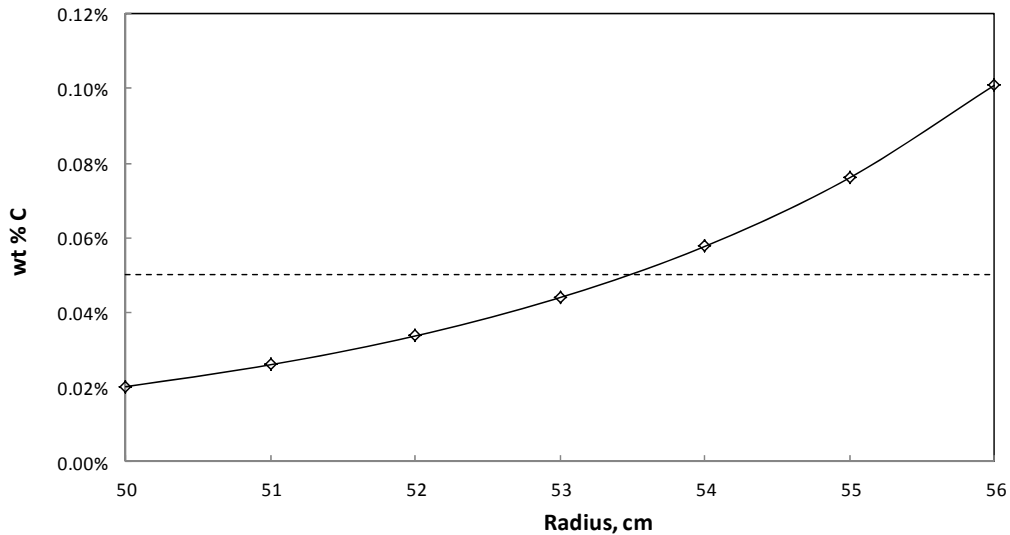


Figure 1. Carbon distribution in a Cr blade rotatating at 40,000 RPM at 1000 K with an average wt% C of 0.05.