Fundamental Aspects of Nuclear Reactor Fuel Elements

Solutions to Problems

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CHAPTER 1

Problem 1.1

The canonical partition function of an ideal gas of particles obeying Fermi-Dirac statistics is

$$\ln Z = -\frac{\mu N}{kT} + \sum_j \ln \left[1 + \exp \left(-\frac{\epsilon_j - \mu}{kT} \right) \right]$$

from Eq. (1.51). (1.51)

However from Eq. (1.15), average energy per particle is

$$U_F = \frac{kT^2}{N} \left(\frac{\partial \ln Z}{\partial T} \right)_V = -\frac{k}{N} \left(\frac{\partial \ln Z}{\partial (1/T)} \right)_V$$

(1.15)'

$$\begin{aligned} \therefore \left(\frac{\partial \ln Z}{\partial (1/T)} \right)_V &= - \left(\frac{\mu N}{k} + \frac{N}{kT} \left(\frac{\partial \mu}{\partial (1/T)} \right)_V \right) \\ &\quad + \sum_j \frac{\partial}{\partial (1/T)} \left\{ \ln \left[1 + \exp \left(-\frac{\epsilon_j - \mu}{kT} \right) \right] \right\} \\ \frac{\partial}{\partial (1/T)} \left\{ \ln \left[1 + \exp \left(-\frac{\epsilon_j - \mu}{kT} \right) \right] \right\} &= \frac{-\frac{\partial}{\partial (1/T)} \left\{ (\epsilon_j - \mu)/kT \right\} \cdot \exp \left(-\frac{\epsilon_j - \mu}{kT} \right)}{1 + \exp \left(-\frac{\epsilon_j - \mu}{kT} \right)} \end{aligned}$$

But from Eq. (1.53)

$$\bar{n}_j = \frac{\exp \left(-\frac{\epsilon_j - \mu}{kT} \right)}{1 + \exp \left(-\frac{\epsilon_j - \mu}{kT} \right)} \quad (1.53)$$

$$\text{and } \frac{\partial}{\partial (1/T)} \left\{ \frac{\epsilon_j - \mu}{kT} \right\} = \frac{\epsilon_j - \mu}{k} - \frac{1}{kT} \left(\frac{\partial \mu}{\partial (1/T)} \right)_V$$

Thus

$$\begin{aligned}
 & \sum_j \frac{\partial}{\partial(\mu/T)} \{ \ln[1 + \exp(-\frac{\epsilon_j - \mu}{kT})] \} \\
 &= - \sum_j \left\{ \frac{\epsilon_j - \mu}{k} - \frac{1}{kT} \left(\frac{\partial \mu}{\partial(\mu/T)} \right)_V \right\} \bar{n}_j \\
 &= -\frac{1}{k} \sum_j \epsilon_j \bar{n}_j + \frac{\mu}{k} \sum_j \bar{n}_j + \frac{1}{kT} \left(\frac{\partial \mu}{\partial(\mu/T)} \right)_V \sum_j \bar{n}_j
 \end{aligned}$$

But $\sum_j \bar{n}_j = N$

$$\begin{aligned}
 \therefore \sum_j \frac{\partial}{\partial(\mu/T)} \{ \ln[1 + \exp(-\frac{\epsilon_j - \mu}{kT})] \} &= -\frac{1}{k} \sum_j \epsilon_j \bar{n}_j + \frac{\mu}{k} N \\
 &\quad + \frac{N}{kT} \left(\frac{\partial \mu}{\partial(\mu/T)} \right)_V
 \end{aligned}$$

$$\begin{aligned}
 \therefore \left[\frac{\partial \ln Z}{\partial(\mu/T)} \right]_V &= -\frac{\mu N}{k} - \frac{N}{kT} \left(\frac{\partial \mu}{\partial(\mu/T)} \right)_V - \frac{1}{k} \sum_j \epsilon_j \bar{n}_j \\
 &\quad + \frac{\mu N}{k} + \frac{N}{kT} \left(\frac{\partial \mu}{\partial(\mu/T)} \right)_V \\
 &= -\frac{1}{k} \sum_j \epsilon_j \bar{n}_j
 \end{aligned}$$

Substituting this into Eq. (1.15)' we get,

$$U_F = -\frac{k}{N} \left[-\frac{1}{k} \sum_j \epsilon_j \bar{n}_j \right] = \frac{1}{N} \sum_j \epsilon_j \bar{n}_j$$

Approximating the summation to an integral

$$U_F \cong \frac{1}{N} \int_0^\infty \epsilon \bar{n}(\epsilon) \mathcal{D}(\epsilon) d\epsilon$$

Problem 1.2

- (a) Assuming that the substance is heated at constant pressure

$$S = \int_0^T c_p \frac{dT}{T}$$

Since phase transformations take place at constant temperatures, the corresponding entropy changes are given simply by

$$\Delta S = \frac{\Delta H}{T}$$

$$\therefore S = \int_0^{T_f} c_{ps}(T) \frac{dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} c_{pl}(T) \frac{dT}{T} + \frac{\Delta H_v}{T_b} + \int_{T_b}^T c_{pg} \frac{dT}{T}$$

(where $c_{pg} = 5/2 R$ for ideal gas)

(b)
$$S = k \left[\ln Z + T \left(\frac{\partial \ln Z}{\partial T} \right)_V \right]$$

For ideal gas, $Z = Z_{tr} = \frac{z_{tr}^N}{N!}$

$$z_{tr} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$\therefore \ln Z = N \ln z_{tr} - \ln N!$$

then $\left(\frac{\partial \ln Z}{\partial T} \right)_V = N \left(\frac{\partial \ln z_{tr}}{\partial T} \right)_V$

$$\begin{aligned}\therefore \left(\frac{\partial \ln Z}{\partial T} \right)_V &= N \frac{\partial}{\partial T} \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m k T}{h^2} \right) + \frac{3}{2} \ln T \right] \\ &= \frac{3}{2} N \frac{\partial \ln T}{\partial T} = \frac{3}{2} \frac{N}{T}\end{aligned}$$

$$\begin{aligned}\therefore S &= k [\ln Z + \frac{3}{2} N] \\ &= k [N \ln z_{tr} - \ln N! + \frac{3}{2} N] \\ &= k \left[N \ln \left\{ V \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right\} - \ln N! + \frac{3}{2} N \right]\end{aligned}$$

but $pV = NkT$ for ideal gas

and $\ln N! \cong N \ln N - N$ (Stirling's approximation)

$$\therefore S = k \left[N \ln \left\{ \frac{NkT}{p} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right\} - N \ln N + N + \frac{3}{2} N \right]$$

$$\therefore S = k N \left[\ln \left\{ \frac{kT}{p} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right\} + \frac{5}{2} \right]$$

Problem 1.3

From Fermi-Dirac statistics, the average occupation number of fermions is

$$\begin{aligned}\bar{n}_j &= \frac{1}{e^{(\alpha + \epsilon_j/kT)} + 1} = e^{-(\alpha + \epsilon_j/kT)} \left\{ 1 + e^{-(\alpha + \epsilon_j/kT)} \right\}^{-1} \\ &= e^{-(\alpha + \epsilon_j/kT)} \left\{ 1 - e^{-(\alpha + \epsilon_j/kT)} + e^{-2(\alpha + \epsilon_j/kT)} - \dots \right\}\end{aligned}$$

First order approximation gives Maxwell-Boltzmann Statistics. Taking 2nd order approximation we get,

$$\begin{aligned}\bar{n}_j &\doteq e^{-(\alpha + \epsilon_j/kT)} \left\{ 1 - e^{-(\alpha + \epsilon_j/kT)} \right\} \\ &= e^{-\alpha} e^{-\epsilon_j/kT} - e^{-2\alpha} e^{-2\epsilon_j/kT}\end{aligned}$$

Energy distribution $n(\epsilon_j)$ = number of particles with energy ϵ_j = number of states available with energy ϵ_j multiplied by the probability of occupation of state ϵ_j .

$$\text{i.e. } n(\epsilon_j) = \mathcal{D}(j) \bar{n}_j$$

Assume classical limit, i.e. energy continuum.

$$\therefore n(\epsilon) = \mathcal{D}(\epsilon) f(\epsilon)$$

$$= 2 \times \frac{V}{4\pi^2} \left(\frac{2m}{h^2} \right)^{3/2} \sqrt{\epsilon} \left\{ e^{-\alpha} e^{-\epsilon/kT} - e^{-2\alpha} e^{-2\epsilon/kT} \right\}$$

Find α from
normalizing $n(\epsilon)$.

To justify classical limit it could be shown that αkT is far above discrete quantum levels.

Normalizing:

$$N = V n_{\text{tot}} = \int_0^{\infty} n(\epsilon) d\epsilon$$

$$N = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left\{ e^{-\alpha} \int_0^{\infty} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon - \frac{e^{-2\alpha}}{2} \int_0^{\infty} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \right\}$$

$$N = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left\{ \frac{e^{-\alpha} \sqrt{\pi} (kT)^{3/2}}{2} - \frac{e^{-2\alpha} \sqrt{\pi} (kT)^{3/2}}{2^{5/2}} \right\}$$

$$N = \mathcal{Z} \left(e^{-\alpha} - \frac{e^{-2\alpha}}{2^{3/2}} \right)$$

Where $\mathcal{Z} = 2V \left(\frac{2\pi m kT}{h^2} \right)^{3/2} =$ partition function
of fermions

Solving for $\bar{e}^\alpha$: $(\bar{e}^\alpha)^2 - \frac{3}{2}(\bar{e}^\alpha) + \frac{2^{3/2}N}{Z} = 0$

$$\bar{e}^\alpha = \sqrt{2} \pm \sqrt{2 - \frac{2^{3/2}N}{Z}}$$

Since we want $\alpha > 0$, we choose negative sign

Numerical estimate shows $Z > 2^{3/2}N$, so the root is real.

Expand the root to 2nd order

$$\bar{e}^\alpha = \sqrt{2} \left(1 - \sqrt{1 - \frac{\sqrt{2}N}{Z}} \right)$$

$$\approx \sqrt{2} \left(\frac{N}{\sqrt{2}Z} + \frac{N^2}{4Z^2} \right)$$

$$= \frac{N}{Z} \left(1 + \frac{1}{2\sqrt{2}} \frac{N}{Z} \right)$$

$$= \underbrace{\frac{n_{\text{tot}}}{2} \left(\frac{h^2}{2\pi m k T} \right)^{3/2}}_{\text{value for M-B statistics} \equiv A} \left(1 + \frac{n_{\text{tot}}}{2^{5/2}} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} \right)$$

value for M-B statistics $\equiv A$

$$\therefore \bar{e}^\alpha = A \left(1 + \frac{A}{2\sqrt{2}} \right)$$

So $n(\epsilon)$ becomes

$$n(\epsilon) = \underbrace{\frac{VA}{2\pi^2} \left(\frac{2m}{h^2} \right)^{3/2} \sqrt{\epsilon}}_{\substack{n(\epsilon) \\ \text{M-B}}} e^{-\epsilon/kT} \left\{ 1 + \frac{A}{2\sqrt{2}} - A e^{-\epsilon/kT} - \frac{A^2}{\sqrt{2}} e^{-\epsilon/kT} - \frac{A^3}{8} e^{-\epsilon/kT} \right\}$$

the last four terms are correction terms in decreasing order of size

$$n(\epsilon) = n_{m-B}(\epsilon) \left\{ \left(1 + \frac{A}{2\sqrt{2}}\right) - \left(A + \frac{A^2}{\sqrt{2}} + \frac{A^3}{8}\right) e^{-\epsilon/kT} \right\}$$

(a) Average energy is

$$\bar{\epsilon} = \int_0^{\infty} \epsilon n(\epsilon) d\epsilon$$

$$= \frac{1}{V n_{tot}} \frac{VA}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \left\{ \left(1 + \frac{A}{2\sqrt{2}}\right) \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon - \left(A + \frac{A^2}{\sqrt{2}} + \frac{A^3}{8}\right) \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon \right\}$$

$$= \frac{2}{\sqrt{\pi} (kT)^{3/2}} \left\{ \left(1 + \frac{A}{2\sqrt{2}}\right) \frac{3}{4} \sqrt{\pi} (kT)^{5/2} - \left(A + \frac{A^2}{\sqrt{2}} + \frac{A^3}{8}\right) \frac{3}{4} \sqrt{\pi} \left(\frac{kT}{2}\right)^{5/2} \right\}$$

$$= \frac{3}{2} kT \left\{ 1 + \frac{A}{2\sqrt{2}} - \frac{A}{4\sqrt{2}} - \frac{A^2}{8} - \frac{A^3}{32\sqrt{2}} \right\}$$

ignore

$$= \frac{3}{2} kT \left(1 + \frac{A}{4\sqrt{2}}\right), \quad A = \frac{n_{tot}}{2} \left(\frac{\hbar^2}{2\pi m kT}\right)^{3/2}$$

$$= \frac{(N/V)}{2} \lambda^3$$

A is very small correction, λ thermal wavelength

The upper limit on $\bar{e}^x$ is approximately the maximum value of A : for neutrons,

$$A_n = \frac{n_{\text{tot}}}{2} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} = \frac{n_{\text{tot}}}{2} \left(\frac{h^2 c^2}{2\pi m c^2} \right)^{3/2} \left(\frac{1}{k T} \right)^{3/2}$$

$$\approx \frac{n_{\text{tot}}}{2} \left(\frac{10^{-42} \text{ MeV}^2 \times 10^{17} \text{ cm}^2}{10 \times 10^3 \text{ MeV}} \right)^{3/2} \left(\frac{10^6}{k T (\text{eV})} \right)^{3/2}$$

$$\approx n_{\text{tot}} (\text{cm}^3) (k T (\text{eV}))^{-3/2} \times 10^{-35}$$

for $n_{\text{tot}} = 10^{10} \text{ cm}^3$, $A_n \approx (k T (\text{eV}))^{-3/2} \times 10^{-25}$

$\therefore$ for $T = 1^\circ \text{K} \sim 10^{-4} \text{ eV}$, $A_n \approx 10^{-19}$

Thus the expression of the F-D $\bar{n}_j$ must converge very quickly and the correction to the M-B value is very small.

(b)

It is stated in Seitz, Modern Theory of Solids (Ch. 4) that the approximation is good for most metals below their melting point.

$(k T \ll \epsilon_f)$

Problem 1.4

The method derived in the text for calculating Z is not applicable here because of the small number of particles. Instead, we must count states of the system. For Fermi-Dirac particles with spin $1/2$, there are 3 energy states $\times$ 2 spin states = 6 single-particle states. The first particle can be in any of the 6 states, & the second can be placed in any of the 5 remaining states. Therefore, the number of states of the system is $6 \times 5 / 2 = 15$, where the denominator 2 accounts for the indistinguishability of the two particles. The distinct states of the system are shown below, with the total energy of the state indicated.

The partition function is:

$$Z = e^{-2E_0/RT} + e^{-2E_1/RT} + e^{-2E_2/RT} + 4e^{-(E_0+E_1)/RT} + 4e^{-(E_0+E_2)/RT} + 4e^{-(E_1+E_2)/RT}$$

Problem 1.5

(a) Consider an equation of state of the form $p(V, T)$.
The differential of β is:

$$d\beta = \left(\frac{\partial \beta}{\partial T}\right)_V dT + \left(\frac{\partial \beta}{\partial V}\right)_T dV \quad (1)$$

or, at constant pressure

$$0 = \left(\frac{\partial \beta}{\partial T}\right)_V + \left(\frac{\partial \beta}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

$$\text{or } \left(\frac{\partial V}{\partial T}\right)_p = - \frac{\left(\frac{\partial \beta}{\partial T}\right)_V}{\left(\frac{\partial \beta}{\partial V}\right)_T} \quad (2)$$

$$\text{By definition } \alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V} \frac{\left(\frac{\partial \beta}{\partial T}\right)_V}{\left(\frac{\partial \beta}{\partial V}\right)_T} \quad [\text{from (2)}]$$

$$\text{and } \beta \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V} \frac{1}{\left(\frac{\partial p}{\partial V}\right)_T} \quad (3)$$

From Eq. (1.28)

$$p = kT \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

so

$$\left(\frac{\partial p}{\partial V}\right)_T = kT \left(\frac{\partial^2 \ln Z}{\partial V^2}\right)_T \quad (5)$$

$$\text{and } \left(\frac{\partial p}{\partial T}\right)_V = kT \frac{\partial}{\partial T} \left[\left(\frac{\partial \ln Z}{\partial V}\right)_T \right]_V + k \left(\frac{\partial \ln Z}{\partial V}\right)_T \quad (6)$$

$\therefore$ Substituting (5) and (6) into (3) and (5) into (4)

$$\alpha = -\frac{1}{VT} \left[\frac{T \frac{\partial^2 \ln Z}{\partial T \partial V} + \left(\frac{\partial \ln Z}{\partial V}\right)_T}{\left(\frac{\partial^2 \ln Z}{\partial V^2}\right)_T} \right] \quad (7)$$

$$\text{and } \beta = -\frac{1}{kTV} \frac{1}{\left(\frac{\partial^2 \ln Z}{\partial V^2}\right)_T} \quad (8)$$

(b) From eq. (2) and the definitions of α and β

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T} = -\left(\frac{V\alpha}{-V\beta}\right) = \frac{\alpha}{\beta} \quad (9)$$

Integrating this $\Delta p = \frac{\alpha}{\beta} \Delta T$ at constant volume.

$$\therefore \Delta p = \frac{1.5 \times 10^{-5}}{5.4 \times 10^{-11}} \times 1 = 3.33 \times 10^6 \text{ N/m}^2 \quad (33 \text{ atm})$$

(c) By definition

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p, \quad C_v = \left(\frac{\partial U}{\partial T}\right)_v \quad (10)$$

$$\begin{aligned} \therefore C_p - C_v &= \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v \\ &= \left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v \quad (\text{since } U + pV = H) \end{aligned}$$

$$\text{But } \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (11)$$

substituting this into the above

$$C_p - C_v = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p$$

Using eq (3) we get,

$$C_p - C_v = \left(\frac{\partial U}{\partial V} \right)_T V\alpha + pV\alpha \quad (12)$$

From part (d), Eq (22):

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{\alpha}{\beta} T - p$$

$$\therefore C_p - C_v = \left(\frac{\alpha}{\beta} T - p \right) V\alpha + pV\alpha = \frac{\alpha^2}{\beta} VT \quad (13)$$

for an ideal gas, $pV = RT$ and

$$\alpha = \frac{1}{V} \frac{R}{p} = \frac{1}{T} ; \quad \beta = \frac{1}{V} \frac{RT}{p^2} = \frac{V}{RT}$$

$$\therefore \frac{C_p - C_v}{C_p} = \frac{(\alpha^2/\beta) VT}{\frac{5}{2}R} = \frac{1}{T} \cdot \frac{RT}{V} VT / \frac{5}{2}R = \underline{\underline{0.4}} \quad (14)$$

for mercury:

$$\begin{aligned} \frac{C_p - C_v}{C_p} &= \frac{(\alpha^2/\beta) VT}{C_p} ; \text{ at } 0^\circ\text{C}, V = 0.074 \text{ cm}^3/\text{gm}, C_p = 0.14 \frac{\text{J}}{\text{gm}^\circ\text{C}} \\ &= \frac{(1.8 \times 10^{-5})^2}{5.4 \times 10^{-11}} \frac{(0.074)(273)}{(0.14) \times 10^6} = \underline{\underline{0.087}} \quad (15) \end{aligned}$$

(d) The 1st law of thermodynamics states

$$dU = TdS - pdV \quad (16)$$

or

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p \quad (17)$$

$$\text{consider: } dF = -p dV - S dT = \left(\frac{\partial F}{\partial V} \right)_T dV + \left(\frac{\partial F}{\partial T} \right)_V dT \quad (18)$$

identifying coefficients of dV and dT in Eq (18):

$$\left(\frac{\partial F}{\partial V} \right)_T = -p \quad \text{and} \quad \left(\frac{\partial F}{\partial T} \right)_V = -S \quad (19)$$

By forming mixed second derivatives

$$-\frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad (\text{Maxwell relation}) \quad (20)$$

Substituting Eq (20) into Eq (17):

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (21)$$

so by comparison between (20) & (21)

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

From part (a) eq. (9)

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha}{\beta} T - p \quad (22)$$

Now differentiating w.r.t. V with constant T

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_T = T \left(\frac{\partial (1/\beta)}{\partial V}\right)_T - \left(\frac{\partial p}{\partial V}\right)_T \quad (23)$$

$$\text{Using eq. (4) in part (a), i.e. } \left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{\beta V} \quad (24)$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_T = \frac{T}{\beta} \left(\frac{\partial \alpha}{\partial V}\right)_T - T \frac{\alpha}{\beta^2} \left(\frac{\partial \beta}{\partial V}\right)_T + \frac{1}{\beta V} \quad (25)$$

$$\text{but } \left(\frac{\partial \beta}{\partial V}\right)_T = \left(\frac{\partial \beta}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial \beta}{\partial p}\right)_T \frac{1}{\beta V} \quad [\text{From eq. (24)}]$$

$$\text{Thus } \left(\frac{\partial^2 U}{\partial V^2}\right)_T = \frac{1}{\beta V} + \frac{T\alpha}{\beta^3 V} \left(\frac{\partial \beta}{\partial p}\right)_T + \frac{T}{\beta} \left(\frac{\partial \alpha}{\partial V}\right)_T \quad (26)$$

$$\text{but } \left(\frac{\partial \alpha}{\partial V}\right)_T = \left(\frac{\partial \alpha}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{\beta V} \left(\frac{\partial \alpha}{\partial p}\right)_T \quad [\text{From eq. (24)}] \quad (27)$$

From the definition of α, β

$$\begin{aligned} \left(\frac{\partial \alpha}{\partial p}\right)_T &= \frac{\partial}{\partial p} \left[\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \right]_T = -\frac{1}{V^2} \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \frac{1}{V} \frac{\partial}{\partial p} \left[\left(\frac{\partial V}{\partial T}\right)_p \right]_T \end{aligned}$$

$$\left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\partial}{\partial T} \left[-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \right]_P = \frac{1}{V^2} \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V} \frac{\partial}{\partial T} \left[\left(\frac{\partial V}{\partial P}\right)_T \right]_P$$

Thus $\left(\frac{\partial \alpha}{\partial P}\right)_T = -\left(\frac{\partial \beta}{\partial T}\right)_P$ (28) [From the previous two eqs.]

$$\begin{aligned} \therefore \left(\frac{\partial \alpha}{\partial V}\right)_T &= -\frac{1}{\beta V} \left(\frac{\partial \alpha}{\partial P}\right)_T \text{ [from (27)]} \\ &= \frac{1}{\beta V} \left(\frac{\partial \beta}{\partial T}\right)_P \text{ [from (28)]} \end{aligned} \quad (29)$$

Substituting (29) into (26) we get,

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_T = \frac{1}{\beta V} \left[1 + T \frac{\alpha}{\beta^2} \left(\frac{\partial \beta}{\partial P}\right)_T + \frac{T}{\beta} \left(\frac{\partial \beta}{\partial T}\right)_P \right] \quad (30)$$

Problem 1.6

For an ideal gas

$$Z = \frac{\zeta_{tr}^N}{N!}$$

$$\zeta_{tr} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$\therefore \ln Z = N \ln \zeta_{tr} - N \ln N + N \quad (\text{Using Stirling's approximation})$$

$$(a) \quad p = kT \left(\frac{\partial \ln Z}{\partial V} \right)_T \quad [\text{From Eq. (1.28)}]$$

$$\left(\frac{\partial \ln Z}{\partial V} \right)_T = \frac{N}{\zeta_{tr}} \left(\frac{\partial \zeta_{tr}}{\partial V} \right)_T = \frac{N}{\zeta_{tr}} \cdot \frac{\zeta_{tr}}{V} = \frac{N}{V}$$

$$\therefore p = \frac{kTN}{V}$$

$$\text{or } \underline{pV = NkT}$$

$$(b) \quad S = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T} \right)_V$$

$$\begin{aligned} \left(\frac{\partial \ln Z}{\partial T} \right)_V &= \frac{N}{\zeta_{tr}} \left(\frac{\partial \zeta_{tr}}{\partial T} \right)_V = \frac{N}{\zeta_{tr}} V \left(\frac{2\pi mk}{h^2} \right)^{3/2} T^{1/2} \\ &= \frac{3}{2} \frac{N}{T} \end{aligned}$$

$$\therefore S = kN \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] - kN \ln N + kN + \frac{3}{2} kN$$

$$\therefore S = kN \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{5}{2} kN$$

$$\text{or } S = R \ln \left[\frac{P}{kT} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{5}{2} R$$

$$[\text{Using } R = kN \text{ and } PV = NkT]$$

(c) From Prob. 1.5c for ideal gas, $C_p = C_v + R$, or

$$C_p = \left(\frac{\partial U}{\partial T} \right)_V + R = \frac{\partial}{\partial T} \left\{ kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \right\} + R$$

$$C_p = R \left\{ 2T \left(\frac{\partial \ln Z}{\partial T} \right)_V + T^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_V \right\} + R$$

$$\left(\partial \ln Z / \partial T \right)_V = 3N/2T \text{ from part (b)}$$

$$\therefore C_p = R \left(3N - \frac{3}{2}N \right) + R = \frac{3}{2}NR + R = \underline{\underline{\frac{5}{2}R}}$$

$$(d) Z = (\mathcal{Z}_{tr} \cdot \mathcal{Z}_{int})^N / N!$$

$$\ln Z = N \ln (\mathcal{Z}_{tr} \cdot \mathcal{Z}_{int}) - N \ln N + N$$

$$\mathcal{Z}_{int} = 1 + e^{-\Delta \epsilon / kT}$$

$$\text{let } \mathcal{Z} = \mathcal{Z}_{tr} \cdot \mathcal{Z}_{int}$$

$$\frac{\partial \mathcal{Z}}{\partial V} = (1 + e^{-\Delta \epsilon / kT}) \frac{\partial \mathcal{Z}_{tr}}{\partial V} = \frac{\mathcal{Z}}{V}$$

$$\left(\frac{\partial \ln Z}{\partial V} \right)_T = \frac{N}{V} \quad (\text{unchanged})$$

Hence (a) part is unchanged, i.e. $PV = NkT$.

Now

$$\begin{aligned} \left(\frac{\partial \ln Z}{\partial T} \right)_V &= N \left(\frac{\partial \ln Z_{tr.}}{\partial T} \right)_V + N \left(\frac{\partial \ln Z_{int.}}{\partial T} \right)_V \\ &= \frac{3}{2} N/T + N \left[\frac{\partial \ln (1 + e^{-\Delta \epsilon / kT})}{\partial T} \right]_V \end{aligned}$$

using $e^{-\Delta \epsilon / kT} \ll 1$,

$$\ln [1 + e^{-\Delta \epsilon / kT}] \cong e^{-\Delta \epsilon / kT}$$

$$\therefore \frac{\partial e^{-\Delta \epsilon / kT}}{\partial T} = \frac{\Delta \epsilon}{kT^2} e^{-\Delta \epsilon / kT}$$

$$\therefore \left(\frac{\partial \ln Z}{\partial T} \right)_V = \frac{3}{2} \frac{N}{T} + \frac{N}{T} \left(\frac{\Delta \epsilon}{kT} \right) e^{-\Delta \epsilon / kT}$$

$$\begin{aligned} S &= kN \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + kN \ln (1 + e^{-\Delta \epsilon / kT}) - kN \ln N \\ &\quad + kN + \frac{3}{2} kN + kN \left(\frac{\Delta \epsilon}{kT} \right) e^{-\Delta \epsilon / kT} \end{aligned}$$

$$\begin{aligned} \therefore S &\cong kN \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + kN e^{-\Delta \epsilon / kT} - kN \ln N \\ &\quad + \frac{5}{2} kN + kN \left(\frac{\Delta \epsilon}{kT} \right) e^{-\Delta \epsilon / kT} \end{aligned}$$

$$\text{or } S = kN \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{5}{2} kN + kN e^{-\Delta \epsilon / kT} \left(1 + \frac{\Delta \epsilon}{kT} \right)$$

additional term

for the heat capacity, the formula from part (c):

$$C_p = R \left\{ 2T \left(\frac{\partial \ln Z}{\partial T} \right)_V + T^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_V \right\} + R$$

still holds because the electronic excitation does not change the fact that the gas is ideal. However, with electronic excitation,

$$\left(\frac{\partial \ln Z}{\partial T} \right)_V = \frac{3}{2} \frac{N}{T} + \frac{N}{T} \left(\frac{\Delta E}{kT} \right) e^{-\Delta E/kT}$$

substituting in C_p equation yields

$$C_p = \frac{5}{2} R + R \left(\frac{\Delta E}{kT} \right)^2 e^{-\Delta E/kT}$$

(additional term)

Problem 1.7

$$\text{let } e^{-(\epsilon_k - \mu)/kT} = a_k$$

From Eq. (1.47)

From Eq. (1.48)

$$\bar{z} = \sum_{N=0}^{\infty} \left[\sum_{\substack{\{n_0, n_1\} \\ (n_0 + n_1 = N)}} a_0^{n_0} a_1^{n_1} \right] = \left(\sum_{n_0=0}^{\infty} a_0^{n_0} \right) \left(\sum_{n_1=0}^{\infty} a_1^{n_1} \right)$$

(to be shown equal)

$$\text{Let } \left[\sum_{\substack{\{n_0, n_1\} \\ (n_0 + n_1 = N)}} a_0^{n_0} a_1^{n_1} \right] = [\text{term}]$$

$$\underline{N=0}$$

$$n_0 = n_1 = 0$$

$$\text{term} = 1$$

$$\underline{N=1}$$

$$n_0 = 1, n_1 = 0 \quad \text{or} \quad n_0 = 0, n_1 = 1$$

$$\text{term} = a_0 + a_1$$

$$\underline{N=2}$$

$$\left. \begin{array}{l} n_0 = 2 \\ n_1 = 0 \end{array} \right\} \text{or} \left. \begin{array}{l} n_0 = 1 \\ n_1 = 1 \end{array} \right\} \text{or} \left. \begin{array}{l} n_0 = 0 \\ n_1 = 2 \end{array} \right\}$$

$$a_0^2 \quad a_0 a_1 \quad a_1^2$$

$$\text{term} = a_0^2 + a_0 a_1 + a_1^2$$

$$\underline{N=3}$$

$$\text{term} = a_0^3 + a_0^2 a_1 + a_0 a_1^2 + a_1^3$$

N=4

$$\text{term} = a_0^4 + a_0^3 a_1 + a_0^2 a_1^2 + a_0 a_1^3 + a_1^4$$

Then RHS of Eq. (1.47) gives,

$$\begin{aligned} \underline{\underline{\cdot}} &= 1 + a_0 + a_1 + a_0^2 + a_0 a_1 + a_1^2 + a_0^3 + a_0^2 a_1 + a_0 a_1^2 \\ &\quad + a_1^3 + a_0^4 + a_0^3 a_1 + a_0^2 a_1^2 + a_0 a_1^3 + a_1^4 + \dots \end{aligned}$$

RHS of Eq. (1.48) gives,

$$\begin{aligned} \underline{\underline{\cdot}} &= (1 + a_0 + a_0^2 + a_0^3 + a_0^4 + \dots) (1 + a_1 + a_1^2 + a_1^3 + a_1^4 + \dots) \\ &= 1 + a_0 + a_1 + a_0^2 + a_0 a_1 + a_1^2 + a_0^3 + a_0^2 a_1 + a_0 a_1^2 + \\ &\quad a_1^3 + a_0^4 + a_0^3 a_1 + a_0^2 a_1^2 + a_0 a_1^3 + a_1^4 + \dots \end{aligned}$$

Thus both the series are identical upto the order 4 as seen above. Complete identity can be established by going to any arbitrary higher order. Therefore Eq. (1.47) and Eq. (1.48) give identical formulation.

CHAPTER 2

Problem 2.1

$$\epsilon_i = h\nu_i \left[\left(j_i + \frac{1}{2} \right) - x_e \left(j_i + \frac{1}{2} \right)^2 \right] \quad (1)$$

Since ϵ_i is a function of $(j_i + \frac{1}{2})$ and it is parabolic, there is a maximum energy level ϵ_i^* corresponding to some quantum number j_i^* . Moreover for $j_i > j_i^*$ ϵ_i will decrease and these energy levels are meaningless. Hence we have to consider only $0 \leq j_i \leq j_i^*$

An approximate maximum quantum number is obtained by

$$\left(\frac{d\epsilon_i}{dj_i} \right)_{j_i^*} = 0$$

$$\text{then } j_i^* \cong \frac{1 - x_e}{2x_e}$$

and this is independent of modes.

Since (1) can be written in the form

$$\varepsilon_i = \frac{1}{2} h \nu_i (1 - \frac{x_e}{2}) + h \nu_i j_i [1 - x_e(j_i + 1)]$$

defining

$$E_c = E_{ceh} + \sum_{i=1}^{3N} \frac{1}{2} h \nu_i (1 - \frac{x_e}{2})$$

the energy of a microstate of the system is

$$E(j_1, j_2, j_3, \dots, j_{3N}) = E_c + \sum_{i=1}^{3N} h \nu_i j_i [1 - x_e(j_i + 1)]$$

Hence, the partition function for the crystal from Eq. (1.12) becomes

$$Z = e^{-E_c/kT} \sum_{\{j_1, j_2, \dots, j_i, \dots, j_{3N}\}} \exp \left\{ -\frac{1}{kT} \sum_{i=1}^{3N} h \nu_i j_i [1 - x_e(j_i + 1)] \right\} \quad \dots (2)$$

Now, in evaluating the sum over microstates, since each of the quantum numbers j_i may have any value from 0 to $j^* \approx (\frac{1}{2x_e} - \frac{1}{2})$, eq (2) may be written as :

$$Z = e^{-E_c/kT} \prod_{i=1}^{3N} \left\{ \sum_{j_i=0}^{j^*} \exp \left\{ -\frac{1}{kT} h \nu_i j_i [1 - x_e(j_i + 1)] \right\} \right\} \quad \dots (3)$$

Now define $z_i = \sum_{j_i=0}^{j^*} \exp \left\{ -\frac{1}{kT} h \nu_i j_i [1 - x_e(j_i + 1)] \right\}$

then $z_i = \sum_{j_i=0}^{j^*} \exp \left(-\frac{h \nu_i}{kT} j_i \right) \cdot \exp \left(\frac{h \nu_i x_e}{kT} (j_i^2 + j_i) \right) \quad \dots (4)$

Using the assumption that x_e is so small that

any exponential function which has X_e in the argument can be approximated by a two-term Taylor series expansion,

$$\exp\left\{\frac{h\nu_i X_e}{kT} (j_i^2 + j_i)\right\} \cong 1 + \frac{h\nu_i}{kT} X_e (j_i^2 + j_i) \quad (5)$$

then (4) becomes,

$$Z_i = \sum_{j_i=0}^{j_i^*} \left[\exp\left(-\frac{h\nu_i}{kT} j_i\right) \right] \left(1 + \frac{h\nu_i}{kT} X_e (j_i^2 + j_i) \right) \quad (6)$$

providing that $j_i^2 \ll \frac{kT}{h\nu_i X_e}$

However, for $j_i \cong j^* \cong \frac{1}{2X_e} - \frac{1}{2}$

$$\exp\left\{-\frac{h\nu_i}{kT} j_i [1 - X_e(j_i + 1)]\right\}_{j_i=j^*} = \exp\left\{-\frac{h\nu_i}{kT} \frac{1}{2} \left(\frac{1}{X_e} - 1\right) \frac{1}{2} (X_e + 1)\right\}$$

neglecting

$$\cong \exp\left\{-\frac{h\nu_i}{kT} \frac{1}{4X_e}\right\}$$

This means that even if $j_i^2 \ll \frac{kT}{h\nu_i X_e}$ is not satisfied for $j_i \cong j^* \exp\left\{-\frac{h\nu_i}{kT} j_i\right\}$ term is so small that the approximation in eq. (6) may be valid for all j_i as $\exp\left(-\frac{h\nu_i}{kT} j_i\right)$ is the multiplying factor. Moreover, the finite sum over j_i from 0 to j^* can be replaced by infinite sum and it then converges.

$$Z_i \cong \sum_{j_i=0}^{\infty} \left[1 + \frac{h\nu_i}{kT} X_e (j_i^2 + j_i) \right] e^{-\frac{h\nu_i}{kT} j_i} \quad (7)$$

for simplicity let $\frac{h\nu_i}{kT} = u_i$

$$\text{then } Z_i = \sum_{j_i=0}^{\infty} e^{-u_i j_i} + u_i X_e \sum_{j_i=0}^{\infty} (j_i^2 + j_i) e^{-u_i j_i} \quad (8)$$

We know that
$$\sum_{j_i=0}^{\infty} e^{-u_i j_i} = \frac{1}{1 - e^{-u_i}} \quad (9)$$

and
$$\begin{aligned} \sum_{j_i=0}^{\infty} (j_i^2 + j_i) e^{-u_i j_i} &= \frac{\partial^2}{\partial u_i^2} \sum_{j_i=0}^{\infty} e^{-u_i j_i} - \frac{\partial}{\partial u_i} \sum_{j_i=0}^{\infty} e^{-u_i j_i} \\ &= \frac{\partial^2}{\partial u_i^2} \left(\frac{1}{1 - e^{-u_i}} \right) - \frac{\partial}{\partial u_i} \left(\frac{1}{1 - e^{-u_i}} \right) \\ &= \frac{\partial}{\partial u_i} \left[\frac{-e^{-u_i}}{(1 - e^{-u_i})^2} \right] + \frac{e^{-u_i}}{(1 - e^{-u_i})^2} \\ &= \frac{e^{-u_i}}{(1 - e^{-u_i})^2} + \frac{2 e^{-u_i} e^{-u_i}}{(1 - e^{-u_i})^3} + \frac{e^{-u_i}}{(1 - e^{-u_i})^2} \\ &= \frac{2 e^{-u_i}}{(1 - e^{-u_i})^2} + \frac{2 e^{-2u_i}}{(1 - e^{-u_i})^3} \\ &= \frac{2 e^{-u_i}}{(1 - e^{-u_i})^3} \quad (10) \end{aligned}$$

Substituting this result into (3) we get,

$$Z_i = \frac{1}{1 - e^{-h\nu_i/kT}} + 2 \chi_e \frac{h\nu_i}{kT} \frac{e^{-\frac{h\nu_i}{kT}}}{(1 - e^{-\frac{h\nu_i}{kT}})^3} \quad (11)$$

Then from eq (3) the total partition function becomes,

$$Z = e^{-E_0/kT} \prod_{i=1}^{3N} \left[\frac{1}{(1 - e^{-\frac{h\nu_i}{kT}})} + 2 \chi_e \left(\frac{h\nu_i}{kT} \right) \frac{e^{-\frac{h\nu_i}{kT}}}{(1 - e^{-\frac{h\nu_i}{kT}})^3} \right] \quad (12)$$

Problem 2.2

Force at j is given by

$$\begin{aligned}
 F_j &= k(u_{j+1} - u_j) - k(u_j - u_{j-1}) \\
 &= m \frac{d^2 u_j}{dt^2} = k(u_{j+1} - 2u_j + u_{j-1}) \quad \dots (1)
 \end{aligned}$$

(b) $u_j = A \sin(jak) e^{-i\omega t}$

$$\frac{du_j}{dt} = -i\omega A \sin(jak) e^{-i\omega t}$$

$$\frac{d^2 u_j}{dt^2} = -\omega^2 A \sin(jak) e^{-i\omega t}$$

Substituting for u_j in eq. (1) we get,

$$\begin{aligned}
 -\omega^2 m A \sin(jak) e^{-i\omega t} &= k [A \sin[(j+1)ak] e^{-i\omega t} \\
 &\quad - 2A \sin(jak) e^{-i\omega t} + A \sin[(j-1)ak] e^{-i\omega t}]
 \end{aligned}$$

$$\therefore -\frac{m\omega^2}{k} \sin(jak) = \sin(jak) \cos(ak) + \cos(jak) \sin(ak)$$

$$-2\sin(jak) + \sin(jak) \cos(ak)$$

$$-\cos(jak) \sin(ak)$$

$$\text{or } \frac{m\omega^2}{k} = 2(1 - \cos(ak))$$

$$\text{or } \omega = \left(\frac{4k}{m} \right)^{1/2} \left| \sin\left(\frac{ka}{2}\right) \right| \quad \dots (2)$$

(c) Assume central differences

$$\frac{du}{dx} \approx \frac{\delta u_j}{\Delta x} = \frac{u_{j+1/2} - u_{j-1/2}}{\Delta x}$$

$$\begin{aligned} \frac{d^2 u}{dx^2} &= \frac{\delta^2 u_j}{(\Delta x)^2} = \frac{\delta u_{j+1/2} - \delta u_{j-1/2}}{(\Delta x)^2} \\ &= \frac{u_{j+1} - 2u_j + u_{j-1}}{(\Delta x)^2} \end{aligned}$$

$$\begin{aligned} \therefore \frac{d^2 u}{dx^2} &= \frac{u_{j+1} - 2u_j + u_{j-1}}{(\Delta x)^2} ; \quad \Delta x = a \\ &= \frac{u_{j+1} - 2u_j + u_{j-1}}{a^2} \end{aligned}$$

Therefore from eq.(1) in part (a)

$$\frac{m}{ka^2} \frac{d^2 u}{dt^2} \approx \frac{d^2 u}{dx^2} \quad (3)$$

(d)

Generalizing the result of part (c) to three dimensions

$$\frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2}$$

or in the finite difference form

$$\begin{aligned} \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} &= \frac{(u_{j+1,k,l} - 2u_{j,k,l} + u_{j-1,k,l})}{a^2} + \frac{(u_{j,k+1,l} - 2u_{j,k,l} + u_{j,k-1,l})}{a^2} \\ &\quad + \frac{(u_{j,k,l+1} - 2u_{j,k,l} + u_{j,k,l-1})}{a^2} \end{aligned}$$

for $u_{j,k,l} = A \sin(ja\bar{k}_x) \sin(ja\bar{k}_y) \sin(ja\bar{k}_z) e^{i\omega t}$

as in part (b)

$$\therefore \frac{m\omega^2}{\kappa} = 2 \left\{ (1 - \cos(a\bar{k}_x)) + (1 - \cos(a\bar{k}_y)) + (1 - \cos(a\bar{k}_z)) \right\} \quad (4)$$

Note that this dispersion relation does not yield ω as a function of $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$ and so the density of states $\mathcal{D}(\omega)$ can not be evaluated by the arguments used for the Debye model.

(e) For long wavelengths $a\bar{k}_x, a\bar{k}_y, a\bar{k}_z \ll 1$
and $\cos(ak) \rightarrow 1 - \frac{(ak)^2}{2}$

Then

$$\frac{m\omega^2}{\kappa} \rightarrow \alpha^2 (k_x^2 + k_y^2 + k_z^2) = \alpha^2 k^2$$

[from eq. (4) in part (d)]

$$\text{or } \omega = \sqrt{\frac{\kappa \alpha^2}{m}} k$$

$$\text{or } \omega = c k$$

and $c = \sqrt{\frac{\kappa \alpha^2}{m}} = \text{Velocity of sound in the medium}$

Problem 2.3

within the context of the Einstein model, graphite has two characteristic vibration frequencies instead of one. The N vibration modes representing vibrations perpendicular to the basal plane in Fig. 4.5 have a single frequency $\omega_{\perp}$ or an Einstein temperature:

$$\Theta_{\perp} = \frac{\hbar \omega_{\perp}}{k} < 300^{\circ}\text{K}$$

Similarly, the $2N$ modes for vibration parallel to the basal planes have a common frequency $\omega_{\parallel}$ or an Einstein temperature:

$$\Theta_{\parallel} = \frac{\hbar \omega_{\parallel}}{k} > 300^{\circ}\text{K}$$

The frequency spectrum for graphite in this model is:

which are widely separated and fall on either side of the frequency for an Einstein temperature at 300°K ($\omega_{300} = \hbar/300k$). The frequency spectrum is:

$$D(\omega) = N\delta(\omega - \omega_{\perp}) + 2N\delta(\omega - \omega_{\parallel}) \quad (1)$$

using $\epsilon_f(1)$ in $\epsilon_f(2.21)$ of the text and then determining U by $\epsilon_f(1.15)$ and C_v from $(\partial U / \partial T)_v$ yields:

$$C_v = R E\left(\frac{\theta_{\perp}}{T}\right) + 2R E\left(\frac{\theta_{\parallel}}{T}\right) \quad (2)$$

where $E(\theta/T)$ is the Einstein function:

$$E(\theta/T) = \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{[e^{\theta/T} - 1]^2} \quad (3)$$

(a) for $T = 300^\circ\text{K}$, $\frac{\theta_{\perp}}{300} < 1$ and $E\left(\frac{\theta_{\perp}}{300}\right) \approx 1$

$\frac{\theta_{\parallel}}{300} > 1$ and $E\left(\frac{\theta_{\parallel}}{300}\right) \approx 0$

$\therefore$ Using $\epsilon_f(2)$:

$$C_v(300^\circ\text{K}) \approx R$$

i.e. at 300°K , only the $\perp$ modes of vibration are excited and they have attained the classical limit.

(b) In general, the variation of C_v with T for graphite is

Problem 2.4

$$(a) \quad \mathcal{D}(\omega) = 3N \left[\frac{3\omega^2}{\omega_D^3} + \eta \delta(\omega - \omega_E) \right] \quad \left. \begin{array}{l} \text{for } 0 < \omega < \omega_a \\ \\ = 0 \quad \text{for } \omega > \omega_a \end{array} \right\} \quad (1)$$

$\mathcal{D}(\omega)$ must satisfy the normalization condition

$$\int_0^{\omega_a} \mathcal{D}(\omega) d\omega = 3N \quad (2)$$

therefore $3N \int_0^{\omega_a} \left[\frac{3\omega^2}{\omega_D^3} + \eta \delta(\omega - \omega_E) \right] d\omega = 3N \quad (3)$

since $0 < \omega_D < \omega_a$ and $0 < \omega_E < \omega_a$ eq.(3) becomes

$$\left[\frac{\omega_a^3}{\omega_D^3} + \eta \right] = 1 \quad (4)$$

(b) From Eq.(2.21)

$$\ln Z = -\frac{E_c}{kT} - \int_0^{\omega_a} \mathcal{D}(\omega) \ln(1 - e^{-\hbar\omega/kT}) d\omega \quad (5)$$

$$= -\frac{E_c}{kT} - \int_0^{\omega_a} 3N \left[\frac{3\omega^2}{\omega_D^3} + \eta \delta(\omega - \omega_E) \right] \ln(1 - e^{-\hbar\omega/kT}) d\omega$$

$$= -\frac{E_c}{kT} - \frac{9N}{\omega_D^3} \int_0^{\omega_a} \omega^2 \ln(1 - e^{-\hbar\omega/kT}) d\omega$$

$$- 3N\eta \int_0^{\omega_a} \delta(\omega - \omega_E) \ln(1 - e^{-\hbar\omega/kT}) d\omega$$

$$\therefore \ln Z = -\frac{E_c}{kT} - \frac{9N}{\omega_D^3} \int_0^{\omega_a} \omega^2 \ln(1 - e^{-\hbar\omega/kT}) d\omega - 3N\eta \ln(1 - e^{-\frac{\hbar\omega_E}{kT}}) \quad (6)$$

Since $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and $U = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V$

$$\begin{aligned}
 U &= E_0 - kT^2 \frac{9N}{\omega_D^3} \int_0^{\omega_0} \frac{\omega^2 \left(-\frac{\hbar\omega}{kT^2}\right) e^{-\frac{\hbar\omega}{kT}}}{\left(1 - e^{-\frac{\hbar\omega}{kT}}\right)} d\omega \\
 &\quad + 3N\eta \frac{kT^2 \left(-\frac{\hbar\omega_E}{kT^2}\right) e^{-\frac{\hbar\omega_E}{kT}}}{\left(1 - e^{-\frac{\hbar\omega_E}{kT}}\right)} \\
 &= E + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_0} \frac{\omega^3}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)} d\omega + \frac{3N\eta \hbar\omega_E}{\left(e^{\frac{\hbar\omega_E}{kT}} - 1\right)}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \left(\frac{\partial U}{\partial T}\right)_V = C_V &= \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_0} \frac{\left(-\frac{\hbar\omega}{kT^2}\right) \left(-e^{\frac{\hbar\omega}{kT}}\right)}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)^2} \omega^3 d\omega \\
 &\quad + \frac{3N\eta \hbar\omega_E \left(-\frac{\hbar\omega_E}{kT^2}\right) \left(-e^{\frac{\hbar\omega_E}{kT}}\right)}{\left(e^{\frac{\hbar\omega_E}{kT}} - 1\right)^2}
 \end{aligned}$$

Now define $\theta_D = \frac{\hbar\omega_D}{k}$, $\theta_E = \frac{\hbar\omega_E}{k}$ and $\theta_0 = \frac{\hbar\omega_0}{k}$

let $x = \frac{\hbar\omega}{kT}$, then using the normalization condition (4) and $Nk = R$, we get,

$$\begin{aligned}
 C_V = \left(\frac{\partial U}{\partial T}\right)_V &= 3R \left\{ 3 \left(\frac{T}{\theta_0}\right)^3 (1-\eta) \int_0^{\theta_0/T} \frac{e^x x^4}{(e^x - 1)^2} dx \right. \\
 &\quad \left. + \eta \frac{(\theta_E/T)^2 e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \right\}
 \end{aligned}$$

where $\left(\frac{T}{\theta_D}\right)^3 = \left(\frac{T}{\theta_0}\right)^3 \left(\frac{\theta_0}{\theta_D}\right)^3 = \left(\frac{T}{\theta_0}\right)^3 \left(\frac{\omega_0}{\omega_D}\right)^3 = \left(\frac{T}{\theta_0}\right)^3 (1-\eta)$ was used.

$$\therefore C_V = 3R \left\{ (1-\eta) H(\theta_0/T) + \eta E(\theta_E/T) \right\}$$

Problem 2.5

Consider a case of two atoms' vibration in one dimension.

Total kinetic energy of the system is

$$E_{kin} = \frac{1}{2} m \dot{x}_1^2 + \frac{1}{2} m \dot{x}_2^2$$

and potential energy of the system is

$$E_{pot}(x_1, x_2) = E_{pot}(0,0) + \left(\frac{\partial E_{pot}}{\partial x_1} \right)_{\substack{x_1=0 \\ x_2=0}} x_1 + \left(\frac{\partial E_{pot}}{\partial x_2} \right)_{\substack{x_1=0 \\ x_2=0}} x_2 + \frac{1}{2} \sum_{i=1}^2 \sum_{j=1}^2 \frac{\partial^2 E_{pot}}{\partial x_i \partial x_j} x_i x_j$$

Since at equilibrium $E_{pot}(0,0) = E_0$ and

$$\frac{\partial E_{pot}}{\partial x_1} = \frac{\partial E_{pot}}{\partial x_2} = 0, \quad \text{defining} \quad \frac{\partial^2 E_{pot}}{\partial x_i \partial x_j} = b_{ij}$$

then

$$E_{pot}(x_1, x_2) = E_0 + \frac{1}{2} (b_{11} x_1^2 + 2b_{12} x_1 x_2 + b_{22} x_2^2)$$

Thus the total energy of this system is

$$E = E_0 + \frac{1}{2} [m(\dot{x}_1^2 + \dot{x}_2^2) + (b_{11} x_1^2 + 2b_{12} x_1 x_2 + b_{22} x_2^2)] \quad (A)$$

(a) Vibration frequencies

Equation of motion of two atoms

$$F_1 = -\left(\frac{\partial E_{\text{pot}}}{\partial x_1}\right)_{x_2} = -(b_{11}x_1 + b_{12}x_2) = m \frac{d^2 x_1}{dt^2} \quad (1)$$

$$F_2 = -\left(\frac{\partial E_{\text{pot}}}{\partial x_2}\right)_{x_1} = -(b_{12}x_1 + b_{22}x_2) = m \frac{d^2 x_2}{dt^2} \quad (2)$$

Assuming the solutions in form of simple harmonic motion,

$$x_1 = C_1 e^{-2\pi i \nu t}, \quad x_2 = C_2 e^{-2\pi i \nu t} \quad (3)$$

and substituting them into (1) and (2), we get,

$$\left. \begin{aligned} b_{11}C_1 + b_{12}C_2 &= 4\pi^2 \nu^2 m C_1 \\ b_{12}C_1 + b_{22}C_2 &= 4\pi^2 \nu^2 m C_2 \end{aligned} \right\} \quad (4)$$

$$\text{or } \left. \begin{aligned} (b_{11} - 4\pi^2 \nu^2 m)C_1 + b_{12}C_2 &= 0 \\ b_{12}C_1 + (b_{22} - 4\pi^2 \nu^2 m)C_2 &= 0 \end{aligned} \right\} \quad (4)$$

For non trivial solution of eq. (4), the determinant of coefficient matrix must vanish.

$$\text{i.e., } \begin{vmatrix} b_{11} - 4\pi^2 \nu^2 m & b_{12} \\ b_{12} & b_{22} - 4\pi^2 \nu^2 m \end{vmatrix} = 0$$

$$\text{or } (b_{11} - 4\pi^2 \nu^2 m)(b_{22} - 4\pi^2 \nu^2 m) - b_{12}^2 = 0$$

$$\text{let } 4\pi^2 \omega^2 m = a \quad (5)$$

$$\text{then } a^2 - (b_{11} + b_{22})a - (b_{12}^2 - b_{11}b_{22}) = 0 \quad (6)$$

solving for a

$$\begin{aligned} a_1 &= \frac{1}{2} \left\{ (b_{11} + b_{22}) - \sqrt{(b_{11} + b_{22})^2 + 4(b_{12}^2 - b_{11}b_{22})} \right\} \\ a_2 &= \frac{1}{2} \left\{ (b_{11} + b_{22}) + \sqrt{(b_{11} + b_{22})^2 + 4(b_{12}^2 - b_{11}b_{22})} \right\} \end{aligned} \quad (7)$$

for $a > 0$, $b_{12}^2 < b_{11}b_{22}$ must be held.

(b) Normal Mode Analysis:-

Now define new coordinates q_i 's as in Eq. (2.7)

$$q_1 = C_{11}X_1 + C_{21}X_2$$

$$q_2 = C_{12}X_1 + C_{22}X_2 \quad (8)$$

If the coefficients C_{ij} are chosen according to the prescription Eq. (2.8), then

$$\sum_j C_{ji} C_{je} = \delta_{ie} \quad (9)$$

i.e. for $i=1, e=1$

$$C_{11}C_{11} + C_{21}C_{21} = 1 \rightarrow C_{11}^2 + C_{21}^2 = 1 \quad (10)$$

$i=1, e=2$

$$C_{11}C_{12} + C_{21}C_{22} = 0$$

$i=2, e=1$

$$C_{12}C_{11} + C_{22}C_{21} = 0$$

$i=2, e=2$

$$C_{12}C_{12} + C_{22}C_{22} = 1 \rightarrow C_{12}^2 + C_{22}^2 = 1 \quad (12)$$

$$\text{from (10)} \quad C_{11}^2 = 1 - C_{21}^2$$

$$\text{from (12)} \quad C_{22}^2 = 1 - C_{12}^2$$

Substituting C_{11}, C_{22} into (11) we get,

$$C_{12}^2 (1 - C_{21}^2) = C_{21}^2 (1 - C_{12}^2)$$

$$\therefore C_{12}^2 = C_{21}^2 \quad \text{i.e. } C_{12} = \pm C_{21} \quad (13)$$

$$\text{hence } C_{11}^2 = C_{22}^2 = 1 - C_{12}^2 \quad (14)$$

$$\text{so if } C_{12} = C_{21}, \text{ from (11) } C_{11} = -C_{22}$$

$$\text{if } C_{12} = -C_{21}, \text{ then } C_{11} = C_{22}$$

Then with these coordinates, the original coordinates can be expressed as

$$\begin{aligned} x_1 &= C_{11} q_1 + C_{12} q_2 \\ x_2 &= C_{21} q_1 + C_{22} q_2 \end{aligned} \quad (15)$$

(c) Total Energy in Normal Mode Coordinates

Substituting eq. (15) into eq. (A)

$$\begin{aligned} E = E_0 &+ \frac{1}{2} \left[m (C_{11} \dot{q}_1 + C_{12} \dot{q}_2)^2 + m (C_{21} \dot{q}_1 + C_{22} \dot{q}_2)^2 \right. \\ &+ b_{11} (C_{11} q_1 + C_{12} q_2)^2 + 2 b_{12} (C_{11} q_1 + C_{12} q_2)(C_{21} q_1 + C_{22} q_2) \\ &\left. + b_{22} (C_{21} q_1 + C_{22} q_2)^2 \right] \quad (16) \end{aligned}$$

$$\begin{aligned} = E_0 &+ \frac{1}{2} m \left[(C_{11}^2 + C_{21}^2) \dot{q}_1^2 + (C_{12}^2 + C_{22}^2) \dot{q}_2^2 + 2 (C_{11} C_{12} + C_{21} C_{22}) \dot{q}_1 \dot{q}_2 \right] \\ &+ \frac{1}{2} \left[(b_{11} C_{11}^2 + 2 b_{12} C_{11} C_{21} + b_{22} C_{21}^2) q_1^2 + 2 (b_{11} C_{11} C_{12} + b_{12} C_{12} C_{21} \right. \\ &\quad \left. + b_{12} C_{11} C_{22} + b_{22} C_{21} C_{22}) q_1 q_2 \right. \\ &\quad \left. + (b_{11} C_{12}^2 + 2 b_{12} C_{12} C_{22} + b_{22} C_{22}^2) q_2^2 \right] \end{aligned}$$

Now using (10), (11) and (12)

$$E = E_0 + \frac{1}{2} m [\dot{q}_1^2 + \dot{q}_2^2] + \frac{1}{2} [\text{same as in previous eq}] \quad (17)$$

From the second term on the right we see that the kinetic energy form checks with Eq.(2.10).

Then we claim that terms in the second bracket on the RHS of eq.(17), i.e. the last term on RHS of (17) is of the form:

$$E_{\text{pot}} - E_0 = \frac{1}{2} 4\pi m \nu_1^2 q_1^2 + \frac{1}{2} 4\pi m \nu_2^2 q_2^2 \quad (18)$$

Using q_1 and q_2 as functions of x_1 and x_2 , we have

$$\begin{aligned} \text{RHS of eq. (18)} &= \frac{1}{2} 4\pi m [\nu_1^2 (C_{11}^2 x_1^2 + 2C_{11}C_{21} x_1 x_2 + C_{21}^2 x_2^2) \\ &\quad + \nu_2^2 (C_{12}^2 x_1^2 + 2C_{12}C_{22} x_1 x_2 + C_{22}^2 x_2^2)] \end{aligned}$$

Identifying coefficients of x_1^2 , $x_1 x_2$, x_2^2 in eq.(A)

$$b_{11} = [\nu_1^2 C_{11}^2 + \nu_2^2 C_{12}^2] 4\pi^2 m$$

$$b_{12} = [\nu_1^2 C_{11}C_{21} + \nu_2^2 C_{12}C_{22}] 4\pi^2 m$$

$$b_{22} = [\nu_1^2 C_{21}^2 + \nu_2^2 C_{22}^2] 4\pi^2 m$$

defining as in eq.(5)

$$4\pi^2 m \nu_1^2 = a_1^2 \quad \text{and} \quad 4\pi^2 m \nu_2^2 = a_2^2$$

then

$$b_{11} = a_1^2 C_{11}^2 + a_2^2 C_{12}^2 \quad (19)$$

$$b_{12} = a_1 C_{11}C_{21} + a_2 C_{12}C_{22} \quad (20)$$

$$b_{22} = a_1^2 C_{21}^2 + a_2^2 C_{22}^2 \quad (21)$$

using (13), $C_{11}^2 = C_{22}^2 = 1 - C_{12}^2$ in (19)

$$b_{11} = a_1(1 - c_{12}^2) + a_2 c_{12}^2$$

$$\text{or } b_{11} - a_1 = (a_2 - a_1) c_{12}^2 \quad \dots (22)$$

$$\text{similarly } b_{22} = a_1 c_{12}^2 + a_2(1 - c_{12}^2)$$

$$\therefore b_{22} - a_2 = -(a_2 - a_1) c_{12}^2 \quad \dots (23)$$

from (22) & (23)

$$b_{11} - a_1 = -(b_{22} - a_2) \quad \dots (24)$$

using (7)

$$b_{11} - a_1 = \frac{1}{2} \left\{ (b_{11} - b_{22}) + \sqrt{(b_{11} - b_{22})^2 + 4b_{12}^2} \right\} \quad (25)$$

$$b_{22} - a_2 = \frac{1}{2} \left\{ -(b_{11} - b_{22}) - \sqrt{(b_{11} - b_{22})^2 + 4b_{12}^2} \right\} \quad (26)$$

so relation (24) is satisfied.

Now we use eqs. (13) and (14) in eq. (20), i.e.

$$c_{12} = c_{21} \quad \text{and} \quad c_{11} = -c_{22}$$

$$\text{or } c_{12} = -c_{21} \quad \text{and} \quad c_{11} = c_{22}$$

$$\begin{aligned} b_{12} &= a_1 c_{11} c_{21} - a_2 c_{21} c_{11} \\ &= (a_1 - a_2) c_{11} c_{21} \end{aligned}$$

$$\therefore b_{12}^2 = (a_1 - a_2)^2 c_{11}^2 c_{21}^2$$

using (10), i.e. $c_{11}^2 = 1 - c_{21}^2$, we get

$$b_{12}^2 = (a_1 - a_2)^2 c_{21}^2 (1 - c_{21}^2)$$

or using $c_{21}^2 = c_{12}^2$

$$b_{12}^2 = (a_1 - a_2)^2 c_{12}^2 (1 - c_{12}^2) \quad \dots (27)$$

from (22)

$$C_{12}^2 = \frac{b_{11} - a_1}{a_2 - a_1} \quad \dots (28)$$

from (23)

$$C_{12}^2 = - \frac{b_{22} - a_2}{a_2 - a_1}$$

$$C_{11}^2 = 1 - C_{12}^2 = 1 + \frac{b_{22} - a_2}{a_2 - a_1} = \frac{b_{22} - a_1}{a_2 - a_1} \quad \dots (29)$$

from (27), (28) and (29)

$$b_{12}^2 = \frac{(b_{11} - a_1)}{(a_2 - a_1)} \cdot \frac{(b_{22} - a_1)}{(a_2 - a_1)} \cdot (a_1 - a_2)^2$$

$$= (b_{11} - a_1)(b_{22} - a_1)$$

i.e. $b_{12}^2 = (b_{11} - a_1)(b_{22} - a_1)$

This is the same as eq. (6).

Therefore, the potential energy term is that given by Eq. (2.10).

Finally, we can define the coefficients C 's

from (28) $C_{12}^2 = \frac{b_{11} - a_1}{a_2 - a_1}$

using (7) for a_1 and $a_2 - a_1$, we get

$$C_{12}^2 = \frac{(b_{11} - b_{22}) + \sqrt{(b_{11} - b_{22})^2 + 4b_{12}^2}}{\sqrt{(b_{11} - b_{22})^2 + 4b_{12}^2}} \quad \dots (30)$$

and from (3) and (14) we evaluate C_{11} , C_{21} and C_{22}

If $b_{11} > b_{22}$, $C_{12}^2 > 1$ and C_{11} and C_{22} are complex.

If $b_{11} < b_{22}$, $C_{12}^2 < 1$ and C_{11} & C_{22} are real.

Problem 2.6

The energy of vibration of the i^{th} mode is given by

$$E_i = (j_i + \frac{1}{2}) h \nu_i$$

At 0°K., if the cohesive energy is chosen as the reference energy state, the residual vibrational energy, when all atoms of the solid are in the lowest quantum state, i.e. $j_i = 0$ (for all i) is the zero point energy, and is given by

$$E_{z.p.} = \frac{1}{2} \sum_{i=1}^{3N} h \nu_i = \frac{1}{2} \int_0^{\omega_D} (\hbar \omega) \mathcal{D}(\omega) d\omega$$

$$\text{from Eq. (2.34)} \quad \mathcal{D}(\omega) = \begin{cases} 9N\omega^2/\omega_D^3 & \text{for } 0 \leq \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases}$$

$$\therefore E_{z.p.} = \frac{9N\hbar}{2\omega_D^3} \int_0^{\omega_D} \omega^3 d\omega$$

$$= \frac{9N\hbar}{2\omega_D^3} \frac{\omega_D^4}{4} = \frac{9}{8} Nk \left(\frac{\hbar \omega_D}{k} \right)$$

$$\text{Using } \theta_D = \frac{\hbar \omega_D}{k}, \quad Nk = R$$

$$E_{z.p.} = \frac{9}{8} R \theta_D$$

Problem 2.7

$$S = k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad \text{Eq. (1.17)}$$

$$\ln Z = -\frac{E_0}{kT} - \int_0^\infty g(\nu) \ln(1 - e^{-h\nu/kT}) d\nu \quad \text{Eq. (2.21)}$$

Assume Einstein model: $g(\nu) = 3N\delta(\nu - \nu_E)$

then

$$\ln Z = -\frac{E_0}{kT} - 3N \ln(1 - e^{-h\nu_E/kT})$$

$$\left. \frac{\partial \ln Z}{\partial T} \right|_V = \frac{E_0}{kT^2} + 3N \frac{e^{-h\nu_E/kT} \left(+ \frac{h\nu_E}{kT^2} \right)}{1 - e^{-h\nu_E/kT}}$$

$$\therefore S = k \left[-\frac{E_0}{kT} - 3N \ln(1 - e^{-h\nu_E/kT}) \right] + kT \left[\frac{E_0}{kT^2} + 3N \frac{e^{-h\nu_E/kT} \left(\frac{h\nu_E}{kT^2} \right)}{1 - e^{-h\nu_E/kT}} \right]$$

$$= -3Nk \ln \frac{h\nu_E}{kT} + 3Nk \left(1 - \frac{h\nu_E}{kT} \right)$$

$$\left(\text{Using } e^{-\frac{h\nu_E}{kT}} \approx 1 - \frac{h\nu_E}{kT} \right)$$

$$\therefore S \approx 3Nk \left(1 - \ln \frac{h\nu_E}{kT} \right)$$

As ν_E increases, S decreases.

Problem 2.8

From Eq. (2.33), $\theta_D = \frac{\hbar \omega_D}{k} = \frac{\hbar}{k} \left(\frac{6\pi^2}{v} \right)^{1/3} \bar{c}$

Omitting constants,

$$\bar{c} \sim \frac{1}{\sqrt{\beta \epsilon}}$$

or $\theta_D \sim \frac{1}{v^{1/3} \sqrt{\beta \epsilon}}, \quad \epsilon \sim 1/v$

then $\theta_D \sim \frac{v^{1/6}}{\beta^{1/2}}$

$$\ln \theta_D = \frac{1}{6} \ln v - \frac{1}{2} \ln \beta + \text{const.}$$

$$\therefore \gamma = -\frac{1}{6} + \frac{1}{2} \frac{d \ln \beta}{d \ln v}$$

but $\beta = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{1}{v} \left[\frac{1}{-\left(\frac{\partial p}{\partial v} \right)_T} \right]$

$$\ln \beta = -\ln v - \ln \left[-\left(\frac{\partial p}{\partial v} \right)_T \right]$$

$$\therefore \frac{d \ln \beta}{d \ln v} = -1 - \frac{d \ln \left[-\left(\frac{\partial p}{\partial v} \right)_T \right]}{d \ln v}$$

$$= -1 - \left\{ \frac{v}{-\left(\frac{\partial p}{\partial v} \right)_T} \left(-\frac{\partial^2 p}{\partial v^2} \right)_T \right\}$$

$$= -1 - \frac{v \left(\frac{\partial^2 p}{\partial v^2} \right)_T}{\left(\frac{\partial p}{\partial v} \right)_T}$$

$$\therefore \gamma = -\frac{1}{6} + \frac{1}{2} \left[-1 - v \frac{\left(\frac{\partial^2 p}{\partial v^2} \right)_T}{\left(\frac{\partial p}{\partial v} \right)_T} \right]$$

$$\text{or } \gamma = -\frac{2}{3} - \frac{1}{2} v \frac{\left(\frac{\partial^2 p}{\partial v^2} \right)_T}{\left(\frac{\partial p}{\partial v} \right)_T}$$

CHAPTER 3

Problem 3.1

(a) The unit cell shown in the sketch accompanying the problem statement is a rectangular parallelepiped with the edges (a , b , and c) of unequal length. According to Fig. 3.6, the lattice type is orthorhombic. The corners of the unit cell do not contain atoms. However, two atoms are equidistant from the corners of the unit cell. In addition, the a - b faces of the unit cell share a pair of atoms at the center of these faces. According to Fig. 3.6, this corresponds to the C-type orthorhombic space lattice.

Therefore, the full description of the α -uranium crystal structure is:

Face-centered orthorhombic space lattice with a basis of 2.

Atoms per unit cell: Each corner has 2 atoms shared among 8 contiguous unit cells. For 8 corners, this contributes 2 atoms to the unit cell. The two a - b faces have 2 atoms at their centers. These are divided between 2 unit cells. $\therefore$ faces contribute 2 atoms. So total atoms per unit cell = 4.

(b) Let: V = volume of unit cell
 n = number of atoms in unit cell
 m = mass of atom

then

$$\text{density} = \rho = \frac{n \text{ atoms/unit cell}}{V \text{ cm}^3/\text{unit cell}} \times m \text{ gms/atom}$$

but $A = m N_{av}$

N_{av} : Avogadro's #

A : atomic mass

$$\therefore \rho = \frac{n A}{V N_{av}}$$

(1) UC

$$a = 4.961 \text{ \AA}, V = \frac{1}{4} a^3 \text{ cc/molecule}$$

$$= \frac{1}{4} (4.961)^3 \times 10^{-24} = 3.06 \times 10^{-23} \text{ cc/molecule}$$

($\therefore$ For NaCl structure 4 molecules/unit cell)

$$\begin{aligned} \therefore \rho &= \frac{(M \text{ gms/mole})}{(V \text{ cm}^3/\text{molecule}) (N_{av} \text{ molecules/mole})} \\ &= \frac{(238 + 12)}{(3.06 \times 10^{-23}) (6.023 \times 10^{23})} = 13.54 \text{ gm/cc.} \end{aligned}$$

$$N_u = \frac{1}{3.06 \times 10^{-23}} = 3.28 \times 10^{22} \text{ U-atoms/cc.}$$

(2) UO₂

$$a = 5.470 \text{ \AA} \quad \text{Fluorite structure -}$$

4 molecules UO₂/unit cell

$$V = \frac{1}{4} a^3 = \frac{1}{4} (5.47)^3 \times 10^{-24} = 4.08 \times 10^{-23} \text{ cc./molecule}$$

$$\rho = \frac{(238 + 16 \times 2)}{(4.08 \times 10^{-23}) (6.023 \times 10^{23})} = 10.97 \text{ gm/cc.}$$

$$N_u = \frac{1}{4.08 \times 10^{-23}} = 2.44 \times 10^{22} \text{ U-atoms/cc.}$$

(3) α -U for FC structure 4-atoms/unit cell

$$V = \frac{1}{4} abc = \frac{1}{4} (8.3 \times 10^{-23})$$

$$= 2.075 \times 10^{-23} \text{ cc./atom}$$

$$\rho = \frac{238}{(2.075 \times 10^{-23})(6.023 \times 10^{23})} = 19.04 \text{ gm./cc.}$$

$$N_u = \frac{1}{2.075 \times 10^{-23}} = 4.82 \times 10^{22} \text{ atom-U/cc.}$$

Fuel	Crystal Structure	Lattice Constant	Theoretical density gm./cc.	Theoretical Uranium density (atoms/cc) $\times 10^{-22}$
UO ₂	Fluorite	5.47 Å	10.97	2.44
UC	NaCl	4.961 Å	13.54	3.28
α -U	Face Centered orthorhombic	a = 2.854 Å b = 5.87 Å c = 4.956 Å	19.04	4.82

Problem 3.2 BCC.

close packed plane (011)
or any {011} plane

$a_0 =$ lattice constant

Minimum interatomic
distance $= d = \frac{\sqrt{3}}{2} a_0$

In a unit cell there are 2 atoms

$$\begin{aligned} \text{taking up space} &= 2 \times \frac{4}{3} \pi \left(\frac{d}{2}\right)^3 = \frac{\pi}{3} d^3 \\ &= \frac{\pi}{3} \left(\frac{\sqrt{3}}{2}\right)^3 a_0^3 = \frac{\pi\sqrt{3}}{8} a_0^3 \end{aligned}$$

Volume of a unit cell $= a_0^3$

Therefore fraction of space occupied by

$$\text{hard sphere atoms} = \frac{\pi\sqrt{3}}{8} = 0.68$$

Therefore void fraction $= 32\%$

by comparison, the fcc lattice has a void fraction of 26%.

Problem 3.3

Let a_0 be the bcc edge length.
and a'_0 be the fcc edge length.

If r_0 is the atomic radius, then for touching nearest-neighbors structure

$$4r_0 = \sqrt{3} a_0$$

$$4r_0 = \sqrt{2} a'_0$$

$$\therefore \frac{a'_0}{a_0} = \frac{\sqrt{3}}{\sqrt{2}} = \sqrt{\frac{3}{2}} = 1.225$$

In fcc there are 4 atoms/unit cell

$$\therefore \text{Solid density} = \frac{4m}{a_0'^3} = \rho_{\text{fcc}}$$

In bcc there are 2 atoms/unit cell

$$\therefore \rho_{\text{bcc}} = \frac{2m}{a_0^3}$$

$$\begin{aligned} \therefore \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} &= \left(\frac{a_0}{a'_0}\right)^3 \times 2 = \frac{2}{3} \times \sqrt{\frac{2}{3}} \times 2 \\ &= \frac{4}{3} \times \sqrt{0.667} = 1.089 \end{aligned}$$

For percentage change in volume, from bcc to fcc of the same mass we have

$$\rho_{fcc} = \frac{m}{V_{fcc}}, \quad \rho_{bcc} = \frac{m}{V_{bcc}}$$

$$\therefore \frac{V_{fcc}}{V_{bcc}} = \frac{\rho_{bcc}}{\rho_{fcc}} = \frac{1}{1.089}$$

$\therefore$ percentage change in Volume

$$= \frac{V_{fcc} - V_{bcc}}{V_{bcc}}$$

$$= \frac{V_{fcc}}{V_{bcc}} - 1$$

$$= - \frac{.089}{1.089}$$

$$= - .082$$

$$= \underline{-8.2\%}$$

CHAPTER 4

Problem 4.1

- I) Coulomb energy between unit negative charge on the sphere and $+e$ at the center of the sphere

$$= \frac{(-1) \cdot e}{r} = -\frac{e}{r}$$

- II) For coulomb energy between unit negative charge and charge inside the sphere, consider a volume element dv

$$dv = s^2 \sin \theta d\theta d\phi ds$$

$$\therefore \text{charge in } dv = -\frac{e}{\frac{4}{3}\pi r_0^3} s^2 \sin \theta d\theta d\phi ds$$

- $\therefore$ coulomb energy between negative unit charge and charge in dv

$$= (-1) \cdot \frac{-e}{\frac{4}{3}\pi r_0^3} (s^2 \sin \theta d\theta d\phi ds) \times \frac{1}{l}$$

Then the total coulomb energy between the unit negative charge and negative charge inside the sphere is given by

$$\Phi = \int_{s=0}^r \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \frac{e}{\frac{4}{3}\pi r_0^3} \cdot \frac{s^2 \sin\theta}{[r^2 + s^2 - 2rs\cos\theta]^{\frac{1}{2}}} d\phi d\theta ds$$

(where $\ell^2 = r^2 + s^2 - 2rs\cos\theta$ was used)

let $r^2 + s^2 - 2rs\cos\theta = \ell$

then for constant s , $2rs\sin\theta d\theta = d\ell$

$$\therefore \Phi = \frac{3e}{2r_0^3} \int_{s=0}^r s^2 \left[\int_0^{\pi} \frac{\sin\theta d\theta}{[r^2 + s^2 - 2rs\cos\theta]^{\frac{1}{2}}} \right] ds$$

$$= \frac{3e}{2r_0^3} \int_{s=0}^r \frac{s^2}{2rs} \int_{(r-s)^2}^{(r+s)^2} \frac{d\ell}{\ell^{\frac{1}{2}}} = \frac{3e}{2r_0^3} \int_0^r \frac{s}{2r} \left[2\ell^{\frac{1}{2}} \right]_{(r-s)^2}^{(r+s)^2} ds$$

$$= \frac{3e}{2r_0^3} \left[\int_0^r \frac{2s^2}{r} ds \right] = \frac{3e}{r r_0^3} \left[\frac{s^3}{3} \right]_0^r = \frac{er^2}{r_0^3}$$

Then the total coulomb energy is the sum of that due to positive charge and that due to negative charge inside the sphere, that is, the sum of I) and II).

$$\therefore \text{Total coulomb energy } \Phi_c = -\frac{e}{r} + \frac{er^2}{r_0^3} \\ = -\frac{e}{r} \left[1 - \left(\frac{r}{r_0} \right)^3 \right]$$

Problem 4.2

$$(a) \quad \rho(r) = \left[\frac{e}{\frac{4}{3}\pi r_0^3} \right] A e^{-r/r_0}$$

Consider a unit negative charge on the sphere of radius r . By the same reason as in problem 4.1 the coulomb energy between a unit negative charge and charge in a volume element dv is

$$d\Phi = -\frac{3Ae(-1)}{4\pi r_0^3} \frac{e^{-s/r_0}}{e} \cdot \frac{s^2 \sin\theta ds d\theta d\phi}{(r^2 + s^2 - 2rs\cos\theta)^{1/2}}$$

$\therefore$ Total coulomb energy between unit negative charge and charge inside the sphere is

$$\Phi = \int_{s=0}^r \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\Phi$$

$$= -\frac{3Ae(2\pi)}{4\pi r_0^3} \int_{s=0}^r s^2 e^{-s/r_0} \left[\int_0^{\pi} \frac{\sin\theta d\theta}{[r^2 + s^2 - 2rs\cos\theta]^{1/2}} \right] ds$$

$$= \frac{3Ae}{2r_0^3} \int_{s=0}^r \frac{2s^2}{r} e^{-s/r_0} ds$$

$$= \frac{3Ae}{r_0^3 r} \left[s^2 e^{-s/r_0} (-r_0) \right]_{s=0}^r + 2r_0 \int_0^r s e^{-s/r_0} ds$$

$$= \frac{3Ae}{r_0^3 r} \left[-r^2 r_0 e^{-r/r_0} + 2r_0 \left(s e^{-s/r_0} (-r_0) \right)_{s=0}^r + r_0 e^{-s/r_0} (-r_0) \right]_{s=0}^r$$

$$= \frac{3Ae}{r_0^3 r} \left[-r^2 r_0 e^{-r/r_0} - 2r_0^2 r e^{-r/r_0} - 2r_0^3 e^{-r/r_0} + 2r_0^3 \right]$$

$$\therefore \Phi = \frac{3Ae}{r} \left[2 - e^{-r/r_0} \left\{ \left(\frac{r}{r_0} \right)^2 + 2 \left(\frac{r}{r_0} \right) + 2 \right\} \right]$$

$\therefore$ Total coulomb energy between a unit charge on the sphere of radius r and charge inside the sphere is

$$\Phi_c = -\frac{e}{r} + \frac{3Ae}{r} \left[2 - e^{-r/r_0} \left\{ \left(\frac{r}{r_0} \right)^2 + 2 \left(\frac{r}{r_0} \right) + 2 \right\} \right]$$

Therefore the coulomb energy between the sphere of radius r and a spherical shell of thickness dr at r is

$$dU_c = 4\pi r^2 \frac{e}{\frac{4}{3}\pi r_0^3} A e^{-r/r_0} dr \Phi_c(r)$$

Hence the total coulomb energy for this model is

$$U_c = \int_0^{r_0} dU_c$$

$$= \frac{3e^2 A}{r_0^3} \int_0^{r_0} dr r^2 e^{-r/r_0} \cdot \frac{e}{r} \left\{ -1 + 3A \left[2 - e^{-r/r_0} \left\{ \left(\frac{r}{r_0} \right)^2 + 2 \left(\frac{r}{r_0} \right) + 2 \right\} \right] \right\}$$

$$\therefore U_c = \frac{3e^2 A}{r_0^3} \int_0^{r_0} \left[(6A-1) r e^{-r/r_0} - \frac{3A}{r_0^2} r^3 e^{-r/r_0} - \frac{6A}{r_0} r^2 e^{-r/r_0} + 6A r e^{-r/r_0} \right] dr$$

Using integration by parts, we get

$$U_c = \frac{3e_c^2 A}{r_0^3} \left[(6A-1)r_0^2 \left(1 - \frac{2}{e}\right) - \frac{3Ar_0^2}{16} \left(6 - \frac{38}{e^2}\right) - \frac{3Ar_0^2}{4} \left(2 - \frac{10}{e^2}\right) - \frac{3Ar_0^2}{2} \left(1 - \frac{3}{e^2}\right) \right]$$

(Here charge e is denoted by e_c to avoid confusion with Napierian $e = 2.71828 \dots$)

Value of A

Since the total negative charge inside the sphere of radius r_0 is unity, then

$$\int_0^{r_0} 4\pi r^2 \xi(r) dr = e_c$$

$$\text{and } \xi(r) = \frac{e_c}{\frac{4}{3}\pi r_0^3} A e^{-r/r_0}$$

$$\therefore \int_0^{r_0} 4\pi r^2 \cdot \frac{e_c A}{\frac{4}{3}\pi r_0^3} e^{-r/r_0} dr = e_c$$

$$\begin{aligned} \therefore A &= \frac{r_0^3}{3 \int_0^{r_0} r^2 e^{-r/r_0} dr} = \frac{1}{3(2-5e^{-1})} \\ &= \frac{e}{3(2e-5)} \end{aligned}$$

$$\begin{aligned} U_c &= \frac{e_c^2}{r_0} 3A \left[(6A-1) \left(1 - \frac{2}{e}\right) - \frac{3A}{8} \left(11 - \frac{51}{e^2}\right) \right] \\ &= \frac{e_c^2}{r_0} \frac{e^2}{(2e-5)^2} \left[\frac{5}{e} \left(1 - \frac{2}{e}\right) - \frac{1}{8} \left(11 - \frac{51}{e^2}\right) \right] \end{aligned}$$

$$e = 2.71828$$

$$U_c = -\frac{e^2}{r_c} \cdot 1.015$$

or
$$U_c = -1.015 \frac{e^2}{r_c} \quad (\text{where } e \text{ is electronic charge})$$

Compare this with the result from constant charge density

$$U_c = -\frac{q}{10} \frac{e^2}{r_c}$$

(b)

$$U(r_c) = U_c(r_c) + U(\text{kinetic})$$

$$E_{\text{coh}} = U(r_{\text{eq}})$$

let $U_c = -\frac{C_1}{r_c}, \quad U_{\text{kinetic}} = \frac{C_2}{r_c^2}$

$$\therefore \left. \frac{\partial U_c}{\partial r_c} \right|_{r_{\text{eq}}} = \frac{C_1}{r_{\text{eq}}^2} - \frac{2C_2}{r_{\text{eq}}^3} = 0$$

$$\therefore r_{\text{eq}} = \frac{2C_2}{C_1}$$

Hence for larger C_1 , r_{eq} becomes smaller,

and
$$E_{\text{coh}} = -\frac{C_1}{r_{\text{eq}}} + \frac{C_2}{r_{\text{eq}}^2}$$

$$= -\frac{C_1^2}{4C_2}$$

Clearly, for larger C_1 , the E_{coh} is larger in magnitude. Hence for non-uniform charge distribution model E_{coh} is larger and r_{eq} is smaller than those for uniform charge density.

Problem 4.3

(a) From Eq. (1.55)

$$p = -\left(\frac{\partial U}{\partial V}\right)_{T=0} \quad (1)$$

From Eq. (4.16) and (4.14), the average energy of an electron at 0°K is U_F , where

$$U_F = \frac{3}{5} \epsilon_F \quad \text{and} \quad \epsilon_F = \left(\frac{\hbar^2}{2m}\right) \left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

Hence,

for Fermi gas at 0°K. containing N electrons,

$$U = \frac{3}{5} N \epsilon_F = \frac{3}{10} \frac{\hbar^2}{m} N \left(3\pi^2 \frac{N}{V}\right)^{2/3} \quad (2)$$

$$\text{i.e. } U = A V^{-2/3}, \quad \text{where } A = \frac{3}{10} \frac{\hbar^2}{m} N (3\pi^2 N)^{2/3} \quad (3)$$

Substituting (3) into (1) we get,

$$p = -\left(\frac{\partial U}{\partial V}\right)_{T=0} = \frac{2}{3} A V^{-5/3} = \frac{2}{3} \frac{U}{V} \quad (4)$$

From the definition of Compressibility at 0°K.

$$\begin{aligned} \frac{1}{\beta_c} &= -V \left(\frac{\partial p}{\partial V}\right)_{T=0} = -V \frac{2}{3} A \frac{d}{dV} V^{-5/3} \\ &= \frac{10}{9} A V^{-5/3} \\ &= \frac{10}{9} \cdot \frac{3}{10} \cdot \frac{\hbar^2}{m} N (3\pi^2 N)^{2/3} V^{-5/3} \end{aligned}$$

$$\therefore \boxed{\frac{1}{\beta_c} = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} \left(\frac{N}{V}\right)^{5/3}}$$

(b) In general we have to go back to Eq. (1.23)

$$p = kT \left(\frac{\partial \ln Z}{\partial V} \right)_T \quad \dots (1)$$

Since free electrons constitute an ideal gas of particles obeying Fermi-Dirac statistics, from Eq. (1.51)

$$\ln Z = - \frac{\mu N}{kT} + \sum_k \ln \left[1 + \exp \left(- \frac{\epsilon_k - \mu}{kT} \right) \right] \quad \dots (2)$$

Now, replacing sum over k with density of state integral

$$\ln Z = - \frac{\mu N}{kT} + \int_0^\infty \mathcal{D}(\epsilon) \ln \left[1 + \exp \left(- \frac{\epsilon - \mu}{kT} \right) \right] d\epsilon \quad \dots (3)$$

For Fermi electrons in volume V from Eq. (4.8)

$$\mathcal{D}(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\epsilon} \quad \dots (4)$$

and chemical potential μ is given in terms of N by Eq. (1.52)

$$N = \sum_k \left[\exp \left(\frac{\epsilon_k - \mu}{kT} \right) + 1 \right]^{-1} \quad \dots (5)$$

$$\text{or } N = \int_0^\infty \mathcal{D}(\epsilon) \left[\exp \left(\frac{\epsilon - \mu}{kT} \right) + 1 \right]^{-1} d\epsilon \quad \dots (6)$$

Using eqs. (4) and (6) we get,

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \sqrt{\epsilon} \left[\exp \left(\frac{\epsilon - \mu}{kT} \right) + 1 \right]^{-1} d\epsilon \quad \dots (7)$$

From this relation between T , N/V and μ , determine μ as a function of T and N/V .

i.e. $\mu = \mu(T, N/V)$

Now substituting eq. (4) into eq. (3) we get

$$\ln Z = N \left\{ -\frac{\mu(T, N/V)}{kT} + \frac{1}{(N/V)} \cdot \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \sqrt{\epsilon} \left[1 + \exp\left(-\frac{\epsilon - \mu(T, N/V)}{kT}\right) \right]^{-1} d\epsilon \right\} \quad (8)$$

Since μ is a function of T and N/V , the bracketed term in eq. (8) is a function of the same two variables, or

$$\ln Z = N G(T, N/V) \quad \dots (9)$$

Substituting eq. (9) into eq. (1), we get,

$$p = kT N \left(\frac{\partial G}{\partial V} \right)_T$$

Since N is constant

$$N \frac{\partial}{\partial V} = \frac{\partial}{\partial (N/V)} = - \left(\frac{N}{V} \right)^2 \frac{\partial}{\partial (N/V)}$$

or

$$p = -kT \left(\frac{N}{V} \right)^2 \left[\frac{\partial G(T, N/V)}{\partial (N/V)} \right]_T$$

(c) Jellium model,

$$E_{\text{coh}} = -\frac{A_{\text{coul}}}{r_s} + \frac{A_f}{r_s^2} \quad \dots (1)$$

$$\frac{dE_{cch}}{dr_s} = \frac{A_{coul}}{r_s^2} - \frac{2A_f}{r_s^3} = 0 \quad \text{at equilibrium.} \quad (2)$$

$$\frac{d^2E_{cch}}{dr_s^2} = -2 \frac{A_{coul}}{r_s^3} + \frac{6A_f}{r_s^4} \quad (3)$$

$$V = r_s^3, \quad r_s = 1.30 \text{ \AA}$$

$$\frac{d^2E_{cch}}{dV^2} = \frac{1}{9r_s^4} \frac{d^2E_{cch}}{dr_s^2} = \frac{1}{9r_s^3} \quad \left(\text{since } \frac{dE_{cch}}{dr_s} = 0 \text{ at equilibrium} \right)$$

$$\begin{aligned} \therefore \frac{1}{\beta} &= \frac{1}{9r_s} \frac{d^2E_{cch}}{dr_s^2} = \frac{1}{9r_s} \left[-2 \frac{A_{coul}}{r_s^3} + \frac{6A_f}{r_s^4} \right] \\ &= \frac{2}{9r_s^3} \left(\frac{A_{coul}}{r_s} \right) \left[3 \frac{A_f/r_{seq.}}{A_{coul.}} - 1 \right] \quad (4) \end{aligned}$$

From $r_{seq.}$ calculation, i.e. eq.(2)

$$\begin{aligned} \frac{A_{coul.}}{r_{seq.}} &= \frac{q}{10} \frac{e^2}{r_{seq.}} \quad \left(\text{since } U_c = -\frac{q}{10} \frac{e^2}{r_c} \text{ Eq.(4.4)} \right) \\ &= -\frac{A_{coul}}{r_c} \end{aligned}$$

$$= 1.6 \times 10^{-18} \text{ nt.m.}$$

$$\text{and } \frac{A_f}{A_{coul}} = \frac{1}{2} r_{seq.}$$

$$\therefore \frac{1}{\beta} = \frac{1}{9V} \frac{A_{coul.}}{r_{seq.}} = \frac{1}{9} \times \frac{1.6 \times 10^{-18} \text{ nt.m}}{(1.3)^3 \times 10^{-24} \text{ cm}^3}$$

$$\therefore \boxed{\beta = 1.2 \times 10^{11} \text{ m}^2/\text{m}^2.}$$

From eq. (4) it is clear that, because of coulomb attraction the value of $1/\beta$ is smaller, i.e. coulomb attraction gives a negative contribution to $1/\beta$. Therefore the value of β will be larger due to the coulomb attraction. Thus the value of β in part (c) will be larger than that in part (a).

Problem 4.4Born - Haber cycle

We want standard free energy of formation $\Delta E_f^0 (0^\circ \text{K})$.

Quantity missing in problem statement is $\Delta E_{\text{sub}, \text{M}}^0 (0^\circ \text{K})$.

Energy balance on cycle gives

$$\Delta E_f^0 (0^\circ \text{K}) = -(\Delta E_{\text{sub}, \text{MX}}^0 (0^\circ \text{K}) + D - \Delta E_{\text{sub}, \text{M}}^0 (0^\circ \text{K}))$$

Problem 4.5

CsCl structure

Fig. 2

a = lattice constant

r_0 = nearest neighbor distance

$$r_0 = \frac{\sqrt{3}}{2} a$$

$(C_s)_0 = \text{Central ion} = C_s \text{ in primary unit cell}$

1st term

The 8 Cl ions on the corners of the unit cell are each shared by 8 adjacent unit cells.

$$\therefore 1^{\text{st}} \text{ term} = \frac{1}{8} \times 8 = 1 \quad \left(\frac{e^2}{r_0} \text{ omitted} \right)$$

The 2nd term consists interactions for all ions in a cube of side $3a$ surrounding the central ion. This shell, consists, 26 unit cells - 6 attached to the faces of the primary unit cell (shown in Fig. 1 above) - 12 connected to the edges and 8 attached to the corners, plus the fraction of the Cl ions on the corners of the primary unit cell which are in the secondary cell.

Face cells (6)

$$(Cs)_0 - Cs \text{ separation} = a = \frac{2}{\sqrt{3}} r_0$$

$$\text{interaction} = -\frac{\sqrt{3}}{2} \times 1 = -\frac{\sqrt{3}}{2} \quad (\text{minus sign because like charges})$$

$$y = (Cs)_0 - Cl \text{ separation} = a \sqrt{\left(\frac{3}{2}\right)^2 + \left(\frac{1}{\sqrt{3}}\right)^2}$$

$$= \frac{2}{\sqrt{3}} r_0 \sqrt{\frac{11}{4}} = r_0 \sqrt{\frac{11}{3}}$$

$$\therefore \text{Interaction} = \frac{4}{2} \times \sqrt{\frac{3}{11}} \quad (4 - \text{because } 4 \text{ Cl ions divided by } 2 - \text{because each is only half in the secondary shell})$$

$$\therefore \text{Total interaction of 6 face cells} = 6 \left(-\frac{\sqrt{3}}{2} + 2\sqrt{\frac{3}{11}} \right)$$

Edge cells (12)

$$(Cs)_0 - Cs \text{ separation} = 2 \frac{a}{\sqrt{2}} = \sqrt{2} a = \sqrt{2} \frac{2}{\sqrt{3}} r_0$$

$$\therefore (Cs)_0 - Cs \text{ interaction} = -\frac{\sqrt{3}}{2\sqrt{2}} \times 1 = -\frac{\sqrt{3}}{2\sqrt{2}}$$

$$\begin{aligned}
 y = (Cs)_0 - Cl \text{ separation} &= \sqrt{\left(\frac{3a}{\sqrt{2}}\right)^2 + \left(\frac{a}{2}\right)^2} \\
 &= a \sqrt{\left(\frac{3}{\sqrt{2}}\right)^2 + \left(\frac{1}{2}\right)^2} \\
 &= a \sqrt{\frac{19}{4}} = \frac{2}{\sqrt{3}} \cdot \frac{\sqrt{19}}{2} r_0 = \sqrt{\frac{19}{3}} r_0
 \end{aligned}$$

$$\therefore \text{Interaction} = \frac{2}{4} \times \sqrt{\frac{3}{19}} \quad \left(\begin{array}{l} 2 - \text{number of Cl ions in} \\ \text{secondary shell} \end{array} \right)$$

4 - each only $\frac{1}{4}$ in the shell

$$\therefore \text{Total interaction of edge cells} = 12 \left(-\frac{\sqrt{3}}{2\sqrt{2}} + \frac{1}{2} \sqrt{\frac{3}{19}} \right)$$

$$(Cs)_0 - Cs \text{ separation} = 2r_0$$

$$\therefore \text{Interaction} = -\frac{1}{2} \times 1 = -\frac{1}{2}$$

$$(Cs)_0 - Cl \text{ separation} = 3r_0 = \sqrt{\frac{27}{3}} r_0$$

$$\therefore \text{Interaction} = \frac{1}{8} \times \sqrt{\frac{3}{27}} \quad \left(\begin{array}{l} 1 - \# \text{ of Cl ions in} \\ \text{secondary shell} \\ 8 - \text{only } \frac{1}{8} \text{ in the} \\ \text{shell} \end{array} \right)$$

$$\therefore \text{Total interaction of 8 corner shells} = 8 \left(-\frac{1}{2} + \frac{1}{8} \sqrt{\frac{3}{27}} \right)$$

$$\text{Interaction due to remainder Cl at the corners of primary cell} = \frac{7}{8} \times 8$$

$\therefore$ Second term in Madelung constant due to secondary shell is

$$= 6 \left(-\frac{\sqrt{3}}{2} + 2\sqrt{\frac{3}{11}} \right) + 12 \left(-\frac{\sqrt{3}}{2\sqrt{2}} + \frac{1}{2} \sqrt{\frac{3}{19}} \right) + 8 \left(-\frac{1}{2} + \frac{1}{8} \sqrt{\frac{3}{27}} \right) + \frac{7}{8} \times 8$$

$$= 1.0706 - 4.964 - 3.667 + 7.000 = -0.56$$

Thus we see that the series for Madelung constant

$$M = 1 - 0.56 + \dots$$

does not converge easily.

Problem 4.6

$$(a) \quad E_{\text{coul}} / \text{UO}_2 \text{ molecule} = - \frac{z^2 M e^2}{a},$$

$$M = 11.6365 \quad \dots (1)$$

$$Z = 2 \quad (\text{oxygen charge})$$

Repulsive potentials

$$\begin{array}{lll} \bar{O}^2 - \bar{O}^2 & \text{interaction} & \phi_{oo}(\tau) = b_{oo} e^{-\tau/\xi_{oo}} \\ U^{+4} - U^{+4} & \text{interaction} & \phi_{uu}(\tau) = b_{uu} e^{-\tau/\xi_{uu}} \\ U^{+4} - \bar{O}^2 & \text{interaction} & \phi_{uo}(\tau) = b_{uo} e^{-\tau/\xi_{uo}} \end{array}$$

$$b_{ij} = 627.32 (n_i n_j)^{1/2} g_i g_j \quad \dots (2)$$

$$\xi_{ij} = \frac{a_0}{\frac{1}{2}(g_i + g_j)} \quad ; \quad n_i = \text{total number of electrons in ion} \quad \dots (3)$$

$$a_0 = \text{Bohr radius for H} = .529$$

$$g_o = 1.06, \quad g_u = 1.62$$

Lattice Sum for Repulsive Potentials

$$E_{\text{rep}}^{0-0} = \frac{1}{2} N_o [6 \phi_{oo}(\tau_{oo})]$$

(since there are 6 nearest neighbour atoms as oxygen is in sc lattice)

The factor $\frac{1}{2}$ avoids counting bonds twice when sum over lattice is taken.

$$N_o = 2 N_{uo_2} \quad \text{and} \quad r_{oc} = \frac{1}{2} a \quad (\text{a - lattice constant of fluorite structure})$$

$$\frac{E_{rep}^{o-o}}{N_{uo_2}} = 6 b_{oo} e^{-\frac{(a/2)}{r_{oc}}}$$

$$E_{rep}^{u-u} = \frac{1}{2} N_u [12 \phi_{uu}(r_{uu})] \quad (\text{since there are 12 nearest neighbours as uranium atoms are in fcc lattice})$$

$$N_u = N_{uo_2} \quad \text{and} \quad r_{uu} = a/\sqrt{2}$$

$$\therefore \frac{E_{rep}^{u-u}}{N_{uo_2}} = 6 b_{uu} e^{-\frac{(a/\sqrt{2})}{r_{uu}}}$$

$$E_{rep}^{u-o} = N_u [8 \phi_{uo}(r_{uo})]$$

(since each U^{+4} atom has 8 nearest neighbour O^{2-} atoms at a distance of $r_{uo} = \frac{\sqrt{3}a}{4}$.)

Also there is no need for the factor $\frac{1}{2}$ as sum is over different species.

$$\therefore \frac{E_{rep}^{u-o}}{N_{uo_2}} = 8 b_{uo} e^{-\frac{(\sqrt{3}a/4)}{r_{uo}}}$$

$$\frac{E_{coh}}{N_{uo_2}} = - \frac{Z^2 M e^2}{a} + 6 b_{oo} e^{-\frac{(a/2)}{r_{oc}}} + 6 b_{uu} e^{-\frac{(a/\sqrt{2})}{r_{uu}}} + 8 b_{uo} e^{-\frac{(\sqrt{3}a/4)}{r_{uo}}} \quad (4)$$

$$(b) \quad \frac{d^2 (E_{coh}/N_{UC_2})}{dV^2} = \frac{1}{\beta V}$$

V = Volume per UC_2 molecule.

$$V = \frac{1}{4} a^3 \quad (\text{since 4 } UC_2 \text{ molecules per cube of length } a, \text{ See Fig. 3.12 (b)})$$

$$\frac{d}{dV} = \frac{da}{dV} \frac{d}{da} = \frac{1}{\frac{3}{4}a^2} \frac{d}{da}$$

$$\begin{aligned} \frac{d^2}{dV^2} &= \frac{d}{da} \left(\frac{1}{\frac{3}{4}a^2} \frac{d}{da} \right) \frac{da}{dV} = \frac{1}{\frac{3}{4}a^2} \left[\frac{1}{\frac{3}{4}a^2} \frac{d^2}{da^2} - \frac{8}{3a^3} \frac{d}{da} \right] \\ &= \frac{16}{9a^4} \left[\frac{d^2}{da^2} - \frac{2}{a} \frac{d}{da} \right] \end{aligned}$$

But $\frac{dE_{coh}}{da} = 0$ (since at equilibrium this condition must be satisfied)

$$\frac{d^2 (E_{coh}/N_{UC_2})}{dV^2} = \frac{16}{9a^4} \frac{d^2 (E_{coh}/N_{UC_2})}{da^2} = \frac{4}{\beta a^3}$$

$$\begin{aligned} \therefore \frac{d^2 [E_{coh}/N_{UC_2}]}{da^2} &= \frac{9a}{4\beta} = -2 \frac{Z^2 M e^2}{a^3} + 6 \left(\frac{1}{2s_{cc}} \right)^2 b_{cc} e^{-a/2s_{cc}} \\ &\quad + 6 \left(\frac{1}{12s_{uv}} \right)^2 b_{uv} e^{-a/12s_{uv}} \\ &\quad + 8 \left(\frac{13}{4s_{uo}} \right)^2 b_{uo} e^{-\sqrt{13}a/4s_{uo}} \end{aligned} \quad (6)$$

$$\boxed{\frac{1}{\beta} = \frac{4}{9a} \frac{d^2 [E_{coh}/N_{UO_2}]}{da^2}} \quad \text{from eq.(6)}$$

(c) From eq.(4) the cohesive energy per molecule of UO_2 is

$$\frac{E_{coh}}{N_{UO_2}} = -\frac{Z^2 M e^2}{a} + 6b_{cc} e^{-a/2s_{cc}} + 6b_{uv} e^{-a/\sqrt{2}s_{uv}} + 8b_{uc} e^{-\sqrt{3}a/4s_{uc}} \quad (7)$$

At equilibrium from (5)

$$\frac{dE_{coh}}{da} = 0$$

$$\text{or } \frac{Z^2 M e^2}{a^2} + 6b_{cc} \left(-\frac{1}{2s_{cc}}\right) e^{-a/2s_{cc}} + 6b_{uv} \left(-\frac{1}{\sqrt{2}s_{uv}}\right) e^{-a/\sqrt{2}s_{uv}} + 8b_{uc} \left(-\frac{\sqrt{3}}{4s_{uc}}\right) e^{-\sqrt{3}a/4s_{uc}} = 0 \quad (8)$$

We can substitute for b_{ij} from eq.(3) and s_{ij} from eq.(4) into eq.(8) and solve for 'a' by trial and error. Resulting value of $a = a_0$ can be substituted into eq.(7) to obtain E_{coh}/N_{UO_2} and into eq.(6) to obtain β .

Problem 4.7

(a) Repulsive potentials:

$$U_{XX}^{\text{rep}} = 12 \phi_{XX}^r(\sqrt{2} r_0)$$

$$U_{XM}^{\text{rep}} = 6 \phi_{XM}^r(r_0)$$

$$U_{MM}^{\text{rep}} \cong 0$$

$$E_{\text{coh}} = \frac{U_{\text{tot}}}{N} = \frac{1}{2} \cdot 12 \cdot \phi_{XX}^r(\sqrt{2} r_0) + 6 \phi_{XM}^r(r_0) - \frac{Me^2}{r_0}$$

$$\therefore E_{\text{coh}} = 6 \phi_{XX}^r(\sqrt{2} r_0) + 6 \phi_{XM}^r(r_0) - \frac{Me^2}{r_0} \quad (1)$$

(b)

$$\phi_{XX}^r(r) = b e^{\frac{2R_X}{\epsilon}} e^{-r/\epsilon}$$

$$\phi_{MX}^r(r) = b e^{\frac{(R_X+R_M)/\epsilon}{e}} e^{-r/\epsilon}$$

Neglecting anion-anion repulsive potential

$$A = b e^{\frac{(R_X+R_M)/\epsilon}{e}}$$

$$b e^{\frac{2R_X/\epsilon}{e}} = b e^{\frac{(R_X+R_M)/\epsilon}{e}} e^{\frac{(R_X-R_M)/\epsilon}{e}} = A f$$

$$\text{where } f = e^{\frac{(R_X-R_M)/\epsilon}{e}}$$

$$E_{\text{coh}} = -179 \text{ kcal/mole} = -749.44 \text{ kJoules/mole}$$

$$A = 2.5 \times 10^4 \text{ kcal/mole} = 10.47 \text{ kJoules/mole}$$

$$\gamma_{\text{ceq}} = 0.93 + 1.81 = 2.79 A^\circ$$

$$\xi = 0.321 A^\circ$$

If anion-anion repulsion is included

$$U = 6A f e^{-\sqrt{2} \gamma_{\text{ceq}} / \xi} + 6A e^{-\gamma_{\text{ceq}} / \xi} - \frac{M e^2}{\gamma_{\text{ceq}}}$$

$$f = e^{\frac{(1.81 - 0.79)/0.321}{2.59}} = e^{2.59} = 13.3$$

$$\frac{-\sqrt{2} \gamma_{\text{ceq}} / \xi}{e} = \frac{-(1.414)(2.79)/0.321}{e} = \frac{-12.41}{e} = 4.1 \times 10^{-6}$$

$$\text{correction factor} = (6)(2.5)(13.3)(4.1) \times 10^{-2}$$

$$= 8.18 \text{ kcal/mole}$$

$$= 34.24 \text{ kJoule/mole}$$

$$\therefore \text{error} = \frac{8.18}{179} \times 100$$

$$= \underline{4.6 \%}$$

Problem 4.8

$$(a) \quad \phi(r) = \phi(r_0) + \left. \frac{d\phi}{dr} \right|_{r_0} (r-r_0) + \frac{1}{2} \left. \frac{d^2\phi}{dr^2} \right|_{r_0} (r-r_0)^2$$

$$\left. \frac{d\phi}{dr} \right|_{r_0} = 0 \quad \text{at equilibrium}$$

$$\phi(r_0) = -D$$

(1)

$$\frac{d\phi}{dr} = D(2\alpha) \{ -\exp[-2\alpha(r-r_0)] + \exp[-\alpha(r-r_0)] \}$$

$$\frac{d^2\phi}{dr^2} = 2\alpha D \{ 2\alpha \exp[-2\alpha(r-r_0)] - \alpha \exp[-\alpha(r-r_0)] \}$$

$$\therefore \left. \frac{d^2\phi}{dr^2} \right|_{r_0} = K = 2\alpha^2 D \quad \dots (2)$$

$$\therefore \boxed{\phi(r) = -D + \alpha^2 D (r-r_0)^2} \quad \dots (3)$$

(b) Lattice sum considering only nearest neighbour interactions is

$$E_{\text{coh}} = \frac{1}{2} N \cdot 6 \cdot \phi(r)$$

$$\text{at } r=r_0, \quad \phi(r) = -D$$

$$\therefore \boxed{E_{\text{coh}} = -3ND} \quad \dots (4)$$

$$(c) \quad \frac{1}{\beta} = V \frac{d^2 E_0}{dV^2}$$

E_0 = Energy of lattice at 0°K. for arbitrary nearest neighbour distance r ;

$$E_{\text{coh}} = E_0(r_0)$$

Lattice sum : (nearest neighbours only)

$$E_0(r) = \frac{1}{2} N \cdot 6 \cdot \phi(r)$$

$$\text{SC lattice } V = Nr^3 \quad \frac{dV}{dr} = 3Nr^2$$

$$\frac{d^2}{dV^2} = \frac{dr}{dV} \frac{d}{dr} \left(\frac{dr}{dV} \frac{d}{dr} \right) = \frac{1}{9N^2 r^4} \frac{d^2}{dr^2}$$

$$\left(\text{as } \frac{d}{dr} E_0 = 0 \text{ at } r=r_0 \right)$$

$$\therefore \frac{1}{\beta_0} = Nr_0^3 \frac{\frac{1}{2} N \cdot 6}{9N^2 r_0^4} \frac{d^2 \phi}{dr^2} \bigg|_{r_0}$$

$$= \frac{\kappa}{3r_0}$$

$$\therefore \boxed{\beta_0 = \frac{3r_0}{\kappa} = \frac{3r_0}{2\alpha^2 D}} \quad \text{from eq. (2)}$$

(d) From Problem 2.2 of Chapter 2, planes interact by force constant κ .

Equilibrium separation at $0^\circ\text{K.} = r_0$

$$\text{Velocity of sound} = c_s = \sqrt{\frac{\kappa r_0^2}{m}}$$

simple cubic lattice, $\frac{V}{N} = r_0^3 = \text{Volume/atom}$

$$\text{Debye frequency } \omega_D = c_s \left(6\pi^2 \frac{N}{V} \right)^{1/3}$$

$$\omega_D = \sqrt{\frac{\kappa r_0^2}{m}} \left(\frac{6\pi^2}{r_0^3} \right)^{1/3}$$

$$= \sqrt{\frac{\kappa}{m}} (6\pi^2)^{1/3}$$

$$\text{Gruneisen constant } \gamma = -\frac{V}{\theta_D} \frac{d\theta_D}{dV}$$

$$= \frac{d\omega_D}{dr_0} = 0$$

Problem 4.9

atom density N per unit area

Pair potential ϕ is

$$\phi = -\frac{C}{r^6} + A e^{-r/\epsilon}$$

$$\# \text{ of atoms in differential ring} = 2\pi r dr N$$

Then, potential (i.e. energy) between top atom and the differential ring, $d\phi$

$$d\phi = 2\pi r dr N \phi(l)$$

$$\text{where } l = \sqrt{a^2 + r^2}$$

So potential between an atom and the plane is given by

$$\begin{aligned} \Phi &= 2\pi N \int_0^{\infty} r \left[-\frac{C}{l^6} + A e^{-l/\epsilon} \right] dr \\ &= 2\pi N \int_0^{\infty} \left\{ \frac{-Cr}{(a^2 + r^2)^3} + A r e^{-\sqrt{a^2 + r^2}/\epsilon} \right\} dr \end{aligned}$$

$$\text{Now } \int_0^{\infty} A r e^{-\sqrt{a^2 + r^2}/\epsilon} dr = A \int_a^{\infty} u e^{-u/\epsilon} du$$

$$\therefore \int_0^{\infty} A r e^{-\sqrt{a^2+r^2}/\xi} dr = -A \xi u e^{-u/\xi} \Big|_a^{\infty} - \xi^2 A e^{-u/\xi} \Big|_a^{\infty}$$

$$= +A \xi a e^{-a/\xi} + \xi^2 A e^{-a/\xi}$$

and $-\int_0^{\infty} \frac{C r dr}{(a^2+r^2)^3} = \frac{C}{4(a^2+r^2)^2} \Big|_0^{\infty} = -\frac{C}{4a^4}$

$$\therefore \Phi = \left\{ -\frac{C}{4a^4} + A \xi a e^{-a/\xi} + A \xi^2 e^{-a/\xi} \right\} 2\pi N$$

$$\text{or } \Phi = 2\pi N \left\{ -\frac{C}{4a^4} + \xi^2 A \left(\frac{a}{\xi} + 1 \right) e^{-a/\xi} \right\}$$

At equilibrium, $\frac{\partial \Phi}{\partial a} = 0$, gives,

$$\frac{C}{\xi^6 A} = \left(\frac{a}{\xi} \right)^6 e^{-a/\xi}$$

For given constants $C/\xi^6 A$, there are two solutions but only larger one is the correct answer.

Problem 4.10

Look at the potential energy of the
O ion.

The contribution due to 2 nearest $\ominus$ ions

is $2Ae^{-r_0/\xi} - 2\frac{q^2}{r_0}$

2 next nearest $\oplus$ ions contribute $2\frac{q^2}{2r_0}$

2 third nearest $\ominus$ ions contribute $-2\frac{q^2}{3r_0}$

$$\text{So } U(r_0) = 2Ae^{-r_0/\xi} - \frac{2q^2}{r_0} \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots\right)$$

$$= 2Ae^{-r_0/\xi} - \frac{2(\ln 2)q^2}{r_0}$$

To find the equilibrium radius

$$\text{let } \frac{\partial U(r_0)}{\partial r_0} = 0$$

$$-A\frac{1}{\xi}e^{-r_0/\xi} + (\ln 2)q^2\frac{1}{r_0^2} = 0$$

$$\text{or } Ae^{-r_0/\xi} = \frac{\xi}{r_0^2}(\ln 2)q^2$$

$$\begin{aligned} \text{So } U_{\text{coh}} &= NU(r_0) = N \left[\frac{2\xi}{r_0^2}(\ln 2)q^2 - 2(\ln 2)\frac{q}{r_0} \right] \\ &= \frac{2N}{r_0}(\ln 2)q^2 \left(\frac{\xi}{r_0} - 1 \right) \end{aligned}$$

Problem 4.11

(a) Consider the De-Broglie wave length of the particle $\lambda = \frac{h}{p}$

Allowable quantized particle energy is

$$n \frac{\lambda}{2} = L \Rightarrow n \lambda = \frac{2L}{\lambda}$$

$$\text{or } n_p = \frac{p 2L}{h} \quad \text{or } n_E = \frac{2L}{h} \sqrt{2mE}$$

$$\text{So } g(E) dE = dn_E = \frac{2L}{h} \sqrt{2m} \frac{1}{2\sqrt{E}} dE = \frac{L\sqrt{m}}{h\sqrt{E}} \sqrt{2} dE$$

For each state there are 2 electrons, and the electrons follow Fermi-Dirac distribution.

Thus

$$N = \int_0^{\infty} \frac{2 g(E) dE}{1 + e^{E/\mu/kT}} \quad \dots (1)$$

at $T=0$

$$\frac{1}{1 + e^{E/\mu/kT}} = 1 \quad \text{for } E \leq \mu$$

$$= 0 \quad \text{for } E > \mu \quad \dots (2)$$

$$\text{So } N = \int_0^{\mu} 2 g(E) dE = \int_0^{\mu} \frac{2L}{h} \sqrt{\frac{2m}{E}} dE$$

$$= \frac{2L}{h} \sqrt{2m} \cdot 2 \cdot \sqrt{\mu} \quad \dots (3)$$

$$\therefore \mu^{\frac{1}{2}} = \frac{Nh}{4\sqrt{2m}L}$$

$$\mu = \left(\frac{Nh}{4\sqrt{2m}L} \right)^2 = \frac{N^2 h^2}{32 m L^2} \quad (4)$$

$$(b) \quad \bar{\epsilon} = \frac{1}{N} \int_0^{\infty} \frac{2\epsilon \mathcal{Z}(\epsilon) d\epsilon}{1 + e^{(\epsilon - \mu)/kT}}$$

$$= \frac{L}{Nh} \sqrt{2m} \int_0^{\infty} \frac{2\sqrt{\epsilon}}{1 + e^{(\epsilon - \mu)/kT}} d\epsilon$$

At $0^\circ K$,

$$\frac{1}{1 + e^{(\epsilon - \mu)/kT}} = 1 \quad \text{for } \epsilon \leq \mu$$

$$= 0 \quad \text{for } \epsilon > \mu$$

$$\text{So } \bar{\epsilon} = \frac{2L}{Nh} \sqrt{2m} \int_0^{\mu} \sqrt{\epsilon} d\epsilon$$

$$= \frac{2L\sqrt{2m}}{Nh} \frac{\mu^{3/2}}{3/2} = \frac{4}{3} \frac{L\sqrt{2m}}{Nh} \left(\frac{Nh}{\sqrt{32m}L} \right)^3$$

$$= \frac{4}{3} \sqrt{2m} \frac{N^2 h^2}{32m \sqrt{32m} L^2}$$

$$= \frac{N^2 h^2}{96 m L^2}$$

CHAPTER 5

Problem 5-1

With multicomponent systems, define μ such that

$$dE = Tds - pdv + \sum_i \mu_i dN_i ; \quad \dots (1)$$

- (a) Set $dE = dv = dN_j = 0$, giving

$$-Tds = \mu_i dN_i \Big|_{E, V, N_j}$$

$$\text{or } \mu_i = -T \left(\frac{\partial S}{\partial N_i} \right)_{E, V, N_j}$$

- (b) Now $F = E - TS$, and from eq.(1)

$$dF = dE - Tds - SdT$$

$$= -SdT - pdv + \sum_i \mu_i dN_i$$

- Set $dT = dv = dN_j = 0$, giving

$$dF = \mu_i dN_i \Big|_{T, V, N_j} \text{ or } \mu_i = \left(\frac{\partial F}{\partial N_i} \right)_{T, V, N_j}$$

- (c) Also $G = E - TS + pV$, and from eq.(1)

$$dG = dE - Tds - SdT + pdv + Vdp$$

$$= -SdT + Vdp + \sum_i \mu_i dN_i$$

- Set $dT = dp = dN_j = 0$, giving

$$dG = \mu_i dN_i \Big|_{T, p, N_j} \text{ or } \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, p, N_j}$$

Problem 5.2

- (a) Consider the electrons inside the metal as phase I and the electrons outside as phase II.

At equilibrium $\mu_I^0 = \mu_{II}^0$

(where the superscript 0 indicates the same reference point)

Phase II is low density, so treat electrons (II) as non-interacting particles (no collisions, no space-charge)

Therefore from classical statistics $Z = \frac{z^N}{N!}$

$$\frac{\partial \ln Z}{\partial N} = \frac{\partial}{\partial N} (N \ln z - (N \ln N - N))$$

$$= \ln(z/N) \quad (\text{where } \ln N! \approx N \ln N - N \text{ is Stirling's approximation})$$

$$\therefore \mu_{II} = -kT \left(\frac{\partial \ln Z}{\partial N} \right)_{V,T} = -kT \ln(Z/N).$$

where $Z = Z_{tr}$ for ideal gas of fermions:

$$Z_{tr} = 2V \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

$$\therefore \mu_{II} = -kT \ln \left\{ \frac{2V_{II}}{N_{II}} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right\}$$

Suppose for common energy reference we choose E_c .

$$\therefore \mu_{I}^{\circ} = \mu_I$$

$$\text{Then } \mu_{II}^{\circ} = \mu_I^{\circ} + \phi + \mu_{II}$$

$$\therefore \mu_{II} = -\phi$$

$$\text{Also } \frac{V_{II}}{N_{II}} = \frac{1}{n_{II}}$$

$$\therefore n_{II} = 2 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-\phi/kT}$$

(b) The rate at which gaseous electrons strike surface $= \frac{1}{4} n \bar{v}$

where $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$ = mean velocity of Boltzmann distribution

$$\text{The surface impingement rate} = j_x = n \sqrt{\frac{kT}{2\pi m}}$$

$$\text{setting } n = n_{II}, m = m_e$$

then electrons in phase II incident on surface is

$$j_{IIx} = n_{II} \sqrt{\frac{kT}{2\pi m_e}}$$

$$= \left(\frac{4\pi m_e k^2}{h^3} \right) T^2 e^{-\phi/kT} \quad \text{per unit time per unit area}$$

If no electrons are reflected from the surface, then at equilibrium the same current is emitted by the metal; using the principle of detailed balance:

$$\therefore j = \left(\frac{4\pi m_e e k^2}{h^3} \right) T^2 e^{-\phi/kT}$$

charge per unit time per unit area

This treatment does not show the validity of the answer in non-equilibrium conditions.

Problem 5.3

$$a) \quad K = \frac{n_e n_{\text{Cs}^+}}{n_{\text{Cs}}} = \frac{\gamma_e \gamma_{\text{Cs}^+}}{\gamma_{\text{Cs}}} e^{-I/kT} \quad \left(\begin{array}{l} \text{from law of} \\ \text{mass action} \end{array} \right)$$

$$\gamma_{\text{Cs}^+} = \left(\frac{2\pi m_{\text{Cs}} kT}{h^2} \right)^{3/2}$$

$$\gamma_{\text{Cs}} = 2 \left(\frac{2\pi m_{\text{Cs}} kT}{h^2} \right)^{3/2} \quad \left(\begin{array}{l} \text{two spin states of} \\ \text{1s electron} \end{array} \right)$$

$$\frac{n_{\text{Cs}^+}}{n_{\text{Cs}}} = \frac{\gamma_e}{n_e} \left(\frac{\gamma_{\text{Cs}^+}}{\gamma_{\text{Cs}}} \right) e^{-I/kT} = \frac{1}{2} \frac{\gamma_e}{n_e} e^{-I/kT}$$

b)

Detailed balance:

$$J_{\text{Cs}^+} = \frac{1}{4} (n\bar{v})_{\text{Cs}^+}$$

$$J_{\text{Cs}} = \frac{1}{4} (n\bar{v})_{\text{Cs}}$$

$$\therefore \frac{J_{\text{Cs}^+}}{J_{\text{Cs}}} = \frac{n_{\text{Cs}^+}}{n_{\text{Cs}}} = \frac{K}{n_e} = \frac{1}{2} \frac{\gamma_e}{n_e} e^{-I/kT}$$

$$z_{e^-} = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2}$$

From the previous problem

$$n_e = 2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\phi/kT} = z_{e^-} e^{-\phi/kT}$$

$$\therefore \frac{n_e}{z_{e^-}} = e^{-\phi/kT}$$

$$\therefore \frac{J_{Cs^+}}{J_{Cs}} = \frac{1}{2} e^{-(I-\phi)/kT}$$

(Saha - Langmuir equation)

Problem 5.4

Eq. (1.51) is $\ln Z = -\frac{\mu N}{kT} + \sum_k \ln [1 + e^{-(\epsilon_k - \mu)/kT}]$

Eq. (1.52) is $N = \sum_k [1 + e^{(\epsilon_k - \mu)/kT}]^{-1}$

Eq. (5.15) is $\mu_i = -kT \left(\frac{\partial \ln Z}{\partial N_i} \right)_{T, V, N_j}$

For a single component system $\mu = \mu(T, N/V)$
and $\left(\frac{\partial}{\partial N} \right)_{V, T} = \frac{1}{V} \left[\frac{\partial}{\partial (N/V)} \right]_{T, V}$

$$\therefore \left[\frac{\partial \ln Z}{\partial N} \right]_{T, V} = -\frac{\mu}{kT} - \frac{N/V}{kT} \left[\frac{\partial \mu}{\partial (N/V)} \right]_{T, V} + \frac{1}{V} \sum_k \frac{\partial}{\partial (N/V)} \ln [1 + e^{-(\epsilon_k - \mu)/kT}]$$

$$\frac{1}{V} \sum_k \frac{\partial}{\partial (N/V)} \ln [1 + e^{-(\epsilon_k - \mu)/kT}] = \frac{1}{V kT} \left[\frac{\partial \mu}{\partial (N/V)} \right]_{T, V} \sum_k [1 + e^{(\epsilon_k - \mu)/kT}]^{-1}$$

Substituting eq. (1.52) into the above, we get

$$\begin{aligned} \left[\frac{\partial \ln Z}{\partial N} \right]_{T, V} &= -\frac{\mu}{kT} - \frac{N/V}{kT} \left[\frac{\partial \mu}{\partial (N/V)} \right]_{T, V} + \frac{N/V}{kT} \left[\frac{\partial \mu}{\partial (N/V)} \right]_{T, V} \\ &= -\frac{\mu}{kT} \end{aligned}$$

$$\therefore \left[\frac{\partial \ln Z}{\partial N} \right]_{T, V} = -\frac{\mu}{kT}$$

This is Eq. (5.15) for a single component system.

Problem 5.5

- a) Following the same steps as discussed in Chap. 5 from Eq. (5.29), writing

$$P_c = P_H, \quad P_A = P_{\text{H}_2} \quad \text{and using } a=1, b=0, c=2$$

$$K_P = \left(\frac{2\pi}{h^2}\right)^{\frac{3}{2}(2-1)} (kT)^{\frac{5}{2}(2-1)} \left(\frac{m_H^2}{m_{\text{H}_2}}\right) \frac{1}{(z_2)_{\text{int}}} e^{-\Delta\epsilon_0/kT}$$

$$\text{Since } \frac{m_H^2}{m_{\text{H}_2}} = \frac{1}{2}, \quad \text{and } \Delta\epsilon_0 = D$$

$$\therefore K_P = \left(\frac{\pi}{h^2}\right)^{3/2} (kT)^{5/2} \frac{e^{-D/kT}}{(z_2)_{\text{int}}}$$

- b) Let α be the dissociation coefficient
Then at equilibrium,

From Perfect Gas law $pV = nRT$ (n is no. of moles)

$$\frac{P_{\text{H}_2}}{1-\alpha} = \frac{P_H}{2\alpha} = \frac{P}{1+\alpha} \quad (P \text{ is total pressure})$$

$$\therefore P_{\text{H}_2} = \frac{1-\alpha}{1+\alpha} P \quad \text{and} \quad P_H = \frac{2\alpha}{1+\alpha} P$$

$$\therefore K_P = \frac{P_H^2}{P_{\text{H}_2}} = \frac{4\alpha^2 P^2}{(1+\alpha)^2} \cdot \frac{1+\alpha}{(1-\alpha)P} = \left(\frac{4\alpha^2}{1-\alpha^2}\right) P$$

$$\therefore \alpha^2 (4P + K_P) = K_P$$

$$\therefore \alpha = \sqrt{\frac{K_P}{4P + K_P}}$$

Problem 5.6

$$\Delta S^\circ = c S_c^\circ - a S_A^\circ - b S_B^\circ$$

$$\Delta (H^\circ - H_0^\circ) = c (H_c^\circ - H_{c0}^\circ) - b (H_B^\circ - H_{B0}^\circ) - a (H_A^\circ - H_{A0}^\circ)$$

Eq. (1.17) gives

$$S_i^\circ = k \ln Z_i^\circ + kT \left(\frac{\partial \ln Z_i^\circ}{\partial T} \right)_V$$

Eq. (1.31) gives

$$H_i^\circ - H_{i0}^\circ = kT \left[T \left(\frac{\partial \ln Z_i^\circ}{\partial T} \right)_V + V \left(\frac{\partial \ln Z_i^\circ}{\partial V} \right)_T \right]$$

$$\frac{S_i^\circ}{R} - \frac{H_i^\circ - H_{i0}^\circ}{RT} = \frac{\ln Z_i^\circ - V \left(\frac{\partial \ln Z_i^\circ}{\partial V} \right)_T}{N} \quad (\text{as } R = Nk)$$

Z_i° = partition function above ground state of i

Eq. (5.18) and (5.19) give

$$Z_i^\circ = \frac{V^{N_i}}{N_i!} \left(\frac{2\pi m_i kT}{h^2} \right)^{\frac{3}{2} N_i} (Z_{i0}^\circ)^{N_i}$$

$$\begin{aligned} \ln Z_i^\circ &= N_i \ln V + \frac{3}{2} N_i \ln \left(\frac{2\pi m_i kT}{h^2} \right) + N_i \ln (Z_{i0}^\circ)_{\text{int.}} \\ &\quad - N_i \ln N_i + N_i \end{aligned}$$

$$\therefore V \left(\frac{\partial \ln Z_i^\circ}{\partial V} \right)_T = N_i$$

$$\therefore \left[\frac{S_i^\circ}{R} - \frac{H_i^\circ - H_{i0}^\circ}{RT} \right] = \ln \left[\left(\frac{2\pi m_i kT}{h^2} \right)^{\frac{3}{2}} (Z_{i0}^\circ)_{\text{int.}} \left(\frac{V}{N_i} \right) \right]$$

$$\therefore \exp \left[\frac{\Delta S^\circ}{R} - \frac{\Delta(H^\circ - H_0^\circ)}{RT} \right] = \frac{\left(\frac{2\pi m_c kT}{h^2} \right)^{3/2 c}}{\left(\frac{2\pi m_B kT}{h^2} \right)^{3/2 b} \left(\frac{2\pi m_A kT}{h^2} \right)^{3/2 a}} \cdot \frac{(\gamma_c^\circ)_{\text{int.}}^c}{(\gamma_B^\circ)_{\text{int.}}^b (\gamma_A^\circ)_{\text{int.}}^a} \cdot \left(\frac{V}{N} \right)^{(c-a-b)}$$

But $\frac{N}{V} = n = \frac{P_0}{kT}$ molecules/cc

Note as P_0 , V and T are same for all three species, $N_A = N_B = N_c = N$

With $P_0 = 1 \text{ atm.} = 10^6 \text{ dynes/cm}^2$,

$$\exp \left[\frac{\Delta S^\circ}{R} - \frac{\Delta(H^\circ - H_0^\circ)}{RT} \right] = \left(\frac{2\pi}{h^2} \right)^{\frac{3}{2}(c-a-b)} \frac{(kT)^{\frac{3}{2}(c-a-b)}}{(10^6)^{(c-a-b)}} \cdot \left(\frac{m_c^c}{m_A^a m_B^b} \right)^{\frac{3}{2}} \cdot \frac{(\gamma_c^\circ)_{\text{int.}}^c}{(\gamma_A^\circ)_{\text{int.}}^a (\gamma_B^\circ)_{\text{int.}}^b}$$

agrees with Eq. (5.29) with additional factor of $(10^6)^{(c-a-b)}$ to convert partial pressures from dynes/cm² in Eq. (5.29) to atmospheres in Eq. (5.59)

Problem 5.7

(a) The total partition function of the system is

$$Z = \frac{z_e^{N_e}}{N_e!} \cdot \frac{z_h^{N_h}}{N_h!} \cdot z_b^{N_b} \quad \text{--- (1)}$$

(b) The criterion for equilibrium is

$$\mu_b = \mu_e + \mu_h \quad \text{--- (2)}$$

$$(c) \quad \mu_b = -kT \frac{\partial \ln Z}{\partial N_b} = -kT \ln z_b \quad \text{--- (3)}$$

$$\mu_e = -kT \ln(z_e/N_e) \quad \text{--- (4)}$$

$$\mu_h = -kT \ln(z_h/N_h) \quad \text{--- (5)}$$

(d) From eqs. (2)-(5) we have

$$z_b = \frac{z_e z_h}{N_e N_h} \quad \therefore N_e N_h = \frac{z_e z_h}{z_b}$$

Referring to the common ground state

$$\frac{z_e z_h}{z_b} = \frac{z_e^0 z_h^0}{z_b^0} e^{-\Delta E_0/kT}$$

Since conduction electrons and holes are to be treated as ideal gas components with purely translational energy and possessing two spin states,

then
$$z_e^0 = 2V \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2}$$

$$z_h^0 = 2V \left(\frac{2\pi m_h kT}{h^2} \right)^{3/2}$$

Bound electrons are treated as 3D oscillators with very large ν

$$z_b^0 = \left(1 - e^{-h\nu/kT} \right)^{-3} \quad \left(\text{as } h\nu/kT \rightarrow \infty \right. \\ \left. z_b^0 \rightarrow 1 \right)$$

$$n_e = \frac{N_e}{V} ; \quad n_h = \frac{N_h}{V} \quad (\text{concentration})$$

$$\therefore n_e n_h = 4 \left(\frac{2\pi m_e kT}{h^2} \right)^3 e^{-\Delta E_c/kT} \quad (m_e = m_h)$$

This is the law of mass action for the mixture.

Problem 5.8

(a)

Phase Rule: $F = C - P + 2 \Rightarrow$ $C = \text{components} = 2 (M \text{ and } O)$
 $P = \text{phases} = 3 (\text{metal, oxide, gas})$
 $F = \text{degrees of freedom} = 1 (T \text{ or } P_{O_2})$

Since the free energy change occurs only in the oxygen compression step, (it is given by Eq. (5.52)) the free energy of the equilibrium mixture G is given by

$$G = N_M G_M^\circ + N_{MO_2} G_{MO_2}^\circ + N_{O_2} [G_{O_2}^\circ + RT \ln P_{O_2}]$$

Criterion of chemical equilibrium is

$$\mu_M + \mu_{O_2} = \mu_{MO_2}$$

$$\mu_M = \left(\frac{\partial G}{\partial N_M} \right)_{T, P_{O_2}, N_{O_2}, N_{MO_2}} = G_M^\circ$$

Similarly

$$\mu_{MO_2} = G_{MO_2}^\circ$$

By Eq. (5.54)

$$\mu_{O_2} = G_{O_2}^\circ + RT \ln P_{O_2}$$

$$\therefore G_M^\circ + G_{O_2}^\circ - G_{MO_2}^\circ = -RT \ln P_{O_2}$$

ΔG° = standard free energy of reaction

$$= G_{MO_2}^\circ - G_{O_2}^\circ - G_M^\circ$$

$$\therefore \Delta G^\circ = RT \ln P_{O_2}$$

- (b) If P_{O_2} is reduced below the equilibrium value, the $MO_2(s)$ phase changes into $M(s)$ and $O_2(g)$. This process continues until the oxide phase has completely disappeared.

Problem 5.9(a) Helium Criterion of Equilibrium:-

$$\mu_g = \mu_s \quad (g - \text{gas} ; s - \text{solid})$$

Reference energy : Isolated gas atom with zero kinetic energy (0°K.)

Gas phase He:

$$\mu_g = -kT \frac{\partial \ln Z_g}{\partial N_g}$$

From Eq. (5.16)

$$Z_g = \frac{z_g^{N_g}}{N_g!}$$

$$\therefore \mu_g = -kT \ln(z_g/N_g)$$

From Eq. (5.18)

$$z_g = \frac{V_g}{\lambda^3}$$

where

$$\lambda = \frac{h}{\sqrt{2\pi m k T}} = \text{thermal-wave length} \quad (\text{Eq. (1.73)})$$

He in solid

Einstein oscillation in 3 dimensions (Eq. (2.19))

$$Z_s = \left\{ \frac{N_s!}{N! (N_s - N)!} \right\} \left[1 - e^{-h\nu/kT} \right]^{-3N} e^{-N\epsilon_g/kT}$$

where the exponential term accounts for the difference between the reference energy and the zero point energy of He atoms in the solid.

$$\therefore \ln Z_s = \ln \left[\frac{N_s!}{N! (N_s - N)!} \right] + 3N \ln z_s^0 - \frac{N\epsilon_g}{kT}$$

where

$$z_s^0 = \left[1 - e^{-h\nu/kT} \right]^{-1} \cong \frac{kT}{h\nu} = \text{single particle partition function of dissolved atom measured from ground vibrational state.}$$

Using Stirling's approximation and taking derivative of $\ln Z_s$ (c.f. Eqs (5.42) and (5.31))

$$\mu_s = -kT \left(\frac{\partial \ln Z_s}{\partial N} \right) = -kT \left[-\ln N + \ln(N_s - N) + 3 \ln \beta_s^0 - \frac{\epsilon_g}{kT} \right]$$

Using criterion of Chemical Equilibrium:

$$\ln \left(\frac{V_g}{\lambda^3 N_g} \right) = -\ln \left(\frac{N}{N_s - N} \right) + \ln (\beta_s^0)^3 - \frac{\epsilon_g}{kT}$$

$$\text{or} \quad \frac{1}{\lambda^3} \frac{V_g}{N_g} \left(\frac{N}{N_s - N} \right) \frac{1}{(\beta_s^0)^3} = e^{-\epsilon_g/kT}$$

Ideal gas law:

$$\frac{N_g}{V_g} = \frac{P}{kT}$$

Dilute Solution:

$$N_s \gg N$$

$$\frac{N}{N_s} = X, \quad \text{atom fraction of dissolved He}$$

$$\therefore \frac{P}{X} = kT \left(\frac{h\nu}{kT} \right)^3 \left(\frac{2\pi m kT}{h^2} \right)^{3/2} e^{\epsilon_g/kT}$$

(b) Hydrogen

In considering the equilibrium

part (a) is applicable except that z_g must be multiplied by 2 to account for the 2 spin states of the 1s electron in the H atom. This factor does not appear for the dissolved H atom, which has been stripped of its electron. In addition the sign of the heat of solution term in μ_s is changed, since it takes energy to force H atoms into a metal, whereas energy is required to force H atoms out of a metal.

Also, we must use N_I instead of N_s for the hydrogen analysis. We set $N_I/N_s = \alpha$, a constant for a given lattice and hydrogen dissolution site.

The H-atom pressure P_I in equilibrium with

an atom fraction x of hydrogen in the metal is therefore obtained by the methods of part (a) as:

$$\frac{P_1}{x} = \frac{2kT}{\alpha} \left(\frac{h\nu}{kT} \right)^3 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-E_H/kT}$$

m = mass of H atom

For the gas phase equilibrium

$K_p = \frac{P_1^2}{P_2}$ is given from the solution to problem 5.5

So

$$P_1 = \sqrt{P_2} \sqrt{K_p} = \sqrt{P_2} \left(\frac{\pi}{h^2} \right)^{3/4} (kT)^{5/4} \frac{e^{-\frac{1}{2}D/kT}}{\sqrt{(z_2)_{int.}}}$$

where D = dissociation energy of $H_2 \cong 103$ Kcal/mole

$(z_2)_{int.}$ = internal partition function of H_2

$$\therefore \frac{\sqrt{P_2}}{x} = \frac{2}{\alpha} \left(\frac{\pi}{h^2} \right)^{-3/4} (kT)^{-1/4} \sqrt{(z_2)_{int.}} \left(\frac{h\nu}{kT} \right)^3 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-(E_H - \frac{1}{2}D)/kT}$$

Fowler-Smithells equation

Problem 5.10

(a) Equilibrium of a single component.

$$\mu^I = \mu^{II}$$

$$\mu^I = \left. \frac{\partial G}{\partial N^I} \right|_{T,P,N^{II}} = \mu^{II} = \left. \frac{\partial G}{\partial N^{II}} \right|_{T,P,N^I}$$

$$G = N^I g^I + N^{II} g^{II}$$

$$\therefore g^I = g^{II}$$

True.(b) For equilibrium $dG|_{T,P} = 0$.

$$\text{So } dG^I = -dG^{II}$$

$$G^I = N_A^I g_A^I + N_B^I g_B^I, \quad G^{II} = N_A^{II} g_A^{II} + N_B^{II} g_B^{II}$$

$$g^I = g_A^I + g_B^I, \quad g^{II} = g_A^{II} + g_B^{II}$$

$$dG^I = dN_A^I g_A^I + dN_B^I g_B^I = dN_A^I g^I + (dN_B^I - dN_A^I) g_B^I$$

$$dG^{II} = dN_A^{II} g_A^{II} + dN_B^{II} g_B^{II} = dN_A^{II} g^{II} + (dN_B^{II} - dN_A^{II}) g_B^{II}$$

$$\text{So } dN_A^I g^I + (dN_B^I - dN_A^I) g_B^I = -[dN_A^{II} g^{II} + (dN_B^{II} - dN_A^{II}) g_B^{II}]$$

$$\text{But } dN_A^I = -dN_A^{II}, \quad dN_B^I = -dN_B^{II}, \quad g_B^I = g_B^{II} \quad (\text{from part c})$$

$$\therefore dN_A^I g^I = -dN_A^{II} g^{II}$$

$$\therefore g^I = g^{II}$$

True.

(c) For equilibrium, $dG = 0$

$$G = N_A^I g_A^I + N_A^{II} g_A^{II} + N_B^I g_B^I + N_B^{II} g_B^{II}$$

$$dG = dN_A^I g_A^I + dN_A^{II} g_A^{II} + dN_B^I g_B^I + dN_B^{II} g_B^{II} = 0$$

$$dN_A^I = -dN_A^{II} = dN_A$$

$$dN_B^I = -dN_B^{II} = dN_B$$

$$\text{So } dG = dN_A (g_A^I - g_A^{II}) + dN_B (g_B^I - g_B^{II}) = 0$$

Since dN_A and dN_B are independent

$$g_A^I = g_A^{II} \quad \text{and} \quad g_B^I = g_B^{II} \quad \underline{\text{True.}}$$

Problem 5.11

From Eq. (5.26) and $M^{\circ} \rightleftharpoons M^{++} + 2e^{-}$

$$\frac{n_e^2 n_{M^{++}}}{n_{M^{\circ}}} = \frac{2 \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} \left(\frac{2\pi m_{M^{++}} kT}{h^2} \right)^{3/2}}{\left[\frac{2\pi m_{M^{\circ}} kT}{h^2} \right]^{3/2}} e^{-I/kT}$$

(factor 2 in the numerator is for the 2 spin states)

$$\therefore \frac{n_e^2 n_{M^{++}}}{n_{M^{\circ}}} = 4 \left(\frac{2\pi m_e kT}{h^2} \right)^3 e^{-I/kT}$$

From the result of problem 5.2,
we have

$$n_e^2 = 2^2 \left(\frac{2\pi m_e kT}{h^2} \right)^3 e^{-2\phi/kT}$$

$$\text{while } n_M = \frac{P}{kT} = \frac{A}{kT} e^{-\Delta H_b/kT} \quad (\text{using clapeyron Eq.})$$

$$\text{Then } n_{M^{++}} = \frac{A}{kT} e^{(2\phi - I - \Delta H_b)/kT}$$

Problem 6.1

(a)

Crystal [1]

Crystal [2]

(Nu atoms of U + 2 atoms of Xe in each crystal)

The binding energy of Xe-Xe in Uranium medium

is $\phi_{\text{Xe-Xe}} = \Phi_{[1]} - \Phi_{[2]}$, where Φ is the total energy of the crystal.

Qualitatively: The bond between Xe atoms is very weak (Lennard-Jones potential)

In addition, the Xe atom is much bigger in size than the U atom and when two Xe atoms are placed side by side at a distance of the U atom lattice constant they repel each other. Therefore the energy of the crystal [2] is higher than the energy of crystal [1],

$$\text{or } \Phi_{[1]} < \Phi_{[2]} \quad \therefore \phi_{\text{Xe-Xe}} \text{ is negative.}$$

$$(b) \quad E_{BE} = [b_{Xe-V} \phi_{Xe-V} + b_{Xe-Xe} \phi_{Xe-Xe} + b_{V-V} \phi_{V-V}]$$

$$1) \quad E_{BE} = 2 \phi_{Xe-V} = \underline{1.2 \text{ eV}}$$

$$2) \quad E_{BE} = [2 \phi_{Xe-V} + \phi_{Xe-Xe}]$$

$$= 1.2 - 0.7 = \underline{0.5 \text{ eV}}$$

$$3) \quad E_{BE} = 4 \phi_{Xe-V} = \underline{2.4 \text{ eV}}$$

$$4) \quad E_{BE} = 8 \phi_{Xe-V} + 4 \phi_{V-V}$$

$$= 4.8 + 0.4 = \underline{5.2 \text{ eV}}$$

(c)

Law of Mass Action: at equilibrium

$$K = \frac{x_D}{x_D^{\nu_D} x_{Xe}^{\nu_{Xe}}} = \left(\frac{z_D}{z_D^{\nu_D} z_{Xe}^{\nu_{Xe}}} \right) e^{E_{BE}/kT}$$

$$\left(\frac{z_D}{z_D^{\nu_D} z_{Xe}^{\nu_{Xe}}} \right) \approx 1 \quad \text{if excess entropy of mixing} \approx 0$$

x is the molar fraction, i.e. $x_i = \frac{N_i}{\sum N_i}$

$$\therefore (N_V + N_{Xe} + N_D)^{\gamma_V + \gamma_{Xe} - 1} \left(\frac{N_D}{N_V^{\gamma_V} N_{Xe}^{\gamma_{Xe}}} \right) = e^{E_{BS}/kT}$$

This holds for each defect process. For 4 processes in equilibrium simultaneously,

$$N_{Xe}^0 = N_{Xe} + \sum_{i=1}^4 \gamma_{Xe_i} N_{D_i}$$

$$N_V^0 = N_V + \sum_{i=1}^4 \gamma_{V_i} N_{D_i}$$

For ① $\gamma_{V_1} = 1, \gamma_{Xe_1} = 2;$

② $\gamma_{V_2} = 1, \gamma_{Xe_2} = 2;$

③ $\gamma_{V_3} = 2, \gamma_{Xe_3} = 2;$

④ $\gamma_{V_4} = 4, \gamma_{Xe_4} = 2$

$$\begin{aligned} \therefore N_{Xe} &= N_{Xe}^0 - 2 \sum_i N_{D_i} \\ &= N_{Xe}^0 - 2(N_{D_1} + N_{D_2} + N_{D_3} + N_{D_4}) \end{aligned}$$

$$N_V = N_V^0 - (N_{D_1} + N_{D_2} + 2N_{D_3} + 4N_{D_4})$$

$$\begin{aligned} \text{From ①, } & \frac{N_{D_1} (N_V^0 + N_{Xe}^0 - 2N_{D_1} - 3N_{D_2} - 4N_{D_3} - 6N_{D_4})^2}{[N_V^0 - N_{D_1} - N_{D_2} - 2N_{D_3} - 4N_{D_4}] [N_{Xe}^0 - 2N_{D_1} - 2N_{D_2} - 2N_{D_3} - 2N_{D_4}]^2} \\ &= e^{\frac{1.2 \text{ eV}}{kT}} \end{aligned} \quad (1)$$

From (2),

$$\frac{N_{D_2} (N_v^0 + N_{xe}^0 - 3N_{D_1} - 2N_{D_2} - 4N_{D_3} - 6N_{D_4})^2}{[N_v^0 - N_{D_1} - N_{D_2} - 2N_{D_3} - 4N_{D_4}]^2 [N_{xe}^0 - 2N_{D_1} - 2N_{D_2} - 2N_{D_3} - 2N_{D_4}]^2} = e^{\frac{0.5 \text{ eV}}{kT}} \quad \text{--- (2)}$$

From (3),

$$\frac{N_{D_3} (N_v^0 + N_{xe}^0 - 3N_{D_1} - 3N_{D_2} - 3N_{D_3} - 6N_{D_4})^3}{[N_v^0 - N_{D_1} - N_{D_2} - 2N_{D_3} - 4N_{D_4}]^2 [N_{xe}^0 - 2N_{D_1} - 2N_{D_2} - 2N_{D_3} - 2N_{D_4}]^2} = e^{\frac{2.4 \text{ eV}}{kT}} \quad \text{--- (3)}$$

From (4),

$$\frac{N_{D_4} (N_v^0 + N_{xe}^0 - 3N_{D_1} - 3N_{D_2} - 4N_{D_3} - 5N_{D_4})^5}{[N_v^0 - N_{D_1} - N_{D_2} - 2N_{D_3} - 4N_{D_4}]^4 [N_{xe}^0 - 2N_{D_1} - 2N_{D_2} - 2N_{D_3} - 2N_{D_4}]^2} = e^{\frac{5.2 \text{ eV}}{kT}} \quad \text{--- (4)}$$

These 4 equations must be solved simultaneously for N_{D_1} , N_{D_2} , N_{D_3} and N_{D_4} .

Problem 6.2

- (a) From problem 1.5 of chapter 1, we know that

$$C_p - C_v = \left(\frac{\alpha^2 V}{\beta} \right) T$$

where α = coefficient of thermal expansion

β = coefficient of compressibility

V = Volume / mole of UO_2

For an ideal crystal well above its Debye Temperature

$$C_v = 3R \frac{J}{\text{gm-atom-}^\circ\text{K}}$$

Since $C_v = 3R H\left(\frac{\theta_D}{T}\right)$ and

$$H\left(\frac{\theta_D}{T}\right) \rightarrow 1 \text{ as } \frac{\theta_D}{T} \rightarrow 0$$

but since there are 3 atoms per molecule of UO_2

$$C_v = 9R \frac{J}{\text{mole } \text{UO}_2 - ^\circ\text{K}}$$

Then

$$C_p = 9R + \left(\frac{\alpha^2 V}{\beta} \right) T = b + cT$$

$$\text{or } b = 9R \text{ and } c = \frac{\alpha^2 V}{\beta}$$

- (b) Frenkel defects on Oxygen sublattice of UO_2 .
Crystal structure - MX_2 (Fluorite)

N_M = number of U^{+4} ions on normal lattice sites

N_x = number of O^{2-} ions on normal lattice sites

N_{SM} = number of U^{+4} lattice sites in MX_2

N_{SX} = number of O^{2-} lattice sites in MX_2

N_{SI} = Interstitial sites in Fluorite structure

N_{XI} = number of O^{2-} ions on interstitial sites

N_{XV} = number of anion vacancies

For the Fluorite structure

$$N_{SX} = 2 N_{SM} \quad \text{--- (1)}$$

$$N_{SI} = N_{SM} \quad \text{--- (2) (in Fig. 3.12 of chapter 3,}$$

the locations in the center of the SC sublattice of O^{2-} ions which are unoccupied by U^{+4} ions are interstitial sites)

Electrical neutrality gives,

$$4 N_M = 2 N_x + 2 N_{XI} \quad \text{--- (3)}$$

Since the cation sublattice is perfect

$$N_M = N_{SM} \quad \text{--- (4)}$$

$$\text{and } N_{SX} = N_x + N_{XV} \quad \text{--- (5)}$$

From (1), (3), (4) and (5), eliminating N_{SX} , N_{SM} , N_M we get

$$N_{XV} = N_{XI} \quad \text{--- (6)}$$

Law of Mass action gives,

$$\frac{N_{XI}}{N_{SI}} \cdot \frac{N_{XV}}{N_{SX}} = K_{FX} \quad \text{--- (7)}$$

Using (1), (2) and (6)

$$\frac{N_{XI}}{N_{SM}} \cdot \frac{N_{XI}}{2 N_{SM}} = K_{FX}$$

$$\therefore \frac{N_{XI}}{N_{SM}} = \sqrt{2 K_{FX}} \quad \text{--- (8)}$$

$$\frac{N_{XI}}{N_{SM}} = \frac{\text{interstitial Oxygen atoms}}{\text{Uranium atom}} = \frac{\text{moles of interstitial Oxygen}}{\text{mole of } UO_2}$$

$$H = E + pV \rightarrow \Delta H = \Delta E + p \Delta V \quad (\text{at constant pressure})$$

So excess enthalpy $H_{ex} \left(\frac{\text{Joules}}{\text{mole-}UO_2} \right)$ and energy of formation of Frenkel defects $E_F \left(\frac{\text{Joules}}{\text{mole of } N_{XI}} \right)$ have a relation

$$H_{ex} \cong \frac{N_{XI}}{N_{SM}} E_F \quad \text{--- (9)}$$

(neglecting $p \Delta V$ term since it is very small)

$$\text{Since } K_{FX} = e^{\frac{\Delta S_{FX}}{R}} e^{-\frac{E_F}{RT}} \quad \text{--- (10)}$$

then

$$H_{ex} = \sqrt{2} E_F e^{\frac{\Delta S_{FX}}{2R}} e^{-\frac{E_F}{2RT}}$$

Problem 6.3

(a) Octahedral Interstitial

(b) $\langle 100 \rangle$ Split Interstitial

E_I = Increase in energy of crystal when one interstitial atom is added. It includes only those atom-atom interactions which are different from those in perfect crystal

(a) Octahedral Interstitial

$$E_I = 2\phi\left(\frac{a}{2}\right) + 4\phi\left(\frac{a}{\sqrt{2}}\right) + 4\phi\left(\frac{\sqrt{3}}{2}a\right) + \phi\left(\frac{3}{2}a\right)$$

(b) Split Interstitial

Compute the energy of the split configuration and subtract the energy of one normal atom before the interstitial was added:

$$E_I = 2\left[4\phi(l_1) + \phi(a-x) + \frac{1}{2}\phi(2x) + 4\phi(l_2) + \phi(a+x)\right] - \left[8\phi\left(\frac{\sqrt{3}}{2}a\right) + 3\phi(a)\right]$$

(The factor $\frac{1}{2}$ in front of $\phi(2x)$ is necessary to avoid counting twice)

From $\frac{dE_I}{dx} = 0$ at equilibrium, solve for $x = x_{eq}$.

Then $E_I(x_{eq})$ should be compared with E_I for octahedral interstitial. The configuration which has smaller value of E_I is energetically favored.

Problem 6.4

(a)

BCC - Octahedral sites

a_0 = lattice constant

d_m = nearest neighbor distance = $\frac{\sqrt{3}}{2} a_0$ (see problem 3.2)

If the atoms of the lattice are regarded as hard spheres, the diameter of a lattice atom is equal to the nearest neighbor distance i.e. $\frac{\sqrt{3}}{2} a_0$.

For an impurity of diameter d_I to fit in the center of the octahedral site, it must fit between atoms "5" and "6", since the distances between other atoms are larger than the distance between "5" and "6", which is the shortest and equal to a .

$$\text{Hence } \frac{\sqrt{3}}{2} a_0 + (d_I)_{\max} = a_0$$

$$\therefore (d_I)_{\max} = \left(1 - \frac{\sqrt{3}}{2}\right) a_0 = \left(\frac{2}{\sqrt{3}} - 1\right) \frac{\sqrt{3}}{2} a_0$$

$$\therefore (d_I)_{\max} = \left(\frac{2}{\sqrt{3}} - 1\right) d_m$$

$$\text{or } \boxed{(d_I)_{\max} = 0.155 d_m}$$

BCC - Tetrahedral site

The interstitial site is $\frac{1}{4}a_0$ down from the middle of the unit cell edge between atoms 1 and 2. Taking a plane through atoms 1, 5, 6 and 2

If d_{I-1} or d_{I-2} are the distances of the interstitial atom from the atoms 1 or 2 respectively, then

$$d_{I-1} \text{ or } d_{I-2} = \sqrt{\left(\frac{1}{4}a_0\right)^2 + \left(\frac{1}{2}a_0\right)^2} = \frac{\sqrt{5}}{4} a_0$$

Next, taking a plane through atoms 3 and 4 which is perpendicular to the unit cell edge 1-2 and includes the interstitial site, again we can

calculate d_{I-3} or d_{I-4} in precisely the same manner. Since in this plane the relative positions of the atoms are same as in the previous plane we get,

$$d_{I-3} \text{ or } d_{I-4} = \frac{\sqrt{5}}{4} a_0$$

Since $d_m = \frac{\sqrt{3}}{2} a_0$ (nearest neighbor distance)

$$\frac{1}{2}(d_I)_{\max} + \frac{1}{2}d_m = \frac{\sqrt{5}}{4} a_0$$

$$\therefore \frac{1}{2}(d_I)_{\max} = \frac{\sqrt{5}}{4} a_0 - \frac{\sqrt{3}}{4} a_0$$

$$\therefore (d_I)_{\max} = \frac{1}{2}(\sqrt{5} - \sqrt{3})a_0$$

$$\therefore (d_I)_{\max} = (\frac{\sqrt{5}}{\sqrt{3}} - 1)d_m$$

$$\boxed{\therefore (d_I)_{\max} = 0.290 d_m}$$

FCC - Lattice (see fig. 6.2 in chapter 6)

$$d_m = \frac{a_0}{\sqrt{2}}$$

FCC - Octahedral site

$$(d_I)_{\max} + 2 \cdot \frac{a_0}{2\sqrt{2}} = a_0$$

$$\therefore (d_I)_{\max} = a_0(1 - \frac{1}{\sqrt{2}}) = (\frac{2}{\sqrt{2}} - 1)d_m$$

$$\boxed{\therefore (d_I)_{\max} = 0.414 d_m}$$

$$\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$$

$$d_{p-3} = \sqrt{\left(\frac{1}{\sqrt{2}}\right)^2 - \left(\frac{1}{2\sqrt{2}}\right)^2} a_0$$

$$= \frac{\sqrt{3}}{2\sqrt{2}} a_0 = d_{P-2}$$

$$d_{H-P} = \frac{1}{3} \frac{\sqrt{3}}{2\sqrt{3}} a_0$$

$$\begin{aligned} \therefore d_{H-2} &= \sqrt{d_{P-2}^2 - d_{H-2}^2} \\ &= \sqrt{\left(\frac{\sqrt{3}}{2\sqrt{2}}\right)^2 - \left(\frac{1}{3} \frac{\sqrt{3}}{2\sqrt{2}}\right)^2} \quad a_0 \\ &= \frac{a_0}{\sqrt{3}} \end{aligned}$$

$$d_{r-2} = \frac{3}{4} d_{H-2} = \frac{\sqrt{3}}{4} a_0$$

$$\therefore \frac{1}{2} (d_i)_{\max} + \frac{1}{2} \frac{a_0}{\sqrt{2}} = \frac{\sqrt{3}}{4} a_0$$

$$\therefore (d_I)_{\max} = a_b \left(\frac{\sqrt{3}}{2} - \frac{\sqrt{2}}{2} \right)$$

$$\therefore (d_1)_{\max} = d_m \left(\sqrt{\frac{3}{2}} - 1 \right)$$

$$\therefore (d_I)_{max} = 0.223 d_m$$

Each side of tetrahedron = $\frac{1}{\sqrt{2}} a_0$

(b) FCC - Tetrahedral

FCC has $6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4$ atoms per unit cell and there are 8 tetrahedral sites.

Then the chemical formula with saturated tetrahedral sites becomes

Interstitial atoms form SC lattice interseding FCC of M. This is like SC lattice of O atoms interseding FCC lattice of U atoms in UO_2 .

Therefore we have Fluorite structure.

FCC - Octahedral

$$\text{Interstitial site/unit cell} = 1 + 12 \times \frac{1}{4} = 4$$

(center of the cell) (edge-center sites)

$\therefore$ Chemical formula is MI

BCC - Tetrahedral

Interstitial sites/unit cell $= 4 \times 6 \times \frac{1}{2} = 12$
(since there are 4 sites on each of the 6 faces and each site is shared by two unit cells)

$$\text{Host atoms/unit cell} = 2$$

$\therefore$ Chemical formula is MI_6

BCC - Octahedral

$$\text{Interstitial sites / unit cell} = 6 \times \frac{1}{2} + 12 \times \frac{1}{4} = 6$$

(on the faces) (on the edges)

$\therefore$ Chemical formula is MI_3

Problem 6.5Schottky Defects in MX_2

$$G - G(0) = N_{VM} E_{VM} + N_{VX} E_{VX} - kT \ln W$$

N_{SM} = Cation sites , N_M = Cations ,

N_{VM} = Cation vacancies , N_{DM} = Cation impurity ,

N_{SX} = Anion sites , N_X = Anions ,

N_{VX} = Anion vacancies

$$N_{SX} = 2 N_{SM}$$

Electrical neutrality gives,

$$q_M N_M + q_D N_{DM} = q_X N_X$$

$$N_{SM} = N_M + N_{VM} + N_{DM}$$

$$N_{SX} = N_X + N_{VX}$$

$$\therefore q_M (N_{SM} - N_{VM} - N_{DM}) + q_D N_{DM} = q_X (N_{SX} - N_{VX})$$

Dividing by q_M gives,

$$N_{SM} - N_{VM} + \left(\frac{q_D}{q_M} - 1 \right) N_{DM} = \frac{q_X}{q_M} N_{SX} - \frac{q_X}{q_M} N_{VX}$$

but $\frac{q_X}{q_M} = \frac{1}{2}$

$$\therefore \frac{q_X}{q_M} N_{SX} = \frac{1}{2} \times 2 N_{SM} = N_{SM}$$

$$\therefore \left(\frac{q_D}{q_M} - 1\right) N_{DM} + \frac{1}{2} N_{VX} = N_{VM}$$

$$\therefore \frac{dN_{VM}}{dN_{VX}} = \frac{1}{2} \quad \dots (1)$$

$$\begin{aligned} \therefore \frac{\partial G}{\partial N_{VX}} &= \frac{\partial N_{VM}}{\partial N_{VX}} \epsilon_{VM} + \epsilon_{VX} - kT \left[\frac{1}{2} \left(\frac{\partial \ln W_M}{\partial N_{VM}} \right) + \frac{\partial \ln W_X}{\partial N_{VX}} \right] \\ &\quad \text{[using (1)]} \\ &= \frac{1}{2} \epsilon_{VM} + \epsilon_{VX} - kT \left[\left(\frac{\partial \ln W_M}{\partial N_{VM}} \right) \frac{1}{2} + \frac{\partial \ln W_X}{\partial N_{VX}} \right] \\ &\quad \text{[using (1)]} \end{aligned}$$

$\therefore$ In equilibrium

$$0 = \frac{\partial G}{\partial N_{VX}} = \frac{1}{2} \epsilon_S - kT \left[-\frac{1}{2} \ln X_{VM} - \ln X_{VX} \right]$$

$$\left(\text{where } \epsilon_S = \epsilon_{VM} + 2\epsilon_{VX} \right.$$

$$X_{VM} = \frac{N_{VM}}{N_{VM} + N_M + N_{DM}}$$

$$X_{VX} = \frac{N_{VX}}{N_{VX} + N_X} \left. \right)$$

$$\therefore -\frac{\epsilon_S}{kT} = \ln X_{VM} + 2 \ln X_{VX} = \ln (X_{VM} X_{VX}^2)$$

$$\text{or } \boxed{X_{VM} X_{VX}^2 = e^{-\epsilon_S/kT}}$$

Problem 6.6

Let $N_{sm} = N_{sx} = N$ be the number of sites
(Cation or anion)

N_m = number of cations on cation sublattice

N_{vm} = number of vacancies on cation sublattice

N_x = number of anions on anion sublattice

N_{vx} = number of vacancies on anion sublattice

N_{si} = number of interstitial sites

N_{im} = number of cation interstitials

Then $N_{sm} = N_m + N_{vm}$ ---- (1)

$N_{sx} = N_x + N_{vx}$ ---- (2)

Also $K_s = \frac{N_{vm} N_{vx}}{N_{sm} N_{sx}} = X_{vm} \cdot X_{vx}$ [eq. (6.32)] ---- (3)

For Frenkel defect

$K_{fm} = \frac{N_{vm} N_{im}}{N_{sm} N_{si}} = X_{vm} \cdot X_{im}$ [eq. (6.34)] ---- (4)

For electrical neutrality,

$N_m + N_{im} = N_x$ ---- (5)

Substituting (1) and (2) into (5) and using

$N_{sm} = N_{sx}$ we get,

$(N_{sm} - N_{vm}) + N_{im} = N_{sx} - N_{vx}$

or $N_{vm} = N_{vx} + N_{im}$

Dividing by $N_{sm} = N_{sx}$ and using the definition

$$x_{vm} = \frac{N_{vm}}{N_{sm}}, \quad x_{vx} = \frac{N_{vx}}{N_{sx}}, \quad x_{im} = \frac{N_{im}}{N_{si}}$$

and also using $\frac{N_{si}}{N_{sm}} = \beta$, we get

$$x_{vm} = x_{vx} + \beta x_{im} \quad \text{--- (6)}$$

Solving eqs. (3), (4) and (6) for x_{vm} , x_{vx} and x_{im} we have, multiplying (6) by x_{vm} and substituting (3) and (4)

$$\begin{aligned} x_{vm}^2 &= x_{vm} \cdot x_{vx} + \beta x_{vm} \cdot x_{im} \\ &= K_s + \beta K_{FM} \end{aligned}$$

$$\therefore x_{vm} = \sqrt{K_s + \beta K_{FM}}$$

then from (3) and (4)

$$x_{vx} = \frac{K_s}{\sqrt{K_s + \beta K_{FM}}}$$

and

$$x_{im} = \frac{K_{FM}}{\sqrt{K_s + \beta K_{FM}}}$$

Problem 6.7

$$\mu_A = \mu_B$$

$$\mu_i = -kT \left(\frac{\partial \ln Z}{\partial N_i} \right)_{T, V, N_j}$$

If the lattice modes are unaffected Z is given by Eq. (5.41) :

$$Z = \frac{N_{SA}!}{N_A! (N_{SA} - N_A)!} \frac{N_A}{z_A} \frac{N_{SB}!}{N_B! (N_{SB} - N_B)!} \frac{N_B}{z_B} \dots (1)$$

N_L = number of host atoms on normal lattice sites

N_A = number of impurity atoms on A sites

N_B = number of impurity atoms on B sites

When the host atoms are present, their vibrational lattice modes will be affected by the presence of impurity atoms on A and B sites. Then the partition function Z of eq.(1) must be multiplied by

$$\prod_{i=1}^{3N_L} (1 - e^{-h\nu_i/kT})^{-1}$$

let α_A = number of lattice modes which are affected by atoms in A site. The frequency of these modes is changed from ν_i to ν_{iA}

α_B = number of lattice modes affected by an atom on B site, with mode frequency change from ν_i to ν_{iB}

$$\therefore \prod_{i=1}^{3N_L} [1 - e^{-h\nu_i/kT}]^{-1} = [1 - e^{-h\nu_{iA}/kT}]^{-\alpha_A N_A} [1 - e^{-h\nu_{iB}/kT}]^{-\alpha_B N_B} [1 - e^{-h\nu_i/kT}]^{-(3N_L - \alpha_A N_A - \alpha_B N_B)}$$

$$\approx \left(\frac{kT}{h\nu_{iA}}\right)^{\alpha_A N_A} \left(\frac{kT}{h\nu_{iB}}\right)^{\alpha_B N_B} \left(\frac{kT}{h\nu_i}\right)^{3N_L - \alpha_A N_A - \alpha_B N_B}$$

$$= \left(\frac{kT}{h\nu_i}\right)^{3N_L} \left(\frac{\nu_i}{\nu_{iA}}\right)^{\alpha_A N_A} \left(\frac{\nu_i}{\nu_{iB}}\right)^{\alpha_B N_B}$$

$$= Z_L^* \left(\frac{\nu_i}{\nu_{iA}}\right)^{\alpha_A N_A} \left(\frac{\nu_i}{\nu_{iB}}\right)^{\alpha_B N_B}$$

$$\therefore Z = Z_L^* \frac{N_{SA}!}{N_A! (N_{SA} - N_A)!} \cdot \frac{N_A}{Z_A} \left(\frac{\nu_i}{\nu_{iA}}\right)^{\alpha_A N_A} \frac{N_{SB}!}{N_B! (N_{SB} - N_B)!} \cdot \frac{N_B}{Z_B} \left(\frac{\nu_i}{\nu_{iB}}\right)^{\alpha_B N_B}$$

$$\therefore \mu_A = -kT \left(\frac{\partial \ln Z}{\partial N_A} \right)_{T, V, N_B} = -kT \ln \left[\frac{Z_A}{x_A} \right] - kT \alpha_A \ln \left(\frac{\nu_i}{\nu_{iA}} \right) \quad (2)$$

$$= -kT \ln \left[\frac{Z_A}{x_A} \left(\frac{\nu_i}{\nu_{iA}} \right)^{\alpha_A} \right]$$

[The first term on the RHS in eq.(2) follows from Eq.(5.42)]

Similarly $\mu_B = -kT \ln \left[\frac{Z_B}{x_B} \left(\frac{\nu_i}{\nu_{iB}} \right)^{\alpha_B} \right]$

Equating μ_A and μ_B in equilibrium and

factoring out ground state energy from z_A and z_B
 we get in the equilibrium,

$$\frac{x_A}{x_B} = \left(\frac{z_A^0}{z_B^0} \right) \left[\left(\frac{\nu_e}{\nu_{eA}} \right)^{z_A} / \left(\frac{\nu_e}{\nu_{eB}} \right)^{z_B} \right] e^{-\Delta E_0/kT}$$

The additional factor due to the alteration of
 lattice modes is

$$\frac{\left(\frac{\nu_e}{\nu_{eA}} \right)^{z_A}}{\left(\frac{\nu_e}{\nu_{eB}} \right)^{z_B}}$$

Problem 6.8

(a) Since the formula is MX_2

$$N_{sx} = 2 N_{sm} \quad \text{--- (1)}$$

The number of anion interstitial sites in the fluorite structure is equal to the number of cation lattice sites

$$N_{si} = N_{sm} \quad \text{--- (2)}$$

Electrical neutrality gives,

$$4 N_M^{+4} + 2 N_M^{+2} = 2 N_x + 2 N_{xi} \quad \text{--- (3)}$$

Filling of sublattice sites gives,

$$\text{Cation: } N_{sm} = N_M^{+4} + N_M^{+2} \quad (\text{assume perfect}) \quad \text{--- (4)}$$

$$\text{Anion: } N_{sx} = N_x + N_{vx} \quad \text{--- (5)}$$

$$(b) \quad \frac{\text{Oxygen}}{\text{Uranium}} = \frac{N_x + N_{xi}}{N_M^{+4} + N_M^{+2}} = 2 + x \quad \text{--- (6)}$$

or from eq.(4),

$$\frac{N_x + N_{xi}}{N_{sm}} = 2 + x$$

Using eq.(5),

$$\frac{N_{sx} - N_{vx} + N_{xi}}{N_{sm}} = 2 + x$$

Using (4) we get,

$$\boxed{x = 2 \left(\frac{N_{xI} - N_{vX}}{N_{sX}} \right)} \quad (7)$$

When hyperstoichiometric ($x > 0$) $N_{xI} > N_{vX}$,
 when hypostoichiometric ($x < 0$) $N_{xI} < N_{vX}$

(c) Combining eqs (3) and (6)

$$4 N_M^{+4} + 2 N_M^{+2} = 2(2+x)(N_M^{+4} + N_M^{+2}) \quad (8)$$

let
$$\gamma = \frac{N_M^{+2}}{N_M^{+4}}$$

then dividing eq (8) by N_M^{+4} gives,

$$\begin{aligned} 4 + 2\gamma &= 2(2+x)(1+\gamma) \\ &= 2(2+x) + 2\gamma(2+x) \end{aligned}$$

$$\therefore 4 - 2(2+x) = \gamma [2(2+x) - 2]$$

$$\therefore \gamma = \frac{2x}{2-4-2x}$$

$$\therefore \boxed{\frac{N_M^{+2}}{N_{SM}} = \frac{N_M^{+2}}{N_M^{+4} + N_M^{+2}} = \frac{\gamma}{1+\gamma} = \frac{2x}{2-4}} \quad (9)$$

$$(d) \quad K_{FX} = \frac{N_{VX} N_{XI}}{N_{SX} N_{SI}} = \frac{2 N_{VX} N_{XI}}{N_{SX}^2} \quad (10)$$

Solving eqs (7) and (10) simultaneously for N_{VX} and N_{XI} gives,

$$\text{from (7), } N_{XI} = \frac{1}{2} x N_{SX} + N_{VX}$$

$$\text{into (10), } \frac{1}{2} N_{SX}^2 K_{FX} = N_{VX} (N_{VX} + \frac{1}{2} x N_{SX})$$

$$\text{let } y_{VX} = \frac{N_{VX}}{N_{SX}} \quad (\text{site fraction of vacancies on anion sublattice})$$

$$\frac{1}{2} K_{FX} = y_{VX} (y_{VX} + \frac{1}{2} x)$$

$$\therefore y_{VX} = \frac{1}{4} x \left\{ \pm \sqrt{1 + \frac{3K_{FX}}{x^2}} - 1 \right\} \quad (11)$$

If $x \geq 0$, choose + sign in the root,

$$y_{VX} = \frac{1}{4} x \left\{ \sqrt{1 + \frac{3K_{FX}}{x^2}} - 1 \right\}$$

If $x < 0$, choose - sign in the root,

$$y_{VX} = \frac{1}{4} (-x) \left\{ \sqrt{1 + \frac{3K_{FX}}{x^2}} + 1 \right\}$$

$$\text{At } x=0, \quad y_{VX}^{(eq)} = \frac{1}{\sqrt{2}} \sqrt{K_{FX}}$$

Problem 6.9BCC lattice - Octahedral interstitial sites

(a) α = number of interstitial sites per lattice site

$\alpha = 3$ for BCC - Octahedral interstitial sites
(from problem 6.3)

β = number of interstitial sites adjacent to a lattice site

$\beta = 6$ for BCC - Octahedral interstitial sites

β' = number of lattice sites adjacent to an interstitial site

$$\beta' = \frac{\beta}{\alpha} = \frac{6}{3} = 2$$

(b) G , the total free energy is a function of

- (1) the number of free vacancies (N_v^f)
- (2) the number of free interstitials ($N_b - N_p$)
- (3) the number of bound pairs (N_p)

$$G = G(0,0,0) + N_v^f g_v + (N_b - N_p) g_b + N_p g_p - kT \ln W$$

(c) g_p can be written as

$$g_p = g_v + g_b - B_p$$

where B_p is the binding energy of the pair.
It is the energy released when a free vacancy and a free interstitial come together.

(d) Combinatorial factor W

$$W = W_p W_b W_v$$

W_p = number of ways of arranging N_p pairs among available sites.

W_b = number of ways of arranging $N_b - N_p$ free interstitial atoms on sites available to them

N_v = number of ways of arranging N_v^+ vacancies on sites available to them.

Modification of divacancy method to calculate W_p

- (1) start with perfect lattice
- (2) Withdraw an atom (create a vacancy) — add an interstitial
- (3) withdraw another atom — add another interstitial

until N_p pairs are created

1st pair

vacancy — withdraw atom from any of N_s sites.
 interstitial — add to any of β adjacent sites

$\therefore \beta N_s$ ways of creating the first pair.

[Do not divide by 2 as in the divacancy case because the two partners are different entities on different sites]

2nd pair

$N_s - 1$ lattice atoms available to be withdrawn.
(neglect possible exclusion of atoms surrounding the existing pair)

$\beta(N_s - 1)$ ways of making second pair

3rd pair

$\beta(N_s - 2)$ ways of making third pair

$\beta[N_s - (N_p - 1)]$ ways of making N_p^{th} pair

$\therefore$ Total number of ways

$$= [\beta N_s][\beta(N_s - 1)][\beta(N_s - 2)] \dots [\beta(N_s - (N_p - 1))]$$

$$= \beta^{N_p} N_s(N_s - 1) \dots [N_s - (N_p - 1)]$$

$$= \beta^{N_p} \frac{N_s!}{(N_s - N_p)!}$$

But remove permutations among the N_p pairs by dividing by $N_p!$

$$\therefore W_p = \frac{\beta^{N_p} N_s!}{(N_s - N_p)! N_p!} \quad (1)$$

Calculation of W_b

If there are N_p pairs, there are $N_b - N_p$ free impurity atoms to be distributed among $N_{SI} - N_p$ sites,

$$\text{But } N_{SI} = \alpha N_s$$

The number of vacant interstitial sites is

$$(\alpha N_s - N_p) - (N_b - N_p) = \alpha N_s - N_b$$

$$\therefore W_b = \frac{(\alpha N_s - N_p)!}{(N_b - N_p)! (\alpha N_s - N_b)!} \quad (2)$$

Calculation of W_v

If there are N_p pairs and $N_b - N_p$ free interstitials in the lattice, the $N_v^{\dagger}$ free vacancies can be distributed among N_s lattice sites except those that are

- (1) already accounted for in the vacancy-interstitial pairs
- (2) nearest neighbors to one of the $N_b - N_p$ interstitial atoms

$\therefore$ available lattice sites on which to distribute $N_v^{\dagger}$ free vacancies is

$$= N_s - N_p - \beta' (N_b - N_p)$$

number of filled lattice sites

$$= N_s - N_p - \beta'(N_b - N_p) - N_v^f$$

$$\therefore W_v = \frac{[N_s - N_p - \beta'(N_b - N_p)]!}{[N_s - N_p - \beta'(N_b - N_p) - N_v^f]! N_v^f!} \quad (3)$$

(e) Equilibrium occurs when

$$\left(\frac{\partial G}{\partial N_v} \right)_{N_p} = 0 \quad \text{and} \quad \left(\frac{\partial G}{\partial N_p} \right)_{N_v} = 0$$

[assuming that the total number of solute atoms and the total number of solvent atoms remain constant]

$$G = G(0,0,0) + N_v^f g_v + (N_b - N_p) g_b + N_p g_p$$

$$- kT \ln W_p W_b W_v$$

where W_p , W_b and W_v are given by eqs. (1) - (3)

$$N_v^f = N_v - N_p \quad (4), \quad N_s = N_a + N_v \quad (5)$$

where N_v = total number of vacancies
and N_a = total number of solvent atoms

Writing, $\left(\frac{\partial G}{\partial N_p} \right)_{N_a, N_b, N_v} = 0$ we get

$$\begin{aligned}
 & -g_v - g_b + g_p - kT \ln \beta - kT \ln(N_s - N_p) + kT \ln N_p \\
 & + kT \ln(\alpha N_s - N_p) - kT \ln(N_b - N_p) - kT(\beta' - 1) \ln[N_s - \beta'(N_b - N_p) - N_p] \\
 & + \beta' kT \ln[N_s - \beta'(N_b - N_p) - N_v] - kT \ln(N_v - N_p) = 0
 \end{aligned}$$

$$\therefore -B_p - kT \ln \beta = kT \ln \left\{ \frac{N_s - N_p}{N_p} \cdot \frac{N_b - N_p}{\alpha N_s - N_p} \cdot \frac{N_s - \beta'(N_b - N_p) - N_p}{[N_s - \beta'(N_b - N_p) - N_v]^2} (N_v - N_p) \right\}$$

$$(\text{since } \beta' = 3, \therefore \beta' - 1 = 2)$$

$$\therefore \frac{(B_p + kT \ln \beta)/kT}{e} = \frac{N_p}{N_b - N_p} \cdot \frac{\alpha N_s - N_p}{N_v - N_p} \cdot \frac{[N_s - \beta'(N_b - N_p) - N_v]^2}{N_s - \beta'(N_b - N_p) - N_p} \cdot \frac{1}{N_s - N_p}$$

Now since $N_p \ll N_s$

$$N_b \ll N_s$$

and $N_v \ll N_s$ we can neglect N_p, N_v

or $\beta'(N_b - N_p)$ in comparison to N_s or αN_s

$$\therefore \exp[(B_p + kT \ln \beta)/kT] \cong \frac{N_p}{N_b - N_p} \cdot \frac{\alpha N_s}{N_v - N_p} \cdot \frac{N_s^2}{N_s} \cdot \frac{1}{N_s}$$

$\alpha N_s = N_{sI}$, number of octahedral interstitial sites

$N_b - N_p = N_b^f$, number of free solute atoms

$N_v - N_p = N_v^f$, number of free vacancies

$$\therefore \frac{N_p N_{sI}}{N_b^f N_v^f} = \exp[(B_p + kT \ln \beta)/kT] \quad (6)$$

where B_p is the binding energy of the pair, i.e.

$$B_p = g_v + g_b - g_p$$

Now taking, $\left(\frac{\partial G}{\partial N_v}\right)_{N_a, N_b, N_p} = 0$ we get, since

$$N_v^f = N_v - N_p \text{ and } N_s = N_a + N_v$$

$$g_v - kT \ln N_s + kT \ln (N_s - N_p) - \alpha kT \ln (\alpha N_s - N_p) + \alpha kT \ln (\alpha N_s - N_b) - kT \ln [N_s - N_p - \beta' (N_b - N_p)] + kT \ln N_v^f = 0$$

$$\therefore \exp[-g_v/kT] = \frac{N_s - N_p}{N_s} \cdot \frac{[\alpha N_s - N_b]^\alpha}{[N_s - N_p]^\alpha} \cdot \frac{N_v^f}{[N_s - N_p - \beta' (N_b - N_p)]}$$

Again neglecting N_p, N_b in comparison to αN_s we get,

$$\frac{N_v^f}{N_s} = \left[1 - \beta' \frac{N_b - N_p}{N_s - N_p}\right] \exp[-g_v/kT]$$

Again neglecting N_p in comparison to N_s , we get,

$$\frac{N_v^f}{N_s} = \left[1 - \beta' \frac{N_b - N_p}{N_s} \right] \exp[-q_v/kT] \quad \text{--- (7)}$$

Now let us define $x_p = \frac{N_p}{N_s}$ --- (8);

$$x_v^f = \frac{N_v^f}{N_s} \quad \text{--- (9);} \quad (x_b^f)' = \frac{N_b^f}{N_{sI}} \quad \text{--- (10);}$$

$$x_b^f = \frac{N_b^f}{N_s} = \alpha (x_b^f)' \quad \text{--- (11)}$$

Therefore from eq. (6),

$$\frac{x_p}{x_v^f (x_b^f)'} = \exp[(B_p + kT \ln \beta)/kT]$$

$$\begin{aligned} \text{or } x_p &= x_v^f (x_b^f)' \cdot \beta \exp(B_p/kT) \\ &= x_v^f x_b^f \frac{\beta}{\alpha} \exp(B_p/kT) \quad \text{from eq. (11) --- (12)} \end{aligned}$$

If we define

$$x_v = \frac{N_v}{N_s} \quad \text{--- (13); then}$$

$$\begin{aligned} x_v &= x_v^f + x_p = x_v^f \left[1 + \frac{x_p}{x_v^f} \right] \\ &= x_v^f \left[1 + \frac{\beta}{\alpha} x_b^f \exp[B_p/kT] \right] \quad \text{--- (14)} \end{aligned}$$

From eq. (7) we get,

$$x_v^f = (1 - \beta' x_b^f) \exp[-q_v/kT] \quad \text{--- (15)}$$

Defining $x_b = \frac{N_b}{N_s}$, we have $x_b^{\ddagger} = x_b - x_p$.

Substituting this in eq.(15) and neglecting second order terms in concentration, x_v becomes,

$$\begin{aligned} x_v &= x_v^{\ddagger} \left\{ 1 + \frac{\beta}{\alpha} x_b^{\ddagger} \exp[B_p/kT] \right\} \quad [\text{from eq. (14)}] \\ &= (1 - \beta' x_b^{\ddagger}) \left\{ 1 + \beta' x_b^{\ddagger} \exp[B_p/kT] \right\} \exp[-q_v/kT] \\ &\quad [\text{from eq. (15)}] \\ &\quad (\text{since } \beta' = \frac{\beta}{\alpha}) \end{aligned}$$

$$\therefore x_v \cong (1 - \beta' x_b^{\ddagger}) \exp[-q_v/kT] + \beta' x_b^{\ddagger} \exp[-(q_v - B_p)/kT] \quad (16)$$

$$\begin{aligned} \text{Since } x_b &= x_b^{\ddagger} + x_p = x_b^{\ddagger} [1 + \beta' x_v^{\ddagger} \exp(B_p/kT)] \quad [\text{from eq. (12)}] \\ &= x_b^{\ddagger} [1 + \beta' (1 - \beta' x_b^{\ddagger}) \exp(-q_v/kT)] \quad [\text{from eq. (15)}] \end{aligned}$$

then $x_b^{\ddagger}$ can be solved for in terms of x_b and substituted in eq.(16). Thus we obtain x_v in terms of x_b .

(f) For the "reaction" the law of mass action is

$$\frac{x_p}{(x_b' - x_p) x_v^{\ddagger}} = \exp(B_p/kT) \quad \text{--- (17)}$$

$$\text{where } x_b' = \frac{N_b}{N_{sI}} = \frac{x_b}{\alpha}$$

$$x_v^f = \exp(-E_v/kT) = \frac{N_v^f}{N_s} = \text{site fraction of free vacancies}$$

Eq.(17) must be compared with eq.(16) for the results of the two approaches.

Problem 6.10

Starting with Eq. (6.11)

$$G(N_v) - G(0) = N_v g_v - kT \ln \left[\frac{(N+N_v)!}{N! N_v!} \right]$$

Neglecting excess entropy

$$g_v \cong \epsilon_v$$

$$\mu_v = \left(\frac{\partial G}{\partial N_v} \right)_{N, T, P}$$

$$G - G(0) = N_v \epsilon_v - kT \left[(N+N_v) \ln(N+N_v) - (N+N_v) - N \ln N + N - N_v \ln N_v + N_v \right]$$

$$\therefore \frac{\partial G}{\partial N_v} = \epsilon_v - kT \left[\ln(N+N_v) - \ln N_v \right]$$

$$\therefore \mu_v = \epsilon_v + kT \ln \left[\frac{N_v}{N+N_v} \right] = \epsilon_v + kT \ln x_v$$

From Eq. (6.12), the equilibrium concentration of vacancies is

$$x_v^{eq} = e^{-\epsilon_v/kT}$$

... at equilibrium $\mu_v = 0$

Problem 6.11

Let n_v = atom fraction vacancies at time t

then
$$\frac{dn_v}{dt} = k^+ - k^- n_v \quad \text{--- (1)}$$

As $t \rightarrow \infty$, equilibrium is approached

$$\therefore (n_v)_{eq.} = e^{-E_v/kT} = \frac{k^+}{k^-} \quad \text{--- (2)}$$

$$\therefore \frac{dn_v}{dt} = -k^+ \left[\frac{n_v}{(n_v)_{eq.}} - 1 \right] \quad \text{--- (3)}$$

Integrating eq.(3) and using the initial condition

$$n_v(0) = n_v^0 \quad \text{--- (4)}$$

yields

$$\frac{n_v - (n_v)_{eq.}}{n_v^0 - (n_v)_{eq.}} = e^{-k^+ t} \quad \text{--- (5)}$$

When the correct value of n_v^0 is used, the left hand side of eq.(5) will plot as a straight line on a semilog plot vs. t . The value of n_v^0 which yields a straight line on such a plot is the correct value and the slope of the line is k^+ . The rate constant k^- can then be determined from eq.(2).

Problem 6.12(a) Anneal of the Irradiated Sample (First Anneal)

$$MC_p \frac{dT}{dt} = K[200 - T] + Mq(T(t)) \quad \text{--- (1)}$$

(Second Anneal)

(Stored energy has been dissipated by first anneal)

$$MC_p \frac{dT'}{dt} = K[200 - T'] \quad \text{--- (2)}$$

Subtract the two equations,

$$MC_p \frac{d}{dt}(T - T') = -K(T - T') + Mq(T)$$

Integrating,

$$Q \equiv \int_0^{\infty} q(T(t)) dt = C_p \int_0^{\infty} d(T - T') + \frac{K}{M} \int_0^{\infty} (T - T') dt$$

The first integral on the right hand side is zero, since in the curve of two anneals, $(T - T')$ at both the end points are zero.

$$\therefore \boxed{Q = \frac{K}{M} \int_0^{\infty} (T - T') dt}$$

This is the area enclosed by the two curves of two anneals. It can be evaluated graphically.

$$Q = \frac{0.44}{10} (4.2 \times 10^3) = 184.8 \text{ Joules/gm}$$

Alternate method

Assume temperature spike — heat released instantaneously at $T_0 = 128^\circ\text{C}$. Temperature rises to $T_{\text{max}} = 279^\circ\text{C}$. in very short time. Neglect the heat exchange term $K(200 - T)$ during the interval compared to $mc_p \frac{dT}{dt}$

$$Q = \int_0^\infty q[T(t)] dt = c_p \int_0^\infty \frac{dT}{dt} dt = c_p \int_{T_0}^{T_{\text{max}}} dT$$

$$= c_p (T_{\text{max}} - T_0)$$

$$\therefore Q = 1.26 (151) = 190.3 \text{ Joules/gm}$$

(b) Energy released per vacancy-interstitial recombination:

Step:1 Move an atom from surface to vacant lattice site inside the solid. — releases E_v of energy and removes Vacancy.

Step:2 Move an atom from interstitial site inside solid to surface — releases E_i of energy and removes an interstitial.

$$\begin{aligned}
 \therefore \text{Total energy released per} &= E_v + E_i \\
 \text{V-i recombination} &= 5.2 + 13.9 \\
 &= 19.1 \text{ eV}
 \end{aligned}$$

Let $x_i = x_v =$ Frenkel pair concentrations
prior to anneal
(atom fractions)

$N_c =$ number of atoms per gm of graphite, then

$$N_c = \frac{1 \text{ gm atom}}{12 \text{ gm}} \times \frac{6 \times 10^{23} \text{ atoms}}{\text{gm atom}} = 5 \times 10^{22} \frac{\text{atoms}}{\text{gm.}}$$

$$\begin{aligned}
 x_i = x_v &= \frac{Q \text{ eV/gm}}{(E_i + E_v) \text{ eV/Frenkel pair} \times N_c \frac{\text{atoms}}{\text{gm}}} = \frac{Q}{N_c (E_i + E_v)} \\
 &= \frac{190.26}{19.1 \times 1.6 \times 10^{-19} \times 5 \times 10^{22}} \\
 &= \frac{190.26}{152.8} \times 10^{-3} \\
 &= 1.25 \times 10^{-3}
 \end{aligned}$$

CHAPTER 7

Problem 7.1

- (a) Since Frenkel disorder on the oxygen sublattice predominates, the concentration of Oxygen vacancies can be obtained from the results of the previous problem 6.2, i.e. from eq. (1), (2), (6) and (8) in the problem 6.2

$$\frac{N_{Vx}}{N_{Ox}} = X_{Vx} = \frac{1}{2} \sqrt{2 K_{Fx}} = \sqrt{\frac{K_{Fx}}{2}} \quad \text{--- (1)}$$

The vacancy concentration on the cation sublattice is obtained for Schottky disorder by the law of mass action

$$X_{Vx}^2 X_{Vm} = K_s \quad \text{--- (2)}$$

Combining (1) and (2)

$$X_{Vm} = \frac{2 K_s}{K_{Fx}} \quad \text{--- (3)}$$

and

$$\begin{aligned} K_{Fx} &= e^{\frac{\Delta S_{Fx}}{k}} e^{-\frac{E_{Fx}}{kT}} \\ &= e^{\frac{63}{8.314}} e^{-\frac{297 \times 10^3}{8.314 \times 1673}} = 10^{-5.98} \quad \text{--- (4)} \end{aligned}$$

$$\begin{aligned} K_s &= e^{\frac{\Delta S_s}{k}} e^{-\frac{E_s}{kT}} \\ &= 1 e^{-\frac{544 \times 10^3}{8.314 \times 1673}} = 10^{-16.93} \quad \text{--- (5)} \end{aligned}$$

Substituting eqs. (4) and (5) into (1) and (3) we get,

$$\left. \begin{aligned} X_{Vx} &= 7.24 \times 10^{-4} \\ X_{Vm} &= 2.24 \times 10^{-11} \end{aligned} \right\} \text{ for pure } \text{UO}_2 \quad \dots (6)$$

(b) Charge balance in UO_2 doped with N_{DM} cation impurity atoms of charge +5 is:

$$4N_M + 5N_{DM} = 2N_x + 2N_{xI} \quad \dots (7)$$

but $N_{SM} = N_M + N_{DM} + N_{Vm} \quad \dots (8)$

and $N_{Sx} = N_x + N_{Vx} \quad \dots (9)$

$$N_{SM} = \frac{1}{2} N_{Sx}, \quad N_{SI} = \frac{1}{2} N_{Sx} \quad \dots (10)$$

(for fluorite structure)

$$\therefore 4(N_{SM} - N_{DM} - N_{Vm}) + 5N_{DM} = 2(N_{Sx} - N_{Vx}) + 2N_{xI}$$

Neglecting N_{Vm} by assumption,

$$N_{DM} = 2(N_{xI} - N_{Vx})$$

Dividing by $N_{SM} = \frac{1}{2} N_{Sx}$

$$\frac{N_{DM}}{N_{SM}} = 4 \left(\frac{N_{xI}}{N_{Sx}} - \frac{N_{Vx}}{N_{Sx}} \right)$$

let

$$\frac{N_{DM}}{N_{SM}} = X_{DM}, \quad \frac{N_{Vx}}{N_{Sx}} = X_{Vx}$$

and by $N_{SI} = \frac{1}{2} N_{SX}$

$$\frac{N_{XI}}{N_{SX}} = \frac{N_{XI}}{2 N_{SI}} = \frac{1}{2} X_{XI}$$

Therefore electrical neutrality gives,

$$X_{DM} = 2 X_{XI} - 4 X_{VX} \quad \dots (11)$$

Law of mass action for Frenkel defects of anion sublattice gives,

$$K_{FX} = X_{VX} X_{XI} \quad \dots (12)$$

Solving eqs (11) and (12) for X_{VX} gives,

$$X_{VX} = \frac{1}{8} X_{DM} \left(\sqrt{1 + 32 \frac{K_{FX}}{X_{DM}^2}} - 1 \right) \quad \dots (13)$$

From eq (2),

$$X_{VM} = \frac{K_S}{X_{VX}^2}$$

Limiting case

(1) Large impurity concentration or $\frac{32 K_{FX}}{X_{DM}^2} \ll 1$

Expanding the square root term in Taylor Series and taking the first 2-terms

$$X_{VX} = \frac{1}{8} X_{DM} \left(1 + 16 \frac{K_{FX}}{X_{DM}^2} - 1 \right) = 2 \frac{K_{FX}}{X_{DM}}$$

$$\therefore X_{VX} = \frac{2 K_{FX}}{X_{DM}} \quad \dots (14)$$

(2) Small impurity concentration $\frac{32 K_{FX}}{X_{DM}^2} \gg 1$

$$\therefore X_{VX} \cong \frac{1}{8} X_{DM} \sqrt{\frac{32 K_{FX}}{X_{DM}^2}}$$

or $\boxed{X_{VX} = \sqrt{\frac{K_{FX}}{2}}}$ (15)

(c) Using the calculated value of K_{FX} and $X_{DM} = 0.1$ in eq. (13), we get,

$$X_{VX} = \frac{1}{8} (0.1) \left(\sqrt{1 + 32 \frac{10^{-5.98}}{10^{-2}}} - 1 \right)$$

$$= 2.1 \times 10^{-5}$$

Now using this in eq. (2) to get X_{VM}

$$X_{VM} = \frac{K_S}{X_{VX}^2} = \frac{10^{-16.73}}{(2.1 \times 10^{-5})^2} = \frac{10^{-6.73}}{(2.1)^2}$$

$$\cong 2.66 \times 10^{-8}$$

$$\therefore \left. \begin{array}{l} X_{VX} = 2.1 \times 10^{-5} \\ X_{VM} = 2.66 \times 10^{-8} \end{array} \right\} \text{ in doped } \text{UO}_2$$

For both U and O,

$$\frac{D_{(\text{doped})}}{D_{(\text{pure})}} = \frac{X_V (\text{doped})}{X_V (\text{pure})}$$

for U $\frac{D_U (\text{doped})}{D_U (\text{pure})} = \frac{(X_{VM}) (\text{doped})}{(X_{VM}) (\text{pure})} = \frac{2.7 \times 10^{-8}}{2.24 \times 10^{-11}} \cong 1.2 \times 10^3$

for O $\frac{D_O (\text{doped})}{D_O (\text{pure})} = \frac{(X_{VX}) (\text{doped})}{(X_{VX}) (\text{pure})} = \frac{2.1 \times 10^{-5}}{7.24 \times 10^{-4}} = 2.9 \times 10^{-2}$

Problem 7.2

$$K = \left(\frac{d^2\phi}{dx^2} \right)_{x=0}$$

$$\phi(x) = \frac{1}{2} \epsilon^* \left[1 - \cos\left(\frac{2\pi x}{a_0}\right) \right]$$

$$\frac{d\phi}{dx} = \frac{1}{2} \epsilon^* \left(\frac{2\pi}{a_0} \right) \sin\left(\frac{2\pi x}{a_0}\right)$$

$$\frac{d^2\phi}{dx^2} = \frac{1}{2} \epsilon^* \left(\frac{2\pi}{a_0} \right)^2 \cos\left(\frac{2\pi x}{a_0}\right)$$

$$\therefore \boxed{K = \frac{2\pi^2}{a_0^2} \epsilon^*} \quad (1)$$

Frequency of vibration is :

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{m}} = \frac{1}{2\pi} \sqrt{\frac{(2\pi)^2 \epsilon^*}{2m a_0^2}} \quad [\text{from (1)}]$$

$$\therefore \boxed{\nu = \sqrt{\frac{\epsilon^*}{2m a_0^2}}} \quad (2)$$

Jump frequency $W = \nu e^{-\epsilon^*/kT}$

$$\therefore \boxed{W = \sqrt{\frac{\epsilon^*}{2m a_0^2}} e^{-\epsilon^*/kT}} \quad (3)$$

Problem 7.3

- (a) For a single degree of vibrational freedom, the energy of the oscillator above the minimum in the potential curve is :

$$\epsilon_j = (j + \frac{1}{2}) h\nu$$

The partition function of a single oscillator is :

$$\begin{aligned} Z &= \sum_{j=0}^{\infty} e^{-\epsilon_j/kT} = \sum_{j=0}^{\infty} e^{-(j+\frac{1}{2}) \frac{h\nu}{kT}} \\ &= e^{-\frac{1}{2} \frac{h\nu}{kT}} \sum_{j=0}^{\infty} e^{-j(\frac{h\nu}{kT})} \end{aligned}$$

$$\text{or } Z = e^{-\frac{1}{2}(\frac{h\nu}{kT})} \left(1 - e^{-\frac{h\nu}{kT}}\right)^{-1}$$

$$\text{let } x = \frac{h\nu}{kT}$$

$$\therefore Z = e^{-\frac{x}{2}} (1 - e^{-x})^{-1} = \frac{1}{x} \left[\frac{x}{e^{x/2} - e^{-x/2}} \right]$$

The bracketed term is the correction factor $f(x)$

$$\therefore f(x) = \frac{e^{x/2} - e^{-x/2}}{x} = \frac{2 \sinh(\frac{x}{2})}{x}$$

$$\text{or } \boxed{f(x) = \frac{\sinh(\frac{x}{2})}{(\frac{x}{2})}} \quad (1)$$

(b) From Eq. (7.34), neglecting lattice effect

$$W = \frac{z^*}{z_{eq}} \cdot \frac{\bar{v}_x}{\delta} e^{-\epsilon^*/kT}$$

where $z^* = z_{tr}^* z_{vib}^* = \frac{\delta \left(\frac{2\pi m kT}{h^2} \right)^{1/2}}{[x^* f(x^*)]^2}$

where $x^* = \frac{h\nu^*}{kT}$

$$z_{eq} = \frac{1}{[x f(x)]^3}$$

$$\therefore W = \delta \left(\frac{2\pi m kT}{h^2} \right)^{1/2} \frac{[x f(x)]^3}{[x^* f(x^*)]^2} \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{1}{\delta} e^{-\epsilon^*/kT}$$

$$\therefore W = \frac{kT}{h} \left(\frac{h\nu}{kT} \right)^3 \left(\frac{kT}{h\nu^*} \right)^2 \frac{[f(x)]^3}{[f(x^*)]^2} e^{-\epsilon^*/kT}$$

$$\therefore W = \frac{\nu^3}{(\nu^*)^2} \frac{[f(x)]^3}{[f(x^*)]^2} e^{-\epsilon^*/kT} \quad \dots (2)$$

(c) From Random Walk Theory

$$D = \frac{1}{6} \lambda^2 \Gamma = \frac{1}{6} \lambda^2 \beta W$$

$$\therefore E = -k \frac{d \ln D}{d \ln T} = -k \frac{d \ln W}{d \ln T}$$

(because λ and β are temperature independent)

From part (b) :

$$\ln W = \ln \left[\frac{\nu^3}{(\nu^*)^2} \right] + 3 \ln[f(x)] - 2 \ln[f(x^*)] - \frac{\epsilon^*}{kT}$$

$$\frac{d \ln W}{d(1/T)} = 3 \left(\frac{h\nu}{k} \right) \left[\frac{d \ln f(x)}{dx} \right]_{x=\frac{h\nu}{kT}} - 2 \left(\frac{h\nu^*}{k} \right) \left[\frac{d \ln f(x)}{dx} \right]_{x=\frac{h\nu^*}{kT}} - \frac{\epsilon^*}{k}$$

From part (a) :

$$\frac{d \ln f(x)}{dx} = \frac{1}{2} \frac{1}{f} \frac{df}{d(\frac{x}{2})} = \frac{1}{2} \frac{\left[\frac{\cosh(\frac{x}{2})}{(\frac{x}{2})} - \frac{\sinh(\frac{x}{2})}{(\frac{x}{2})^2} \right]}{\frac{\sinh(\frac{x}{2})}{(\frac{x}{2})}}$$

$$\text{or } \frac{d \ln f(x)}{dx} = \frac{1}{2} \left[\coth\left(\frac{x}{2}\right) - \frac{1}{(\frac{x}{2})} \right]$$

$$\therefore E = -k \frac{d \ln W}{d(1/T)} = \epsilon^* + k \left\{ 2 \left(\frac{h\nu^*}{k} \right) \frac{1}{2} \left[\coth\left(\frac{h\nu^*}{2kT}\right) - \frac{2kT}{h\nu^*} \right] - 3 \left(\frac{h\nu}{k} \right) \frac{1}{2} \left[\coth\left(\frac{h\nu}{2kT}\right) - \frac{2kT}{h\nu} \right] \right\}$$

$$\therefore E = \epsilon^* + kT \left\{ 1 + \left(\frac{h\nu^*}{kT} \right) \coth\left(\frac{h\nu^*}{2kT}\right) - \frac{3}{2} \left(\frac{h\nu}{kT} \right) \coth\left(\frac{h\nu}{2kT}\right) \right\}$$

... (3)

(d) Isotope effect

D_1 = diffusivity of hydrogen

D_2 = diffusivity of deuterium

$D = \frac{1}{6} \lambda^2 \beta W$, but λ and β are the properties of the host lattice, not the diffusing atom, therefore

$$\frac{D_1}{D_2} = \frac{W_1}{W_2}$$

Using the result of the part (b), i.e. eq. (2) for W_1 and W_2 :

$$\frac{D_1}{D_2} = \left(\frac{\nu_1}{\nu_2} \right)^3 \left(\frac{\nu_2^*}{\nu_1^*} \right)^2 \left[\frac{f(x_1)}{f(x_2)} \right]^3 \left[\frac{f(x_2^*)}{f(x_1^*)} \right]^2$$

For simple harmonic oscillator,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

where K is the force constant (or the second derivative of the potential energy curve) and m is the mass of the diffusing atom.

Since K is the same for both the isotopes

$$\left(\frac{\nu_1}{\nu_2}\right)^3 = \left(\frac{m_2}{m_1}\right)^{3/2} = 2^{3/2};$$

$$\left(\frac{\nu_2^*}{\nu_1^*}\right)^2 = \left(\frac{m_1}{m_2}\right) = \frac{1}{2}$$

$$x_2 = \frac{h\nu_2}{kT} = \left(\frac{h\nu_1}{kT}\right)\left(\frac{\nu_2}{\nu_1}\right) = x_1 \left(\frac{m_1}{m_2}\right)^{1/2} = \frac{x_1}{\sqrt{2}}$$

similarly, $x_2^* = \frac{x_1^*}{\sqrt{2}}$

Dropping the subscript 1 on x_1 , the diffusivity ratio is :

$$\boxed{\frac{D_1}{D_2} = \sqrt{2} \left[\frac{f(x)}{f\left(\frac{x}{\sqrt{2}}\right)} \right]^3 \left[\frac{f\left(\frac{x^*}{\sqrt{2}}\right)}{f(x^*)} \right]^2} \quad \dots (4)$$

(e) At 300°K ,

$$x = \frac{h\nu}{kT} = \frac{1350}{300} = 4.5; \quad \frac{x}{\sqrt{2}} = 3.182$$

and $x^* = \frac{h\nu^*}{kT} = \frac{2300}{300} = 7.66; \quad \frac{x^*}{\sqrt{2}} = 5.42$

$$\therefore \frac{D_{\text{Hydrogen}}}{D_{\text{Deuterium}}} = \frac{D_1}{D_2} = \sqrt{2} \left[\frac{f(x)}{f\left(\frac{x}{\sqrt{2}}\right)} \right]^3 \left[\frac{f\left(\frac{x^*}{\sqrt{2}}\right)}{f(x^*)} \right]^2$$

$$\therefore \frac{D_{\text{Hycl.}}}{D_{\text{Deut}}} = \sqrt{2} \left[\frac{\left(\frac{e^{\frac{4.5}{2}} - e^{-\frac{4.5}{2}}}{4.5} \right)}{\left(\frac{e^{\frac{3.182}{2}} - e^{-\frac{3.182}{2}}}{3.182} \right)} \right]^3 \left[\frac{\left(\frac{e^{\frac{5.42}{2}} - e^{-\frac{5.42}{2}}}{5.42} \right)}{\left(\frac{e^{\frac{7.66}{2}} - e^{-\frac{7.66}{2}}}{7.66} \right)} \right]^2$$

$$= \sqrt{2} \times 2.8 \times 0.211$$

$$= \underline{0.836}$$

At 1000° K,

$$x = \frac{h\nu}{kT} = \underline{1.35}, \quad \frac{x}{\sqrt{2}} = \underline{0.95}$$

$$\text{and } x^* = \frac{h\nu^*}{kT} = \underline{2.30}, \quad \frac{x^*}{\sqrt{2}} = \underline{1.63}$$

$$\therefore \frac{D_{\text{Hycl.}}}{D_{\text{Deut.}}} = \sqrt{2} \left[\frac{\left(\frac{e^{\frac{0.95}{2}} - e^{-\frac{0.95}{2}}}{0.95} \right)}{\left(\frac{e^{\frac{1.35}{2}} - e^{-\frac{1.35}{2}}}{1.35} \right)} \right]^{-3} \left[\frac{\left(\frac{e^{\frac{1.63}{2}} - e^{-\frac{1.63}{2}}}{1.63} \right)}{\left(\frac{e^{\frac{2.3}{2}} - e^{-\frac{2.3}{2}}}{2.3} \right)} \right]^2$$

$$= \sqrt{2} \times 1.1 \times 0.81$$

$$= \underline{1.26}$$

Problem 7.4

Substitutional Migration with FCC lattice octahedral
equilibrium sites

$$\lambda = \frac{a_0}{\sqrt{2}} \quad ; \quad \beta = 12 \quad ; \quad (\text{all edge center positions})$$

$$\begin{aligned} \therefore D &= \frac{1}{6} \lambda^2 \Gamma \\ &= \frac{1}{6} \left(\frac{a_0}{\sqrt{2}} \right)^2 12 W \end{aligned}$$

$$\therefore \boxed{D = a_0^2 W}$$

Problem 7.5

(a) Either by (i) the Einstein relation

$$\overline{x^2} \cong 6Dt$$

or by (ii) recognising that solutions of the unsteady state diffusion problems of this sort depend upon the variable $(x^2/4Dt)$, and a value of the variable of approximately unity is needed to produce a significant change in the concentration,

$$\begin{aligned} \therefore D_{\min.} &\cong \frac{(\overline{x^2})_{\min.}}{6t_{\max.}} = \frac{(2 \times 10^{-4})^2 \text{ cm}^2}{6 \times 3.14 \times 10^7 \text{ sec}} \\ &= 2 \times 10^{-16} \text{ cm}^2/\text{sec} \end{aligned}$$

(b) For BCC interstitial diffusion,

$$D = \frac{1}{6} a_0^2 \nu e^{\frac{s^*}{k}} e^{-\frac{E^*}{kT}}$$

$$E^* = 60 \text{ kcal/mole}$$

Estimates

$$a_0 \cong 3\text{\AA} = 3 \times 10^{-8} \text{ cm}$$

$$\nu \cong 10^{13} \text{ sec}^{-1}$$

$$s^* \cong 0$$

$$\therefore \frac{E^*}{kT_{\min}} = \ln \left(\frac{a_0^2 \nu e^{\frac{s^*}{k}}}{6D} \right) \cong \ln(10^{13}) = 30$$

$$\therefore kT_{\min.} = \frac{60}{30} = 2, \quad T_{\min.} = 1000^\circ \text{K.}$$

CHAPTER 8

Problem 8.1

- (a) $\frac{a_0}{2}$ $[110]$ edge dislocation in the (111) plane in the FCC lattice.

The extra half sheet of atoms which forms the edge dislocation must be perpendicular to the slip plane [i.e., the (111) plane] and also must be perpendicular to the Burgers Vector (i.e. $[110]$)

The extra half sheet in the fcc lattice is very wrinkled. We need to pick out a row of atoms in the (111) planes which is perpendicular to the $[110]$ direction. A cut $\perp$ to the extra half sheet would reveal that it consists of the atoms shown with an "x" in the sketch below.

Continuation of the "X" atoms in the (111) planes above and below the one in the sketch shows that the extra half sheet consists of two adjacent (110) planes in the fcc structure.

b)

$\frac{a_0}{2} [111]$ edge dislocation in the (110) plane of bcc lattice. Extra half sheet must simultaneously be $\perp$ to $[111]$ direction and to the (110) plane. Half sheet consists of three adjacent (111) planes. (x's in sketch)

Problem 8.2

$$E_{el} = \frac{1}{2E} (\sigma_{rr}^2 + \sigma_{\theta\theta}^2 + \sigma_{zz}^2) - \frac{\nu}{E} (\sigma_{rr}\sigma_{zz} + \sigma_{rr}\sigma_{\theta\theta} + \sigma_{\theta\theta}\sigma_{zz}) \\ + \frac{1}{2G} (\sigma_{r\theta}^2 + \sigma_{\theta z}^2 + \sigma_{rz}^2) \quad \text{--- [Eq. (A-26)]}$$

From Fig. 8.8

$$\sigma_{rr} = \sigma_{\theta\theta} = \frac{Gb}{2\pi(1-\nu)} \frac{\sin\theta}{r} = \frac{K\sin\theta}{r} \\ \text{[where } K = \frac{Gb}{2\pi(1-\nu)} \text{]}$$

$$\sigma_{r\theta} = -\frac{Gb}{2\pi(1-\nu)} \frac{\cos\theta}{r} \\ = -\frac{K\cos\theta}{r}$$

$$\sigma_{zz} = \frac{Gb\nu}{2\pi(1-\nu)} \frac{\sin\theta}{r} = 2\nu\sigma_{rr} = \frac{2K\nu\sin\theta}{r}$$

Substituting:

$$E_{el} = \frac{1}{2E} \frac{K^2}{r^2} (\sin^2\theta + \sin^2\theta + 4\nu^2\sin^2\theta) \\ - \frac{\nu K^2}{Er^2} (2\nu\sin^2\theta + \sin^2\theta + 2\nu\sin^2\theta) \\ + \frac{1}{2G} \frac{K^2}{r^2} \cos^2\theta$$

$$\therefore E_{el} = \frac{K^2}{r^2} \left\{ \frac{2}{2E} \sin^2\theta (1+2\nu^2) - \frac{\nu}{E} \sin^2\theta (1+4\nu) \right. \\ \left. + \frac{1}{2G} \cos^2\theta \right\}$$

$$\therefore E_{el} = \frac{K^2}{r^2} \frac{1}{E} \sin^2\theta [1+2\nu^2-\nu-4\nu^2] + \frac{K^2}{r^2} \left(\frac{1+\nu}{E} \right) \cos^2\theta$$

$$2G = \frac{E}{1+\nu} \quad \text{--- [Eq. (A-20)]}$$

$$\therefore E_{el} = \frac{K^2}{r^2} \frac{1}{E} \left\{ (1-2\nu)(1+\nu) \sin^2 \theta + (1+\nu) \cos^2 \theta \right\}$$

Replace $\frac{1+\nu}{E}$ by $\frac{1}{2G}$

$$\frac{K^2}{2G} = \frac{G^2 b^2}{4\pi^2 (1-\nu)^2} \frac{1}{2G} = \frac{G b^2}{8\pi^2 (1-\nu)^2}$$

$$\therefore E_{el} = \frac{G b^2}{8\pi^2 (1-\nu)^2} \cdot \frac{1}{r^2} \left\{ (1-2\nu) \sin^2 \theta + \cos^2 \theta \right\}$$

Line Tension:

$$\tau = \int_0^{2\pi} d\theta \int_{r_d}^R r dr E_{el}$$

$$\begin{aligned} \therefore \tau &= \frac{G b^2}{8\pi^2 (1-\nu)^2} \int_{r_d}^R \frac{dr}{r} \left\{ (1-2\nu) \int_0^{2\pi} \sin^2 \theta d\theta + \int_0^{2\pi} \cos^2 \theta d\theta \right\} \\ &= \frac{G b^2}{8\pi^2 (1-\nu)^2} \ln\left(\frac{R}{r_d}\right) \pi \left\{ (1-2\nu) + 1 \right\} \end{aligned}$$

$$\therefore \tau = \frac{G b^2}{4\pi (1-\nu)} \ln\left(\frac{R}{r_d}\right)$$

Problem 8.3

$$F_{12} = \text{Force exerted by ① on ②} = -F_{21}$$

From Eq. (8.13)

$$F_{12} = -(\sigma_{xy})_1 b_{\perp} + (\sigma_{xx})_1 b_{\parallel} \quad [\text{Eq. (8.13)}]$$

where $(\sigma_{xy})_1$ and $(\sigma_{xx})_1$ are the stress fields of ① at the position of ②.

Eq. (8.22) :

$$(\sigma_{xy})_1 = (\cos^2 \theta - \sin^2 \theta) (\sigma_{r\theta})_1$$

$$(\sigma_{xx})_1 = (\sigma_{rr})_1 - 2 \sin \theta \cos \theta (\sigma_{r\theta})_1$$

Apply equations in Fig. 8.8 to ①

(note : use θ' , not θ , here)

$$(\sigma_{rr})_1 = \frac{Gb}{2\pi(1-\nu)} \frac{\sin \theta'}{r} = \frac{K \sin \theta'}{r}$$

$$(\sigma_{r\theta})_1 = -\frac{Gb}{2\pi(1-\nu)} \frac{\cos \theta'}{r} = -\frac{K \cos \theta'}{r}$$

$$\text{where } K = \frac{Gb}{2\pi(1-\nu)}$$

$$\theta' = \pi + \theta$$

$$\cos \theta' = -\cos \theta, \quad \sin \theta' = -\sin \theta$$

$$(\sigma_{rr})_1 = -\frac{K}{r} \sin \theta, \quad (\sigma_{r\theta})_1 = \frac{K}{r} \cos \theta$$

$$\therefore (\sigma_{xy})_1 = \frac{K}{r} (\cos^2 \theta - \sin^2 \theta) \cos \theta$$

$$(\sigma_{xx})_1 = \frac{K}{r} (-\sin \theta - 2 \sin \theta \cos^2 \theta) = -\frac{K}{r} \sin \theta (1 + 2 \cos^2 \theta)$$

Substituting in Eq. (8.13) we get,

$$F_{12} = \frac{Kb}{r} \left[-\cos \theta (\cos^2 \theta - \sin^2 \theta) \underline{i} - \sin \theta (1 + 2 \cos^2 \theta) \underline{j} \right]$$

$$\therefore F_{12} = -\frac{Gb^2}{2\pi(1-\nu)r} \left[\cos \theta (\cos^2 \theta - \sin^2 \theta) \underline{i} + \sin \theta (1 + 2 \cos^2 \theta) \underline{j} \right]$$

This is Eq. (8.23) For F_{21} , remove minus sign.

$$\theta' = \frac{\pi}{2} + \theta$$

$$\sin \theta' = \cos \theta, \quad \cos \theta' = -\sin \theta$$

$$(\sigma_{rr})_1 = \frac{K}{r} \cos \theta, \quad (\sigma_{r\theta})_1 = \frac{K}{r} \sin \theta$$

$$(\sigma_{xy})_1 = \frac{K}{r} (\cos^2 \theta - \sin^2 \theta) \sin \theta$$

$$(\sigma_{xx})_1 = \frac{K}{r} (\cos \theta - 2 \sin^2 \theta \cos \theta)$$

$$\therefore F_{12} = \frac{Kb}{r} \left[-\sin \theta (\cos^2 \theta - \sin^2 \theta) \underline{i} + \cos \theta (1 - 2 \sin^2 \theta) \underline{j} \right]$$

but $1 - 2\sin^2\theta = \cos^2\theta - \sin^2\theta$

$$F_{12} = - \frac{Gb^2}{2\pi(1-\nu)\tau} (\cos^2\theta - \sin^2\theta) (\sin\theta \underline{i} - \cos\theta \underline{j})$$

For F_{21} , remove minus sign.

Problem 8.4

a)

For $\underline{b}$ to be independent of θ :

$$b_e \cos \theta + b_s \cos(\pi/2 - \theta) = b$$

$$b_e \sin \theta = b_s \sin(\pi/2 - \theta)$$

Solving:

$$b_s = b \sin \theta$$

$$b_e = b \cos \theta$$

At (A)

$$\left. \begin{array}{l} b_e = b \\ b_s = 0 \end{array} \right\} \text{pure edge}$$

At (C)

$$\left. \begin{array}{l} b_e = -b \\ b_s = 0 \end{array} \right\} \text{pure edge, of opposite sign as at (A)}$$

At (B)

$$\left. \begin{array}{l} b_e = 0 \\ b_s = b \end{array} \right\} \text{pure screw}$$

At (D)

$$\left. \begin{array}{l} b_e = 0 \\ b_s = -b \end{array} \right\} \text{pure screw of opposite sign as at (B)}$$

b) F_e = Force on edge component (in x-direction)

$$F_e = \sigma_{yx} b_e \quad \text{--- [Eq. (8.13)]}$$

[Choose sign to give + force at (A)]

F_s = Force on screw component
(in z-direction)

Fig. (8.11): Shear stress in the direction of screw dislocation produces force at right angles to it. For geometry of circular loop, screw component lies along x-axis, not z-axis.

F = resultant force

θ' = angle of resultant force from x-axis

$$\tan \theta' = \frac{F_s}{F_e} = \frac{b_s}{b_e} = \frac{\sin \theta}{\cos \theta} = \tan \theta$$

$\therefore \theta' = \theta$, or the resultant force is along radially outward.

$$\begin{aligned} F &= \sqrt{F_s^2 + F_e^2} = \sigma_{yx} \sqrt{b_e^2 + b_s^2} \\ &= \sigma_{yx} b \sqrt{\cos^2 \theta + \sin^2 \theta} \end{aligned}$$

$$\therefore \boxed{F = \sigma_{yx} b}$$

Problem 8.5

a)

$$\underline{n = 3}$$

$$\text{Let } K' = \frac{Gb}{2\pi(1-\nu)\sigma_{xy}}$$

$$x_2 = d, \quad x_3 = L$$

Eq. (8.38) for $i = 2, 3$:

$$\frac{1}{d} - \frac{1}{L-d} = \frac{1}{K'} \quad \text{--- (1)}$$

$$\frac{1}{L} + \frac{1}{L-d} = \frac{1}{K'} \quad \text{--- (2)}$$

From (1)

$$\text{Let } d = d/K'$$

$$L = L/K'$$

$$\therefore \frac{1}{d} - \frac{1}{L-d} = 1 \quad \text{--- (3)}$$

$$\frac{1}{L} + \frac{1}{L-d} = 1 \quad \text{--- (4)}$$

From (3)

$$L = \frac{2d - d^2}{1-d} \quad \text{--- (5)}$$

Substitute (5) into (4):

$$\frac{1-d}{d(2-d)} + \frac{1-d}{d} = 1$$

or:

$$2d^2 - 6d + 3 = 0$$

Solutions: $D = 2.37$, $L = 0.64$ [from (5)]

and $D = 0.64$, $L = 2.37$

Reject the first set because L must be greater than D .

$\therefore D = 0.64$ and $L = 2.37 K'$

From Eq. (8.39), for $n=3$, $L = 6 K'$

$$K' = \frac{Gb}{2\pi(1-\nu)\sigma_{xy}} \quad , \quad \text{units of cm}$$

$$K' \sum_{\substack{j=1 \\ j \neq i}}^n \frac{1}{x_i - x_j} = 1 \quad \text{--- (1)}$$

Continuous distribution:

$f(x')dx' = \text{number of dislocations in } x' \text{ to } x'+dx'$

$$K' \lim_{\epsilon \rightarrow 0} \left\{ \int_0^{x-\epsilon} \frac{f(x')dx'}{x-x'} + \int_{x+\epsilon}^L \frac{f(x')dx'}{x-x'} \right\} = 1 \quad \text{--- (2)}$$

$$\int_0^L f(x)dx = n \quad \text{--- (3)} \quad (f=0 \text{ for } x>L)$$

solution is: $f(x) = \frac{2n}{\pi L} \left(\frac{L-x}{x} \right)^{1/2}$

and $L = 2nK'$

Check integrals:

Let $x = L \sin^2 \theta$

$$\frac{L-x}{x} = \frac{L-L\sin^2\theta}{L\sin^2\theta} = \frac{\cos^2\theta}{\sin^2\theta}$$

Eq. (3) becomes,

with $dx = 2L \sin\theta \cos\theta d\theta$

and when $x=0$, $\theta=0$

and $x=L$, $\theta=\pi/2$

$$\begin{aligned} \therefore \frac{2\eta}{\pi L} \int_0^{\pi/2} L \frac{\cos\theta}{\sin\theta} (2\sin\theta \cos\theta) d\theta &= \frac{4\eta}{\pi} \int_0^{\pi/2} \cos^2\theta d\theta \\ &= \frac{4\eta}{\pi} \frac{\pi}{4} = \eta \quad (\text{OK}) \end{aligned}$$

Eq. (2) gives with $x' = L \sin^2 \theta$ and since $K' = \frac{L}{2\eta}$

$$\begin{aligned} \frac{L}{2\eta} \lim_{\epsilon \rightarrow 0} \left\{ \int_0^{x-\epsilon} \frac{f(x') dx'}{x-x'} + \int_{x+\epsilon}^L \frac{f(x') dx'}{x-x'} \right\} \\ = \frac{2}{\pi} \lim_{\delta \rightarrow 0} \left\{ \int_0^{\sin^{-1}\sqrt{\frac{x}{L}-\delta}} \frac{\cos^2\theta d\theta}{\frac{x}{L} - \sin^2\theta} + \int_{\sin^{-1}\sqrt{\frac{x}{L}+\delta}}^{\pi/2} \frac{\cos^2\theta d\theta}{\frac{x}{L} - \sin^2\theta} \right\} \end{aligned}$$

The term in $\{ \}$ above can be shown to be equal to $\pi/2$. Thus eq. (2) is satisfied also.

Evaluation of the integral in $\{ \}$ (Courtesy of H. Amster)

Let

$$I \equiv \lim_{\delta \rightarrow 0} \left[\int_0^{\eta-\delta} \frac{\cos^2\theta d\theta}{\sin^2\eta - \sin^2\theta} + \int_{\eta+\delta}^{\pi/2} \frac{\cos^2\theta d\theta}{\sin^2\eta - \sin^2\theta} \right]$$

where $\frac{x}{L} = \sin^2 \eta$ or $\eta = \sin^{-1} \sqrt{\frac{x}{L}}$

This is known as the "Cauchy Principal Value" of the integral (sometimes called the "Principal Part" of the integral) and written

$$I = P \int_0^{\pi/2} \frac{\cos^2 \theta d\theta}{\sin^2 \eta - \sin^2 \theta}$$

Without the P (i.e. with $\delta=0$) the integral does not exist (even though its "Principal Part" does.)

With $\delta=0$, both parts of integrals do not exist, but by making $\delta>0$, the $\pm\infty$ contributions cancel each other to give a finite limit.

Since there is no closed contour, the contour integration can't help. The indefinite integral must be sought.

$$\int \frac{\cos^2 \theta d\theta}{\sin^2 \eta - \sin^2 \theta} \equiv \int \frac{(\sin^2 \eta - \sin^2 \theta) + 1 - \sin^2 \eta}{\sin^2 \eta - \sin^2 \theta} d\theta$$

$$= \theta + \cos^2 \eta \int \frac{d\theta}{\sin^2 \eta - \sin^2 \theta}$$

Consider

$$\begin{aligned} \theta \Big|_{\theta=0}^{\eta-\delta} + \theta \Big|_{\eta+\delta}^{\pi/2} &= \eta - \delta + \pi/2 - (\eta + \delta) \\ &= \pi/2 - 2\delta \xrightarrow{\delta \rightarrow 0} \pi/2 \end{aligned}$$

Thus, $I = \pi/2 + J \cos^2 \eta$

where $J = \text{P} \int_0^{\pi/2} \frac{d\theta}{\sin^2 \eta - \sin^2 \theta}$

See Dwight P. 94 : $b=1$; $a=\sin \eta$

$$\therefore b^2 > a^2 \quad \& \quad \sqrt{b^2 - a^2} = \cos \eta$$

$$\therefore \int \frac{d\theta}{\sin^2 \eta - \sin^2 \theta} = \frac{1}{2 \cos \eta \sin \eta} \ln \left| \frac{\cot \eta \tan \theta + \sin \eta}{\cos \eta \tan \theta - \sin \eta} \right|$$

$$J = \lim_{\delta \rightarrow 0} \frac{1}{2 \cos \eta \sin \eta} \ln \left| \frac{[\theta = \eta - \delta] [\theta = \pi/2]}{[\theta = 0] [\theta = \eta + \delta]} \right|$$

$$\therefore \cos^2 \eta J = \lim_{\delta \rightarrow 0} \frac{1}{2} \cot \eta \ln \left| \frac{\left[\frac{\cos \eta \tan(\eta - \delta) + \sin \eta}{\cos \eta \tan(\eta - \delta) - \sin \eta} \right] [1]}{[-1] \left[\frac{\cos \eta \tan(\eta + \delta) + \sin \eta}{\cos \eta \tan(\eta + \delta) - \sin \eta} \right]} \right|$$

$$= \frac{1}{2} \cot \eta \ln 1 = 0$$

$$\therefore I = \pi/2 + J \cos^2 \eta$$

$$= \pi/2$$

Problem 8.6

a)

$$\sin \frac{\theta}{2} = \frac{a_0}{2d} \approx \frac{\theta}{2}$$

$$\therefore \theta = \frac{a_0}{d}$$

b) Energy/unit length of edge dislocation $\perp$ to the diagram $= \tau_d$

Each edge dislocation is associated with a distance d in the direction along the grain boundary in the diagram.

$$\gamma_{gb} = \frac{\tau_d}{d} = \frac{Gb^2}{4\pi(1-\nu)} \ln\left(\frac{d}{b}\right) / d$$

[Using Eq. (8.9)]

$$d = \frac{a_0}{\theta} \approx \frac{b}{\theta} \quad \text{or} \quad \frac{b}{d} = \theta$$

$$\therefore \gamma_{gb} = - \frac{Gb}{4\pi(1-\nu)} \theta \ln \theta$$

CHAPTER 9

Problem 9.1

From fundamental thermodynamic relation,

$$du = Tds - pdv$$

For an isentropic process, $ds = 0$

$$\therefore du = -pdv \quad dv = v_c dv_r$$

$$\therefore \Delta U = -p \Delta v = -p v_c \Delta v_r$$

(a)

$$\Delta U_0 = - \frac{20000 \times 1.01 \times 10^6 \times 414 \times 0.1}{4.186 \times 10^{10}} \approx -2000 \times 10^{-3}$$

$$\approx -20 \text{ kcal/mole} = -83.72 \text{ kJ/mole}$$

The curve P_0-1 plotted on the diagram shows this process.

(b)

The path of expansion can be obtained by the following iterative scheme

$$U_1 = U_0 + \Delta U_0 = 220 - 20 = 200 \text{ kcal/mole}$$

From $v_r = 0.6$, $U_1 = 200 \text{ kcal/mole}$, find

$$P_1 = 16000 \text{ atm.}$$

$$\Delta U_1 \approx -16000 \times 10^{-3} \approx -16 \text{ kcal/mole}$$

$$U_2 = U_1 + \Delta U_1 = 200 - 16 = 184 \text{ kcal/mole.}$$

$v_r = 0.7$, $U_2 = 184 \text{ kcal/mole}$, find $P_2 = 12500 \text{ atm}$

$$\Delta U_2 \approx -12500 \times 10^{-3} = -12.5 \text{ kcal/mole}$$

$$U_3 = U_2 + \Delta U_2 = 184 - 12.5 = 171.5 \text{ kcal/mole}$$

$$P_3 = 9200 \text{ atm} , \Delta U_3 = -9.2 \text{ kcal/mole}$$

$$U_4 = U_3 + \Delta U_3 = 171.5 - 9.2 = 162.3 \text{ kcal/mole}$$

$$P_4 = 6200 \text{ atm} , \Delta U_4 = -6.2 \text{ kcal/mole}$$

$$U_5 = 158 \text{ kcal/mole} , V_r \cong 0.97 , P_5 = 4600 \text{ atm}$$

$$U_6 = 157.3 \text{ kcal/mole} , V_r = 1.0 , P_6 = 4400 \text{ atm}$$

$$U_7 = 154.9 \text{ kcal/mole} , V_r = 1.1 , P_7 = 3400 \text{ atm}$$

(i) Because along the isentropic path, $du = -p dv$ and p decreases as the fuel expands, Thus although ΔV is uniformly changed, ΔU keeps decreasing as the state of the material moves down the path. The dotted line is the straight line extension of the line segment P_0-1 .

(ii) The discontinuity occurs at the saturated liquid line. After this the fluid is in the two phase region. In this region dv is much larger, due to vaporization, so that the slope is different from outside.

(c) At $p = 1000 \text{ atm}$, the fluid is in a liquid-gas phase.

Problem 9.2

Neglecting electronic excitation, the specific heat at constant volume of gaseous PuO_2 at high temperature will have contributions from translation, rotation and vibration of the molecule.

Linear Molecule

● = Plutonium
○ = Oxygen

(a) Rotation

(b) Vibration

As in the case of UO_2 there will be three translational modes giving $\frac{3}{2}R$, two rotational modes giving $2 \times \frac{1}{2}R$ and four vibrational modes giving

$4 \times (2 \times \frac{1}{2}R)$ $\therefore$ Molar heat capacity $C_v = (\frac{3}{2} + 1 + 4)R$

$$= \frac{13}{2}R$$

Non-linear Molecule

Rotation

For a non-linear molecule, there will be an additional rotational mode about x-axis as shown. However for the non-linear molecule there will be only $3N - 6 = 3 \times 3 - 6 = 3$ vibrational modes as against $3N - 5 = 4$ for the linear molecule. (see Thermodynamics by Lewis, Randall, Pitzer and Brewer pp. 59-60)

Therefore we have $\frac{3}{2}R$ from translation,

$\frac{3}{2}R$ from rotation and $3 \times (2 \times \frac{1}{2}R)$ from vibration.

$$\therefore \text{Molar heat capacity} = C_v = \left(\frac{3}{2} + \frac{3}{2} + 3\right)R$$
$$= 6R$$

Problem 9.3

The vapor pressure of the solid is

$$-RT \ln P_s^\circ = \Delta H_s - T \Delta S_s \quad \dots (1)$$

The vapor pressure of the liquid is

$$-RT \ln P_l^\circ = \Delta H_l - T \Delta S_l \quad \dots (2)$$

At the melting point $T = T_f$, and the solid and liquid phases are in equilibrium,

$$G_l = G_s$$

$$H_l - T_f S_l = H_s - T_f S_s$$

$$\therefore H_l - H_s = T_f (S_l - S_s)$$

$$\therefore \Delta S_f = S_l - S_s = \frac{\Delta H_f}{T_f}$$

$$\begin{aligned} \therefore \Delta S_s &= S_g - S_s = S_g - S_l + S_l - S_s \\ &= \Delta S_l + \frac{\Delta H_f}{T_f} \end{aligned}$$

$$\therefore \Delta S_l = \Delta S_s - \frac{\Delta H_f}{T_f} \quad \dots (3)$$

At the triple point the heat of sublimation equals the sum of the heats of fusion and the heat of vaporization:

$$\ell_{13} = \ell_{12} + \ell_{23}$$

$$\text{or } \Delta H_s = \Delta H_l + \Delta H_f \quad \therefore \Delta H_l = \Delta H_s - \Delta H_f \quad \dots (4)$$

If the enthalpy differences are independent of T , then eq. (4) holds at all temperatures

Substituting eqs. (3) and (4) into (2) and using (1) for ΔH_s we get,

$$\begin{aligned} -RT \ln P_i^\circ &= \Delta H_s - \Delta H_f - T \Delta S_s + \frac{T}{T_f} \Delta H_f \\ &= -RT \ln P_s^\circ - \Delta H_f \left(1 - \frac{T}{T_f}\right) \end{aligned}$$

$$\therefore RT \ln \frac{P_i^\circ}{P_s^\circ} = \Delta H_f \left(1 - \frac{T}{T_f}\right)$$

$$\therefore P_i^\circ = P_s^\circ \exp \left[\frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \right]$$

(for $T > T_f$, $P_s^\circ(T)$ is the extrapolated vapor pressure curve over the solid)

Start from the Clausius-Clapeyron equation for the solid-liquid equilibrium:

$$\frac{dp}{dT_f} = \frac{\Delta H_f}{T_f \Delta V_f}$$

$$\therefore \frac{dT_f}{T_f} = \frac{\Delta V_f}{\Delta H_f} dp$$

Integrating:

$$\ln \frac{T_{f2}}{T_{f1}} \cong \frac{\Delta V_f}{\Delta H_f} (P_2 - P_1)$$

where p_1 is 1 atmosphere and T_{f1} is the melting point at 1 atm

$$\text{or } T_{f2} = T_{f1} \exp \left[\frac{\Delta V_f}{\Delta H_f} (p_2 - p_1) \right]$$

Therefore for an increase in the applied pressure

$(p_2 - p_1) > 0$, there are two cases for the melting point temperature:

- i) $T_{f2} > T_{f1}$, if $\Delta V_f > 0$ (i.e. if the material expands on melting)
- ii) $T_{f2} < T_{f1}$, if $\Delta V_f < 0$ (i.e. if the material expands with solidification)

Problem 9.4

(a) From Fig. 9.4, $p \cong 0.04$ atm. at $T = 3100^\circ\text{K}$.

$$v_g = \frac{RT}{p_g} = \frac{82 \frac{\text{cm}^3\text{-atm}}{\text{mole}^\circ\text{K}} \times 3100^\circ\text{K}}{0.04 \text{ atm}}$$

$$= 6 \times 10^6 \text{ cm}^3/\text{mole}$$

$$v_l = \frac{(238+32) \text{ gm/mole}}{\rho_l \text{ gm/cm}^3}$$

From Fig. 9.3 $\rho_l = 8.8 \text{ gm/cm}^3$.

$$\therefore v_l = \frac{270}{8.8} \cong 30 \text{ cm}^3/\text{mole}$$

$$v = v_l x_l + (1-x_l)v_g = 60 \text{ cm}^3/\text{mole}$$

solving for x_l gives,

$$\begin{aligned} \text{mole fraction } x_l &= \frac{1 - v/v_g}{1 - v_l/v_g} = 1 - \frac{v - v_l}{v_g} = 1 - \frac{30}{6 \times 10^6} \\ &= 1 - 5 \times 10^{-6} \end{aligned}$$

$$\begin{aligned} \text{volume fraction of liquid} &= \frac{x_l v_l}{v} \cong \frac{v_l}{v} = \frac{1}{2} \end{aligned}$$

(b) $U = x_l U_l + (1-x_l)U_g$

$$\begin{aligned} \Delta H_{\text{vap.}} &= \text{latent heat of vaporization} = 119.1 \text{ kcal/mole} \\ &= 498.6 \text{ kJ/mole} \end{aligned}$$

$$\Delta H_{\text{vap}} = H_g - H_l = U_g - U_l + p(v_g - v_l)$$

v_l is negligible compared to v_g

$$\therefore \Delta H_{\text{vap}} = U_g - U_l + p v_g = U_g - U_l + RT$$

$$\text{or } U_g - U_l = \Delta H_{\text{vap}} - RT = 119.1 - 1.98 \times 10^{-3} \times 3100$$

$$\therefore \Delta U_{\text{vap}} = U_g - U_l = 119.1 - 6.1 = 113 \text{ kcal/mole}$$

$$= \underline{472.3 \text{ kJ/mole}}$$

With reference state as ideal gas at 0°K .

$$U_g = \frac{13}{2} RT = 40 \text{ kcal/mole}$$

$$= \underline{167.2 \text{ kJ/mole}}$$

$$U = x_l U_l + (1 - x_l) U_g$$

$$\cong U_l + 5 \times 10^{-6} U_g \cong U_l \quad (\text{as the second term is negligible})$$

(c) From Eq. (9.35) ($p_s = p = \text{vapor pressure}$)

$$\left(\frac{dU}{dT}\right)_s \cong \left(\frac{dU_l}{dT}\right)_s = c_{pe} - T \left(\frac{dv_l}{dT}\right)_p \left(\frac{dp}{dT}\right) - p \left(\frac{dv_l}{dT}\right)_s$$

$\alpha_l = \text{liquid thermal coefficient of expansion}$

$$\alpha_l = \frac{1}{v_l} \left(\frac{dv_l}{dT}\right)_p = -\frac{1}{\rho_l} \left(\frac{d\rho_l}{dT}\right)_p \quad (\rho_l = \text{liquid density})$$

From Fig 9.3 ,

$$\alpha_l = 7.5 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$$

Assume

$$\left(\frac{dv_l}{dT}\right)_p \cong \left(\frac{dv_l}{dT}\right)_{\text{saturation}} \quad (\text{see Fig. 9.1})$$

$$= \alpha_l v_l$$

$$\begin{aligned} \therefore \left(\frac{dU_l}{dT}\right)_s &= C_{pe} - \left[T \frac{dp}{dT} + p\right] \left(\frac{dv_l}{dT}\right)_s \\ &= C_{pe} - \left[v_g T \frac{dp}{dT} + p v_g\right] \alpha_l \left(\frac{v_l}{v_g}\right) \end{aligned}$$

$$p v_g = RT \quad \therefore v_g = \frac{RT}{p}$$

$$\begin{aligned} \therefore \left[v_g T \frac{dp}{dT} + p v_g\right] &= \frac{RT^2}{p} \frac{dp}{dT} + RT \\ &= -R \frac{d \ln p}{d(1/T)} + RT = -\Delta H_{\text{vap}} + RT \\ &= -\Delta U_{\text{vap}} \end{aligned}$$

$$\begin{aligned} \therefore \left(\frac{dU_l}{dT}\right)_s &= C_{pe} + \Delta U_{\text{vap}} \alpha_l \frac{v_l}{v_g} \\ &= C_{pe} \left[1 + \frac{\Delta U_{\text{vap}}}{C_{pe}} \alpha_l \frac{v_l}{v_g}\right] \end{aligned}$$

$$\frac{\Delta U_{\text{vap}}}{C_{pe}} \alpha_l \frac{v_l}{v_g} = \frac{113 \times 10^3 \text{ cal/mole}}{18 \text{ cal/mole-}^\circ\text{K}} \times 7.5 \times 10^{-5} \times \frac{30}{6 \times 10^6} \cong 2.35 \times 10^{-6}$$

$$\therefore \left(\frac{dU_l}{dT}\right)_s \cong C_{pe}$$

Problem 9.5

From Eq. (9.37) :

$$\frac{1}{\gamma} = \frac{1}{V} \left(\frac{\partial U}{\partial P} \right)_V$$

But $\left(\frac{\partial U}{\partial P} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V$

and $\left(\frac{\partial U}{\partial T} \right)_V = C_V$, $\left(\frac{\partial T}{\partial P} \right)_V = \frac{\beta}{\alpha}$

(from problem 1.5 d)

$$\therefore \frac{1}{\gamma} = \frac{1}{V} C_V \frac{\beta}{\alpha}$$

or

$$\boxed{\gamma = \frac{\alpha V}{\beta C_V}}$$

CHAPTER 10

Problem 10.1

where $\alpha_{\text{U}} \sigma_{\text{U}}^f$ is the capture cross-section of U^{238}

Nuclide Balances

for Pu:
$$\frac{dN_{\text{Pu}}}{dt} = -\sigma_{\text{Pu}} N_{\text{Pu}} \phi + \alpha_{\text{U}} \sigma_{\text{U}}^f N_{\text{U}} \phi \quad \dots (1)$$

for U^{238} :
$$\frac{dN_{\text{U}}}{dt} = -(1 + \alpha_{\text{U}}) \sigma_{\text{U}}^f N_{\text{U}} \phi \quad \dots (2)$$

for F.P. pairs:
$$\frac{dN_{\text{F.P.}}}{dt} = \sigma_{\text{Pu}} N_{\text{Pu}} \phi + \sigma_{\text{U}}^f N_{\text{U}} \phi \quad \dots (3)$$

Definition of Burnup:
$$\beta \equiv \frac{N_{\text{F.P.}}}{N_{\text{U}}^0 + N_{\text{Pu}}^0} \quad \dots (4)$$

Combine eqs. (3) and (4)

$$\frac{d\beta}{dt} = \frac{\sigma_{\text{Pu}} N_{\text{Pu}} + \sigma_{\text{U}}^f N_{\text{U}}}{N_{\text{U}}^0 + N_{\text{Pu}}^0} \phi \quad \dots (5)$$

Transform the time variable to the burnup variable in eqs (1) and (2) by use of eq. (5),

i.e. $\frac{d}{d\beta} = \frac{d}{dt} \frac{dt}{d\beta}$ this gives,

$$\frac{dN_{Pu}}{d\beta} = \frac{dN_{Pu}/dt}{d\beta/dt} = \frac{-\sigma_{Pu} N_{Pu} + \alpha_U \sigma_U^f N_U}{\sigma_U N_{Pu} + \sigma_U^f N_U} (N_U^0 + N_{Pu}^0) \quad (6)$$

$$\text{and } \frac{dN_U}{d\beta} = - \frac{(1 + \alpha_U) \sigma_U^f N_U}{\sigma_{Pu} N_{Pu} + \sigma_U^f N_U} (N_U^0 + N_{Pu}^0) \quad (7)$$

Solve eqs. (6) and (7) subject to $N_{Pu}(0) = N_{Pu}^0$ and $N_U(0) = N_U^0$

Approximate Solution

Rewrite (6) and (7) as,

$$\frac{dN_{Pu}}{d\beta} = \frac{-1 + \alpha_U \left(\frac{\sigma_U^f N_U}{\sigma_{Pu} N_{Pu}} \right)}{1 + \left(\frac{\sigma_U^f N_U}{\sigma_{Pu} N_{Pu}} \right)} (N_U^0 + N_{Pu}^0) \quad (8)$$

$$\frac{dN_U}{d\beta} = - \frac{(1 + \alpha_U) \left(\frac{\sigma_U^f N_U}{\sigma_{Pu} N_{Pu}} \right)}{1 + \left(\frac{\sigma_U^f N_U}{\sigma_{Pu} N_{Pu}} \right)} (N_U^0 + N_{Pu}^0) \quad (9)$$

The conversion ratio is:

$$C = \frac{\alpha_U \sigma_U^f N_U \phi}{\sigma_{Pu} N_{Pu} \phi} = \frac{\alpha_U \sigma_U^f N_U}{\sigma_{Pu} N_{Pu}} \quad (10)$$

Then eqs. (8) and (9) become,

$$\frac{dN_{Pu}}{d\beta} = \frac{-(1 - C) (N_U^0 + N_{Pu}^0)}{1 + (C/\alpha_U)} \quad (11)$$

$$\frac{dN_u}{d\beta} = - \left(\frac{1+\alpha_u}{\alpha_u} \right) C \frac{(N_u^0 + N_{Pu}^0)}{1 + (C/\alpha_u)} \dots (12)$$

The approximation consists of setting $C \cong \text{constant}$, independent of burnup for the purpose of solving eqs (11) and (12).

This gives:

$$N_{Pu} = N_{Pu}^0 - \left(\frac{1-C}{1+C/\alpha_u} \right) (N_u^0 + N_{Pu}^0) \beta \dots (13)$$

and

$$N_u = N_u^0 - \left[\frac{(1+\alpha_u)C}{1+C/\alpha_u} \right] (N_u^0 + N_{Pu}^0) \beta \dots (14)$$

The plutonium fraction is:

$$q = \frac{N_{Pu}}{N_{Pu} + N_u} \dots (15)$$

Substituting eqs (13) and (14) into eq (15) gives,

$$q = \frac{q_0 - \left(\frac{1-C}{1+C/\alpha_u} \right) \beta}{1-\beta}$$

Problem 10.2

$$T_{Na} = \text{sodium temperature at mid plane} = 470 + \frac{1}{2} (650 - 470) = \underline{560^\circ \text{C}}$$

Sodium Film Temperature Drop:-

q_{Na} = heat flux from clad surface to coolant

$$q_{Na} = \frac{\phi}{2\pi R_c} = h_{Na} (T_{co} - T_{Na})$$

$$\therefore T_{co} - T_{Na} = \frac{\phi}{2\pi R_c h_{Na}} = \frac{550}{2\pi \times 0.315 \times 12} = \underline{23^\circ \text{C}}$$

(since $\phi = 550$ Watts/cm, $2R_c = 0.63$ cm
and $h_{Na} = 12$ Watts/cm²·°C)

$$\begin{aligned}\therefore T_{co} &= T_{Na} + 23^\circ\text{C} \\ &= 560 + 23 = \underline{583^\circ\text{C}}\end{aligned}$$

Temperature Drop through Cladding:-

Average heat flux through cladding $= q_c$

$$q_c = \frac{\rho}{2\pi(R_c - \frac{1}{2}t_c)} = \frac{k_c}{t_c} (T_{ci} - T_{co})$$

For stainless steel, $k_c = 0.22 \text{ Watts/cm-}^\circ\text{C}$

$$\frac{k_c}{t_c} = \frac{22 \times 10^{-2}}{4 \times 10^{-2}} = 5.5 \text{ Watts/cm}^2\text{-}^\circ\text{C}$$

$$\therefore T_{ci} - T_{co} = \frac{550}{2\pi(0.315 - 0.02) \times 5.5} = \underline{54^\circ\text{C}}$$

$$\therefore T_{ci} = \underline{637^\circ\text{C}} \quad \text{--- (1)}$$

$q_f = \text{surface heat flux from fuel}$

$$= \frac{\rho}{2\pi R}$$

From Eq. (10.63)

$$\int_{T_s}^{T_o} k dT = \frac{\rho}{4\pi}$$

$$\text{or, } \int_0^{T_o} k dT - \int_0^{T_s} k dT = \frac{\rho}{4\pi} = \frac{550}{4\pi} = \underline{43.8 \text{ Watts/cm}} \quad \text{--- (2)}$$

For the gas conductivity use Eq. (10.102),

$$k_g = 15.8 \times 10^{-6} (900)^{0.79} = 3.4 \times 10^{-3} \frac{\text{Watts}}{\text{cm-}^\circ\text{C}}$$

(Average temperature in the gas $= 900^\circ\text{K}$)

Then $q_f = \frac{k_g}{t_g} (T_s - T_{ci}) = \frac{\rho}{2\pi R} \dots (3)$

Gap Closure

Fuel thermal expansion $= \frac{\Delta R}{R} = \alpha_F (\bar{T}_f - T_a)$

$(T_a = \text{fabrication temp.} = 25^\circ\text{C})$

Clad thermal expansion $= \frac{\Delta R_c}{R_c} = \alpha_c (\bar{T}_c - T_a)$

Hot fuel radius $= R_f^{\text{hot}} = R_f^{\text{cold}} [1 + \alpha_F (\bar{T}_f - T_a)]$

Hot clad inner radius $= R_c^{\text{hot}} - t_c^{\text{hot}}$

$R_{ci}^{\text{hot}} = R_c^{\text{cold}} [1 + \alpha_c (\bar{T}_c - T_a)] - t_c^{\text{hot}}$

gap width $t_g^{\text{hot}} = R_{ci}^{\text{hot}} - R_f^{\text{hot}}$
and $t_g^{\text{cold}} = R_{ci}^{\text{cold}} - R_f^{\text{cold}} \quad \left. \vphantom{\begin{matrix} t_g^{\text{hot}} \\ t_g^{\text{cold}} \end{matrix}} \right\} \Rightarrow$

$t_g^{\text{hot}} - t_g^{\text{cold}} = R_{ci}^{\text{cold}} \alpha_c (\bar{T}_c - T_a) - R_f^{\text{cold}} \alpha_F (\bar{T}_f - T_a)$

Inserting numbers,

$\bar{T}_c = \frac{1}{2} (637 + 583) = 610^\circ\text{C.}, T_a = 25^\circ\text{C.}$

$\alpha_F \cong 1.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1} \quad (\text{Fig. 10.8})$

$\alpha_c \cong 1.8 \times 10^{-5} \text{ } ^\circ\text{C}^{-1} \quad (\text{Fig. 10.9})$

$R_f^{\text{cold}} = 0.315 - 0.04 - 0.007 = 0.268 \text{ cm.}$

$R_{ci}^{\text{cold}} = 0.315 - 0.04 = 0.275 \text{ cm}$

$\therefore t_g^{\text{hot}} - t_g^{\text{cold}} = 0.275 \times 1.8 \times 10^{-5} (610 - 25) - 0.268 \times 1.2 \times 10^{-5} (\bar{T}_f - T_a)$

$$\therefore t_g^{\text{hot}} - t_g^{\text{cold}} = 2.9 \times 10^{-3} - 3.22 \times 10^{-6} (\bar{T}_f - T_a) \dots (4)$$

Iterative Procedure

$$\text{Assume } t_g = t_g^{\text{cold}} = 7 \times 10^{-3} \text{ cm.}$$

$$\begin{aligned} \text{Then from eq. (3)} \quad T_s - T_{ci} &= \frac{\rho}{2\pi R \left(\frac{k_g}{t_g} \right)} \\ &= \frac{550}{2\pi \times 0.263 \times \left(\frac{3.4 \times 10^{-3}}{7 \times 10^{-3}} \right)} \\ &= 695^\circ\text{C} \end{aligned}$$

$$\therefore T_s = 637 + 695 = \underline{1332^\circ\text{C}}$$

$$\text{From Fig. (10.20) : } \int_0^{1332} k dT = \underline{51 \text{ Watts/cm}}$$

$$\begin{aligned} \text{Therefore from eq. (2)} \quad \int_0^{T_c} k dT &= 43.8 + 51 \\ &= \underline{94.8 \text{ Watts/cm.}} \end{aligned}$$

$$\text{From Fig. (10.20) : } T_0 \cong \underline{2700^\circ\text{C}}$$

Estimating $\bar{T}_f$;

$$\text{Assuming a parabolic profile } \frac{T - T_s}{T_0 - T_s} = 1 - \left(\frac{r}{R} \right)^2$$

$$T = T_s + (T_0 - T_s) \left[1 - \left(\frac{r}{R} \right)^2 \right] = T_0 - (T_0 - T_s) \left(\frac{r}{R} \right)^2$$

$$\begin{aligned} \text{Then } \bar{T}_f &\cong \frac{1}{\pi R^2} \int_0^R \left[T_0 - (T_0 - T_s) \left(\frac{r}{R} \right)^2 \right] 2\pi r dr \\ &= \frac{2}{R^2} T_0 \frac{R^2}{2} - \frac{2}{R^4} (T_0 - T_s) \frac{R^4}{4} \end{aligned}$$

$$\therefore \bar{T}_f = T_0 - \frac{1}{2} (T_0 - T_s) = \frac{1}{2} (T_0 + T_s)$$

Then $\bar{T}_f = \frac{1}{2} (1332 + 2700) = 2016^\circ\text{C}$

From eq. (4)

$$\begin{aligned} t_g^{\text{hot}} &= t_g^{\text{cold}} + 2.9 \times 10^{-3} - 3.22 \times 10^{-6} (2016 - 25) \\ &= 7 \times 10^{-3} + 2.9 \times 10^{-3} - 6.45 \times 10^{-3} \\ &= 3.45 \times 10^{-3} \text{ cm} \end{aligned}$$

1st Iteration

$$\frac{k_g}{t_g} = \frac{3.4}{3.45} = 0.985 \text{ Watts/cm}^2\text{-}^\circ\text{C}$$

$$\begin{aligned} \therefore T_s - T_{ci} &= \frac{550}{2\pi \times 0.263 [1 + 1.2 \times 10^{-5} (2016 - 25)] \times 0.985} \\ &= \frac{550}{2\pi \times 0.275 \times 0.985} = 323^\circ\text{C} \end{aligned}$$

$$\therefore T_s^{(2)} = 637 + 323 = 960^\circ\text{C}$$

From Fig. (10.20) $\int_0^{960} k dT = 41 \text{ Watts/cm}$

$$\therefore \int_0^{T_0} k dT = 43.8 + 41 = 84.8 \text{ cm}$$

$$\therefore T_0^{(2)} = \underline{2520^\circ\text{C}} \quad [\text{from Fig. (10.20)}]$$

$$\therefore \bar{T}_f = \frac{1}{2} (2520 + 960) = 1740^\circ\text{C}$$

and $t_g^{\text{hot}} = 7 \times 10^{-3} + 2.9 \times 10^{-3} - 3.22 (1740 - 25) \times 10^{-6}$
 $= 4.525 \times 10^{-3} \text{ cm}$

Repeat the iterations until convergence

Final values $T_0 \cong 2530^\circ\text{C}$, $T_s \cong 1050^\circ\text{C}$

Problem 10.3

a) For no loss of Plutonium:

$$\frac{1}{\pi R^2} \int_0^R \frac{q(r)}{q_0} 2\pi r dr = 1 \quad \text{--- (1)}$$

$$\therefore 1 = 1 + \frac{D}{\pi R^2} \int_0^R \left\{ \exp \left[-2\alpha \left(\frac{r-r^*}{R} \right) \right] - 2 \exp \left[-\alpha \left(\frac{r-r^*}{R} \right) \right] \right\} 2\pi r dr$$

$$\text{or } \int_0^R \exp \left[-2\alpha \left(\frac{r-r^*}{R} \right) \right] r dr = 2 \int_0^R \exp \left[-\alpha \left(\frac{r-r^*}{R} \right) \right] r dr$$

$$\text{Let } \eta = \frac{r}{R}, \quad \eta^* = \frac{r^*}{R}$$

$$\text{Then } \int_0^1 \exp \left[-2\alpha (\eta - \eta^*) \right] \eta d\eta = 2 \int_0^1 \exp \left[-\alpha (\eta - \eta^*) \right] \eta d\eta$$

$$\text{or } e^{2\alpha\eta^*} \int_0^1 \eta e^{-2\alpha\eta} d\eta = 2e^{\alpha\eta^*} \int_0^1 \eta e^{-\alpha\eta} d\eta$$

Integrating,

$$\frac{1}{8} e^{\alpha\eta^*} \left[1 - (2\alpha+1)e^{-2\alpha} \right] = 1 - (\alpha+1)e^{-\alpha}$$

$$\text{For } \alpha=10 \quad e^{-2\alpha} \cong 0 \quad \text{and} \quad e^{-\alpha} \cong 0$$

Therefore

$$e^{\alpha\eta^*} = 8$$

$$\text{or } \eta^* = \frac{1}{\alpha} \ln 8 = \frac{\ln 8}{10} = \underline{0.207}$$

$$b) \quad \frac{q(0)}{q_0} = 1 + D \left\{ e^{2\alpha\eta^*} - 2e^{\alpha\eta^*} \right\}$$

$$\therefore \frac{q(0)}{q_c} = 1 + 10^{-2} \{64 - 2 \times 8\} = 1 + 10^{-2} \times 48$$

$$= \underline{1.48}$$

Then $q(0) = 1.48 \times 20\% \cong \underline{30\%}$

For the minimum Plutonium concentration:

Making $\frac{dq(r)}{dr} = 0$ and with a little of algebra yields,

$q(r)$ is minimum at $r = r^*$

$$\frac{q(r^*)}{q_c} = 1 - D' = 0.99$$

or $q(r^*) = 0.99 \times 20\% = \underline{19.8\%}$

$$c) \quad H(r) = \bar{H} \frac{q(r)}{q_0}$$

with $\bar{H}$ = Average power density of fuel

With constant thermal conductivity Eq.(10.49) reduces to:

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) = - \frac{\bar{H}}{k} \frac{q(r)}{q_0} \quad \text{--- (2)}$$

Boundary Conditions: i) $T(R) = T_s$

ii) $T(0) = T_0$

For the initial plutonium distribution, $\frac{q(r)}{q_0} = 1$,

$\bar{H} = H_0$, initial power density.

Temperature distribution is given by Eq.(10.52):

$$T - T_s = \frac{1}{4} \frac{H_0 R^2}{k} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad \text{--- (3)}$$

For non-uniform plutonium distribution:

Integrating eq (2),

$$r \frac{dT}{dr} = - \frac{\bar{H}}{k} \int r \frac{q(r)}{q_0} dr + A$$

Changing variable to $\eta = \frac{r}{R}$;

$$\eta \frac{dT}{d\eta} = - \frac{\bar{H} R^2}{k} \int \eta \frac{q(\eta)}{q_0} d\eta + A$$

$$\begin{aligned}
 \therefore \eta \frac{dT}{d\eta} &= -\frac{\bar{H}R^2}{2k} \eta^2 - \frac{\bar{H}R^2 D}{k} \left\{ e^{2\alpha\eta^*} \int \eta e^{-2\alpha\eta} d\eta \right. \\
 &\quad \left. - 2e^{\alpha\eta^*} \int \eta e^{-\alpha\eta} d\eta \right\} + A \\
 &= -\frac{\bar{H}R^2}{2k} \eta^2 + \frac{\bar{H}R^2 D}{\alpha^2 k} \left\{ \frac{e^{2\alpha\eta^*} e^{-2\alpha\eta}}{4} (1+2\alpha\eta) \right. \\
 &\quad \left. - 2e^{\alpha\eta^*} e^{-\alpha\eta} (1+\alpha\eta) \right\} + A
 \end{aligned}$$

B.C. At $\eta=0$, $\frac{dT}{d\eta} = 0$

$$\therefore A = -\frac{\bar{H}R^2 D}{\alpha^2 k} \left\{ \frac{1}{4} e^{2\alpha\eta^*} - 2e^{\alpha\eta^*} \right\}$$

With $e^{\alpha\eta^*} = 8$, $e^{2\alpha\eta^*} = 64$

$$A = -\frac{\bar{H}R^2 D}{\alpha^2 k} \left\{ \frac{64}{4} - 2 \times 8 \right\} = 0$$

Then

$$\begin{aligned}
 \frac{dT}{d\eta} &= -\frac{\bar{H}R^2}{k} \left\{ \frac{\eta}{2} - \frac{D}{4\alpha^2} e^{2\alpha\eta^*} \left(\frac{1+2\alpha\eta}{\eta} \right) \right. \\
 &\quad \left. + \frac{2D}{\alpha^2} e^{\alpha\eta^*} \left(\frac{1+\alpha\eta}{\eta} \right) e^{-\alpha\eta} \right\}
 \end{aligned}$$

Integrating from $\eta=1$ to $\eta=\eta$, $T=T_s$ to $T=T$
yields:

$$\begin{aligned}
 T - T_s &= \frac{\bar{H}R^2}{k} \left\{ \frac{1}{4}(1-\eta^2) - \frac{D}{4\alpha^2} e^{2\alpha\eta^*} \left[F(2\alpha, \eta) + (e^{-2\alpha\eta} - e^{-2\alpha}) \right] \right. \\
 &\quad \left. + \frac{2D}{\alpha^2} e^{\alpha\eta^*} \left[F(\alpha, \eta) + (e^{-\alpha\eta} - e^{-\alpha}) \right] \right\} \quad \dots (4)
 \end{aligned}$$

With $F(\alpha, \eta) = \int_{\eta}^1 \frac{e^{-\alpha\eta}}{\eta} d\eta$;

d) $H \sim \rho$ (linear power of rod)

For T_0 to be the same before and after redistribution:

$$\frac{\rho_0}{\rho} = \frac{H_0}{H} = 1 + \frac{D}{\alpha^2} \left\{ 8e^{\alpha\eta^*} [F(\alpha, 0) + (1 - e^{-\alpha})] - e^{2\alpha\eta^*} [F(2\alpha, 0) + (1 - e^{-2\alpha})] \right\}$$

(using eqs. (3) and (4) and putting $\eta=0$ in these)

since $8e^{\alpha\eta^*} = e^{2\alpha\eta^*}$ and neglecting $e^{-\alpha}$ and $e^{-2\alpha}$

We get,

$$\begin{aligned} \frac{\rho_0}{\rho} &= 1 + \frac{8D}{\alpha^2} e^{\alpha\eta^*} [F(\alpha, 0) - F(2\alpha, 0)] \\ &= 1 + \frac{8D}{\alpha^2} e^{\alpha\eta^*} \int_0^1 \frac{e^{-\alpha\eta} - e^{-2\alpha\eta}}{\eta} d\eta \end{aligned}$$

Examine the behavior of the integral near $\eta=0$

$$e^{-\alpha\eta} \rightarrow 1 - \alpha\eta + \frac{1}{2}\alpha^2\eta^2 - \dots + \dots$$

$$e^{-2\alpha\eta} \rightarrow 1 - 2\alpha\eta + 2\alpha^2\eta^2 - \dots + \dots$$

$$\therefore \frac{e^{-\alpha\eta} - e^{-2\alpha\eta}}{\eta} = \alpha - \frac{3}{2}\alpha^2\eta + \dots \text{ (negligible near } \eta=0 \text{)}$$

$\therefore \text{Integral} \cong \frac{1}{5} \alpha$ (estimate of area on plot)

$$\frac{\rho_0}{\rho} = 1 + \frac{8D e^{\alpha \eta^*}}{\alpha^2} \left(\frac{1}{5} \alpha \right) = 1 + \frac{64}{5} \times 10^{-3}$$

$$= \underline{1.013}$$

Approximately 1.3% reduction in power is needed in order to keep T_0 constant. The effect is small because volume where η changes (near $r=0$) contains little mass.

Problem 10.4

a)

$$\text{Area per channel} = L^2 = \pi R^2 = \text{Area of unit cell}$$

$$\therefore R = \frac{L}{\sqrt{\pi}}$$

There are N_p fuel pellets $/\text{cm}^3$, each of radius R_p and contains fully enriched $U^{235}O_2$.

$$\text{Heat produced / pellet} = \sigma_{fiss} N_f \phi \left(\frac{4}{3} \pi R_p^3 \right) \times 3.07 \times 10^{11} \text{ watts/pellet}$$

$$\text{Heat generation rate } / \text{cm}^3 = H = 3.07 \times 10^{11} \times \sigma_{fiss} \times N_f \phi \left(\frac{4}{3} \pi R_p^3 \right) \times N_p$$

--- (1)

P = Linear power per channel

$$P = \pi (R^2 - R_0^2) H \quad \text{--- (2)}$$

b) Temperature distribution in graphite:

$$\frac{1}{r} \frac{d}{dr} \left(r k_g \frac{dT}{dr} \right) + H = 0 \quad \text{--- (3)}$$

where H is given by (1).

k_g = thermal conductivity of graphite

B.C.

$$T(R_0) = T_s = \text{temperature of the surface of coolant channel} \quad \text{--- (4)}$$

$$\left(\frac{dT}{dr} \right)_{r=R} = 0 \quad [\text{by definition of unit cell}] \quad \text{--- (5)}$$

Integrating we get

$$r \frac{dT}{dr} = -\frac{1}{2} \frac{H}{k_g} r^2 + C_1$$

Using (5) we get,

$$C_1 = \frac{1}{2} \frac{H}{k_g} R^2 \quad \text{--- (6)}$$

Integrating once more

$$T = -\frac{1}{4} \frac{H}{k_g} r^2 + \frac{1}{2} \frac{H}{k_g} R^2 \ln r + C_2$$

Using (4) we get,

$$T_s = -\frac{1}{4} \frac{H}{k_g} R_0^2 + \frac{1}{2} \frac{H}{k_g} R^2 \ln R_0 + C_2$$

$\therefore$ Temperature distribution in graphite is

$$T - T_s = \frac{1}{4} \frac{H}{k_g} \left\{ R_0^2 - r^2 + 2R^2 \ln \left(\frac{r}{R_0} \right) \right\} \quad \text{--- (7)}$$

c) Temperature distribution in and around pellet:

Let T^* = Temperature far away from pellet equal to the value given by (7) for radial location r of pellet in unit cell.

H_p = power density in pellet

$$H_p = \sigma_{fiss.} N_f \phi \times 3.07 \times 10^{11} \text{ --- (8)}$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 k_p \frac{dT}{dr} \right) + H_p = 0 \text{ --- (9)}$$

k_p = thermal conductivity of fuel material in pellet.

Integrate once:

$$r^2 \frac{dT}{dr} = -\frac{1}{3} \frac{H_p}{k_p} r^3 + C_1$$

$$\frac{dT}{dr} = 0 \text{ at } r=0 \therefore C_1 = 0$$

Integrate once more:

$$T = -\frac{1}{6} \frac{H_p}{k_p} r^2 + C_2 \text{ --- (10)}$$

In graphite near pellet

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 k_g \frac{dT}{dr} \right) = 0$$

Integrate once:

$$r^2 \frac{dT}{dr} = C_3 \text{ --- (11)}$$

Determine C_3 by relating heat flows at interface: ($r=R_p$)

$$\left. -k_p \frac{dT}{dr} \right|_{R_p} \underset{\text{(pellet)}}{=} = \left. -k_g \frac{dT}{dr} \right|_{R_p} \underset{\text{(graphite)}}{=}$$

From (10) and (11)

$$-k_p \left(-\frac{1}{3} \frac{H_p}{k_p} R_p \right) = -k_g \left(\frac{C_3}{R_p^2} \right)$$

$$\therefore C_3 = -\frac{1}{3} \frac{H_p}{k_g} R_p^3 \quad \text{--- (12)}$$

Integrating (11) once more

$$T = -\frac{C_3}{r} + C_4 = \frac{1}{3} \frac{H_p}{k_g} \frac{R_p^3}{r} + C_4 \quad \text{--- (13)}$$

Now the temperature in graphite far from pellet is equal to T^* given by (7).

$$\therefore C_4 = T^*$$

Equality of temperatures at the interface $r=R_p$ gives, from (10) and (13)

$$-\frac{1}{6} \frac{H_p}{k_p} R_p^2 + C_2 = \frac{1}{3} \frac{H_p}{k_g} \frac{R_p^3}{R_p} + T^*$$

This determines C_2 .

Therefore the distribution in the pellet is from (10)

$$\boxed{T - T^* = \frac{1}{6} \frac{H_p}{k_p} (R_p^2 - r^2) + \frac{1}{3} \frac{H_p}{k_g} R_p^2} \quad (0 \leq r \leq R_p) \quad \text{--- (14)}$$

and in the graphite near the pellet is from (13)

$$\boxed{T - T^* = \frac{1}{3} \frac{H_p}{k_g} \frac{R_p^3}{r}} \quad (r \geq R_p) \quad \text{--- (15)}$$

Problem 10.5

Random Spherical Pores of Same Diameter Obstacles
in Glide Plane Analysis:

C = Number of spherical pores / cc (total volume)

r_p = Radius of each pore.

(a)

The volume $(2r_p)(1\text{cm}^2)$ contains the centers of $C(2r_p)$ pores, each of which intersects the plane
 $\therefore$ There are $2r_p C$ intersections/cm².

$$\therefore \text{Area / Intersection} = \frac{1}{2r_p C} = \ell^2$$

$$\therefore \text{Average distance between intersections} = \ell = 1/\sqrt{2r_p C}$$

(b) ℓ = radius of circle formed by intersection of pore with plane

$$\boxed{s = r_p \sqrt{1 - (y/r_p)^2}} \quad (\text{length of chord})$$

Assume - of the pores which intersect the plane, the distances of their centers from the plane is randomly distributed

or $p(y) dy =$ probability of a given pore being within a distance y and $y+dy$ from the plane;

$$p(y) = \frac{1}{r_p} \quad \left(\text{since } \int_0^{r_p} p(y) dy = \int_0^{r_p} \frac{dy}{r_p} = 1 \right)$$

$A(y) =$ Area of circle formed in the plane with center of the pore a distance y from the plane

$$A(y) = \pi s^2 = \pi r_p^2 [1 - (y/r_p)^2]$$

$\bar{A} =$ Average area of circle

$$\bar{A} = \int_0^{r_p} A(y) p(y) dy = \frac{\pi r_p^2}{r_p} \int_0^{r_p} [1 - (y/r_p)^2] dy$$

$$\text{Let } \eta = \frac{y}{r_p}$$

$$\therefore \bar{A} = \pi r_p^2 \int_0^1 (1 - \eta^2) d\eta$$

$$= \frac{2}{3} \pi r_p^2$$

(c)

$P_c =$ Fraction of area of plane occupied by intersecting circles

$$\begin{aligned} P_c &= \left(\frac{\text{intersections}}{\text{cm}^2} \right) \left(\frac{\text{area}}{\text{intersection}} \right) \\ &= (2\gamma_p C) \bar{A} \\ &= 2\gamma_p C \left(\frac{2}{3} \pi \gamma_p^2 \right) \\ &= \frac{4}{3} \pi \gamma_p^3 C \\ &= P \quad (\text{porosity}) \end{aligned}$$

Problem 10.6

Initial porosity = P_0

Conductivity is given by Eq. (10.40) ;

$$k_0 = k_s (1 - P^{2/3}) \quad \text{independent of temperature}$$

a) Energy Equation

$$k_0 \frac{d^2 T}{dx^2} + H_c = 0 ;$$

Integrating : $\frac{dT}{dx} = -\frac{H_c}{k} x + A ;$

Boundary Condition: i) At $x=0$, $\frac{dT}{dx} = 0$

This gives $A = 0$

Integrating again : $T = -\frac{1}{2} \frac{H_c}{k_0} x^2 + B$

Boundary Condition: ii) At $x=L$, $T = T_s$

This gives $B = T_s + \frac{1}{2} \frac{H_c}{k_0} L^2$

Therefore :

$$T - T_s = \frac{1}{2} \frac{H_0}{k_0} L^2 \left(1 - \frac{x^2}{L^2}\right)$$

Also : $T(0) = T_m$.

$$\therefore H_0 = \frac{2k_0(T_m - T_s)}{L^2} = \frac{2k_s(1 - P_0^{2/3})(T_m - T_s)}{L^2}$$

b) After restructuring

From Eq. (10.40) $k_1 = k_s (1 - P_1^{2/3})$

$$T = -\frac{1}{2} \frac{H}{k_1} x^2 + Ax + B$$

$$\text{and } \frac{dT}{dx} = -\frac{H}{k_1} x + A$$

B.C. i) $\frac{dT}{dx} = 0$ at $x = x_0$

This gives, $A = \frac{H}{k_1} x_0$

B.C. ii) $T = T_s$ at $x = L$

This gives, $B = T_s + \frac{1}{2} \frac{H}{k_1} L^2 - \frac{HX_0L}{k_1}$

Mass balance gives, $s_0L = s_1(L - x_0)$

$$\therefore \frac{x_0}{L} = 1 - \frac{s_0}{s_1} = 1 - \frac{1-p_0}{1-p_1}$$

Now we have $T(x_0) = T_m$, then

$$T_m = -\frac{1}{2} \frac{H}{k_1} x_0^2 + \frac{HX_0^2}{k_1} + \left(T_s + \frac{1}{2} \frac{H}{k_1} L^2 - \frac{HX_0L}{k_1} \right)$$

$$\therefore T_m - T_s = \frac{HX_0^2}{2k_1} + \frac{HL^2}{2k_1} - \frac{HX_0L}{k_1}$$

$$\begin{aligned} \text{or } H &= \frac{T_m - T_s}{\frac{1}{2} \left(\frac{L^2}{k_1} \right) \left[1 - 2 \frac{x_0}{L} + \left(\frac{x_0}{L} \right)^2 \right]} \\ &= \frac{2k_1(T_m - T_s)}{L^2 \left(1 - \frac{x_0}{L} \right)^2} = \frac{2k_1(T_m - T_s)}{L^2 \left(s_0/s_1 \right)^2} \end{aligned}$$

or rearranging:

$$\begin{aligned} H &= \frac{2k_0(T_m - T_s)}{L^2} \cdot \frac{k_1}{k_0} \cdot \frac{L^2}{L^2 \left(1 - \frac{x_0}{L} \right)^2} \\ &= H_0 \left(\frac{1-p_1^{2/3}}{1-p_0^{2/3}} \right) \left(\frac{1-p_1}{1-p_0} \right)^2 \end{aligned}$$

Therefore

$$\frac{H}{H_0} = \left(\frac{1-p_1^{2/3}}{1-p_0^{2/3}} \right) \left(\frac{1-p_1}{1-p_0} \right)^2$$

Problem 10.7

a)

After half restructuring we have two regions and void.

Region ① = Columnar grain region with density = ρ_1

Region ② = Unrestructured region with density = ρ_0

(initial value)

Since reactor power is constant the power density in the unrestructured region is $H_2 = H_0$.

H_2 = power density in region ②

H_1 = power density in region ①

$$\frac{H_1}{H_2} = \frac{\rho_1}{\rho_0} \quad \text{--- (1)}$$

Mass balance (per unit area)

$$\text{Initial} = \rho_0 L$$

$$\text{Final} = \rho_0 (L - x_1) + \rho_1 (x_1 - x_0)$$

Equating and dividing by $\rho_0 L$

$$1 = \left(1 - \frac{x_1}{L}\right) + \frac{\rho_1}{\rho_0} \left(\frac{x_1}{L} - \frac{x_0}{L}\right)$$

$$\therefore \left(\frac{s_1}{s_0} - 1\right) \left(\frac{x_1}{L}\right) = \left(\frac{s_1}{s_0}\right) \left(\frac{x_0}{L}\right) \quad \text{--- (2)}$$

Final value of the central void occurs when $x_1 = L$

$$\text{or} \quad \frac{x_{cf}}{L} = \frac{s_1/s_0 - 1}{s_1/s_0} = 1 - \frac{s_0}{s_1} \quad \text{--- (3)}$$

$$\text{For this problem} \quad \frac{x_0}{x_{cf}} = \frac{1}{2}$$

$$\text{or} \quad \frac{x_0}{L} = \frac{1}{2} \left(1 - \frac{s_0}{s_1}\right) \quad \text{--- (4)}$$

Using this in eq (2) we get,

$$\left(\frac{s_1}{s_0} - 1\right) \left(\frac{x_1}{L}\right) = \left(\frac{s_1}{s_0}\right) \frac{1}{2} \left(1 - \frac{s_0}{s_1}\right)$$

$$\therefore \boxed{\frac{x_1}{L} = \frac{1}{2}} \quad \text{--- (5)}$$

b) Integrating the heat conduction equation, we get

$$\text{Region ①:} \quad T_1(x) = -\frac{1}{2} \frac{H_1}{k_1} x^2 + A_1 x + B_1; \quad \frac{dT_1}{dx} = -\frac{H_1}{k_1} x + A_1 \quad \text{--- (6)}$$

$$\text{Region ②:} \quad T_2(x) = -\frac{1}{2} \frac{H_2}{k_2} x^2 + A_2 x + B_2; \quad \frac{dT_2}{dx} = -\frac{H_2}{k_2} x + A_2 \quad \text{--- (7)}$$

$$\text{B.C.} \quad \text{i) } \left(\frac{dT_1}{dx}\right)_{x_0} = 0 \quad \text{--- (8)}$$

$$\text{ii) } k_1 \left(\frac{dT_1}{dx}\right)_{x_1} = k_2 \left(\frac{dT_2}{dx}\right)_{x_1} \quad \text{--- (9)}$$

$$\text{iii)} \quad T_1(x_1) = T_2(x_1) \quad \text{--- (10)}$$

$$\text{iv)} \quad T_2(L) = T_s \quad \text{--- (11)}$$

From (8) :

$$A_1 = \frac{H_1}{k_1} x_0 = \frac{H_2}{k_2} L \left(\frac{H_1}{H_2} \right) \left(\frac{k_2}{k_1} \right) \left(\frac{x_0}{L} \right)$$

$$= \frac{H_2}{k_2} L \left(\frac{s_1}{s_c} \right) \left(\frac{k_2}{k_1} \right) \frac{1}{2} \left(1 - \frac{s_c}{s_1} \right) \quad \text{--- (12)}$$

[using (1) and (4)]

From (9) :

$$-H_1 x_1 + k_1 A_1 = -H_2 x_1 + k_2 A_2$$

$$\therefore -H_1 x_1 + H_1 x_0 = -H_2 x_1 + k_2 A_2 \quad [\text{using (12)}]$$

$$\therefore A_2 = \frac{1}{k_2} \left\{ H_1 x_0 - (H_1 - H_2) x_1 \right\}$$

$$= \frac{H_1 x_0}{k_2} \left\{ 1 - \left(1 - \frac{s_c}{s_1} \right) \left(\frac{x_1}{x_0} \right) \right\} \quad [\text{using (1)}]$$

$$= \frac{H_1 x_0}{k_2} \left\{ 1 - \frac{\left(1 - \frac{s_c}{s_1} \right) \frac{s_1}{s_c}}{\left(\frac{s_1}{s_c} - 1 \right)} \right\} \quad [\text{using (2)}]$$

$$= \frac{H_1 x_0}{k_2} \{ 1 - 1 \} = 0 \quad \text{--- (13)}$$

From (11) :

$$T_s = -\frac{1}{2} \frac{H_2}{k_2} L^2 + B_2$$

$$\therefore B_2 = T_s + \frac{1}{2} \frac{H_2}{k_2} L^2 \quad \text{--- (14)}$$

From (10):

$$-\frac{1}{2} \frac{H_1}{k_1} x_1^2 + \frac{H_1}{k_1} x_0 x_1 + B_1 = -\frac{1}{2} \frac{H_2}{k_2} x_1^2 + T_5 + \frac{1}{2} \frac{H_2}{k_2} L^2$$

[using (12), (13) and (14)]

$$\therefore B_1 = T_5 + \frac{1}{2} \frac{H_2}{k_2} L^2 \left[1 - \left(\frac{x_1}{L} \right)^2 \right] + \frac{1}{2} \frac{H_1}{k_1} L^2 \left\{ \left(\frac{x_1}{L} \right)^2 - 2 \left(\frac{x_0}{L} \right) \left(\frac{x_1}{L} \right) \right\}$$

$$\text{or } B_1 = T_5 + \frac{1}{2} \frac{H_2}{k_2} L^2 \left[1 - \left(\frac{x_1}{L} \right)^2 \right] + \frac{1}{2} \frac{H_2}{k_2} L^2 \left(\frac{H_1}{H_2} \right) \left(\frac{k_2}{k_1} \right) \left\{ \left(\frac{x_1}{L} \right) \left[\left(\frac{x_1}{L} \right) - 2 \left(\frac{x_0}{L} \right) \right] \right\}$$

$$\text{or } B_1 = T_5 + \left(\frac{1}{2} \frac{H_2}{k_2} L^2 \right) \left\{ 1 - \left(\frac{x_1}{L} \right)^2 + \left(\frac{s_1}{s_0} \right) \left(\frac{k_2}{k_1} \right) \left(\frac{x_1}{L} \right) \left(\frac{x_1}{L} - 2 \frac{x_0}{L} \right) \right\} \quad \text{--- (15)}$$

This determines the temperature profiles in the two regions.

c) At the edge of the central void

$$T_1(x_0) = -\frac{1}{2} \frac{H_1}{k_1} x_0^2 + A_1 x_0 + B_1 \quad \text{--- (16)}$$

$$-\frac{1}{2} \frac{H_1}{k_1} x_0^2 + A_1 x_0 = -\left(\frac{1}{2} \frac{H_2}{k_2} L^2 \right) \left(\frac{s_1}{s_0} \right) \left(\frac{k_2}{k_1} \right) \left(\frac{x_0}{L} \right)^2 + 2 \left(\frac{1}{2} \frac{H_2}{k_2} L^2 \right) \left(\frac{s_1}{s_0} \right) \left(\frac{k_2}{k_1} \right) \left(\frac{x_0}{L} \right)^2$$

[using (1) and (12)]

$$= \frac{1}{2} \frac{H_2}{k_2} L^2 \left(\frac{s_1}{s_0} \right) \left(\frac{k_2}{k_1} \right) \left(\frac{x_0}{L} \right)^2$$

combining with (15) and (16):

$$T_1(x_c) - T_s = \left(\frac{1}{2} \frac{H_2}{k_2} L^2 \right) \left\{ \frac{s_1}{s_c} \frac{k_2}{k_1} \left(\frac{x_c}{L} \right)^2 + 1 - \left(\frac{x_1}{L} \right)^2 + \frac{s_1}{s_c} \frac{k_2}{k_1} \left(\frac{x_1}{L} \right) \left(\frac{x_1}{L} - 2 \frac{x_c}{L} \right) \right\}$$

But from Problem 10.6, with $H_c = H_2$,

$$\frac{1}{2} \frac{H_2}{k_2} L^2 = T_m - T_s \quad ; \quad (T_m = \text{initial centerline temperature before restructuring})$$

$$\begin{aligned} \therefore \frac{T_1(x_c) - T_s}{T_m - T_s} &= \frac{s_1}{s_c} \frac{k_2}{k_1} \left[\left(\frac{x_c}{L} \right)^2 + \left(\frac{x_1}{L} \right)^2 - 2 \left(\frac{x_1}{L} \right) \left(\frac{x_c}{L} \right) \right] + 1 - \left(\frac{x_1}{L} \right)^2 \\ &= \frac{s_1}{s_c} \frac{k_2}{k_1} \left(\frac{x_1}{L} - \frac{x_c}{L} \right)^2 + 1 - \left(\frac{x_1}{L} \right)^2 \quad \text{--- (17)} \end{aligned}$$

With $k_2 = k_c$ and from Problem 10.6 $\frac{s_1}{s_c} = \frac{1 - P_1}{1 - P_0}$

and $\frac{k_2}{k_1} = \frac{1 - P_0^{2/3}}{1 - P_1^{2/3}}$

Using (4) and (5)

$$\frac{x_1}{L} - \frac{x_c}{L} = \frac{1}{2} - \frac{1}{2} + \frac{1}{2} \frac{s_0}{s_1} = \frac{1}{2} \frac{1 - P_0}{1 - P_1}$$

$$1 - \left(\frac{x_1}{L} \right)^2 = 1 - \left(\frac{1}{2} \right)^2 = \frac{3}{4}$$

$$\therefore \boxed{\frac{T_1(x_c) - T_s}{T_m - T_s} = \frac{1}{4} \left(\frac{1 - P_0}{1 - P_1} \right) \left(\frac{1 - P_0^{2/3}}{1 - P_1^{2/3}} \right) + \frac{3}{4}} \quad \text{--- (18)}$$

Problem 10.8 Multicollision Effect upon α

$$T_r^{(1)} = T_i + \alpha(T_s - T_i) = \alpha T_s + (1-\alpha)T_i$$

$$\alpha = \frac{T_r^{(2)} - T_r^{(1)}}{T_s - T_r^{(1)}}$$

$$\begin{aligned} \therefore T_r^{(2)} &= T_r^{(1)} + \alpha[T_s - T_r^{(1)}] = \alpha T_s + (1-\alpha)T_r^{(1)} \\ &= \alpha T_s + (1-\alpha)\{\alpha T_s + (1-\alpha)T_i\} \\ &= [\alpha + \alpha(1-\alpha)]T_s + (1-\alpha)^2 T_i \end{aligned}$$

If there are 3 collisions,

$$\begin{aligned} T_r^{(3)} &= T_r^{(2)} + \alpha(T_s - T_r^{(2)}) = \alpha T_s + (1-\alpha)T_r^{(2)} \\ &= \alpha T_s + (1-\alpha)\alpha(2-\alpha)T_s + (1-\alpha)^3 T_i \\ &= \alpha T_s [1 + (1-\alpha)(2-\alpha)] + (1-\alpha)^3 T_i \end{aligned}$$

$$\alpha_{eff} = \frac{T_r^{(3)} - T_i}{T_s - T_i}$$

$$\alpha_{eff.} = \frac{\alpha [1 + (1-\alpha)(2-\alpha)] T_s + [(1-\alpha)^3 - 1] T_i}{T_s - T_i}$$

$$(1-\alpha)^3 - 1 = -3\alpha + 3\alpha^2 - \alpha^3 = \alpha(-3 + 3\alpha - \alpha^2)$$

$$\begin{aligned} \therefore \frac{\alpha_{eff.}}{\alpha} &= \frac{[1 + (1-\alpha)(2-\alpha)] T_s - (\alpha^2 - 3\alpha + 3) T_i}{T_s - T_i} \\ &= \frac{[1 + 2 - 3\alpha + \alpha^2] T_s - (\alpha^2 - 3\alpha + 3) T_i}{T_s - T_i} \end{aligned}$$

$$\therefore \alpha_{eff.} = \alpha(\alpha^2 - 3\alpha + 3) = \alpha[1 + (1-\alpha)(2-\alpha)]$$

General expression for n collisions is:

$$\alpha_{eff.} = \alpha [1 + (1-\alpha)(2-\alpha) \dots (n-1-\alpha)]$$

Problem 10.9

a)

The slope of temperature in the gap is

$$\frac{dT}{dx} = - \frac{T_s - T_c}{q_f + t_{gap} + q_c} \quad \dots (1)$$

$$\text{Heat flux in the gap} = q = -k \frac{dT}{dx} = h_{gap} (T_s - T_c) \dots (2)$$

From (1) and (2), we get,

$$k_{gap} \frac{(T_s - T_c)}{q_f + t_{gap} + q_c} = h_{gap} (T_s - T_c)$$

$$\therefore \boxed{h_{gap} = \frac{k_{gap}}{q_f + t_{gap} + q_c}}$$

b)

$$q_f = 2 \left(\frac{2-\alpha}{\alpha} \right) \left(\frac{\gamma}{1+\gamma} \right) \left(\frac{k}{\mu C_p} \right)_{fuel} \lambda$$

For He, $\gamma = \frac{5}{3}$. For VO_2 , $\alpha = 0.1$

$$\frac{k}{\mu C_p} \cong 0.7, \quad \lambda = \frac{\lambda_0}{P} \left(\frac{T}{273} \right)$$

Mean free path in Helium at 1 atm pressure and room temperature is $0.17 \mu\text{m}$ (see p. 70, chapter 10)

$$\therefore \text{At } 1000^\circ\text{K. } \lambda = \frac{0.17 \times 10^{-6} \times 1000}{300}$$

$$= 0.056 \times 10^{-5} \text{ m.}$$

$$= 5.6 \times 10^{-7} \text{ m.}$$

$$\therefore q_f = 2 \left(\frac{\frac{5}{3}}{1 + \frac{5}{3}} \right) \times 0.7 \times 5.6 \times 10^{-7} \times \left(\frac{2-\alpha}{\alpha} \right)_{\text{fuel}}$$

$$= \frac{5}{4} \times 0.7 \times 5.6 \times 10^{-7} \times \left(\frac{2-\alpha}{\alpha} \right)_{\text{fuel}}$$

$$= 4.9 \times 10^{-7} \times \left(\frac{2-0.1}{0.1} \right)$$

$$= 19 \times 4.9 \times 10^{-7} = 93.1 \times 10^{-7} \text{ m.}$$

$$= \underline{9.31 \mu\text{m}}$$

$$q_c = 4.9 \times 10^{-7} \left(\frac{2-\alpha}{\alpha} \right)_{\text{cladding}}$$

$$= 4.9 \times 10^{-7} \left(\frac{2-0.2}{0.2} \right) = 9 \times 4.9 \times 10^{-7} \text{ m}$$

$$= \underline{4.41 \mu\text{m}}$$

$$k_{\text{gap}} = 15.8 \times 10^{-6} \times (1000)^{0.79} = 15.8 \times 10^{-6} \times 235$$

$$= 3.72 \times 10^{-3} \text{ Watts/cm-}^\circ\text{C}$$

$$\therefore \left| \frac{dT}{dx} \right| = \text{slope} = \frac{q}{k_{\text{gap}}} = \frac{1200}{3.72 \times 10^{-3}}$$

$$= \underline{3.22 \times 10^5} \text{ }^\circ\text{C/cm}$$

$$\begin{aligned}\therefore \text{Temperature jump at fuel end} &= q_f \times \text{slope} \\ &= 9.31 \times 10^{-4} \text{ cm} \times 3.22 \times 10^5 \text{ }^\circ\text{C/cm} \\ &= \underline{300^\circ\text{C}}\end{aligned}$$

$$\begin{aligned}\text{Temperature jump at cladding end} &= q_c \times \text{slope} \\ &= 4.41 \times 10^{-4} \times 3.22 \times 10^5 \text{ }^\circ\text{C} \\ &= \underline{142^\circ\text{C}}\end{aligned}$$

Problem 10.10

We have from Eq. (10.94) for overall heat transfer coefficient U ,

$$\begin{aligned}\frac{1}{U} &= \frac{1}{h_{\text{gap}}} + \frac{t_c}{k_c} + \frac{1}{h_{\text{coolant}}} \\ &= 1 + \frac{1}{9} + \frac{1}{12} = \frac{36+4+3}{36} = \frac{43}{36}\end{aligned}$$

$$\therefore U = \underline{0.84} \text{ Watts/cm}^2\text{-}^\circ\text{C}.$$

$$\text{Heat flux} = U(T_s - T_{\text{coolant}}) = \frac{\rho}{2\pi R_c}$$

(R_c - outside radius of cladding)

$$\therefore q = \frac{800}{\pi(0.7)} = 0.84(T_s - 500)$$

$$\therefore T_s = 500 + 433 = 933^\circ\text{C}.$$

$$\begin{aligned}\int_{T_s}^{T_{\text{MP}}} k dT &= \int_0^{T_{\text{MP}}} k dT - \int_0^{T_s} k dT = 93 - 40 \\ &= 53 \text{ Watts/cm}\end{aligned}$$

[Using Eq. (10.66) and Fig. (10.40)]

From Eq. (10.65) with $T^* = T_{\text{MP}}$

$$\int_{T_s}^{T_{\text{MP}}} k dT = \frac{\rho}{4\pi} \left[1 - \left(\frac{r_m}{R} \right)^2 \right]$$

$$\begin{aligned}\therefore \left(\frac{\gamma_m}{R}\right)^2 &= 1 - \frac{4\pi}{\rho} \int_{T_b}^{T_{mp}} k dT \\ &= 1 - 0.83 = 0.17\end{aligned}$$

$$\therefore \left(\frac{\gamma_m}{R}\right) = \sqrt{0.17} = \underline{0.412}$$

CHAPTER 11

Problem 11.1

For the gaseous state H_2O/H_2 equilibrium:

At $1500^\circ K$,

$$\Delta G_{H_2O}^{\circ*} = -58.9 + 13.1 \times 1.5 = -39.2 \text{ kcal/mole}$$

* This value is given in metric system of units in the problem statement.

$$\Delta G_{H_2O}^{\circ} = -RT \ln K_{H_2O} = -RT \ln \left[\frac{P_{H_2O}}{P_{H_2} \sqrt{P_{O_2}}} \right]$$

$$\text{For } \frac{P_{H_2O}}{P_{H_2}} = 1,$$

$$RT \ln P_{O_2} = 2 \Delta G_{H_2O}^{\circ} = -78.4 \quad \dots (1)$$

O_2 equilibrium above UO_{2+x} at $1500^\circ K$:

$$\overline{\Delta G}_{O_2} = RT \ln P_{O_2} = \overline{\Delta H}_{O_2}^* - \overline{\Delta S}_{O_2}^* \left(\frac{T}{10^3} \right) \text{ kcal/mole}$$

* These values are given in metric units in the problem statement.

Using $RT \ln P_{O_2}$ value from eq.(1), we get,

$$\begin{aligned} -78.4 &= -125 + 1.6 \times 10^4 x - 1.5(-29 + 6.6 \times 10^3 x) \\ &= -125 + 43.5 + 1.6 \times 10^4 x - 0.99 \times 10^4 x \end{aligned}$$

$$\therefore -78.4 = -81.5 + 0.61 \times 10^4 x$$

$$\therefore x = \frac{3.1}{0.61 \times 10^4}$$

$$= \underline{5.1 \times 10^{-4}}$$

The stoichiometry is :

Problem 11.2

$P_{O_2} = \text{constant}$ (with radius)

$$\overline{\Delta G}_{O_2} = RT \ln P_{O_2} = \overline{\Delta H}_{O_2}^* - T \overline{\Delta S}_{O_2}^*$$

* These values are given in metric units in the problem statement.

$$= -65 + 120RTx$$

(T in units of 10^3 K)

$$\therefore x = \frac{1}{120} \left\{ \ln P_{O_2} + \frac{65}{RT} \right\} \quad \text{--- (1)}$$

Parabolic Profile

$$\frac{T - T_s}{T_0 - T_s} = 1 - \left(\frac{r}{R}\right)^2$$

a) Average value of $x = \bar{x}$

$$\bar{x} = \frac{1}{\pi R^2} \int_0^R 2\pi r x(r) dr$$

$$\text{let } \eta = \left(\frac{r}{R}\right)^2; \text{ then } T = T_s + (T_0 - T_s)(1 - \eta) \quad \text{--- (2)}$$

$$\text{and } \bar{x} = \int_0^1 x(\eta) d\eta = \frac{1}{120} \int_0^1 \left\{ \ln P_{O_2} + \frac{65}{RT_s \left[1 + \frac{T_0 - T_s}{T_s}(1 - \eta) \right]} \right\} d\eta$$

[Using (1) and (2)]

Integrating and solving for $\ln P_{O_2}$, we obtain:

$$\ln P_{O_2} = 120 \bar{x} - \frac{65}{R(T_0 - T_s)} \ln \left(\frac{T_0}{T_s} \right) \quad \text{--- (3)}$$

$$\bar{x} = .05$$

$$\therefore \ln P_{O_2} = 120 \times .05 - \frac{65}{1.98 \times 1.5} \ln(2.5)$$

$$= -14.1$$

$$\therefore P_{O_2} = \underline{7.5 \times 10^{-7}} \text{ atm}$$

b) From eq. (1),

$$x = \frac{1}{120} \left\{ \ln P_{O_2} + \frac{65}{R} \frac{1}{T} \right\}$$

$$= -\frac{14.1}{120} + \frac{65}{120 \times 1.98} \frac{1}{T} \quad (T \text{ in units of } 10^3 \text{ } ^\circ K.)$$

$$= -0.1175 + \frac{0.274}{T}$$

τ/R	η	$T/10^3$ ($^\circ K$)	x
0	0	2.50	(-0.0079)
0.2	0.04	2.44	(-0.0052)
0.4	0.16	2.26	(+0.0037)
0.6	0.36	1.96	+0.022
0.8	0.64	1.54	+0.060
1.0	1.00	1.00	+0.156

(Note: The negative values of x are not correct. The ΔG_{O_2} approximation used here is valid only for $x > \sim +.005$)

c) At $r=R$, $\bar{\Delta G}_{O_2} = RT_s \ln P_{O_2}$

$$= 1.98 \times 1.00 (-14.1)$$

$$= -28 \text{ kcal/mole}$$

From Fig. 12.7, ΔG_{Zr}° for the reaction,

$$Zr + O_2(g) = ZrO_2$$

at $1000^\circ K$ is $\cong -220 \text{ kcal/mole}$

Since $\bar{\Delta G}_{O_2} > \Delta G_{Zr}^\circ$, the cladding should be oxidized thermodynamically. However, as soon as the oxide layer is formed the rate of further oxidation reduces drastically as the oxygen has to diffuse through the oxide layer. This prevents catastrophic corrosion of the cladding.

Problem 11.3

(a)

From Fig. 10.4, the volume of Gas plenum

$$V_p = \frac{\pi}{4} (0.6)^2 \times 66$$

$$= \underline{18.66 \text{ cm}^3}$$

Volume of fuel

$$V_f = \frac{\pi}{4} (0.6)^2 \times [112 + 30 + 46]$$

$$= \frac{\pi}{4} \times 0.36 \times 188$$

$$= \underline{53.16 \text{ cm}^3}$$

Let us assume that the density of fuel is 90% of theoretical density.

$$\text{i.e. } \rho_f = 0.9 \times 10.43 \text{ gm/cm}^3$$

Then the number of fuel atoms in a rod are

$$N_f = \frac{\rho_f V_f}{M_f} N_{AV}$$

$$= \frac{0.9 \times 10.43 \times 6.02 \times 10^{23} \times 53.16}{270} = 1.17 \times 10^{24}$$

If N_c are number of carbon atoms, then

$$\frac{N_c M_c}{N_f M_f} = \frac{5}{10^6} \quad (\text{i.e. 5 ppm by weight})$$

$$\therefore N_c = \frac{5}{10^6} \times \frac{270}{12} \times 1.17 \times 10^{24}$$

$$= \underline{1.32 \times 10^{20}}$$

Then the number of carbon atoms in the gas plenum $= N_c' = \frac{N_c}{2} = \underline{0.66 \times 10^{20}}$ atoms

Let us assume that CO and CO₂ are ideal gases.

Then their partial pressures p_{CO} and p_{CO_2} will be proportional to their numbers of molecules.

i.e. $\frac{p_{CO_2}}{p_{CO}} = \frac{N_{CO_2}}{N_{CO}}$ or $\frac{p_{CO_2}}{p} = \frac{N_{CO_2}}{N_{CO_2} + N_{CO}}$

$$= \frac{N_{CO_2}}{N_c'}$$

where p is the total pressure

$$\therefore p V_p = N_c' k T$$

$$k = 1.38 \times 10^{-16} \text{ erg/molecule} \cdot ^\circ K$$

$$T \cong 900^\circ K, \quad 1 \text{ atm} = 1.0133 \times 10^6 \text{ dynes/cm}^2$$

$$\therefore p = \frac{N_c' k T}{V_p} = \frac{0.66 \times 10^{20} \times 1.38 \times 10^{-16} \times 900}{18.66} = 0.44 \times 10^6 \text{ dynes/cm}^2$$

$$= \underline{0.44 \text{ atm}}$$

(b)

Oxygen balance:
 (neglect oxygen in O_2)

Basis 1 gm mole $\text{UO}_{2.005}$

initial O = 2.005 gm atoms O in fuel

final O → in fuel = $2+x$ gm atoms O
 in gas, let $\gamma \equiv (P_{\text{CO}_2} / P_{\text{CO}})$

N_c = gm atoms carbon per mole UO_2

$$N_c = 44 \times 10^{-6} \times \frac{270}{12} = 10^{-3}$$

Let

$f \equiv$ fraction of gas as CO_2

$$f = \frac{P_{\text{CO}_2}}{P_{\text{CO}} + P_{\text{CO}_2}} = \frac{\gamma}{\gamma + 1}$$

Now,

$$\text{gm atoms O in gas} = 2 N_c f + N_c (1-f)$$

(as CO_2) (as CO)

$$= N_c \left(\frac{2\gamma}{1+\gamma} + \frac{1}{1+\gamma} \right)$$

$$= \left(\frac{2\gamma+1}{\gamma+1} \right) N_c$$

$$\therefore 2.005 = (2+x) + \left(\frac{2\gamma+1}{\gamma+1} \right) N_c$$

↑
initial O
in fuel

↑
final O
in fuel

O in gas as CO, CO_2

$$\text{or, } 0.005 = x + \left(\frac{2\gamma + 1}{\gamma + 1} \right) 10^{-3} \quad (1)$$

Equilibrium
gas phase:

$$\Delta G_c^\circ = -282 + 86.8 \frac{T}{10^3} \text{ in [kJ/mole]}$$

$$= -151.8 \text{ @ } 1500^\circ \text{K}$$

$$\frac{P_{\text{CO}_2} / P_{\text{CO}}}{\sqrt{P_{\text{O}_2}}} = e^{-\Delta G_c^\circ / RT}$$

$$\text{or, } RT \ln \gamma = \frac{1}{2} \Delta G_{\text{O}_2} - \Delta G_c^\circ \quad (2)$$

$$\Delta G_{\text{O}_2} = RT \ln P_{\text{O}_2}$$

Fuel oxygen potential:

$$\Delta G_{\text{O}_2} = \Delta H_{\text{O}_2} - T \Delta S_{\text{O}_2}$$

$$\Delta G_{\text{O}_2} = -523 + 121 \left(\frac{T}{10^3} \right) + \left(6.7 \times 10^4 - 2.8 \times 10^4 \left(\frac{T}{10^3} \right) \right) \times$$

$$\text{at } T = 1500^\circ \text{K}$$

$$\Delta G_{\text{O}_2} = -341.5 + 2.5 \times 10^4 \times \left[\frac{\text{kJ}}{\text{mole}} \right]$$

Now, using ΔG_c° & ΔG_{O_2} in (2), obtain

$$\ln \gamma = -1.52 + 10^3 x \quad (3)$$

Combine (1) & (3)

$$5 = \ln \gamma + 1.52 + \left(\frac{2\gamma + 1}{\gamma + 1} \right) \quad (4)$$

Solving (4), $\gamma = 5$. Substituting in (3) yields $x = 0.003$

Problem 11.4

Since it is a hypostoichiometric mixed oxide,

$$V_u = 4 \quad ; \quad V_{Pu} = 4 - \frac{2x}{q} \quad [\text{from Eq. (11.15)}]$$

$$q = 0.2, \quad x = 0.02 \quad (\text{since } O/M = 1.98)$$

$$\therefore V_{Pu} = 4 - \frac{0.04}{0.2} = \underline{3.80}$$

From Fig. (11.13) using Javed and Roberts plot
(as it corresponds to a temperature range
1400–1700°C. which is closer to 2241°C. than
Markin and McIver plot temperature range)

$$\bar{\Delta S}_{O_2}^* = -55 \text{ eu} \quad (\text{for } V_{Pu} = 3.8)$$

$$\text{From Fig. (11.4)} \quad \bar{\Delta H}_{O_2}^* = -220 \text{ kcal/mole}$$

[Javed & Roberts plot]

$$\begin{aligned} \therefore \bar{\Delta G}_{O_2} &= \bar{\Delta H}_{O_2}^* - \bar{\Delta S}_{O_2}^* (T/10^3) \quad [\text{from Eq. (11.14)}] \\ &= -220 + 55 \times 2.241 \\ &\cong -220 + 123 = \underline{-97 \text{ kcal/mole}} \end{aligned}$$

Then from Eq. (11.4)

$$RT \ln P_{O_2} = \bar{\Delta G}_{O_2} = -97 \text{ kcal/mole} \quad \text{--- (1)}$$

(* These values are given in metric units in the text.)

For atomic Oxygen:

Equilibrium requires

$$K_p = \frac{P_{\text{O}}}{\sqrt{P_{\text{O}_2}}} \quad \text{--- (2)}$$

$$\therefore \ln K_p = \ln P_{\text{O}} - \frac{1}{2} \ln P_{\text{O}_2}$$

$$\therefore \ln P_{\text{O}} = \ln K_p + \frac{1}{2} \ln P_{\text{O}_2} \quad \text{--- (3)}$$

From Table 11.2, for the reaction

$$\Delta H^\circ = 122.5 \text{ kcal/mole}, \quad \Delta S^\circ = 32.2 \text{ e.u.}$$

$$\therefore K = \frac{P_{\text{O}}^2}{P_{\text{O}_2}} = K_p^2 = e^{-\Delta G^\circ/RT}$$

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ(T/10^3) \quad [K_p \text{ -defined in eq (2)}]$$

$$= 122.5 - 2.241 \times 32.2$$

$$= 122.5 - 72.1 = 50.4 \text{ kcal/mole}$$

$$\therefore K_p = e^{-\frac{\Delta G^\circ}{2RT}} = e^{-\frac{50.4}{2 \times 1.98 \times 2241}}$$

$$\therefore \ln K_p = -\frac{50.4}{2 \times 1.98 \times 2241}$$

[*These values are given in metric units in the text.]

From eq.(3),

$$\ln P_0 = \ln K_p + \frac{1}{2} \ln P_{O_2}$$

$$= - \frac{50.4}{2 \times 1.98 \times 2241} - \frac{97}{2 RT}$$

[using eq.(1)]

$$= - \frac{50.4 + 97}{2 \times 1.98 \times 2241}$$

$$= - \frac{147.4}{8.86} = -16.6$$

$$\therefore \log P_0 = - \frac{16.6}{2.303}$$

$$= -7.21$$

$$\therefore P_0 = \frac{10^{-7.21}}{\quad} \text{ atm}$$

Problem 11.5

UO_{2.2} at 1600°C.

$$T = 1600 + 273 = 1873^\circ \text{K.}$$

$$(a) \quad \overline{\Delta G}_{O_2} = \overline{\Delta H}_{O_2}(x) - \left(\frac{T}{10^3}\right) \overline{\Delta S}_{O_2}(x)$$

From Fig. 11.10, for $x = 0.2$

$$\overline{\Delta H}_{O_2} = -315 \text{ kJ/mole}$$

$$\overline{\Delta S}_{O_2} = -126 \text{ J/mole-}^\circ\text{K.}$$

$$\begin{aligned} \therefore \overline{\Delta G}_{O_2} &= -315 + 1.873 \times 126 \\ &= -79 \text{ kJ/mole} \end{aligned}$$

$$\begin{aligned} \therefore p_{O_2} &= \exp\left(\frac{\overline{\Delta G}_{O_2}}{RT}\right) = \exp\left(-\frac{79}{8.31 \times 1.873}\right) \\ &= 6.2 \times 10^{-3} \text{ atm.} \end{aligned}$$

From Fig. 11.6, $p_{O_2} = 10^{-2} \text{ atm.}$

(b) Following $p_{O_2} = 10^{-2} \text{ atm.}$ isobar, U₅O₁₃ precipitates out at point Q. (see fig.)

$T = 1350^\circ\text{C.}$ The other equilibrium phase is

UO_{2.256}. (last digit approximate)

(c) Cooling at constant O/U to 800°C. , (point R) the two phases present are UO_{2.17} at R' and UO_{2.23} at R''.

Relative amounts:-

Basic - 1 mole of UO_{2.2} initially.

Let f = fraction of $\text{UO}_{2.17}$ in the mixture

$$\text{Oxygen balance: } 2.17f + 2.23(1-f) = 2.2$$

$$\therefore f = \underline{0.5}$$

$$p_{\text{O}_2} \cong \underline{5 \times 10^{-10}} \text{ atm at this temp.}$$

CHAPTER 12

Problem 12.1

$$\text{Elemental yield} = \frac{\text{Number of Zr atoms at time } T}{\text{Number of heavy metal atoms fissioned}}$$

$$= \frac{1}{\dot{F}T} \sum_{j=90}^{99} N_{Zr, j}$$

$$\underline{A = 90}$$

Neglecting species with half lives shorter than $\sim$ day, the decay chain reduces to

$$\underline{5.77}$$

The growth of Sr^{90} is governed by ;

$$\frac{dN_{\text{Sr}}}{dt} = Y_{90} \dot{F} - N_{\text{Sr}} \lambda_{\text{Sr}} ; \text{ and } N_{\text{Sr}}(0) = 0$$

$$\therefore N_{\text{Sr}}(T) = \frac{Y_{90} \dot{F}}{\lambda_{\text{Sr}}} (1 - e^{-\lambda_{\text{Sr}} T})$$

$$\lambda_{\text{Sr}^{90}} = \frac{0.693}{28 \times 365} = 0.678 \times 10^{-4} \text{ days}^{-1}; T = 100 \text{ days};$$

$$Y_{90} = 5.77$$

$$\therefore N_{\text{Sr}}^{90}(T) = \frac{5.77 \dot{F}}{0.678 \times 10^{-4}} (1 - e^{-0.678 \times 10^{-4} \times 10^2})$$

$$= 851 \times 10^2 \dot{F} \times 0.00675 = 574.42 \dot{F}$$

$$\therefore N_{\text{Zr}}^{90}(T) = Y_{90} \dot{F} T - N_{\text{Sr}}^{90} = (577 - 574.42) \dot{F} = \underline{2.57 \dot{F}}$$

$$\underline{A = 91}$$

The decay chain reduces to:

For the first reaction:

$$\begin{aligned} \frac{dN_{Y^{91}}}{dt} &= \gamma_{91} \dot{F} - \lambda_{Y^{91}} N_{Y^{91}}, \text{ and } N_{Y^{91}}(0) = 0 \text{ gives} \\ N_{Y^{91}}(T) &= \frac{\gamma_{91} \dot{F} (1 - e^{-\lambda_{Y^{91}} T})}{\lambda_{Y^{91}}}; \quad \lambda_{Y^{91}} = \frac{0.693}{58d} = 0.0119 \text{ day}^{-1} \\ &= \frac{5.4 \dot{F}}{0.0119} (1 - e^{-1.19}) = F \times 453.78 \times 0.6958 = 315.7 \dot{F} \end{aligned}$$

$$\therefore N_{Z_r^{91}}(T) = \gamma_{91} \dot{F} T - N_{Y^{91}}(T) = (540 - 315.7) \dot{F} = 224.3 \dot{F}$$

From the second reaction:

$$N_{Z_r^{91}}(T) = \gamma'_{91} \dot{F} T = 44 \dot{F}$$

$$\text{So: } N_{Z_r^{91}}(T) = (224.3 + 44) \dot{F} = \underline{268.3 \dot{F}}$$

$$\underline{A = 92}$$

The decay chain reduces to:

$$\therefore N_{Z_r^{92}}(T) = \gamma_{Z_r^{92}} \dot{F} T = \underline{603 \dot{F}}$$

$$\underline{A = 93}$$

The decay chain reduces to:

$$\therefore N_{Z_r^{93}}(T) = \gamma_{Z_r^{93}} \dot{F} T = \underline{645 \dot{F}}$$

$$\underline{A = 94}$$

The decay chain reduces to:

fission $\rightarrow$ stable Zr^{94} ($\gamma = 6.4$)

$$\therefore N_{Zr^{94}}(T) = \gamma_{Zr^{94}} \dot{F} T = \underline{640 \dot{F}}$$

$$\underline{A = 95}$$

The decay chain reduces to:

fission $\rightarrow$ $65d - Zr^{95} \rightarrow Nb^{95}$
($\gamma = 6.2$)

$$\lambda_{Zr^{95}} = \frac{0.693}{65d} = 0.01066 \text{ day}^{-1}$$

$$\frac{dN_{Zr^{95}}}{dt} = \gamma_{95} \dot{F} - N_{Zr^{95}} \lambda_{Zr^{95}} ; N_{Zr^{95}}(0) = 0 \text{ gives}$$

$$N_{Zr^{95}}(T) = \frac{6.2 \dot{F}}{0.01066} (1 - e^{-0.01066 \times 100}) = \underline{381.3 \dot{F}}$$

$$\underline{A = 96}$$

The decay chain reduces to:

fission $\rightarrow$ Zr^{96} ($\gamma = 6.33$)

$$\therefore N_{Zr^{96}}(T) = \gamma_{96} \dot{F} T = \underline{633 \dot{F}}$$

$$\underline{A = 97}$$

The decay chain reduces to:

fission $\rightarrow$ $17h - Zr^{97} \rightarrow Nb^{97}$
($\gamma = 5.9$)

$$\lambda_{Zr^{97}} = \frac{0.693}{17h} = \frac{0.693}{\frac{17}{24} \text{ day}} = 0.978 \text{ day}^{-1}$$

$$\frac{dN_{Zr^{97}}}{dt} = \gamma_{97} \dot{F} - N_{Zr^{97}} \lambda_{Zr^{97}} ; N_{Zr^{97}}(0) = 0, \text{ gives,}$$

$$N_{Zr^{97}}(T) = \frac{5.9 \dot{F}}{0.978} (1 - e^{-0.978}) = \underline{6.03 \dot{F}}$$

$$\underline{A = 98}$$

Neglect N_{Zr}^{98} as $N_{Zr}^{98}(T)$ will be very small

$$\underline{A = 99}$$

Neglect $N_{Zr}^{99}(T)$

Therefore:

$$\text{Elemental yield} = \frac{1}{\dot{F} T} \sum_{A=90}^{99} N_{Zr}^A(T)$$

$$Y_{Zr} = \frac{1}{100 \dot{F}} (2.57 + 268.3 + 603 + 645 + 640 + 381.3 + 633 + 6.03) \dot{F}$$

$$= \frac{3179.2 \dot{F}}{100 \dot{F}} = 31.79\%$$

$$\therefore \boxed{Y_{Zr} = 31.79\%} \quad (\text{after 100 days of irradiation})$$

Problem 12.2

a) 10^{12} oxide phase particle/cm³ of fuel.

∴ The volume occupied by one particle is

$$\frac{4}{3} \pi R^3 = 10^{-12} \text{ cm}^3.$$

$$\therefore R = \underline{0.62 \times 10^{-4} \text{ cm.}}$$

b) Since $Y_{Zr} > Y_{Ba-Sr}$, growth of oxide particles is controlled by rate of diffusion of Ba-Sr to oxide particle surface.

Diffusion of Ba-Sr in fuel annulus

$\dot{F}$ = fissions/cm³-sec ; Y_{Ba-Sr} = elemental yield of Ba-Sr

Quasi-stationary approximation is used since concentration of Ba-Sr in fuel is a slowly increasing function of time.

$$\frac{D}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = -Y_{Ba-Sr} \dot{F}$$

where

D = Diffusion coefficient of Ba^{+2} and Sr^{+2} ions in UO_2

C = Concentration of Ba-Sr in fuel at position r

Boundary Conditions:-

i) $C(R) = 0$ (oxide particle a perfect sink)

ii) $\left(\frac{dC}{dr}\right)_R = 0$ (by definition of "unit cell")

Solution

Let $u = rC$, then:

$$\frac{d^2u}{dr^2} = -\left(\frac{V_{Ba-Sr} \dot{F}}{D}\right) r = -Kr$$

$$\text{where } K = \frac{V_{Ba-Sr} \dot{F}}{D}$$

Integrating twice we get

$$u(r) = -\frac{1}{6} Kr^3 + Ar + B ; \quad \frac{du}{dr} = -\frac{1}{2} Kr^2 + A$$

B.C. i) $u(R) = 0$

ii) $\frac{1}{R} \left(\frac{du}{dr}\right)_R - \frac{u(R)}{R^2} = 0$

From i) $0 = -\frac{1}{6} KR^3 + AR + B$

From ii) $0 = -\frac{1}{2} KR + \frac{A}{R} + \frac{1}{6} KR - \frac{A}{R} - \frac{B}{R^2}$

$$\therefore B = -\frac{1}{3} KR^3, \quad A = \frac{\frac{1}{3} KR^3 + \frac{1}{6} KR^3}{R}$$

$$\therefore C(r) = \frac{u(r)}{r} = -\frac{1}{6} Kr^2 + \frac{1}{6} KR^2 + \frac{1}{3} K \frac{R^3}{R} - \frac{1}{3} K \frac{R^3}{r}$$

c) Growth of oxide particle

$J_{\text{Ba-Sr}}$ = Flux of Ba-Sr ions to outer surface of oxide particle, atoms/cm²-sec.

$$V_{\text{ox}} \cong 7 \times 10^{-23} \text{ cm}^3/\text{atom}$$

= Volume of oxide phase per atom of Ba or Sr.

Number of atoms of Ba-Sr in an oxide

$$\text{particle} = \frac{\frac{4}{3} \pi R^3}{V_{\text{ox}}}$$

The rate of influx of Ba-Sr atoms in the oxide particle = $4\pi R^2 J_{\text{Ba-Sr}}$

$$\therefore \frac{d}{dt} \left[\frac{\frac{4}{3} \pi R^3}{V_{\text{ox}}} \right] = 4\pi R^2 J_{\text{Ba-Sr}}$$

$$\therefore \boxed{\frac{dR}{dt} = V_{\text{ox}} J_{\text{Ba-Sr}}}$$

$$J_{\text{Ba-Sr}} = D \left(\frac{dc}{dr} \right)_R = \frac{D}{R} \left[\left(\frac{du}{dr} \right)_R - \frac{u}{R} \right]$$

$$= D \left[-\frac{1}{3} KR + \frac{1}{3} K \frac{R^3}{R^2} \right]$$

$$= \frac{KD}{3R^2} [R^3 - R^3] \cong \frac{KD R^3}{3R^2}$$

$$KD = \gamma_{\text{Ba-Sr}} \dot{F}$$

$$\therefore \frac{dR}{dt} = \frac{Y_{Ba-Sr} \dot{F} R^3 v_{ox}}{3R^2}$$

Integrating with $R(0) = 0$, we get,

$$R^3 = v_{ox} Y_{Ba-Sr} \dot{F} t R^3$$

This result could be arrived at by assuming that all Ba-Sr created in volume $\frac{4}{3}\pi R^3$ collect in sphere of radius R .

As a function of burnup:

$$\beta = \frac{\dot{F} t}{N_{HM}^0}, \text{ where } N_{HM}^0 = \text{Heavy metal atom density of fuel at time } t=0.$$

Then

$$\frac{R}{R} = (v_{ox} Y_{Ba-Sr} N_{HM}^0 \beta)^{1/3}$$

d) Inserting numbers:

$$\begin{aligned} \frac{R}{R} &= [7 \times 10^{-23} \times 0.1 \times 2.5 \times 10^{22} \times 0.05]^{1/3} \\ &= 0.26 \end{aligned}$$

$$\begin{aligned} \therefore R &= 0.26 R = 0.26 \times 62 \times 10^{-6} = 16 \times 10^{-6} \text{ cm.} \\ &= \underline{0.16 \mu\text{m}} \end{aligned}$$

Concentration profile:-

$$C = -\frac{1}{6} K r^2 + \frac{1}{3} K \frac{R^3}{R} + \frac{1}{6} K R^2 - \frac{1}{3} K \frac{R^3}{r}$$

$$\text{or } C(r) = \frac{Y_{\text{Ba-Sr}} \dot{F}}{6D} \left[2R^3 \left(\frac{r-R}{rR} \right) - (r^2 - R^2) \right] \quad (r \geq R)$$

[Eq. (13.60)]

or

$$\text{atom fraction Ba-Sr in fuel} = \frac{C(r)}{N_{\text{HM}}^0} = \left(\frac{Y_{\text{Ba-Sr}} \dot{F} R^2}{6 N_{\text{HM}}^0 D} \right) \left\{ 2 \left[\frac{(r/R) - (R/R)}{(r/R)(R/R)} \right] - \left[\left(\frac{r}{R} \right)^2 - \left(\frac{R}{R} \right)^2 \right] \right\}$$

$\frac{r}{R}$	Atom fraction Ba-Sr in fuel ($\times 10^9$)
0.26	0
0.30	2.0
0.40	5.2
0.50	7.0
0.60	8.1
0.70	8.8
0.80	9.2
0.90	9.4
1.00	9.5

Problem 12.3

a) $\overline{\Delta H}_{O_2}^* = \underline{-65} \text{ kcal/mole} \quad \text{--- (1)}$

$$V_U = 2(2+x) = 4+2x$$

$$\therefore x = \frac{1}{2}(V_U - 4)$$

$$\overline{\Delta S}_{O_2}^* = -120 R x \text{ cal/mole-}^\circ K$$

[* These values are
given in metric
units in the problem
statement.]

[See problem 11.2]

$$= -120 \times 1.98 \times \frac{1}{2} (V_U - 4)$$

$$= \underline{-118.8 (V_U - 4)} \text{ cal/mole-}^\circ K. \quad \text{--- (2)}$$

b) Initial number of atoms:

$$\text{uranium} = N_U^\circ$$

$$\text{oxygen} = \left(\frac{O}{M}\right) N_U^\circ = 2 N_U^\circ = N_O^\circ$$

Final number of atoms:

$$N_U = (1-\beta) N_U^\circ$$

Let N_1 be the number of atoms of +3 valence
and N_2 be the number of atoms of zero valence
(element)

Then since $\gamma=1$ for both f.p.1 and 2

$$N_1 = \beta N_U^\circ$$

$$N_2 = \beta N_U^\circ$$

Charge balance gives,

$$2 N_O^\circ = V_U N_U + 3 N_1 + 0 N_2$$

$$\therefore 2 N_0^\circ = V_U(1-\beta) N_U^\circ + 3\beta N_U^\circ$$

$$\therefore 2 \left(\frac{N_0^\circ}{N_U^\circ} \right) = V_U(1-\beta) + 3\beta$$

$$\text{But } \frac{N_0^\circ}{N_U^\circ} = 2$$

$$\therefore V_U = \frac{4-3\beta}{1-\beta} ;$$

$$\text{or } V_U - 4 = \frac{4-3\beta}{1-\beta} - 4 = \frac{\beta}{1-\beta}$$

$$\text{At 5\% burnup, } \beta = 0.05$$

$$\therefore V_U - 4 = \frac{0.05}{0.95} = 0.0526$$

$$\therefore \overline{\Delta S}_{O_2} = -118.8 \times 0.0526 \quad [\text{Using eq. (2)}]$$

$$= -6.25 \text{ cal/mole-}^\circ\text{K.}$$

$\therefore$ Oxygen potential at 1000°K. is

$$\begin{aligned} \overline{\Delta G}_{O_2} &= \overline{\Delta H}_{O_2} - T \overline{\Delta S}_{O_2} \\ &= -65 + \frac{1000 \times 6.25}{10^3} \text{ kcal/mole} \\ &= -65 + 6.25 \\ &= -58.75 \text{ kcal/mole} \\ &= -246 \text{ kJ/mole} \end{aligned}$$

Problem 12.4

- a) For ideal solution of Mo in metallic inclusions and of MoO_2 in fuel, the distribution of molybdenum is governed by:

$$K = e^{-\Delta G_{\text{Mo}}^{\circ}/RT} = \frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m P_{\text{O}_2}} \quad [\text{Eq. (12.17)}]$$

At 2000°K ,

$$\begin{aligned} \Delta G_{\text{Mo}}^{\circ} &= -574 + 164 \times 2 \\ &= -246 \text{ kJ/mole} \end{aligned}$$

$$\therefore \text{Oxygen potential} = \bar{\Delta G}_{\text{O}_2} = RT \ln P_{\text{O}_2}$$

$$= \Delta G_{\text{Mo}}^{\circ} + RT \ln \left(\frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m} \right)$$

$$\begin{aligned} RT \ln \left(\frac{y_{\text{Mo}}^f}{y_{\text{Mo}}^m} \right) &= 8.28 \times 2 \times \ln \left(\frac{0.08}{10} \right) \\ &= -80 \text{ kJ/mole} \end{aligned}$$

$$\therefore \bar{\Delta G}_{\text{O}_2} = -246 - 80 = -326 \text{ kJ/mole}$$

b)

There are 10^{-2} gms. of metallic inclusions per gm. of fuel.

or $10^{-2}/100$ gm. atoms of metallic inclusions per $1/10 \text{ cm}^3$ of fuel. But 10% of the inclusions consists of Mo.

$\therefore$ the Noble Metal concentration (gm atom/ cm^3 fuel)

$$\text{is: } N_{\text{NM}} = \frac{0.9 \times 10^{-4}}{1/10} = 9 \times 10^{-4} \text{ gm atoms/cm}^3 \text{ fuel of NM}$$

$$\begin{aligned}
 N_U^0 + N_{Pu}^0 &= \text{the initial heavy metal concentration} = 10 \text{ gms/cm}^3 \times \frac{1}{270 \text{ gm/g atom}} \\
 &= 3.7 \times 10^{-2} \frac{\text{g atom of HM}}{\text{cm}^3 \text{ of fuel}}
 \end{aligned}$$

Using Eq. (12.16)

$$\begin{aligned}
 \beta &= \frac{1}{Y_{NM}} \frac{N_{NM}}{(N_U^0 + N_{Pu}^0)} \\
 &= \frac{1}{0.456} \times \frac{9 \times 10^{-4}}{3.7 \times 10^{-2}} = \underline{0.053}
 \end{aligned}$$

(Y_{NM} obtained from Table 12.1,
using the value for mixed oxide)

Therefore the burnup $\beta = 5.3\%$

- c) If no Mo is lost or gained in unit volume, $(Y_{Mo}^f)^*$ and $(Y_{Mo}^m)^*$ would have been the compositions of the fuel and metallic inclusions respectively.

Expected total Mo concentration after 5.3% burnup from Eq. (12.16) is:

$$\begin{aligned}
 N_{Mo}^* &= (0.206) \times \beta \times (N_U^0 + N_{Pu}^0) \quad (\text{using Table 12.1}) \\
 &= (0.206) \times (0.053) \times (3.7 \times 10^{-2}) \quad [\text{using part (b)}] \\
 &= 4 \times 10^{-4}
 \end{aligned}$$

$$(N_{M_o}^{incl})^* = M_o \text{ in metallic inclusions, g atom/cm}^3 \text{ fuel} \\ \cong 10^{-3} \frac{\text{g atoms inclusions}}{\text{cm}^3 \text{ of fuel}} \times (y_{M_o}^m)^*$$

[where it is assumed that the metallic inclusions are principally Noble Metals and then the result of part (b) is used.]

$$(N_{M_o}^f)^* = M_o \text{ in fuel matrix, g atom/cm}^3 \text{ fuel} \\ = 3.7 \times 10^{-2} \frac{\text{g atom of fuel}}{\text{cm}^3 \text{ of fuel}} \times (y_{M_o}^f)^*$$

$$\therefore N_{M_o}^* = (N_{M_o}^{incl})^* + (N_{M_o}^f)^* = 10^{-3} (y_{M_o}^m)^* + 3.7 \times 10^{-2} (y_{M_o}^f)^*$$

However, the ratio $(y_{M_o}^f)^*/(y_{M_o}^m)^*$ is fixed by $\overline{\Delta G_{O_2}}$ and is the same as the measured value (despite loss or gain of total M_o)

$$\therefore (y_{M_o}^f)^* = \left(\frac{.08}{10}\right) (y_{M_o}^m)^*$$

$$\text{and } N_{M_o}^* = (y_{M_o}^m)^* \left[10^{-3} + 3.7 \times 10^{-2} \times \frac{.08}{10} \right] \\ = 1.3 \times 10^{-3} (y_{M_o}^m)^*$$

$$\therefore (y_{M_o}^m)^* = \frac{N_{M_o}^*}{1.3 \times 10^{-3}} = \frac{4 \times 10^{-4}}{1.3 \times 10^{-3}} \\ = \underline{0.31}$$

$\therefore$ The metallic inclusions should have contained

about 31% Mo if none of this element had been lost from this spot in the fuel. The fact that only 10% of the inclusions was Mo means that $\sim 2/3$ of the Mo produced by fission at the radial location where the measurements were made was removed by some migration process to other radial positions in the fuel pin.

Problem 12.5

$$(a) \quad RT \ln P_{O_2} = \overline{\Delta G}_{O_2} = \overline{\Delta H}_{O_2} - \overline{\Delta S}_{O_2}(T/10^3) \quad \dots (1)$$

At $T = 1000^\circ K$, using the results of problem 12.3, expressed in metric units

$$\overline{\Delta G}_{O_2} = -272 + 500(V_U - 4) \text{ kJ/mole} \quad \dots (2)$$

Oxygen Balance:-

Let N_O^0 = Initial number of oxygen atoms per unit Volume of fuel

N_U = Number of uranium atoms/unit volume

N_I = Number of +3 valence fission product atoms/unit volume

N_O^c = Number of oxygen atoms absorbed per unit area of cladding

charge balance in fuel gives,

$$2(N_O^0 - \frac{2\pi R}{\pi R^2} N_O^c) = V_U N_U + 3N_I \quad \dots (3)$$

$$N_O^c = \left(\frac{O}{M}\right) N_U^0 = 2N_U^0 \text{ (for initially stoichiometric fuel)}$$

$$N_U = (1-\beta) N_U^0$$

$$N_I = \beta N_U^0$$

Then eq.(3) gives,

$$2\left(2 - \frac{2}{R} \frac{N_O^c}{N_U^0}\right) = (1-\beta)V_U + 3\beta \quad \dots (4)$$

Solving, we get,

$$V_u - 4 = \frac{\beta}{1-\beta} - \frac{4 N_o^c}{(1-\beta) R N_u^o} \quad \text{--- (5)}$$

Substituting eq. (5) into eq. (2) we get,

$$\overline{\Delta G}_{O_2} = -272 + 500 \left[\frac{\beta}{1-\beta} - \frac{4 N_o^c}{(1-\beta) R N_u^o} \right]$$

At $T = 1000^\circ K$,

$$\overline{\Delta G}_{O_2} = RT \ln P_{O_2} = 8.314 \ln P_{O_2} \text{ kJ/mole}$$

$$[R = 8.314 \text{ J/mole-}^\circ K.]$$

$$\therefore P_{O_2} = \exp \left\{ -32.7 + 60 \left(\frac{\beta}{1-\beta} - \frac{4 N_o^c}{(1-\beta) R N_u^o} \right) \right\} \quad \text{--- (6)}$$

Cladding corrosion kinetics:-

$$\frac{dN_o^c}{dt} = C = k_{\text{corr}} P_{O_2} \quad \text{--- (7)}$$

$$\beta = \frac{\dot{F}t}{N_u^o}$$

Then using eq. (6) in (7) and converting from time variable to β variable, we get,

$$\dot{F} \frac{d}{d\beta} (N_o^c / N_u^o) = k_{\text{corr}} \exp \left\{ -32.7 + 60 \left(\frac{\beta}{1-\beta} - \frac{4 N_o^c}{(1-\beta) R N_u^o} \right) \right\} \quad \text{--- (8)}$$

Fraction of oxygen
absorbed by cladding

= X

$$\begin{aligned} \therefore X &= \frac{2\pi R N_0^c}{\pi R^2 N_0^o} \\ &= \frac{N_0^c}{R(\frac{1}{2}N_0^o)} = \frac{N_0^c}{R N_0^o} \quad \left[\left(\frac{Q}{M}\right)_0 = 2 \right] \end{aligned}$$

Let $A = \frac{k_{\text{corr}}}{R \dot{F}} = \text{dimensionless corrosion rate}$

Then eq.(8) becomes,

$$\frac{dx}{d\beta} = A \exp \left\{ -32.7 + 60 \left(\frac{\beta}{1-\beta} - \frac{4x}{1-\beta} \right) \right\}$$

with initial condition $x(0) = 0$.

---(9)

- (b) Eqn (9) is a non-linear equation, which is to be integrated numerically with $A = 10^{12}$ to obtain $x(\beta)$ as a function of burnup, β

Combining eqs(2) and (5) we get,

$$\overline{\Delta G_{O_2}}(\beta) = -272 + 500 \left[\frac{\beta}{1-\beta} - \frac{4x(\beta)}{1-\beta} \right]$$

---(10)

This is to be compared with the result from problem 12.3, namely,

$$\Delta G_{O_2}(\beta) = -272 + 500 \frac{\beta}{1-\beta} \quad \text{--- (11)}$$

Burnup β (%)	Fraction* of oxygen absorbed by clad $X(\beta)$	$\Delta G_{O_2}(\beta)$ for problem 12.5 eq. (10) (kJ/mole)	$\Delta G_{O_2}(\beta)$ for problem 12.3 eq. (11) (kJ/mole)
0.0	0.0	-272.00	-272.00
0.5	0.037×10^{-3}	-269.56	-269.49
1.0	0.086×10^{-3}	-267.12	-266.95
1.5	0.152×10^{-3}	-264.69	-264.39
2.0	0.240×10^{-3}	-262.29	-261.80
2.5	0.358×10^{-3}	-259.91	-259.18
3.0	0.513×10^{-3}	-257.59	-256.54
3.5	0.718×10^{-3}	-255.35	-253.87
4.0	0.983×10^{-3}	-253.22	-251.17
4.5	1.324×10^{-3}	-251.21	-248.44
5.0	1.752×10^{-3}	-249.37	-245.68
5.5	2.279×10^{-3}	-247.72	-242.90
6.0	2.913×10^{-3}	-246.28	-240.09
6.5	3.655×10^{-3}	-245.06	-237.24
7.0	4.504×10^{-3}	-244.05	-234.37
7.5	5.449×10^{-3}	-243.24	-231.46
8.0	6.480×10^{-3}	-242.61	-228.52
8.5	7.582×10^{-3}	-242.12	-225.55
9.0	8.741×10^{-3}	-241.76	-222.55
9.5	9.945×10^{-3}	-241.49	-219.51
10.0	11.180×10^{-3}	-241.29	-216.44

(* Values obtained using a predictor-corrector method)
Eq. (9) was solved numerically for burnup ranging from 0 to 10%, using a Runge-Kutta and a predictor-corrector method. The results of the two methods agree well with each other and are shown in the table above.

PROBLEM 12.6

(a) Substitute (12.13) - (12.16) into (12.22) and (12.23)

$$Y_{Mo}^f = \frac{f_{Mo} Y_{Mo} \beta}{(1-q)(1-\beta) + q(1-\beta) + (Y_{Y-RE} + f_{Mo} Y_{Mo} + Y_{Zr-Nb} - Y_{Ba-Sr})\beta}$$

$$= \frac{f_{Mo} Y_{Mo}}{\frac{1-\beta}{\beta} + Y_{Y-RE} + f_{Mo} Y_{Mo} + Y_{Zr-Nb} - Y_{Ba-Sr}} \quad \text{--- (1)}$$

and

$$Y_{Mo}^m = \frac{(1-f_{Mo}) Y_{Mo}}{Y_{NM} + (1-f_{Mo}) Y_{Mo}} \quad \text{--- (2)}$$

Given $\beta = 0.08$, and $f_{Mo} = 0.5$, and using the yields in the last column of table 12.1

$$Y_{Mo}^f = \frac{(0.5)(0.206)}{\frac{1-0.08}{0.08} + 0.493 + (0.5)(0.206) + 0.219 - 0.109} = 0.0084$$

$$Y_{Mo}^m = \frac{(0.5)(0.206)}{(0.456) + (0.5)(0.206)} = 0.184$$

(b) For an ideal solution of MoO_2 in the fuel, Raoult's Law is obeyed
and $P_{MoO_2} = P_{MoO_2}^0$
where $P_{MoO_2}^0$ is the vapor pressure of pure MoO_2

$$P_{MoO_2}^0 = \exp \left[- \frac{\Delta G_{vap, MoO_2}^0}{RT} \right]$$

$$\text{at } 2000^\circ K \quad P_{MoO_2}^0 = \exp \left[- \frac{561 - 203(2.0)}{(8.31)(2.0)} \right] = 8.9 \times 10^{-5} \text{ atm}$$

i. $P_{\text{MoO}_2} = (0.0084)(8.9 \times 10^{-5}) = 7.48 \times 10^{-7} \text{ atm}$
 This pressure is far too low for vapor transport of MoO_2

(C). Consider the reactions

ΔG_1° is given by equation (12.18) = $-137.1 + 39.3(T/10^3)$ Kcal/mole

$$\Delta G_2^\circ = 510 - 194(T/1000), \text{ KJ/mole}$$

Multiply reaction (1) by $\frac{1}{2}$, and add to reaction (2)

$$\Delta G_3^\circ = \frac{1}{2} \Delta G_1^\circ + \Delta G_2^\circ = \frac{1}{2}(-574) + 510 + \left[\frac{1}{2}(164) - 194\right](T/10^3)$$

$$= 223 - 112(T/10^3)$$

at $T = 2000^\circ \text{K}$ $\Delta G_3^\circ = -1.3 \text{ KJ/mole}$

The equilibrium of equation (3) is

$$\exp\left(-\frac{\Delta G_3^\circ}{RT}\right) = \frac{P_{\text{MoO}_3}}{\sqrt{P_{\text{O}_2}} \cdot Y_{\text{Mo}}^f}$$

or $RT \ln P_{\text{MoO}_3} = \frac{1}{2} RT \ln P_{\text{O}_2} + RT \ln Y_{\text{Mo}}^f - \Delta G_3^\circ$

But $RT \ln P_{\text{O}_2} = \Delta \bar{G}_{\text{O}_2} = \text{oxygen potential of fuel}$

$$\therefore P_{\text{MoO}_3} = Y_{\text{Mo}}^f \exp\left[\frac{\frac{1}{2} \Delta \bar{G}_{\text{O}_2} - \Delta G_3^\circ}{RT}\right]$$

at 2000°K

$$P_{\text{H}_2\text{O}_2} = 0.0084 \exp \left[\frac{\frac{1}{2}(-300) - (-1.3)}{(8.31)(2.0)} \right]$$

$$= 1.1 \times 10^{-6} \text{ atm}$$

This pressure is also too low for vapor transport migration

Problem 12.7

Eq. (12.44)

$$\left(\frac{\Delta V}{V}\right)_{\text{Solid fp}} = \left(\sum y_i \frac{v_i}{v_0} - 1\right) \beta$$

If the fission gases are treated as a solid:

$$y_{\text{Xe-Kr}} = 0.25$$

$$v_{\text{Xe-Kr}} = B = 85 \text{ \AA}^3 \quad (v_0 = 41 \text{ \AA}^3)$$

$$0.25 \left(\frac{85}{41}\right) = 0.518 \quad \text{be added to table 12.6}$$

$\therefore$ The sum tabulated in Tab. 12.6 becomes: $1.324 + 0.518$
 $= 1.842$

$$\text{and } \left(\frac{\Delta V}{V}\right)_{\text{Solid}} = 0.842 \beta$$

or

$$\underline{\underline{0.84\% / \text{atom}\% \text{ burnup}}}$$

Problem 12.8

at equilibrium, the oxygen partial pressure established by the reaction: $\frac{2}{3} \text{Cr}(s) + \text{O}_2(g) = \frac{2}{3} \text{Cr}_2\text{O}_3(s)$ must be the same as that over the final O/M of the fuel. The fuel O/M is reduced from 2.01 to a value (O/M)_f at which

$$\left(\overline{\Delta G_{\text{O}_2}}\right)_f = \Delta G_{\text{Cr}_2\text{O}_3/\text{Cr}}^\circ = -560 \text{ kJ/mole}$$

From Fig. 11.12 at 800°C, we find (O/M)_f = 1.994. The oxygen removed from the fuel reacts with chromium to form a layer of Cr₂O₃. The thickness of the layer is found by an oxygen balance:

$$\text{gm-atoms heavy metals per cm length} = \frac{10.9 \text{ gm oxide}}{\text{cm}^3} \times \pi R^2 \frac{\text{cm}^3}{\text{cm}} \times \frac{1 \text{ gm-atom heavy metal}}{270 \text{ gm oxide}}$$

$$\text{oxygen reacted with chromium} = (2.01 - 1.994) \times 10.9 \times \pi R^2 / 270$$

$$\text{gm-atoms chromium oxidized} = \frac{2}{3} (2.01 - 1.994) \times 10.9 \times \pi R^2 / 270$$

$$\text{gm atoms chromium per cm} = \frac{7.2 \text{ gm Cr}}{\text{cm}^3} \times 2\pi R t_c \frac{\text{cm}^3}{\text{cm}} \times \frac{1 \text{ gm atom Cr}}{52 \text{ gm Cr}}$$

$$\text{fraction of Cr oxidized} = \frac{\text{gm atoms oxidized}}{\text{gm atoms Cr}}$$

$$= \frac{\frac{2}{3} (2.01 - 1.994) \times 10.9 \times \pi R^2 / 270}{7.2 \times 2\pi R t_c / 52}$$

$$\text{using } R = 3 \text{ mm, } t_c = 0.4 \text{ mm,}$$

$$\text{fraction Cr oxidized} = 0.012 \quad (1.2\%)$$

CHAPTER 13

Problem 13.1

a) Determine R :-

$$\left(\frac{4}{3}\pi R^3\right) N = 1$$

$$\therefore R = \left(\frac{3}{4\pi N}\right)^{1/3}$$

Small bubble (dense gas limit)

$$m = \frac{4}{3} \frac{\pi R^3}{B} \quad \text{--- (1)}$$

Initial State:- N bubbles/cc of radius R_0 , matrix gas concentration = C_0 ;

Balance of gas in bubble :

$$\frac{dm}{dt} = 4\pi R D_{xe} C - bm \quad \text{--- (2) [Eq. (13.157)]}$$

Balance of gas in fuel + bubble

C = average concentration at time t
(assuming $R \gg R_0$)

Total gas (bubble + fuel) at time t

$$= \left(\frac{4}{3}\pi R^3\right) C_0 + \frac{4}{3} \frac{\pi R_0^3}{B} + (Y_{xe} \dot{F} t) \left(\frac{4}{3}\pi R^3\right)$$

i.e. Total gas = initially present in bubble + fuel + that produced by fission

This is also equal to :

$$\text{Total gas at time } t = \left(\frac{4}{3}\pi R^3\right)C + \left(\frac{4}{3}\pi R^3\right)\frac{1}{B}$$

Equating the two we get,

$$R^3(C - C_0) + \frac{1}{B}(R^3 - R_0^3) = R^3 \gamma_{xe} \dot{F} t \quad \text{--- (3)}$$

From eq (1) we get,

$$\frac{dm}{dt} = \frac{4\pi R^2}{B} \frac{dR}{dt}$$

Equating with (2), we get,

$$\frac{4\pi R^2}{B} \frac{dR}{dt} = 4\pi R D_{xe} C - \frac{4}{3}\pi R^3 b$$

$$\text{or } \boxed{\frac{dR}{dt} = \frac{B D_{xe} C}{R} - \frac{R}{3} b} \quad \text{--- (4)}$$

Equations (3) and (4) must be solved simultaneously (numerically);

b) Define :

$$\tau = bt = \text{dimensionless time}$$

$$\eta = \frac{R}{R_0} = \text{dimensionless bubble radius}$$

$$\theta = \frac{C}{C_0} = \text{dimensionless bubble concentration}$$

With these definitions eqs. (3) and (4) reduce to:

$$\theta = 1 + A_2 \tau + A_3(1-\eta^3) \quad \text{--- (5)}$$

$$\text{and } \frac{d\eta}{d\tau} = A_1 \frac{\theta}{\eta} - \frac{1}{3}\eta \quad \text{--- (6)}$$

where:

$$A_1 = \frac{B D_{Xe} C_0}{b R_0^2} \quad \text{--- (7)}$$

$$A_2 = \frac{Y_{Xe} \dot{F}}{C_0 b} \quad \text{--- (8)}$$

$$\text{and } A_3 = \frac{R_0^3}{R^3 C_0 B} \quad \text{--- (9)}$$

Combining (5) and (6) we get,

$$\frac{d\eta}{d\tau} = \frac{A_1(1+A_3)}{\eta} + \frac{A_1 A_2 \tau}{\eta} - A_1 A_3 \eta^2 - \frac{1}{3}\eta \quad \text{--- (10)}$$

with initial condition $\eta(0)=1$

c) For initial shrinkage by resolution, we must have, $\frac{d\eta}{d\tau} < 0$ for $\tau=0$ and $\eta(0)=1$.

i.e. we must have $A_1 < \frac{1}{3}$ from eq.(10)

Substituting numerical values

$$\begin{aligned} A_1 &= \frac{85 \times 10^{-24} \text{ cm}^3 \times 10^{-14} \text{ cm}^2/\text{sec} \times 5.2 \times 10^{17} \text{ gas atoms/cm}^3}{10^{-5} \text{ sec}^{-1} \times 400 \times 10^{-16} \text{ cm}^2} \\ &= \frac{85 \times 5.2}{400} = \underline{1.105} \end{aligned}$$

Since $A_1 > \frac{1}{3}$, there is no initial shrinkage.

$$A_2 = \frac{0.26 \times 10^{13} \text{ fissions/cm}^3\text{-sec}}{5.2 \times 10^{17} \text{ gas atoms/cm}^3 \times 10^{-5} \text{ sec}^{-1}}$$

$$= \frac{2.6}{5.2} = 0.50$$

$$\begin{aligned} A_3 &= \frac{R_0^3}{Q^3 C_0 B} = \frac{R_0^3}{\frac{3}{4\pi N} C_0 B} = \frac{4\pi N R_0^3}{3 C_0 B} \\ &= \frac{8 \times 10^3 \times 10^{-24} \text{ cm}^3 \times 4 \times \pi \times 1.3 \times 10^{13} \text{ bubbles/cm}^3}{3 \times 5.2 \times 10^{17} \text{ gas atoms/cm}^3 \times 85 \times 10^{-24} \text{ cm}^3} \\ &= \frac{32 \pi \times 1.3 \times 10^1}{3 \times 5.2 \times 85} = 0.98 \times 10^{-2} \end{aligned}$$

Introducing these values in eq.(10) we get,

$$\frac{d\eta}{d\tau} = \frac{1.115}{\eta} + 0.552 \frac{\tau}{\eta} - 0.010\eta^2 - \frac{1}{3}\eta \quad \dots(11)$$

with $\eta(0) = 1$

Finite Difference scheme for solving eq.(11) :

$$\frac{d\eta}{d\tau} \cong \frac{\eta_{i+1} - \eta_i}{h} \quad (\text{Forward difference scheme})$$

$$\text{or } \eta_{i+1} = \eta_i + h \left[\frac{1.115}{\eta_i} + 0.552 \frac{i h}{\eta_i} - 0.01\eta_i^2 - \frac{1}{3}\eta_i \right]$$

(where $\tau = ih$ has been used)

$$\text{and } \eta_0 = 1$$

This equation was solved with $h = 0.2$ and the following results were obtained.

For $h=0.2$

i	τ	η	i	τ	η
0	0	1.00	11	2.2	2.17
1	0.2	1.17	12	2.4	2.24
2	0.4	1.32	13	2.6	2.30
3	0.6	1.44	14	2.8	2.37
4	0.8	1.56	15	3.0	2.43
5	1.0	1.66	16	3.2	2.50
6	1.2	1.76	17	3.4	2.56
7	1.4	1.85	18	3.6	2.61
8	1.6	1.93	19	3.8	2.67
9	1.8	2.01	20	4.0	2.73
10	2.0	2.09			

The shape of this function is:

A more interesting case would be when $A_1 < \frac{1}{3}$.
For this case, there is a minimum bubble radius.

The differential equation (10), with values:

$A_1 = 0.1$, $A_2 = 0.5$; $A_3 = 1$ was solved numerically

$$\therefore \frac{d\eta}{d\tau} = \frac{0.2}{\eta} + 0.05 \frac{\tau}{\eta} - 0.1\eta^2 - \frac{1}{3}\eta; \quad \eta(0) = 1$$

The result is the following:

$h = 0.2$

i	τ	η	i	τ	η
0	0.0	1.000	11	2.2	0.840
1	0.2	0.955	12	2.4	0.846
2	0.4	0.919	13	2.6	0.853
3	0.6	0.891	14	2.8	0.862
4	0.8	0.869	15	3.0	0.870
5	1.0	0.854	16	3.2	0.880
6	1.2	0.843	17	3.4	0.890
7	1.4	0.837	18	3.6	0.900
8	1.6	0.834	19	3.8	0.910
9	1.8	0.834	20	4.0	0.921
10	2.0	0.836			

The shape of this function is:

Problem 13.2

a) From Eq. (7.24),

$$\sqrt{r^2} = \sqrt{6D_b t} = \sqrt{\frac{9a^4 D_s t}{\pi R^4}} \quad (1)$$

[Using Eq. (13.214)]

Numerically,

$$a = 3 \text{ \AA}$$

$$t = 40 \times 24 \times 3600 = 3.456 \times 10^6 \text{ sec.}$$

$$R = 10 \text{ \AA}$$

$$T = 1400^\circ \text{C.} = 1673^\circ \text{K.}$$

$$D_s = 4 \times 10^5 e^{-108/RT} \quad \frac{\text{cm}^2}{\text{sec}} \quad [\text{Eq. (13.216)}]$$

$$= 2.77 \times 10^{-9} \frac{\text{cm}^2}{\text{sec}}$$

Inserting in (1),

$$\sqrt{r^2} = \left(\frac{9 \times 3^4 \times \text{\AA}^4 \times 2.77 \times 10^{-9} \frac{\text{cm}^2}{\text{sec}} \times 3.456 \times 10^6 \text{ sec.}}{\pi 10^4 \text{\AA}^4} \right)^{1/2}$$

$$= 0.015 \text{ cm.}$$

b) Thermal Gradient Migration:-

$$r = \frac{3D_s Q_s^* a}{R k T^2} \left(\frac{dT}{dx} \right) t \quad [\text{Eq. (13.219)}]$$

$$= \frac{3 \times 2.77 \times 10^{-9} \frac{\text{cm}^2}{\text{sec}} \times 100 \times 10^3 \frac{\text{cal}}{\text{mole}} \times 4.18 \frac{\text{joule}}{\text{cal}} \times 3 \text{ \AA} \times 2000^\circ \text{K/cm.}}{10 \text{ \AA} \times 1.380 \times 10^{-23} \frac{\text{joule}}{^\circ \text{K}} \times (1673)^\circ \text{K}^2 \times 6.02 \times 10^{23} \frac{\text{molecules}}{\text{mole}}}$$

$$= 0.310 \text{ cm.}$$

Problem 13.3Overall gas balance (neglecting $C_4, C_5, \dots$ etc.)

$$C_0 = C_1 + 2C_2 + 3C_3 \quad \text{--- (1)}$$

a) Kinetic Equations:

$$\frac{dC_1}{dt} = -2k_{11}C_1^2 - k_{12}C_1C_2 \quad \text{--- (2)}$$

$$\frac{dC_2}{dt} = k_{11}C_1^2 - k_{12}C_1C_2 \quad \text{--- (3)}$$

$$\frac{dC_3}{dt} = k_{12}C_1C_2 \quad \text{--- (4)}$$

(neglect $k_{13}C_1C_3$ term)

This is a self consistent set. Note that $\frac{d}{dt}$ of eq. (1) is satisfied identically by eqs. (2)-(4).

Initial conditions for these eqs. are

$$C_1(0) = C_0 \quad \text{--- (5)}$$

$$C_2(0) = C_3(0) = 0$$

 k_{11} and k_{12} are given by,

$$k_{11} = \frac{\bar{z}_{11} \Omega D_{Xe}}{a^2}; \quad \bar{z}_{11} \cong 12; \quad k_{12} = \frac{\bar{z}_{12} \Omega D_{Xe}}{a^2}; \quad \bar{z}_{12} \cong 24 \quad \text{--- (6)}$$

b) Let $\theta_1 = \frac{C_1}{C_0}; \quad \theta_2 = \frac{C_2}{C_0}; \quad \theta_3 = \frac{C_3}{C_0}$

$$\tau = C_0 k_{11} t$$

Then eqs (2)-(4) become:

$$\frac{d\theta_1}{d\tau} = -2\theta_1^2 - \frac{1}{2}\theta_1\theta_2 \quad \text{--- (7)}$$

$$\frac{d\theta_2}{d\tau} = \theta_1^2 - \frac{1}{2} \theta_1 \theta_2 \quad \text{--- (8)}$$

$$\frac{d\theta_3}{d\tau} = \frac{1}{2} \theta_1 \theta_2 \quad \text{--- (9)}$$

$$\text{and } \theta_1 + 2\theta_2 + 3\theta_3 = 1 \quad \text{--- (10)}$$

Initial Conditions:-

$$\theta_1(0) = 1; \quad \theta_2(0) = \theta_3(0) = 0$$

Numerical solutions of eqs. (7), (8) and (9) are as follows:

$$\theta_1^{n+1} = \theta_1^n + h(-2\theta_1^n - \frac{1}{2}\theta_1^n \theta_2^n)$$

$$\theta_2^{n+1} = \theta_2^n + h(\theta_1^n - \frac{1}{2}\theta_1^n \theta_2^n)$$

$$\theta_3^{n+1} = \theta_3^n + h(\frac{1}{2}\theta_1^n \theta_2^n)$$

(Superscript n stands for the value at n th time step.)

$$\text{with } \theta_1^0 = 1, \quad \theta_2^0 = \theta_3^0 = 0$$

Solved numerically for $h = 0.2$ gives:

$h=0.2$

i	τ	θ_1	θ_2	θ_3	$\theta_1 + 2\theta_2 + 3\theta_3$
0	0.0	1.000	0.000	0.000	1.000
1	0.2	0.600	0.200	0.000	1.000
2	0.4	0.444	0.260	0.012	1.000
3	0.6	0.353	0.287	0.023	1.000
4	0.8	0.293	0.302	0.033	0.999
5	1.0	0.250	0.311	0.042	0.999
6	1.2	0.217	0.315	0.050	0.999
7	1.4	0.191	0.318	0.057	0.999

i	τ	θ_1	θ_2	θ_3	$\theta_1 + 2\theta_2 + 3\theta_3$
8	1.6	0.170	0.319	0.063	0.999
9	1.8	0.153	0.319	0.068	0.999
10	2.0	0.139	0.319	0.073	0.999
11	2.2	0.127	0.319	0.078	1.000
12	2.4	0.116	0.318	0.082	1.000
13	2.6	0.107	0.317	0.085	1.000
14	2.8	0.099	0.316	0.089	1.000
15	3.0	0.092	0.315	0.092	1.000
16	3.2	0.085	0.313	0.095	1.000
17	3.4	0.080	0.312	0.098	1.000
18	3.6	0.075	0.311	0.100	1.000
19	3.8	0.070	0.310	0.102	1.000
20	4.0	0.066	0.309	0.105	1.000

The shapes of these curves are:

c) The nucleation time t_c is given by:

$$\left(\frac{dc_2}{dt}\right)_{t_c} = 0 \quad [\text{Eq. (13.123)}]$$

From the numerical solution θ_2 is maximum for $\tau = 1.9$

$$\therefore t_c = \frac{\tau}{C_0 k_{11}},$$

$$\begin{aligned} \text{with } k_{11} &= \frac{12 \times \Omega \times D_{Xe}}{a^2} = 12 \times a \times D_{Xe} \\ &= 12 \times 3 \times 10^{-8} \text{ cm} \times 10^{-14} \text{ cm}^2/\text{sec} \\ &= 36 \times 10^{-22} \text{ cm}^3/\text{sec}. \end{aligned}$$

$$\begin{aligned} \text{and, } t_c &= \frac{1.9}{10^{17} \text{ /cc} \times 36 \times 10^{-22} \text{ cc/sec}} \\ &= 5.27 \times 10^3 \text{ sec.} = \underline{1.46 \text{ hr.}} \end{aligned}$$

At $t = t_c$

$$\frac{C_1}{C_0} = \theta_1 \cong 0.146 = 14.6 \% \text{ remains atomically dispersed}$$

$$2\theta_2 \cong 0.638 = 63.8 \% \text{ in diatomic clusters}$$

$$3\theta_3 \cong 0.216 = 21.6 \% \text{ in triatomic clusters}$$

Problem 13.4

Initially : type(I) :- $p_1 = \frac{2\gamma}{r_1}$

type(II) :- $p_2 = \frac{2\gamma}{r_2}$

$$r_2 = 0.5 r_1$$

Initial volume

occupied by bubbles $= \frac{4}{3} \pi n (r_1^3 + r_2^3),$

where n = number of bubbles of each type
(total $2n$ bubbles)

By ideal gas law, let N_i be the number of gas atoms in bubble type (i).

$$\begin{aligned} N_i &= p_i \left(\frac{4}{3} \pi r_i^3 \right) / kT \\ &= \frac{4}{3} \pi \left(\frac{2\gamma}{kT} \right) r_i^2 \quad (i=1,2) \end{aligned}$$

We have 3 types of collisions :

$$\begin{aligned} &(I) + (I) \\ &(I) + (II) \\ &\quad \text{or} \\ &(II) + (I) \\ &(II) + (II) \end{aligned} \left. \vphantom{\begin{aligned} &(I) + (I) \\ &(I) + (II) \\ &\quad \text{or} \\ &(II) + (I) \\ &(II) + (II) \end{aligned}} \right\} \text{same type}$$

Since in actual process the rate of coalescence of smaller bubbles may be faster than that for larger ones, it is not possible to get explicit expression due to complex process of collision, simply an approach is indicated by random motion of bubbles.

Assume that the probability of each type of collision is the same $= \frac{1}{4}$

Then we finish with n total bubbles:

$\frac{n}{4}$ bubbles of type $[(I)+(I)]$; $\frac{n}{4}$ bubbles of type $[(II)+(II)]$;

$\frac{n}{2}$ bubbles of type $[(I)+(II)]$

Moles of gas in bubbles (or number of gas atoms)

$$N = N_i + N_j = \frac{4}{3} \pi \left(\frac{2\gamma}{kT} \right) (r_i^2 + r_j^2)$$

For ideal gas $p = \frac{2\gamma}{r}$ and $p \left(\frac{4}{3} \pi r^3 \right) = NkT$

$$\therefore r = \frac{2\gamma}{p} = 2\gamma \left(\frac{NkT}{\frac{4}{3} \pi r^3} \right)^{-1}$$

$$\text{This gives } r = \sqrt{r_i^2 + r_j^2}$$

$\therefore$ Final volume of gas is:

$$V = \frac{4}{3} \pi n \left\{ \frac{1}{4} (r_1^2 + r_1^2)^{3/2} + \frac{1}{4} (r_2^2 + r_2^2)^{3/2} + \frac{1}{2} (r_1^2 + r_2^2)^{3/2} \right\}$$

$$\therefore \text{Swelling} = \frac{V - V_{\text{initial}}}{V_{\text{initial}}} = \frac{V}{V_{\text{initial}}} - 1$$

$$V_{\text{initial}} = \frac{4}{3} \pi n (r_1^3 + r_2^3)$$

$$\therefore \text{Swelling } \frac{\Delta V}{V} = \frac{\frac{1}{\sqrt{2}} (r_1^3 + r_2^3) + \frac{1}{2} (r_1^2 + r_2^2)^{3/2}}{r_1^3 + r_2^3} - 1$$

$$r_2 = 0.5 r_1$$

$$\therefore \frac{\Delta V}{V} = \frac{1}{\sqrt{2}} + \frac{\frac{1}{2} r_2^3 (1+4)^{3/2}}{r_2^3 (1+8)} - 1$$

$$= 0.707 + \frac{5\sqrt{5}}{18} - 1$$

$$= \underline{0.328}$$

Problem 13.5

a) For no radiation: $X_V = X_V^{eq} = e^{-E_V/kT}$

With E_F = energy of formation of
Vacancies

$$\therefore D_U^{th} = a_0^2 \nu e^{-(E_V^* + E_V)/kT}$$

b) When recombination is the only means of destruction, then equilibrium of destruction and production rates gives [see Eqs. (13.186) and (13.187)]

$$Y_{Vi} \dot{F} = k_{iv} C_V C_i \quad \dots (1)$$

[Where it is assumed that C_V^{eq} and $C_i^{eq} \approx 0$]

But $C_V = C_i$, and $C_V = \frac{X_V}{\Omega} \approx \frac{X_V}{a_0^3}$

$$\therefore X_V = a_0^3 C_V = a_0^3 \sqrt{\frac{Y_{Vi} \dot{F}}{k_{iv}}} \quad [\text{using (1)}]$$

From Eq. (13.42),

$$k_{iv} = \frac{z_{iv} \Omega D_i}{a_0^2} = z_{iv} a_0 D_i$$

Where D_i = interstitial diffusion coefficient

Then:

$$X_V = a_0^3 \sqrt{\frac{Y_{Vi} \dot{F}}{z_{iv} a_0 D_i}}$$

X_V replaces X_V^{eq}

and

$$D_U^{rad} = a_0^2 \nu \left\{ a_0^3 \sqrt{\frac{Y_{Vi} \dot{F}}{z_{iv} a_0 D_i}} \right\} e^{-E_V^*/kT}$$

but since

$$D_i = a_0^2 \nu e^{-E_i^*/kT}$$

We get:

$$D_U = \left(\frac{a_0^7 Y_{Vi} \dot{F} \nu}{z_{iv}} \right)^{1/2} e^{-(E_V^* - \frac{1}{2} E_i^*)/kT}$$

c)

Problem 13.6

Condition of mechanical equilibrium for bubble of radius r is:

$$p = \frac{2\gamma}{r} \quad \text{and} \quad p\left(\frac{4}{3}\pi r^3\right) = mkT$$

$$\therefore m = \left[\frac{8\pi}{3} \frac{\gamma}{kT} \right] r^2 = Cr^2 \quad \text{--- (1)}$$

Eq. (1) holds for all bubbles. ($r=R$ or $r=R^*$)

If the large bubble expands by dR^* , it sweeps out a volume of $4\pi R^{*2} dR^*$. This volume contains N bubbles of radius R per cc, and each bubble contains

$$m = CR^2$$

gas atoms by eq. (1). Therefore the number of additional gas atoms acquired by the large bubble as a result of expansion by dR^* is

$$dm^* = 4\pi R^{*2} dR^* N C R^2 \quad \text{--- (2)}$$

However to maintain mechanical equilibrium according to eq. (1), the number of additional gas atoms required is given by

$$\begin{aligned} dm^{*'} &= \frac{d(CR^{*2})}{dR^*} dR^* \\ &= 2CR^* dR^* \quad \text{--- (3)} \end{aligned}$$

The bubble will tend to grow spontaneously if $dm^* > dm^{*'}$

or if $4\pi R^{*2} N C R^2 > 2 C R^*$

$\therefore$ The critical radius is given by

$$R^* \geq \frac{1}{2\pi N R^2} \quad \text{--- (4)}$$

If $\frac{R^*}{R} = 10$, then from eq.(4),

$$N = \frac{1}{2\pi \times 10 \times R^3}$$

But $V_b = \frac{4}{3}\pi R^3$ (Volume of a bubble)

$$\therefore N V_b = \Delta V = \frac{\frac{4}{3}\pi R^3}{2\pi \times 10 \times R^3} = \frac{2}{30} = 0.0667$$

$$\begin{aligned} \therefore \text{Swelling is } \frac{\Delta V}{V} &= \frac{0.0667}{1 - 0.0667} \\ &= \frac{0.0667}{0.9333} = \underline{7.2\%} \end{aligned}$$

Problem 13.7

a) $v = MF$ [from Eq. (13.220)]

where $F = \text{force on interstitial} = -\nabla V$

[from Eq. (13.223)]

$M = \text{mobility of interstitial}$

$$= \frac{D_i}{kT} \quad [\text{from Eq. (13.221)}]$$

$$\therefore \boxed{v = -\frac{D_i}{kT} \nabla V} \quad \text{--- (1)}$$

b) $J_i = \text{interstitial flux}$

$$J_i = \underbrace{-D_i \nabla C_i}_{\text{concentration gradient}} + \underbrace{C_i v}_{\text{drift}}$$

$$\therefore \boxed{J_i = -D_i \left(\nabla C_i + \frac{C_i}{kT} \nabla V \right)} \quad \text{--- (2)}$$

c) Continuity equation is:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot J_i$$

$$\therefore \frac{\partial C_i}{\partial t} = D_i \nabla \cdot \left(\nabla C_i + \frac{C_i}{kT} \nabla V \right) \quad [\text{from eq. (2)}]$$

or $\boxed{\frac{\partial C_i}{\partial t} = D_i \left(\nabla^2 C_i + \frac{C_i}{kT} \nabla^2 V + \frac{1}{kT} \nabla C_i \cdot \nabla V \right)}$

--- (3)

d) Steady state : $\frac{\partial C_i}{\partial t} = 0$ --- (4)

$$V = -B/r$$

In cylindrical coordinates,

$$\nabla^2 C_i = \frac{1}{r} \frac{d}{dr} \left(r \frac{dC_i}{dr} \right) \quad \text{--- (5)}$$

$$\nabla^2 V = \frac{1}{r} \frac{d}{dr} \left[r \frac{d}{dr} \left(-\frac{B}{r} \right) \right] = -\frac{B}{r^3} \quad \text{--- (6)}$$

$$\nabla C_i \cdot \nabla V = \frac{dC_i}{dr} \cdot \frac{dV}{dr} = \frac{B}{r^2} \frac{dC_i}{dr} \quad \text{--- (7)}$$

Continuity equation becomes,

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dC_i}{dr} \right) - \frac{A C_i}{r^3} + \frac{A}{r^2} \frac{dC_i}{dr} = 0 \quad \text{--- (8)}$$

[Using (4), (5), (6) and (7) in (3)]

where $A = B/kT$ = characteristic range of interaction

Let $C_i(r) = e^{A/r} U(r)$

then substituting this in (8) we get,

$$\boxed{\frac{d^2 U}{dr^2} + \left(\frac{1}{r} - \frac{A}{r^2} \right) \frac{dU}{dr} = 0} \quad \text{--- (9)}$$

e) With $A=0$, $C_i(r) = U(r)$

and the differential equation (9) becomes,

$$\frac{d^2 C_i}{dr^2} + \frac{1}{r} \frac{dC_i}{dr} = 0 \quad \text{--- (10)}$$

By inspection the solution to this equation is seen to be

$$C_i(r) = K \ln r + K' \quad \text{--- (11)}$$

where K and K' are constants of integration.

Using the boundary conditions specified in the problem

$$C_i(R_d) = C_i^{eq} = 0 \quad \text{--- (12)}$$

$$\text{and } C_i(R) = C_i \quad (\text{specified}) \quad \text{--- (13)}$$

$$\therefore 0 = K \ln R_d + K' \quad [\text{using (12) in (11)}]$$

$$\text{and } C_i = K \ln R + K' \quad [\text{using (13) in (11)}]$$

Subtracting we get,

$$C_i = K \ln \left(\frac{R}{R_d} \right)$$

$$\text{or } K = \frac{C_i}{\ln \left(\frac{R}{R_d} \right)} \quad \text{--- (14)}$$

The flux per unit length of dislocation line (with flux positive, when directed towards the dislocation line) is:

$$\begin{aligned} J_i^d &= 2\pi R_d \left[D_i \left(\frac{dC_i}{dr} \right)_{R_d} \right] \\ &= 2\pi R_d \left[\frac{D_i K}{R_d} \right] = \frac{2\pi D_i C_i}{\ln(R/R_d)} \quad [\text{using (14)}] \end{aligned}$$

$$\therefore \boxed{J_i^d = \frac{2\pi D_i C_i}{\ln(R/R_d)}} \quad \text{--- (15) [Compare this with Eq. (13.89)]}$$

f) Let $W = \frac{du}{dr}$

Substituting in eq. (9) we get,

$$\frac{dW}{dr} + \left(\frac{1}{r} - \frac{A}{r^2} \right) W = 0$$

$$\text{or } \frac{dW}{W} = - \left(\frac{1}{r} - \frac{A}{r^2} \right) dr$$

Integrating:

$$\ln W = -\ln r - \frac{A}{r} + \ln K_1 \quad \left[\ln K_1 \text{ is a constant of integration} \right]$$

$$\text{or } W = \frac{du}{dr} = K_1 \frac{e^{-A/r}}{r} \quad \text{--- (16)}$$

Boundary conditions:

$$\text{At } r = R_d, \quad C_i = C_i^{eq} \cong 0$$

$$\therefore U(R_d) = C_i^{eq} e^{-A/R_d} \cong 0 \quad \text{--- (17)}$$

$$\text{At } r = R, \quad C_i = C_i \text{ (specified)}$$

$$\therefore U(R) = C_i e^{-A/R} \quad \text{--- (18)}$$

Now integrate (16) from R_d to R :

$$\int_{U(R_d)}^{U(R)} du = U(R) - U(R_d) = K_1 \int_{R_d}^R \frac{e^{-A/r}}{r} dr$$

or the constant K_1 is:

$$K_1 = \frac{C_i e^{-A/R}}{\int_{R_d}^R \frac{e^{-A/r}}{r} dr} \quad \left[\text{using (17) and (18)} \right] \quad \text{--- (19)}$$

Flux at the core of dislocation from eq.(2) is

$$J = -D_i \left[\left(\frac{dC_i}{dr} \right)_{R_d} + \frac{C_i^{eq}}{kT} \frac{B}{R_d^2} \right]$$

since $C_i^{eq} \cong 0$

$$J \cong -D_i \left(\frac{dC_i}{dr} \right)_{R_d} \quad \text{--- (20)}$$

but $\frac{dC_i}{dr} = -\frac{A}{r^2} e^{A/r} u + e^{A/r} \frac{du}{dr}$

$$\therefore \left(\frac{dC_i}{dr} \right)_{R_d} = -\frac{A}{R_d^2} e^{A/R_d} C_i^{eq} e^{-A/R_d} + e^{A/R_d} \left(\frac{du}{dr} \right)_{R_d}$$

Again since $C_i^{eq} \cong 0$,

$$\therefore \left(\frac{dC_i}{dr} \right)_{R_d} = e^{A/R_d} \left(\frac{du}{dr} \right)_{R_d} \quad \text{--- (21)}$$

$$\therefore J \cong -D_i e^{A/R_d} \left(\frac{du}{dr} \right)_{R_d} \quad [\text{from (20) and (21)}]$$

But $\left(\frac{du}{dr} \right)_{R_d} = K_1 \frac{e^{-A/R_d}}{R_d} \quad [\text{from eq. (16)}]$

$$= \frac{C_i e^{(-A/R_d - A/R)}}{R_d \int_{R_d}^R \frac{e^{-A/r}}{r} dr}$$

Now since $A/a \cong 0$, then

$$\left(\frac{du}{dr} \right)_{R_d} = \frac{C_i e^{-A/R_d}}{R_d \int_{R_d}^R \frac{e^{-A/r}}{r} dr} \quad \text{--- (23)}$$

From (22) and (23),

$$J = - \frac{D_i C_i}{R_d \int_{R_d}^R \frac{e^{-A/r}}{r} dr} \quad \text{(This current is positive, when directed outward from dislocation line)} \quad \text{---(24)}$$

The area per unit length of dislocation line is:

$$2\pi R_d$$

$\therefore$ Flux of interstitials into a unit length of dislocation line is:

$$J_i^d = -2\pi R_d J$$

$$\therefore J_i^d = \frac{2\pi D_i C_i}{\int_{R_d}^R \frac{e^{-A/r}}{r} dr} \quad \text{[using (24)]} \quad \text{--- (25)}$$

[This equation replaces Eq. (13.89) for interstitials]

Now in order that the solution to part e) i.e. eq.(15) equals that of part f) i.e. eq.(25), replace R_d in eq.(15) by R_{di} and equate the resulting J_i^d expression to that in (25). We obtain

$$\ln(R/R_{di}) = \int_{R_d}^R \frac{e^{-A/r}}{r} dr \quad \text{--- (26)}$$

Let

$$\eta = r/R_d, \quad \eta_f = R/R_d$$

$$\frac{A}{R_d} = 0.1$$

$$\ln \left(\frac{\eta_f}{(R_{di}/R_d)} \right) = \int_1^{\eta_f} \frac{e^{-0.1/\eta}}{\eta} d\eta$$

Now write: $e^{-0.1/\eta} = 1 - (1 - e^{-0.1/\eta})$

$$\therefore \ln \eta_f - \ln (R_{di}/R_d) = \int_1^{\eta_f} \frac{d\eta}{\eta} - \int_1^{\eta_f} \frac{1 - e^{-0.1/\eta}}{\eta} d\eta$$

But $\int_1^{\eta_f} \frac{d\eta}{\eta} = \ln \eta_f$

$$\therefore \ln (R_{di}/R_d) = \int_1^{\eta_f} \frac{1 - e^{-0.1/\eta}}{\eta} d\eta$$

$$\therefore \frac{R_{di}}{R_d} = \exp \left\{ \int_1^{\eta_f} \left(\frac{1 - e^{-0.1/\eta}}{\eta} \right) d\eta \right\}$$

Expand $e^{-0.1/\eta}$ in Taylor series:

$$e^{-0.1/\eta} = 1 - \frac{0.1}{\eta} + \frac{1}{2} \frac{0.01}{\eta^2} - \frac{1}{6} \frac{0.001}{\eta^3} + \dots$$

Also since $(1 - e^{-0.1/\eta}) \rightarrow 0$ as $\eta \rightarrow \infty$, then we can replace the limit of integration from η_f to ∞ .

$$\begin{aligned} \therefore \int_1^{\infty} \left(\frac{1 - e^{-0.1/\eta}}{\eta} \right) d\eta &= 0.1 \int_1^{\infty} \frac{d\eta}{\eta^2} - \frac{0.01}{2} \int_1^{\infty} \frac{d\eta}{\eta^3} + \frac{0.001}{6} \int_1^{\infty} \frac{d\eta}{\eta^4} + \dots \\ &= 0.1 - \frac{0.01}{2 \times 2} + \frac{0.001}{6 \times 3} + \dots \end{aligned}$$

$$\therefore \int_1^{\infty} \left(\frac{1 - e^{-0.1/\eta}}{\eta} \right) d\eta = 0.1 - 2.5 \times 10^{-3} + 5.5 \times 10^{-5} + \dots$$

$$= 0.0976$$

$$\therefore \frac{R_{di}}{R_d} = \exp[0.0976]$$

$$= \underline{1.10} \quad \text{--- (27)}$$

g) For $s_d = 10^{10} \text{ cm}^{-2}$, R is determined by

$$\pi R^2 = 1/s_d$$

$$\therefore R = \frac{1}{\sqrt{\pi s_d}} = 5.6 \times 10^{-6} \text{ cm.}$$

For vacancies:

$$\frac{2\pi}{\ln(R/R_d)} = \frac{2\pi}{\ln\left(\frac{5.6 \times 10^{-6}}{6 \times 10^{-8}}\right)} = 1.38$$

$$\therefore Z_v = \frac{1}{\frac{1}{24} + \frac{1}{1.38}} = \underline{1.31}$$

For interstitials:

$$\frac{2\pi}{\ln(R/R_{di})} = \frac{2\pi}{\ln\left(\frac{5.6 \times 10^{-6}}{1.1 \times 6 \times 10^{-8}}\right)} = 1.41$$

[using (27)]

$$Z_i = \frac{1}{\frac{1}{24} + \frac{1}{1.41}} = 1.335$$

$$\therefore \frac{Z_i - Z_v}{Z_v} \cong \underline{2\%}$$

Problem 13.8Mean ff path length through bubble of radius R

Assume parallel beam of ff's.

s = track length for impact
parameter b

= chord length through circle

$$= 2R \sin \theta = 2R \sqrt{1 - \left(\frac{b}{R}\right)^2}$$

Let $p(b)db$ = probability of ff striking with
impact parameter in (b, db)
(assuming it in fact does strike
the bubble!)

$$p(b)db = K 2\pi b db = \frac{2}{R^2} b db$$

$$\text{Since } \int_0^R p(b)db = 1 = 2\pi K \int_0^R b db = \pi R^2 K$$

$$\therefore \bar{s} = \int_0^R p(b) s(b) db$$

$$= 4R \int_0^R \sqrt{1 - \left(\frac{b}{R}\right)^2} \frac{b db}{R^2} = 4R \int_0^1 \sqrt{1 - \eta^2} \eta d\eta$$

$$\text{Let } \omega = \eta^2 ; \therefore d\omega = 2\eta d\eta$$

$$\therefore \frac{\bar{s}}{R} = 2 \int_0^1 \sqrt{1 - \omega} d\omega = 2 \left[-\frac{2}{3} (1 - \omega)^{3/2} \right]_0^1 = \frac{4}{3}$$

$$\therefore \boxed{\bar{s} = \frac{4}{3} R}$$

Problem 13.9

a) After low temperature irradiation, t_i

$$C_{01} = Y_{Xe} \dot{F} t_i = 0.25 \times 5 \times 10^{13} \times 10^6 \\ = \underline{1.25 \times 10^{19} \frac{\text{atoms}}{\text{cc}}} \quad \text{--- (1)}$$

b) Let $m_1 = \text{gas atoms/bubble}$

$$C_{01} = m_1 N \quad \text{--- (2)}$$

From Eq. (13.16),

$$m_1 = \frac{4}{3} \pi R_1^2 \left(\frac{2\gamma}{kT} \right) \quad \text{--- (3)}$$

(assuming R_1 large enough for ideal gas law to apply)

Using (1) and (2) and solving for R_1 .

$$R_1 \cong \frac{1}{2} \sqrt{\frac{kT}{2\gamma} \frac{Y_{Xe} \dot{F} t_i}{N}} \quad \text{--- (4) [where } \frac{4}{3} \pi \cong 4 \text{ is used]}$$

Putting numbers,

$$R_1 = \underline{175 \text{ \AA}}$$

c) Swelling

$$\left(\frac{\Delta V}{V} \right)_1 = \left(\frac{4}{3} \pi R_1^3 \right) N \quad \text{--- (5)} \\ = 2.1 \times 10^{-3} = \underline{0.2 \%}$$

d) After second low-temperature irradiation, consider one bubble. From Eq. (13.117)

$$\frac{\text{gas atoms redissolved}}{\text{sec-bubble}} = b m \quad \text{--- (6)}$$

$$\therefore \frac{dm}{dt} = -bm \quad \text{--- (7)}$$

Integrate from $m=m_1$ at $t=0$ to $m=m_2$ at $t=t_2$

$$\frac{m_2}{m_1} = e^{-bt_2} \quad \text{--- (8)}$$

and: $bt_2 = (2 \times 10^{-19})(5 \times 10^{13}) \times 10^5 = 1$

$$\therefore \frac{m_2}{m_1} = 0.37$$

Using (3)

$$\frac{R_2}{R_1} = \sqrt{\frac{m_2}{m_1}} = 0.61$$

$$\therefore R_2 = \underline{106 \text{ \AA}}$$

e) Swelling at t_2 ;

$$\begin{aligned} \left(\frac{\Delta V}{V}\right)_2 &= \left(\frac{4}{3}\pi R_2^3\right)N = \left(\frac{\Delta V}{V}\right)_1 \left(\frac{R_2}{R_1}\right)^3 \\ &= 2.1 \times 10^{-3} \times (0.61)^3 = 4.7 \times 10^{-4} \cong \underline{0.05\%} \end{aligned}$$

f) Gas in solution at t_2 ;

$$\begin{aligned} \text{Total gas present} &= Y_{Xe} \dot{F}(t_1 + t_2) \\ &= Y_{Xe} \dot{F} t_1 \left(1 + \frac{t_2}{t_1}\right) = C_{O1} \left(1 + \frac{t_2}{t_1}\right) \end{aligned}$$

$$\text{Gas in bubbles at } t_2 = m_2 N = \left(\frac{m_2}{m_1}\right) m_1 N = \left(\frac{m_2}{m_1}\right) C_{O1}$$

$$\begin{aligned} C_{O2} = \text{gas in solution at } t_2 &= C_{O1} \left(1 + \frac{t_2}{t_1} - \frac{m_2}{m_1}\right) \\ &= C_{O1} (1 + 0.1 - 0.37) = 0.73 C_{O1} \end{aligned}$$

$$\therefore C_{O2} = \underline{0.91 \times 10^{19} \frac{\text{gas atoms}}{\text{cm}^3}}$$

Problem 13.10

dV = spherical shell of thickness dr ;
where $R \leq r \leq R + \mu$

Ω = probability of striking the bubble = solid angle subtended by bubble from dV = $\frac{A}{4\pi y^2}$

where A = area of spherical cap of sphere of radius $= y$ and angle $= \alpha$

$$y = \sqrt{R^2 - r^2}$$

$$\sin \alpha = \frac{R}{r}$$

$$\cos \alpha = \sqrt{1 - \left(\frac{R}{r}\right)^2}$$

$$dA = 2\pi y^2 d(\cos \theta)$$

$$A = 2\pi y^2 (1 - \cos \alpha)$$

$$= 2\pi y^2 \left[1 - \sqrt{1 - \left(\frac{R}{r}\right)^2} \right]$$

$$\therefore \Omega = \frac{A}{4\pi y^2} = \frac{1}{2} \left[1 - \sqrt{1 - (R/r)^2} \right]$$

Check on limits:

$$\left(\frac{R}{r}\right)^2 \rightarrow 0 \quad ; \quad \Omega \rightarrow \frac{R^2}{4r^2} \quad (\text{OK})$$

$$\left(\frac{R}{r}\right)^2 \rightarrow 1 \quad ; \quad \Omega \rightarrow \frac{1}{2} \quad (\text{OK})$$

let $Q = \text{ff's cutting bubble / sec.} = 2\dot{F} \int_R^{R+u} \Omega 4\pi r^2 dr$

[factor 2 because 2 ff's emitted per fission]

$$Q = 4\pi\dot{F} \int_R^{R+u} \left[1 - \sqrt{1 - (R/r)^2} \right] r^2 dr$$

or with $x = \frac{r}{R}$, $Q = 4\pi\dot{F}R^3 \int_1^{1+u/R} \left[1 - \sqrt{1 - \frac{1}{x^2}} \right] x^2 dx$

Let $G(u/R) = \int_1^{1+u/R} \left[1 - \sqrt{1 - \frac{1}{x^2}} \right] x^2 dx$

$$G = \int_1^{1+u/R} [x^2 - x\sqrt{x^2 - 1}] dx = \left[\frac{x^3}{3} - \frac{(x^2 - 1)^{\frac{3}{2}}}{3} \right]_1^{1+u/R}$$

$$G = \frac{1}{3} \left\{ \left(1 + \frac{u}{R}\right)^3 - 1 - \left[\left(1 + \frac{u}{R}\right)^2 - 1 \right]^{\frac{3}{2}} \right\}$$

Limit of G as $\mu/R \gg 1$:

$$\text{let } 1 + \frac{\mu}{R} = A$$

$$G = \frac{1}{3} \left\{ A^3 - 1 - [A^2 - 1]^{\frac{3}{2}} \right\} = \frac{1}{3} \left\{ A^3 - 1 - A^3 \left(1 - \frac{1}{A^2} \right)^{\frac{3}{2}} \right\}$$

$$\approx \frac{1}{3} \left\{ A^3 - 1 - A^3 \left(1 - \frac{3}{2A^2} \right) \right\} = \frac{1}{3} \left(\frac{3A}{2} - 1 \right)$$

$$\approx \frac{1}{2} A = \frac{1}{2} \left(1 + \frac{\mu}{R} \right) \approx \frac{1}{2} \frac{\mu}{R}$$

$$\therefore Q = 4\pi \dot{F} R^3 \left(\frac{1}{2} \frac{\mu}{R} \right) = \underline{\underline{2\pi \dot{F} R^2 \mu}}$$

Limit of G as $\mu/R \rightarrow 0$:

$$G = \frac{1}{3} \left\{ \left(1 + \frac{3\mu}{R} \right) - 1 - \left[\left(1 + \frac{2\mu}{R} \right) - 1 \right]^{\frac{3}{2}} \right\} = \frac{1}{3} \left\{ \frac{3\mu}{R} - \left(\frac{2\mu}{R} \right)^{\frac{3}{2}} \right\} \approx \frac{\mu}{R}$$

$$\text{and } Q = 4\pi \dot{F} R^3 \left(\frac{\mu}{R} \right) = \underline{\underline{4\pi \dot{F} R^2 \mu}}$$

b) Each ff which intersects bubble redissolves Δm gas atoms

$$\therefore \frac{\text{gas atoms redissolved}}{\text{sec. - bubble}} = Q \Delta m = 4\pi \dot{F} R^3 G(\mu/R) \Delta m$$

or
$$b = 4\pi \dot{F} R^3 G(\mu/R) \frac{\Delta m}{m}$$

where $m =$ Number of gas atoms per bubble
(equilibrium bubble)

$$P \left(\frac{4}{3} \pi R^3 \right) = m k T \quad \text{and} \quad P = \frac{2\gamma}{R}$$

$$\therefore m = \frac{8\pi\gamma R^2}{3kT} \left(\frac{\text{gas atoms}}{\text{bubble}} \right)$$

$$\therefore b = \frac{3kT \Delta m R G(\mu/R)}{2\gamma}$$

for $\mu/R \gg 1$

$$b = \frac{3kT \Delta m \mu}{4\gamma}$$

for $\mu/R \ll 1$

$$b = \frac{3kT \Delta m \mu}{2\gamma}$$

CHAPTER 14

Problem 14.1

- a) Radius of central void after restructuring is complete: All the pores in the region $0 \leq r \leq 0.8R$ contribute to the final central void.

$$P_0 \pi (0.8R)^2 = \pi r_{of}^2$$

$$\text{or } \boxed{\frac{r_{of}}{R} = 0.8 \sqrt{P_0}} \quad \text{--- (1)}$$

- b) For constant thermal conductivity, the heat conduction equation in the fuel is:

$$\frac{k}{r} \frac{d}{dr} \left(r \frac{dT}{dr} \right) = -H \quad \text{--- (2)}$$

B.C.

$$T(R) = T_s \quad \text{--- (3)}$$

$$\left(\frac{dT}{dr} \right)_{r_0} = 0 \quad \text{--- (4)}$$

If the rod is operated at constant linear power, the average heat generation rate in the columnar grain region is: [From Eq. (10.54)]

$$\bar{H} = \frac{P}{\pi R^2 (1 - \frac{r_0^2}{R^2})} = \frac{H_0 \cdot 1028}{1 - (\frac{r_0}{R})^2} \quad \text{--- (5)}$$

Where H_0 is the initial power density of the fuel. Since r_0 starts at 0 and increases

to the value given by eq.(1) when restructuring is complete, r_0/R increases with time and therefore $\bar{H}$ increases with time

Assume that the local power density in the columnar region is equal to the average power density throughout the region, or that H in eq.(2) is equal to $\bar{H}$ given by eq.(5) for all $r_0 \leq r \leq 0.8R$.

Then the solution to eqs.(2)-(4) in the zone $r_0 \leq r \leq 0.8R$ is

$$T_1(r) = -\frac{1}{4} \frac{\bar{H}}{k} r^2 + A \ln r + B \quad \text{--- (6)}$$

where $T_1(r)$ is the temperature distribution in this region. A and B are constants of integration.

From B.C.(4),

$$A = \frac{1}{2} \frac{\bar{H}}{k} r_0^2 = \frac{1}{2} \frac{H_0 R^2}{k} \left(\frac{\bar{H}}{H_0} \right) \left(\frac{r_0}{R} \right)^2 \quad \text{--- (7)}$$

In the unstructured region $0.8R \leq r \leq R$, H in eq.(2) is equal to H_0 , and the temperature distribution $T_2(r)$ is given by:

$$T_2(r) = -\frac{1}{4} \frac{H_0}{k} r^2 + c \ln r + D \quad \text{--- (8)}$$

Using B.C.(3),

$$T_s = -\frac{1}{4} \frac{H_0}{k} R^2 + c \ln R + D \quad \text{--- (9)}$$

Matching the two solutions at $r=0.8R$:

$$T_1(0.8R) = T_2(0.8R) \quad \text{--- (11)}$$

and
$$\left(\frac{dT_1}{dr}\right)_{0.8R} = \left(\frac{dT_2}{dr}\right)_{0.8R} \quad \text{--- (12)}$$

[Note: k is constant throughout the region $r_0 \leq r \leq R$]

Using (6) and (8) in (11) yields:

$$-\frac{1}{4} \frac{\bar{H}}{k} (0.8R)^2 + A \ln(0.8R) + B = -\frac{1}{4} \frac{H_0}{k} (0.8R)^2 + C \ln(0.8R) + D \quad \text{--- (13)}$$

Using (6) and (8) in (12) yields:

$$-\frac{1}{2} \frac{\bar{H}}{k} (0.8R) + \frac{A}{(0.8R)} = -\frac{1}{2} \frac{H_0}{k} (0.8R) + \frac{C}{(0.8R)} \quad \text{--- (14)}$$

Solving (14) for C gives:

$$C = A - \frac{1}{2} \left(\frac{\bar{H} - H_0}{k} \right) (0.8R)^2 = A - \frac{1}{2} \frac{H_0 R^2}{k} (0.64) \left(\frac{\bar{H}}{H_0} - 1 \right) \quad \text{--- (15)}$$

Using eq (7) for A , we get,

$$C = \frac{1}{2} \frac{H_0 R^2}{k} \left[\left(\frac{r_0}{R} \right)^2 \left(\frac{\bar{H}}{H_0} \right) - 0.64 \left(\frac{\bar{H}}{H_0} - 1 \right) \right] \quad \text{--- (16)}$$

Solving eq (9) for D

$$D = T_s + \frac{1}{4} \frac{H_0 R^2}{k} - C \ln R \quad \text{--- (17)}$$

where C is given by eq. (16)

Now using (13) and (17) to determine B :

$$B = \frac{1}{4} \left(\frac{\bar{H} - H_0}{k} \right) (0.8R)^2 + (C-A) \ln(0.8R) + T_s + \frac{1}{4} \frac{H_0}{k} R^2 - C \ln R$$

Substituting into (6):

$$T_1(r) - T_s = -\frac{1}{4} \frac{\bar{H}}{k} r^2 + A \ln r + \frac{1}{4} \left(\frac{\bar{H} - H_0}{k} \right) (0.8R)^2 + (C-A) \ln(0.8R) + \frac{1}{4} \frac{H_0}{k} R^2 - C \ln R$$

$$\text{but } C \ln R = [A + (C-A)] \ln R = A \ln R + (C-A) \ln R$$

$$\therefore T_1(r) - T_s = -\frac{1}{4} \frac{\bar{H}}{k} r^2 + \frac{1}{4} \frac{H_0 R^2}{k} + \frac{1}{4} \left(\frac{\bar{H} - H_0}{k} \right) (0.8R)^2 + A \ln \left(\frac{r}{R} \right) + (C-A) \ln(0.8)$$

Using (7) for A and (15) for (C-A) we get:

$$T_1(r) - T_s = \frac{1}{4} \left(\frac{H_0 R^2}{k} \right) \left\{ 0.36 + \frac{\bar{H}}{H_0} \left(0.64 - \frac{r^2}{R^2} \right) \right\} + \frac{H_0 R^2}{2k} \left(\frac{\bar{H}}{H_0} \right) \left(\frac{r_0}{R} \right)^2 \ln \left(\frac{r}{R} \right) - \frac{H_0 R^2}{2k} \left[0.64 \ln(0.8) \right] \left(\frac{\bar{H}}{H_0} - 1 \right)$$

$$\text{But } \frac{\bar{H}}{H_0} = \frac{1}{1 - \left(\frac{r_0}{R} \right)^2} \quad [\text{from eq. (5)}]$$

$$\text{Also } H_0 = \frac{\rho}{\pi R^2}, \text{ then}$$

$$T_1(r) - T_s = \frac{\rho}{4\pi k} \left\{ 0.36 + \frac{0.64 - \left(\frac{r}{R} \right)^2}{1 - \left(\frac{r_0}{R} \right)^2} + 2 \left[\frac{\left(\frac{r_0}{R} \right)^2}{1 - \left(\frac{r_0}{R} \right)^2} \right] \left[\ln \left(\frac{r}{R} \right) - 0.64 \ln(0.8) \right] \right\}$$

Eq. (18) gives the temperature distribution in the columnar grain region as a function of (r_0/R) . The central void radius starts at $r_0=0$ when $t=0$ and grows to r_{0f} given by eq. (1) at the end of restructuring. We have assumed that the variation of (r_0/R) is known as a function of time.

Therefore the temperature distribution in the columnar grain region is a function of both r and t , or $T(r,t)$.

- c) The time to complete restructuring = Time for a pore at the outer edge of columnar grain region to migrate to the final central void position $r_0 = r_{0f}$

The pore velocity is a known function of temperature, but as a result of the solution in b), the temperature is a function of r and t . Therefore the velocity of a pore is a function of r and t , $v_p(r,t)$, which is presumed known.

Let r = radial position of a pore which started
at $r = 0.8R$ at $t=0$.

$$v_p(r,t) = \frac{dr}{dt} \quad \text{--- (19)}$$

$$r(0) = 0.8R \quad \text{--- (20)}$$

Eq. (19) must be integrated numerically, obtaining v_p as a function of T from pore migration theory and $T_i(r,t)$ from eq. (18). Eq. (19) must be integrated from $r=0.8R$ upto $r=r_{of} = 0.8\sqrt{B} R$. The time at which this is reached is t_f .

d) The pore velocity is given by combination of Eqs. (14.6) and (14.9):

$$v_p(T, p) = \frac{C}{p T^{3/2}} \exp(-\Delta H_{vap}/RT) \quad \text{--- (21)}$$

Where C is a constant

In the as-fabricated (cold) fuel, the number of gas atoms in each pore is given by:

$$p_0 \left(\frac{4}{3} \pi r_{p_0}^3 \right) = m k T_a \quad \text{--- (22)}$$

When heated to a temperature T and subject to the condition of mechanical equilibrium:

$$p \left(\frac{4}{3} \pi r_p^3 \right) = m k T \quad \text{--- (23)}$$

$$\text{and } p = \frac{2\gamma}{r_p} \quad \text{--- (24)}$$

Dividing (22) by (23) we get:

$$\frac{p_0}{p} \left(\frac{\gamma_{p_0}}{\gamma_p} \right)^3 = \frac{T_a}{T} \quad \text{--- (25)}$$

Eliminating γ_p between (24) and (25) yields:

$$p = \left(\frac{1}{p_0} \frac{T_a}{T} \right)^{1/2} \left(\frac{2\gamma}{\gamma_{p_0}} \right)^{3/2} \quad \text{--- (26)}$$

Substituting (26) into (21) gives:

$$v_p(T) = C \left(\frac{p_0}{T_a} \right)^{1/2} \left(\frac{\gamma_{p_0}}{2\gamma} \right)^{3/2} \frac{\exp(-\Delta H_{\text{vap}}/RT)}{T}$$

--- (27)

Problem 14.2

a) Pore Migration in Mixed Oxide Fuels (Raoult's Law binary)

See figure on the next page.

Δq = mole fraction of PuO_2 on hot side — that on cold side

q_0 = mole fraction of PuO_2 on cold side

At steady state:

$$\frac{J_{\text{Pu}}}{J_{\text{U}} + J_{\text{Pu}}} = q_0 \quad \text{--- (1)}$$

$$J_{\text{U}} = \frac{D_{\text{g}}}{kT\delta} [p_{\text{U}}^{\text{H}} - p_{\text{U}}^{\text{C}}] \quad \text{--- (2)}$$

$$J_{\text{Pu}} = \frac{D_{\text{g}}}{kT\delta} [p_{\text{Pu}}^{\text{H}} - p_{\text{Pu}}^{\text{C}}] \quad \text{--- (3)}$$

where p_i^{H} = partial pressure of i on hot side of pore

p_i^{C} = partial pressure of i on cold side of pore

($i = \text{U}, \text{Pu}$)

Assuming Raoult's Law for both UO_2 and PuO_2 in mixture:

$$p_{\text{U}}^{\text{H}} = (1 - q_{\text{H}}) f_{\text{U}}(T_{\text{H}}) \quad \text{--- (4)} \quad (q_{\text{H}} = q_0 + \Delta q)$$

$$p_{\text{Pu}}^{\text{H}} = q_{\text{H}} p_{\text{Pu}}^{\circ}(T_{\text{H}}) \quad \text{--- (5)} \quad \left[\begin{array}{l} T_{\text{H}} = \text{hot side temp.} \\ T_{\text{C}} = \text{cold side temp.} \end{array} \right]$$

$$p_c^u = (1 - q_0) f_u(T_c) \quad \text{--- (6)}$$

$$p_c^u = q_0 p_u^u(T_c) \quad \text{--- (7)}$$

$$f_i(T) \text{ or } p_i^u(T) = A_i \exp\left(-\frac{\Delta H_i}{kT}\right) \quad \text{--- (8)}$$

Since the temperature drop across the pore is small (thin pore)

$$p_i^u(T_h) = p_i^u(T_c) + \left(\frac{dp_i^u}{dx}\right) \delta \quad \text{--- (9)}$$

but

$$\frac{dp_i^u}{dx} = \left(\frac{dp_i^u}{dT}\right) \left(\frac{dT}{dx}\right) \quad \text{--- (10)}$$

where $\frac{dT}{dx}$ is the temperature gradient.

From (8):

$$\frac{dp_i^u}{dT} = \frac{A_i \Delta H_i}{kT^2} \exp\left(-\frac{\Delta H_i}{kT}\right) \quad \text{--- (11)}$$

$$\therefore p_i^o(T_H) \cong p_i^o(T_C) + \frac{A_i \Delta H_i}{k T_C^2} \exp\left(-\frac{\Delta H_i}{k T_C}\right) \frac{dT}{dx} \delta \quad \text{--- (12)}$$

Using (12) with $i = U$ in (4):

$$p_U^H = (1 - q_H) \left[f_U + \frac{A_U \Delta H_U}{k T^2} \exp\left(-\frac{\Delta H_U}{k T}\right) \left(\frac{dT}{dx}\right) \delta \right] \quad \text{--- (13)}$$

where the subscript "C" used on temperature was dropped.

Using (13) and (6) into (2) we get,

$$J_U = \left(\frac{Dg}{kT\delta}\right) \left\{ (1 - q_H) \left[f_U + \frac{A_U \Delta H_U}{k T^2} \exp\left(-\frac{\Delta H_U}{k T}\right) \left(\frac{dT}{dx}\right) \delta \right] - (1 - q_0) f_U \right\}$$

[we approximate $f_U(T_C) \cong f_U(T_H) = f_U(T)$]

Using (8) for f_U :

$$J_U = \left(\frac{Dg}{kT\delta}\right) \left\{ \frac{(1 - q_H) \left(\frac{dT}{dx}\right) \delta A_U \Delta H_U \exp\left(-\frac{\Delta H_U}{k T}\right)}{k T^2} - A_U \exp\left(-\frac{\Delta H_U}{k T}\right) (q_H - q_0) \right\} \quad \text{--- (14)}$$

Similarly for PuO_2 :

Replace $(1 - q_H)$ by q_H and $(1 - q_0)$ by q_0

$$J_{Pu} = \left(\frac{Dg}{kT\delta}\right) \left\{ \frac{q_H \left(\frac{dT}{dx}\right) \delta A_{Pu} \Delta H_{Pu} \exp\left(-\frac{\Delta H_{Pu}}{k T}\right)}{k T^2} + A_{Pu} \exp\left(-\frac{\Delta H_{Pu}}{k T}\right) (q_H - q_0) \right\} \quad \text{--- (15)}$$

In order to determine q_H , substitute (14) and (15) into (1):

$$\text{Let } B_i = \frac{A_i \Delta H_i \exp\left(-\frac{\Delta H_i}{kT}\right) \left(\frac{dT}{dx}\right) \delta}{kT^2} \quad (i=U, Pu)$$

Also note that:

$$f_U \text{ or } p_{Pu}^0 = A_i \exp\left(-\frac{\Delta H_i}{kT}\right)$$

Combining the above two equations:

$$B_U = \frac{\Delta H_U f_U}{kT^2} \frac{dT}{dx} \delta \quad \text{and} \quad B_{Pu} = \frac{\Delta H_{Pu} p_{Pu}^0}{kT^2} \frac{dT}{dx} \delta$$

Eqs. (14) and (15) become --- (16)

$$J_U = \frac{Dq}{kT\delta} \left[B_U(1-q_H) - f_U(q_H - q_0) \right] \quad \text{--- (14a)}$$

$$J_{Pu} = \frac{Dq}{kT\delta} \left[B_{Pu} q_H + p_{Pu}^0 (q_H - q_0) \right] \quad \text{--- (15a)}$$

Substituting into eq. (1):

$$q_0 = \frac{B_{Pu} q_H + p_{Pu}^0 (q_H - q_0)}{B_U + (B_{Pu} - B_U) q_H + (p_{Pu}^0 - f_U) (q_H - q_0)}$$

Assume $q_H \cong q_0$, except in $q_H - q_0 = \Delta q$

$$\begin{aligned} \therefore B_U q_0 + (B_{Pu} - B_U) q_0^2 + (p_{Pu}^0 - f_U) q_0 \Delta q \\ = B_{Pu} q_0 + p_{Pu}^0 \Delta q \end{aligned}$$

$$\begin{aligned} \text{or } \Delta q &= q_H - q_0 \\ &= \frac{B_U - B_{Pu}}{\frac{f_U}{1-q_0} + \frac{p_{Pu}^0}{q_0}} \end{aligned}$$

using (16) :

$$\Delta q = \left[\frac{\Delta H_U f_U - \Delta H_{Pu} p_{Pu}^0}{\frac{f_U}{1-q_0} + \frac{p_{Pu}^0}{q_0}} \right] \frac{\delta}{kT^2} \left(\frac{dT}{dx} \right)$$

--- (17)

b) Pore Velocity:

$$v_p = \frac{J_{Pu} + J_U}{N}$$

where N = total density of heavy metal atoms $(U+Pu)/cc$

Using (14a) and (15a) :

$$J_{Pu} + J_U = \frac{D_g}{kT\delta} \left[B_U + (B_{Pu} - B_U)q_H + (p_{Pu}^0 - f_U)\Delta q \right]$$

Approximate q_H by q_0 in the above :

$$\begin{aligned} \therefore v_p &= \frac{D_g}{kT\delta N} \left[\left[\Delta H_U f_U (1-q_0) + \Delta H_{Pu} p_{Pu}^0 q_0 \right] \right. \\ &\quad \left. - \frac{(f_U - p_{Pu}^0)(\Delta H_U f_U - \Delta H_{Pu} p_{Pu}^0)}{\frac{f_U}{1-q_0} + \frac{p_{Pu}^0}{q_0}} \right] \left(\frac{\delta}{kT^2} \right) \left(\frac{dT}{dx} \right) \end{aligned}$$

In pure UO_2 , the pore velocity is :

$$(v_p)_{UO_2} = \frac{D_g \Delta H_U p_U^0}{k^2 T^3 N} \left(\frac{dT}{dx} \right) \quad \left[\text{Note: Here } \Delta H_U \text{ and } p_U^0 \text{ refer to pure } UO_2 \right]$$

$$\therefore \frac{v_p}{(v_p)_{\text{uo}_2}} = (1-q_0) \frac{f_u}{p_u^0} + \gamma q_0 - \frac{(f_u - p_{pu}^0) \left(\frac{f_u}{p_u^0} - \gamma \right)}{\frac{f_u}{1-q_0} + \frac{p_{pu}^0}{q_0}} \quad \text{--- (18)}$$

$$\text{where } \gamma = \frac{\Delta H_{pu} p_{pu}^0}{\Delta H_u p_u^0} \quad \text{--- (19)}$$

is a known function
of temperature

Pu Diffusion Equation:

Coordinate system moves with velocity v_p of pore. In the coordinate system the solid "flows" in $-z$ direction with velocity v_p . Balance over slice dz :

$$J_d^{\text{in}} - J_d^{\text{out}} = \text{net diffusion current of Pu into slice}$$

$$J_c^{\text{in}} - J_c^{\text{out}} = \text{net convection of Pu into slice}$$

C = concentration of Pu in gms/cc ; D_s = diffusion coefficient of Pu in solid

$$J_d^{\text{in}} = -D_s \frac{dC}{dz}$$

$$J_d^{\text{out}} = J_d^{\text{in}} + \left(\frac{dJ_d^{\text{in}}}{dz} \right) dz = J_d^{\text{in}} - \left(D_s \frac{d^2C}{dz^2} \right) dz$$

$$\therefore \text{net input by diffusion} = D_s \frac{d^2C}{dz^2} dz$$

Also: $J_c^{\text{in}} = v_p C (z + dz) = v_p \left[C + \frac{dC}{dz} dz \right]$

$$J_c^{\text{out}} = v_p C$$

$$\therefore \text{net input by convection} = v_p \frac{dC}{dz} dz$$

At steady state, with no sources or sinks:

net input by diffusion

$$+ \text{net input by convection} = 0$$

$$\text{or } \boxed{D_s \frac{d^2C}{dz^2} + v_p \frac{dC}{dz} = 0}$$

Converting to q

$$q = \frac{C \frac{\text{gms Pu}}{\text{cc}}}{\rho_s \frac{\text{gms (U+Pu)}}{\text{cc}}} \quad (\rho_s = \text{density of oxide} = \text{constant})$$

$$\therefore \boxed{D_s \frac{d^2q}{dz^2} + v_p \frac{dq}{dz} = 0}$$

B.C. i) $q(0) = q_0 + \Delta q$; ii) $q(\infty) = q_0$

Solution:

$$\text{let } u = \frac{dq}{dz}$$

$$\therefore \frac{du}{dz} + \frac{v_p}{D_s} u = 0$$

Integrating we get,

$$u = \frac{dq}{dz} = A e^{-\frac{v_p}{D_s} z} \quad (\text{where } A \text{ is a constant})$$

Integrating again:

$$\begin{aligned} q &= \frac{AD_s}{v_p} e^{-\frac{v_p}{D_s} z} + B \\ &= A' e^{-\frac{v_p}{D_s} z} + B \end{aligned}$$

From B.C. ii) , $B = q_0$

From B.C. i) , $q_0 + \Delta q = A' + q_0$

$$\therefore A' = \Delta q$$

Therefore the complete solution is:

$$q(z) - q_0 = \Delta q \exp\left(-\frac{v_p}{D_s} z\right)$$

Problem 14.3

- a) The excess plutonium contained in the distribution in front of each moving pore is given by multiplying the answer to problem 14.2 c) by the solid density ρ_s and integrating over all distances from the front face:

$$A = \rho_s (\pi R_p^2) \int_0^{\infty} (q - q_0) dz \quad \text{atoms excess Pu/pore}$$

[R_p = radius of a pore]

z is the distance from the front face. Using the expression for $q - q_0$:

$$A = \rho_s (\pi R_p^2) \Delta q \int_0^{\infty} e^{-\frac{v_p}{D_s} z} dz = \frac{\rho_s \pi R_p^2 \Delta q D_s}{v_p} \quad \text{--- (1)}$$

where the radius of the pore r_p is given by:

$$V_p = \pi R_p^2 \delta$$

- b) Since the excess Pu in front of each pore is equal to the deficiency of Pu left behind at the initial location of the pore, the quantity of Pu lost from the volume element as a result of departure of the initial number N_{p0} of pores is $N_{p0} A$. The lost pores are replaced by N_p pores which have migrated to radial position r from positions further out. Each of the newly arrived pores supplies an excess of Pu of amount A per pore. Therefore the net gain of Pu in the volume element due to pore motion is:

$$(N_p - N_{p0}) A \quad \text{per unit volume.}$$

In the solid at time t , the porosity P is related to the pore concentration by:

$$P = N_p V_p \quad \text{--- (2)}$$

The total mass of heavy metals in the volume element is $\rho_s (1-P)$, and in the absence of the P_u carried by the pores (i.e. if A were zero), the amount of P_u in the unit volume would be $q_0 \rho_s (1-P)$.

When P_u is carried by the pores, the amount of P_u in the volume element is:

$$q_0 \rho_s (1-P) + (N_p - N_{p0}) A.$$

or the average P_u fraction in the volume element is:

$$\bar{q} = \frac{q_0 \rho_s (1-P) + (N_p - N_{p0}) A}{\rho_s (1-P)} \quad \text{--- (3)}$$

Using (1) and (2) in (3) we get:

$$\bar{q} = q_0 + \left(\frac{P - P_0}{1-P} \right) \frac{\Delta q D_s}{\delta v_p} \quad \text{--- (4)}$$

Now Δq is given by the final eq. (17) in problem 14.2 a) solution. Similarly, v_p is given by:

$$v_p = \left\{ D_g \frac{\Delta H_u P_u^0 \Omega}{k^2 T^3} \left(\frac{dT}{dr} \right) \right\} x \quad \text{--- (5)}$$

where x is given by eqs. (18) and (19) of problem 14.2.

Also Δq from eq (17) of problem 14.2 is:

$$\Delta q = \gamma \frac{\delta}{k T^2} \left(\frac{dT}{dr} \right) \quad \text{--- (6)}$$

where γ is the bracketed coefficient in the formula in the problem 14.2 a) solution.

Inserting (5) and (6) into (4) yields:

$$\bar{q} = q_0 + \left(\frac{P-P_0}{1-P} \right) \frac{\gamma}{X \Delta H_u} \frac{D_s}{D_g} \frac{kT}{P_u^0 \Omega} \quad \text{--- (7)}$$

The variation of P_u^0 and D_s with temperature is given by:

$$P_u^0 = 10^6 \exp(\Delta S_u/R) \exp(-\Delta H_u/RT) \quad \text{--- [Eq. (14.4)]}$$

--- (8)

$$D_s = D_s^0 \exp(-E_d/RT) \quad \text{--- (9)}$$

Where E_d is the activation energy for solid state diffusion of Pu in the mixed oxide and D_s^0 is the pre-exponential factor of the diffusivity.

Substituting (8) and (9) into (7) yields:

$$\bar{q} = q_0 + C \left(\frac{P-P_0}{1-P} \right) \exp\left(\frac{\Delta H_u - E_d}{RT}\right) \quad \text{--- (10)}$$

where C is a dimensionless number which is approximately temperature independent.

$$C = \frac{\gamma}{X \Delta H_u} \frac{D_s^0}{D_g} \frac{kT}{10^6 \exp(\Delta S_u/R) \Omega}$$

Thus, plutonium redistribution by pore migration depends directly upon the porosity redistribution through the term $(P-P_0)/(1-P)$ and upon the temperature distribution which appears in the exponential term. The temperature distribution is also affected by restructuring, so that porosity redistribution affects plutonium redistribution indirectly through the temperature profile $T(r)$.

Problem 14.4

Balance on slice dx wide and unit length $\perp$ to diagram on terrace (steady state)

η = surface concentration of adsorbed atoms
(atoms/cm²)

Net input by surface diffusion = $D_s \frac{d^2\eta}{dx^2} dx$

Let $\bar{z} = \frac{\rho}{\sqrt{2\pi m k T}} = \text{impingement rate from gas, atoms/cm}^2\text{-sec.}$

Input from gas phase = $\bar{z} dx$

Let κ = desorption rate constant
= reciprocal of mean life time on surface

$\kappa = \nu_i \exp(-E_b/kT)$, sec⁻¹

Output by desorption = $\kappa \eta dx$

Balance:

$$\boxed{D_s \frac{d^2\eta}{dx^2} = -\bar{z} + \kappa \eta} \quad \text{--- (1)}$$

Let $\xi = \frac{x}{(\lambda_0/2)} = \text{dimensionless distance}$

Balance becomes:

$$\frac{d^2 n}{d\xi^2} = \beta^2 n - C \quad \text{or} \quad \frac{d^2 n}{d\xi^2} - \beta^2 n = C \quad \text{--- (2)}$$

Where $\beta^2 = \frac{\kappa \lambda_0^2}{4 D_s} \text{--- (2a)}, \quad C = \frac{3 \lambda_0^2}{4 D_s} \text{--- (2b)}$

Homogeneous Solution:

$$n_H(\xi) = A \sinh \beta \xi + B \cosh \beta \xi$$

Particular solution:

$$n_P(\xi) = C/\beta^2$$

$$\therefore n(\xi) = A \sinh \beta \xi + B \cosh \beta \xi + C/\beta^2 \quad \text{--- (3)}$$

Boundary conditions:

$$\left(\frac{dn}{d\xi} \right)_0 = 0 \quad (\text{by symmetry}) \quad \text{--- (4)}$$

$$n(l) = 0 \quad (\text{ledges are perfect sinks}) \quad \text{--- (5)}$$

From first B.C. $A = 0$,

From second B.C.

$$B = -\frac{C}{\beta^2 \cosh \beta}$$

$$\therefore \boxed{n(\xi) = \frac{C}{\beta^2} \left[1 - \frac{\cosh \beta \xi}{\cosh \beta} \right]} \quad \text{--- (6)}$$

$$J = \text{flux to ledge} = -D_s \left(\frac{dn}{dx} \right)_{x=\lambda_0/2} = -\frac{2}{\lambda_0} D_s \left(\frac{dn}{d\xi} \right)_1$$

From eq. (6),

$$\frac{dn}{d\xi} = -\frac{C}{\beta} \frac{\sinh \beta \xi}{\cosh \beta}$$

$$\therefore J = \frac{2CD_s}{\lambda_0 \beta} \tanh \beta \quad \text{--- (7)}$$

Total rate at which atoms strike one-half of terrace = $\frac{3}{2} \lambda_0$

$\therefore \alpha$ = condensation coefficient

$$= \frac{J}{\frac{3}{2}(\lambda_0/2)}$$

$$\therefore \alpha = \frac{2CD_s}{\frac{3}{2}\lambda_0(\lambda_0/2)} \frac{\tanh \beta}{\beta}$$

Using definition of C from eq.(2b)

$$\frac{4CD_s}{\frac{3}{2}\lambda_0^2} = 1$$

$$\therefore \boxed{\alpha = \frac{\tanh \beta}{\beta}} \quad \text{--- (8)}$$

where β is given by eq.(2a).

Problem 14.5

a) Fixed temperature distribution :

$$T = T_s + \left(\frac{dT}{dx}\right)x$$

$t(T, T')$ = Time for pore to move from T to T'

$$dt = \frac{dx}{v_p(x)} = \frac{dT}{\left(\frac{dT}{dx}\right)v_p(T)}$$

$$t(T, T') = \frac{1}{\left(\frac{dT}{dx}\right)} \int_T^{T'} \frac{dT}{v_p(T)}$$

$$v_p = v_p^+ \exp(-\Delta H_{vap}/kT) \left(\frac{dT}{dx}\right)$$

$$\therefore t(T, T') = \frac{1}{\left(\frac{dT}{dx}\right)^2} \cdot \frac{1}{v_p^+} \int_T^{T'} e^{\Delta H_{vap}/kT} dT$$

Text, following Eq. (14.38) :

$$\int_T^{T'} e^{\Delta H_{vap}/kT} dT = - \frac{\Delta H_{vap}}{k} \int_{\frac{\Delta H_{vap}}{kT}}^{\frac{\Delta H_{vap}}{kT'}} \left(\frac{e^u}{u^2} \right) du$$

$$\cong \frac{\Delta H_{vap}}{k} \left(\frac{kT}{\Delta H_{vap}} \right)^2 \left\{ \exp\left(\frac{\Delta H_{vap}}{kT}\right) - \exp\left(\frac{\Delta H_{vap}}{kT'}\right) \right\}$$

Since $T < T'$, neglect the second term $\exp\left(\frac{\Delta H_{vap}}{kT'}\right)$

$$\therefore t(T) \cong \frac{1}{\left(\frac{dT}{dx}\right)^2} \cdot \frac{1}{v_p^+} \cdot \frac{\Delta H_{vap}}{k} \left(\frac{kT}{\Delta H_{vap}} \right)^2 \exp\left(\frac{\Delta H_{vap}}{kT}\right) \quad \text{--- (1)}$$

Note: t is independent of T' because most of the time is spent in moving in the low temperature region.

- b) At time t all pores, which were originally at positions, where temperature $\geq T$, reach the hot face.

Let $T(t)$ be the inverse of eq.(1). The position from which pores just reach the hot face in time t is:

$$x = \frac{T(t) - T_s}{(dT/dx)}$$

All porosity from x to L_0 is removed from the slab in time t .

Initial void volume in zone from x to L_0 (per unit area $\perp$ to $\frac{dT}{dx}$) = $P_0(L_0 - x)$

All of this volume is removed, or the thickness of the densified slab is:

$$L = L_0 - P_0(L_0 - x),$$

or

$$L(t) = L_0(1 - P_0) + P_0 \frac{T(t) - T_s}{(dT/dx)}$$

where $T(t)$ is obtained from solving eq.(1) for T in terms of t .

Problem 14.6

Grain size obeys the following equation with time:

$$\frac{d(d)}{dt} = k \left(\frac{1}{d} - \frac{1 + 2000 \Omega \dot{F} t}{d_m^0} \right) \quad \text{--- (1)}$$

[Eq. (14.63)]

where $k = 5.2 \times 10^7 \exp \left[-\frac{270}{R(T/10^3)} \right]$ [Eq. (14.61)]

and $d_m^0 = 2200 \exp \left[-\frac{63}{R(T/10^3)} \right]$ [Eq. (14.62)]

At $T = 1600^\circ \text{K}$,

$$\begin{aligned} k &= 5.2 \times 10^7 \exp \left[-\frac{270}{8.314 \times 1.6} \right] \\ &= \underline{0.0803} \frac{\mu\text{m}^2}{\text{hr}} = \underline{1.925} \frac{\mu\text{m}^2}{\text{days}} \\ d_m^0 &= 2200 \exp \left[-\frac{63}{8.314 \times 1.6} \right] \\ &= \underline{19.35} \mu\text{m} \end{aligned}$$

$$\begin{aligned} \Omega &= \underline{41 \times 10^{-24}} \text{ cm}^3, \quad \dot{F} = 6.1 \times 10^{12} \times 24 \times 3600 \frac{\text{fissions}}{\text{cm}^3 \cdot \text{days}} \\ &= \underline{5.28 \times 10^{17}} \frac{\text{fissions}}{\text{cm}^3 \cdot \text{days}} \end{aligned}$$

Then eq. (1) becomes,

$$\frac{d(d)}{dt} = 1.925 \left(\frac{1}{d} - \frac{1 + 2 \times 10^3 \times 4.1 \times 10^{-23} \times 5.28 \times 10^{17} t}{d_m^0} \right)$$

$$\therefore \frac{d(d)}{dt} = 1.925 \left(\frac{1}{d} - \frac{1 + 0.043t}{19.35} \right) \quad \text{--- (2)}$$

In absence of irradiation, $\dot{F}=0$,

$$\therefore \frac{d(d)}{dt} = 1.925 \left(\frac{1}{d} - \frac{1}{19.35} \right) \quad \text{--- (3)}$$

In both eqs (2) and (3) time t is in days and d is in μm . They are solved numerically using a Runge-Kutta method. The initial condition in both the equations is $d_0 = 9 \mu\text{m}$.

$\dot{F} = 6.1 \times 10^{12} \frac{\text{fissions}}{\text{cm}^2 \cdot \text{sec}}$		$\dot{F} = 0$	
Time t (Days)	Grain Size d (μm)	t (days)	d (μm)
0	9.00	0	9.00
3	9.31	40	12.21
6	9.57	80	14.07
9	9.77	120	15.32
12	9.92	160	16.22
15	10.03	200	16.89
18	10.09	240	17.40
21	10.12	280	17.79
24	10.10	320	18.10
27	10.05	360	18.37
30	9.96	400	18.54
33	9.84		
36	9.69		
39	9.45

Problem 14.7

- a) The velocity of the particle according to the surface diffusion mechanism is given by Eq. (13.219) :

$$v = \frac{3 D_s Q_s^* a_0}{k T^2 R} \left(\frac{dT}{dx} \right) \quad \text{--- (1)}$$

The distance covered in time dt is :

$$dx = v dt$$

$$\text{or } t = \int_0^x \frac{dx}{v} = \int_{T_0}^{T(x)} \frac{dT}{v \left(\frac{dT}{dx} \right)}$$

But $\frac{dT}{dx}$ is a constant

$$\therefore T(x) = T_0 + \left(\frac{dT}{dx} \right) x$$

$$\therefore t = \frac{1}{\left(\frac{dT}{dx} \right)} \int_{T_0}^{T_0 + \left(\frac{dT}{dx} \right) x} \frac{dT}{v} \quad \text{--- (2)}$$

The principal temperature variation of v is due to the surface diffusivity $D_s = D_{0s} e^{-E_s/kT}$, so that (1) becomes:

$$v = \frac{3 D_{0s} Q_s^* a_0}{k T_0^2} \left(\frac{dT}{dx} \right) \frac{e^{-E_s/kT}}{R} \quad \text{--- (1a)}$$

Substituting (1a) into (2) yields:

$$t = \frac{k T_0^2 R}{3 D_{0s} Q_s^* a_0 \left(\frac{dT}{dx} \right)^2} \int_{T_0}^{T_0 + \left(\frac{dT}{dx} \right) x} \exp(E_s/kT) dT \quad \text{--- (2a)}$$

Let $\theta = \frac{T}{T_0}$ and $C = \frac{E_s}{k T_0}$

$$\therefore \int_{T_0}^{T_0 + (dT/dx)x} \exp(E_s/kT) \frac{dT}{T^2} = T_0 \int_1^{1 + \frac{1}{T_0} \left(\frac{dT}{dx}\right)x} \exp(C/\theta) d\theta$$

Using approximate method following Eq. (14.38):

$$\int_1^{1 + \frac{1}{T_0} \left(\frac{dT}{dx}\right)x} \exp(C/\theta) d\theta = \frac{1}{C} \left[\exp(C) - \exp\left(\frac{C}{1 + \frac{1}{T_0} \left(\frac{dT}{dx}\right)x}\right) \right]$$

$$\therefore t = \frac{(k T_0)^2 T_0^2 R}{3 D_{0s} Q_s^* a_0 \left(\frac{dT}{dx}\right)^2 E_s} \left\{ \exp(C) - \exp\left(\frac{C}{1 + \frac{1}{T_0} \left(\frac{dT}{dx}\right)x}\right) \right\} \quad \text{--- (3)}$$

For small x :

$$\begin{aligned} \exp\left(\frac{C}{1 + \frac{1}{T_0} \left(\frac{dT}{dx}\right)x}\right) &\cong \exp\left[C\left(1 - \frac{1}{T_0} \left(\frac{dT}{dx}\right)x\right)\right] \\ &= e^C \exp\left(-\frac{C}{T_0} \left[\frac{dT}{dx}\right]x\right) \end{aligned}$$

$$\text{or } t = AR \left\{ 1 - \exp\left[-\frac{C}{T_0} \left(\frac{dT}{dx}\right)x\right] \right\}$$

where $A = \frac{(k T_0)^2 T_0^2 e^C}{3 D_{0s} Q_s^* a_0 \left(dT/dx\right)^2 E_s}$

$$\text{or } x = -\frac{T_0}{C \left(\frac{dT}{dx}\right)} \ln \left[1 - \frac{t}{AR} \right] \quad \text{--- (4)}$$

- b) The particles found in the range x to $x+dx$ at time t are those which have a radius between R and $R+dR$, where x , R and t are related by eq.(4) of part a)

$$g dx = f dR$$

or
$$g(x,t) = \frac{f(R)}{\left| \left(\frac{\partial x}{\partial R} \right)_t \right|} \quad \text{--- (5)}$$

where $\left(\frac{\partial x}{\partial R} \right)_t$ is obtained from $x(R,t)$ of part A, i.e. eq.(4).

14.8

(a) velocity of migration in temperature gradient.

let j = flux of salt from hot $\rightarrow$ cold, $\frac{\text{gms}}{\text{cm}^2 \cdot \text{sec}}$

In time Δt , $j l^2 \Delta t$ gms of salt are transferred from the hot to the cold end. This corresponds to $j l^2 \Delta t / \rho_s$ cm^3 of salt transferred. But the volume transported is also given by $l^2 \Delta x$, so that

$$\frac{j l^2 \Delta t}{\rho_s} = l^2 \Delta x$$

$$v = \frac{\Delta x}{\Delta t} = j / \rho_s \quad (1)$$

Fick's Law *

$$j = \frac{D}{l} \Delta C \approx \frac{D}{l} \left(\frac{dC}{dT} \right) \Delta T = D \left(\frac{dC}{dT} \right) \nabla T \quad (2)$$

$$\frac{dC}{dT} = A \frac{\Delta H}{RT^2} e^{-\Delta H/RT} \quad (3)$$

Combining (1) - (3):

$$v = \frac{D \Delta H A e^{-\Delta H/RT}}{\rho_s R T^2} \nabla T$$

* note: this problem does not involve thermal diffusion (i.e. the Soret effect)

(b) Rate of brine flow to a pot

Let J_{BC} = r-flux of brine cubes at r and t , $\text{cm}^2\text{-sec}^{-1}$

$$J_{BC} = N v \quad (1)$$

General Conservation Equation: $\frac{\partial N}{\partial t} + \nabla \cdot J_{BC} = 0$

Most frequently, the flux in continuity equations is given by Fick's first law (i.e. diffusion). In the present case, no diffusion (or random walk) occurs. the flux is given by (1). In spherical coordinates (radial component only), the continuity equation is:

$$\frac{\partial N}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 J_{BC}) = 0 \quad (2)$$

Substituting (1) into (2) yields:

$$\frac{\partial N}{\partial t} = \left(2 \frac{v}{r} + \frac{dv}{dr} \right) N + v \frac{\partial N}{\partial r} \quad (3)$$

the sign of v has been changed and positive v means movement inwards. the coefficients of N and $\partial N / \partial r$ in Eq. (3) are known functions of r . Eq. (3) is to be solved subject to the conditions (only two needed):

$$N(r, 0) = N_0 \quad \text{and} \quad N(\infty, t) = N_0 \quad (4)$$

Finally, the volume of brine reaching the pot surface per unit time

$$= 4\pi R^2 J_{BC}(R) \ell^3 = 4\pi R^2 \ell^3 v(R) N(R, t) \quad (5)$$

Problem 14.9

Egn 14.6 :

$$v_p = \frac{(\text{const}) \times D_g e^{-\Delta H/kT}}{(kT)^2} \cdot \frac{1}{T} \left(\frac{dT}{dx} \right)$$

Egn 14.9:

$$D_g = (\text{const}) \times \left(\frac{T^{3/2}}{P} \right)$$

therefore,

$$v_p = (\text{const}) \times \frac{e^{-\Delta H/kT}}{P T^{3/2}} \cdot \frac{dT}{dx} \quad (1)$$

let n_0 = initial number of gas atoms in pore per cm^2 pore area

Ideal gas law then becomes,

$$\delta P_0 = n_0 k T_0$$

$$\therefore n_0 = \frac{\delta P_0}{k T_0} \quad (2)$$

Gas atoms added to pore per cm^2 area in traveling distance $x = Cox$

Thus,

$$\delta p = (n_0 + c_0 x) kT$$

or

$$\frac{p}{p_0} = \left(1 + \frac{c_0 x}{n_0}\right) \frac{T_0}{T}$$

But,

$$T(x) = T_0 + \left(\frac{dT}{dx}\right)x \text{ for linear temp. distrib.}$$

$$\therefore x = \frac{T - T_0}{(dT/dx)}$$

and therefore

$$\frac{p}{p_0} = \left[1 + \frac{c_0}{n_0} \left(\frac{T - T_0}{dT/dx}\right)\right] \frac{T}{T_0}$$

Substituting into (1) and using (2) for n_0 ,
obtain:

$$v_p = (\text{const}) \times \frac{e^{-\Delta H/kT} (dT/dx)}{\left[p_0 + \frac{c_0 k T_0}{\delta} \frac{T - T_0}{(dT/dx)}\right] \left(\frac{T}{T_0}\right) T^{3/2}} \quad (3)$$

Problem 14.10

- (a) Molecular diffusion of VO_2 in the inert gas in the central void causes VO_2 to be vaporized from hot portions of the inner surface of the central void and be condensed on colder portions. In diagram (a), the plugs are hotter than the walls of the segments of central void, as can be shown by an approximate temperature calculation (the method of obtaining the exact temperature distribution is outlined in part (b) of this solution):

The temperature on the fuel axis in the plug is

$$T_0 = T_s + HR^2/4k \quad (1)$$

If the initial radius of the central void is r_{0i} , the temperature at the edge of the central void in diagram (a) is: *

$$T(r_{0i}) = T_s + \left(\frac{HR^2}{4k}\right) \left\{ 1 - \left(\frac{r_{0i}}{R}\right)^2 + \left(\frac{r_{0i}}{R}\right)^2 \ln\left(\frac{r_{0i}}{R}\right) \right\} \quad (2)$$

Since the bracketed term in Eq. (2) is always < 1 , then $T_0 > T(r_{0i})$. Hence the vapor pressure of the fuel is greater at the surface of the plugs exposed to the central void than it is on the cylindrical walls of the central void segments. $\therefore \text{VO}_2$ vaporizes from the plugs moves along the central void by diffusion in the gas and condenses on the walls of the central void segments.

As the plug shrinks in size (and eventually opens up), the radius of the central void decreases. All temperature nonuniformities are eliminated when all of the material in the plugs is redeposited uniformly on the walls of the central void, which then decreases in radius.

* Eq. (2) is the solution of Eq. (10.49) in the text with boundary conditions given by Eqs. (10.50) and (10.51)

(b) at any time t during restructuring, let,

$r_0(z)$ = radius of central void at axial location z , including the shape of the plug at the end near $z=0$ (see drawing on right of diagram for coordinate system).

The temperature distribution in the solid portion of the fuel is determined by solution of the conduction equation:

$$\nabla^2 T = -H/k \quad (3)$$

where

$$\nabla^2 T = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \quad (4)$$

Boundary conditions for Eq (3) are:

$$\left(\frac{\partial T}{\partial z} \right)_{z=0} = 0 \quad (\text{by symmetry}) \quad (5)$$

$$\left(\frac{\partial T}{\partial z} \right)_{z=L} = 0 \quad (\text{by symmetry}) \quad (6)$$

$$T(R, z) = T_s \quad (\text{at outer fuel surface}) \quad (7)$$

$$\left(\frac{\partial T}{\partial r} \right)_{r=r_0(z)} = 0 \quad (\text{neglecting heat transport in the gas phase}) \quad (8)$$

The diffusion equation is solved for the distribution of the VO_2 partial pressure in the gas $p(r, z)$:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial p}{\partial r} \right) + \frac{\partial^2 p}{\partial z^2} = 0 \quad (9)$$

Boundary conditions:

$$\left(\frac{\partial p}{\partial z} \right)_{z=L} = 0 \quad (\text{symmetry}) \quad (10)$$

$$\left(\frac{\partial p}{\partial z} \right)_{z=0} = 0 \quad (\text{symmetry}) \quad (11)$$

$$p(r_0(z), z) = P[T(r_0(z), z)] \quad (\text{from temperature solution}) \quad (12)$$

The time dependence enters via the rate of change of the inner surface radius of the central void. The radial flux of CO_2 from (or to) the vapor and the surface is

$$J_r = - \frac{D_g}{RT_0} \left(\frac{\partial p}{\partial r} \right)_{r=r_0}$$

The velocity of growth (or shrinkage) of the solid surface is:

$$\frac{dr_0}{dt} = \rho_s J_r = - \frac{\rho_s D_g}{RT_0} \left(\frac{\partial p}{\partial r} \right)_{r=r_0} \quad (13)$$

where ρ_s = solid fuel density.

Solution Procedure

1. Starting at time t when $r_0(z)$ is known, solve Eqs (3)-(8) for $T(r, z)$ in the solid and hence for $T(r_0(z), z)$, at the central void surface. This determines the surface vapor pressure of CO_2 by Eq (12).
2. Solve Eqs (9)-(12) for the CO_2 partial pressure distribution inside the gas space, $p(r, z)$.
3. Calculate the time rate of change of the central void radius as a function of z by Eq (13).
4. Taking a small time step Δt , calculate the new shape of the central void at $t + \Delta t$ by:

$$r_0(z) \Big|_{t+\Delta t} = r_0(z) \Big|_t + \left(\frac{dr_0}{dt} \right)_{t,z} \Delta t \quad (14)$$
5. Return to step 1 + repeat until the final state is achieved (i.e. until r_0 no longer depends upon z).

CHAPTER 15

Problem 15.1

Assume all f.f. tracks are $\perp$ to surface

F.P. balance in vaporization zone ($0 \leq x \leq l_{sp}$) & 1 cm^2 area

(C_i = conc. of f.p. i in vaporization zone)

1) Input by stopping of recoils = $(\frac{1}{2} \gamma_i \dot{F}) l_{sp} \frac{\text{atoms } i}{\text{sec-cm}^2}$

(only $\frac{1}{2}$ of recoils which stop in bulk, stop in surface layer)

2) Output by vaporization:

$$I_{ff}^{\text{rec}} = \frac{1}{4} (2\dot{F}) \mu_{ff} = \text{ff's crossing unit area of surface / sec}$$

Each f.f. removes $(\pi R_{sp}^2 l_{sp}) C_i$ atoms

$$\therefore \text{output} = I_{ff}^{\text{rec}} (\pi R_{sp}^2 l_{sp}) C_i \text{ atoms/sec-cm}^2$$

3) At steady state:

$$\frac{1}{2} \gamma_i \dot{F} = I_{ff}^{\text{rec}} \pi R_{sp}^2 C_i$$

I_i^{TS} = release rate of f.p. i by thermal spike mechanism

then

$$I_i^{TS} = I_{ff}^{rec} \pi R_{sp}^2 l_{sp} C_i = \frac{1}{2} \gamma_i \dot{F} l_{sp}$$

$$\frac{I_i^{TS}}{I_i^{rec}} = \frac{\frac{1}{2} \gamma_i \dot{F} l_{sp}}{\frac{1}{4} \gamma_i \dot{F} \mu_{ffi}} = \frac{1}{2} \frac{l_{sp}}{\mu_{ffi}} = \frac{1}{2} \frac{70}{7 \times 10^4}$$

$(\mu_{ffi} \cong 7 \mu)$

$$\therefore \frac{I_i^{TS}}{I_i^{rec}} = 5 \times 10^{-4}$$

$\therefore$ mechanism is negligible

$$\alpha_U = \frac{\text{UO}_2 \text{ molecules vaporized}}{\text{ff recoil}} = \frac{\pi R_{sp}^2 l_{sp}}{\Omega}$$

$(\Omega = \text{volume / UO}_2 \text{ molecule} \cong 41 \text{ \AA}^3)$

$$\therefore \alpha_U = \frac{\pi (20)^2 70}{41} \cong \underline{2000}$$

Problem 15.2

Consider a fission fragment emerging from surface at angle $\cos^{-1} \eta$ after traversing a distance r of fuel:

- distance through gas = t_g/η
- energy after passage through gas in gap = E

$$E = E_s \left(1 - \frac{t_g}{\eta \mu_g} \right) = E_s \left(1 - \frac{t_g E_0}{\eta \mu_g^0 E_s} \right)$$

If $E=0$, when f.f. particle reaches clad, then

$$1 - \frac{t_g E_0}{\eta \mu_g^0 E_s} = 0$$

$$\therefore E_s = \frac{t_g E_0}{\eta \mu_g^0} = E_0 \left(1 - \frac{r}{\mu_{ff}} \right)$$

$$\text{or } 1 - \frac{r}{\mu_{ff}} = \frac{t_g}{\eta \mu_g^0} \quad \text{--- (1)}$$

- c) At a given polar angle $\cos^{-1}\eta$, all the f.f.s created at r , where $r_m < r < \mu_{ff}$ will be stopped in the gas, where r_m is defined by eq. (1).

or
$$\frac{r_m}{\mu_{ff}} = 1 - \frac{t_g}{\eta \mu_g^0} \quad \text{and}$$

$$0 \leq \frac{r_m}{\mu_{ff}} \leq 1 \quad \text{or} \quad \eta > \frac{t_g}{\mu_g^0}$$

$Y\dot{F}$ = source strength of f.f.s in f.f.s/cm³-sec
f.f. current at surface of fuel due to generation in dV :

$$dj = \frac{Y\dot{F}dV}{4\pi} \left(\frac{\eta}{r^2} \right) = \frac{Y\dot{F}}{2} dr d\eta \eta$$

Let j' = current at surface which will stop in the gas

$$\begin{aligned} \text{then } j' &= \frac{Y\dot{F}}{2} \int_0^1 d\eta \left[\int_{r_m}^{\mu_{ff}} dr \right] \eta \\ &= \frac{Y\dot{F}}{2} \int_0^1 [\mu_{ff} - r_m(\eta)] \eta d\eta \\ &= \frac{1}{4} \mu_{ff} Y\dot{F} \left\{ 1 - 2 \int_0^1 \frac{r_m(\eta)}{\mu_{ff}} \eta d\eta \right\} \end{aligned}$$

for η integration: $\eta > \frac{t_g}{\mu_g^0}$, use above formula

and for $\eta < \frac{t_g}{\mu_g^0}$, $r_m = 0$

$$\begin{aligned}\therefore 2 \int_0^1 \frac{r_m(\eta)}{\mu_{ff}} \eta d\eta &= 2 \int_{t_g/\mu_g^0}^1 \left(1 - \frac{t_g}{\eta \mu_g^0}\right) \eta d\eta \\ &= \left(1 - \frac{t_g}{\mu_g^0}\right)^2\end{aligned}$$

Therefore :

$$j' = \frac{1}{4} \mu_{ff} \dot{\gamma} F \left[1 - \left(1 - \frac{t_g}{\mu_g^0}\right)^2 \right]$$

By comparison with the recoil formula:

$$I^{rec} = \frac{1}{4} \mu_{ff} \dot{\gamma} F$$

and

$$\eta_{rec} = \frac{j'}{I^{rec}} = 1 - \left(1 - \frac{t_g}{\mu_g^0}\right)^2$$

$$\text{for } \frac{t_g}{\mu_g^0} \leq 1$$

$$\eta_{rec} \cong 2 \frac{t_g}{\mu_g^0}$$

Typical fuel-clad gap = 8×10^{-3} cm.;

$$\mu_g^0 = 2 \text{ cm. (at 1 atm)}$$

$$\therefore \eta_{rec} = \frac{2 \times 8 \times 10^{-3}}{2}$$

$$= 8 \times 10^{-3}$$

Problem 15.3

- a) P = power/unit length ;
 H = Volumetric heat source in fuel rod, watts/cc
 $\dot{F}$ = fission density, fissions/cc-sec

$$H_0 = 3.07 \times 10^{-11} \frac{\text{Watt-sec}}{\text{fission}} \dot{F}$$

$$P = \pi R^2 H_0$$

γ = fission product yield (elemental)

combining :

$$\gamma \dot{F} = \frac{\gamma P}{\pi (3.07 \times 10^{-11}) R^2}$$

b)

$\gamma \dot{F}$ = rate of production of f.p./unit volume

$\therefore$ Diffusion equation is :

$$\frac{\partial C}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \gamma \dot{F} \quad \text{--- (1)}$$

I.C. $C(r, 0) = 0 \quad \text{--- (2)}$

B.C. i) $\left(\frac{dC}{dr} \right)_{r=0} = 0 \quad \text{--- (3)}$

ii) $C(R) = 0 \quad \text{--- (4)}$

Define Dimensionless variables:

$$\xi = \frac{r}{R} ; \quad T = \left(\frac{D}{R^2 \gamma \dot{F}} \right) C ; \quad \theta = \frac{Dt}{R^2}$$

Eqs (1)–(4) become:

$$\frac{\partial T}{\partial \theta} = \frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial T}{\partial \xi} \right) + 1 \quad \text{--- (5)}$$

I.C.

$$T(\xi, 0) = 0 \quad \text{--- (6)}$$

B.C.

$$i) \quad T(0, \theta) = \text{finite} \quad \text{--- (7)}$$

$$ii) \quad T(1, \theta) = 0 \quad \text{--- (8)}$$

c) Solution by Laplace Transform Method

p = transform variable

$$q = \sqrt{p}$$

$$\bar{C}(\xi) = \text{Laplace transform of } T(\xi, \theta)$$

$$\text{Transform of } \frac{\partial T}{\partial \theta} = p \bar{C}(\xi) \text{ since } T(\xi, 0) = 0$$

$$\therefore q^2 \bar{C} = \frac{1}{\xi} \frac{d}{d\xi} \left(\xi \frac{d\bar{C}}{d\xi} \right) + \frac{1}{p} \quad \text{--- (9)}$$

$$\bar{C}(0) = \text{finite} \quad \text{--- (10)}$$

$$\bar{C}(1) = 0 \quad \text{--- (11)}$$

$$\text{Let } \eta = q\xi$$

$$\text{then: } \frac{d^2 \bar{C}}{d\eta^2} + \frac{1}{\eta} \frac{d\bar{C}}{d\eta} - \bar{C} = -\frac{1}{p^2} \quad \text{--- (12)}$$

Homogeneous Solution:

$$\bar{C}_H = A I_0(\eta) + B K_0(\eta)$$

I_0, K_0 = modified Bessel functions

By B.C., eq. (10): B must be zero, as $\bar{C}(0)$ is finite.

Particular Solution:

$$\bar{C}_p = \frac{1}{p^2}$$

$\therefore$ General solution is :

$$\bar{C}(\eta) = A I_0(\eta) + \frac{1}{p^2}$$

$$\text{or } \bar{C}(\xi) = A I_0(q\xi) + \frac{1}{p^2}$$

using (11) :

$$0 = A I_0(q) + \frac{1}{p^2}$$

$$\therefore A = - \frac{1}{p^2 I_0(q)}$$

$$\therefore \bar{C}(\xi) = \frac{1}{p^2} \left[1 - \frac{I_0(q\xi)}{I_0(q)} \right] \quad \text{--- (13)}$$

Surface flux of f.p.s

$$J = -D \left(\frac{\partial C}{\partial r} \right)_R = -\frac{D}{R} \left(\frac{\partial C}{\partial \xi} \right)_1$$

$$\left(\frac{J}{R Y F} \right) = -\frac{D}{R^2 Y F} \left(\frac{\partial C}{\partial \xi} \right)_1 = -\left(\frac{\partial T}{\partial \xi} \right)_1$$

Taking transform:

$$\frac{\bar{J}}{R Y F} = -\left(\frac{d\bar{C}}{d\xi} \right)_1$$

From (13):

$$\begin{aligned} \frac{d\bar{C}}{d\xi} &= -\frac{1}{p^2 I_0(q)} \frac{d}{d\xi} I_0(q\xi) = -\frac{q}{p^2 I_0(q)} \frac{d}{d(q\xi)} [I_0(q\xi)] \\ &= -\frac{q}{p^2} \frac{I_1(q\xi)}{I_0(q\xi)} \end{aligned}$$

therefore:

$$\boxed{\frac{\bar{J}}{RY\dot{F}} = \frac{1}{q^3} \frac{I_1(q)}{I_0(q)}} \quad \text{--- (14)}$$

Long time approximation:

$$\text{As } t \rightarrow \infty, \quad q \rightarrow 0$$

$$I_1(q) \rightarrow \frac{1}{2}q, \quad I_0(q) \rightarrow 1$$

$$\therefore \frac{\bar{J}}{RY\dot{F}} = \frac{1}{2p}$$

Inverting:

$$\boxed{\frac{J}{RY\dot{F}} = \frac{1}{2}} \quad \text{--- (15)}$$

Short time approximation:

$$\text{As } t \rightarrow 0, \quad q \rightarrow \infty$$

$$I_1(q) \rightarrow \frac{e^q}{\sqrt{2\pi q}} \left[1 - \frac{3}{8q} + \dots \right]$$

$$I_0(q) \rightarrow \frac{e^q}{\sqrt{2\pi q}} \left[1 + \frac{1}{8q} + \dots \right]$$

$$\therefore \frac{\bar{J}}{RY\dot{F}} = \frac{1}{q^3} \left[\frac{1 - \frac{3}{8q}}{1 + \frac{1}{8q}} \right] - \frac{1}{q^3} \left(1 - \frac{1}{2q} + \dots \right)$$

Inverting: (Carslaw & Jaeger, app.V, nos. 8 & 9)

$$\boxed{\frac{J}{RY\dot{F}} = 2 \sqrt{\frac{\theta}{\pi}} - \theta} \quad \text{--- (16)}$$

Problem 15.4

Diffusion equation in the cladding is:

$$\frac{\partial C_{cl}}{\partial t} = D_{cl} \frac{\partial^2 C_{cl}}{\partial x^2}$$

Initial Condition:

$$C_{cl}(0, x) = 0$$

Boundary Conditions:

$$i) C_{cl}(t, \infty) = 0$$

$$ii) \text{ Let } C_{Na} = \text{concentration of F.P. in sodium}$$

distribution coefficient

$$m = \frac{C_{cl}(t, 0)}{C_{Na}(t)} = \text{constant}$$

Balance on F.P. in the sodium

$$t_g \frac{dC_{Na}}{dt} = J - \left[-D_{cl} \left(\frac{\partial C_{cl}}{\partial x} \right)_0 \right]$$

where J is a constant given by eq. (15) of problem 15.3 ;

$$\therefore \boxed{\frac{t_g}{m} \left(\frac{\partial C_{cl}}{\partial t} \right)_{x=0} = J + D_{cl} \left(\frac{\partial C_{cl}}{\partial x} \right)_0}$$

Dimensionless variables:-

$$\theta = \frac{D_{cl} t}{t_g^2}, \text{ dimensionless time}$$

$$\zeta = \frac{x}{t_g}, \text{ dimensionless distance}$$

$$C = \left(\frac{D_{cl}}{m t_g J} \right) C_{cl}, \text{ dimensionless concentration}$$

Diffusion Equation becomes

$$\frac{\partial C}{\partial \theta} = \frac{\partial^2 C}{\partial \zeta^2} \quad \text{--- (1)}$$

$$\text{with } C(0, \zeta) = 0 \quad \text{--- (2)}$$

$$C(\theta, \infty) = 0 \quad \text{--- (3)}$$

$$\text{and } \left(\frac{\partial C}{\partial \theta} \right)_{\zeta=0} = 1 + m \left(\frac{\partial C}{\partial \zeta} \right)_0 \quad \text{--- (4)}$$

Solution by Laplace Transform

Let p = transform variable

and $q = \sqrt{p}$

Transform eq. (1) with initial condition (2):

$$\frac{d^2 \bar{C}}{d\zeta^2} = q^2 \bar{C} \quad \text{or} \quad \frac{d^2 \bar{C}}{d\zeta^2} - q^2 \bar{C} = 0 \quad \text{--- (5)}$$

$$\text{Transform of (3):} \quad \bar{C}(\infty) = 0 \quad \text{--- (6)}$$

$$\text{Transform of (4):} \quad q^2 \bar{C}(0) = \frac{1}{q^2} + m \left(\frac{d\bar{C}}{d\zeta} \right)_0 \quad \text{--- (7)}$$

Solution of (5) is

$$\bar{C} = A e^{-q\zeta} + B e^{q\zeta}$$

$B = 0$ to satisfy (6)

To satisfy (7):

$$q^2 A = \frac{1}{q^2} - m A q ,$$

or $A = \frac{1}{q^3(m+q)}$

Therefore:

$$\bar{C}(s, q) = \frac{e^{-qs}}{q^3(m+q)}$$

To invert, see p.495, Carslaw & Jaeger, no 16.

Inverting:

$$C(\theta, \zeta) = \frac{1}{m^2} \left\{ e^{m\zeta} e^{m^2\theta} \operatorname{erfc}\left(m\sqrt{\theta} + \frac{\zeta}{2\sqrt{\theta}}\right) - \operatorname{erfc}\left(\frac{\zeta}{2\sqrt{\theta}}\right) \right\} + \frac{1}{m} \left\{ 2\sqrt{\frac{\theta}{\pi}} e^{-\zeta^2/4\theta} - \zeta \operatorname{erfc}\left(\frac{\zeta}{2\sqrt{\theta}}\right) \right\}$$

Problem 15.5

$$a) \quad \eta_g(\beta_1) = \eta_o + \left(\frac{Y_{ke} V_f}{\Omega} \right) \beta_1 \bar{f}^*(P_1) \quad \text{--- (1)}$$

Since initial high power operation does not enhance release in subsequent lower power cycle:

$$\eta_g(\beta_2) = \eta_g(\beta_1) + \left(\frac{Y_{ke} V_f}{\Omega} \right) (\beta_2 - \beta_1) \bar{f}^*(P_2)$$

Adding we get;

$$\eta_g(\beta_2) = \eta_o + \left(\frac{Y_{ke} V_f}{\Omega} \right) [\beta_1 \bar{f}^*(P_1) + (\beta_2 - \beta_1) \bar{f}^*(P_2)] \quad \text{--- (2)}$$

For the third power cycle at β_3 , the fractional release is the same as if the operation from β_1 to β_3 had been at β_3

$$\eta_g(\beta_3) = \eta_g(\beta_1) + \left(\frac{Y_{ke} V_f}{\Omega} \right) (\beta_3 - \beta_1) \bar{f}^*(P_3)$$

Using (1):

$$\eta_g(\beta_3) = \eta_o + \left(\frac{Y_{ke} V_f}{\Omega} \right) \left\{ \beta_1 \bar{f}^*(P_1) + (\beta_3 - \beta_1) \bar{f}^*(P_3) \right\} \quad \text{--- (3)}$$

b) Coolant outlet temperature = Temperature of gas in plenum
 $= T_p$

Also: Coolant temperature rise, $(T_p - T_{in}) \propto$ linear power

$$\therefore \frac{T_p - T_{in}}{T_1 - T_{in}} = \frac{\rho}{\rho_1} \quad \text{--- (4)}$$

Only open voidage = that of plenum, volume V_p

$$p_g = \frac{n_g R T_p}{V_p} = \frac{n_g R T_{in}}{V_p} \left[1 + \frac{\rho}{\rho_1} \left(\frac{T_1}{T_{in}} - 1 \right) \right] \quad \text{--- (5)}$$

[using (4)]

$$0 \leq \beta \leq \beta_1, \quad n_g = n_o, \quad \rho = \rho_1$$

$\therefore$ pressure between $0 \leq \beta \leq \beta_1$ is:

$$\boxed{(p_g)_{0-1} = \frac{n_o R T_{in}}{V_p} \left(\frac{T_1}{T_{in}} \right)} \quad \text{--- (6)}$$

$$\beta_1 \leq \beta \leq \beta_2, \quad n_g = n_g(\beta_1) \quad [\text{Eq. (1)}], \quad \rho = \rho_2$$

$$(p_g)_{1-2} = \left(\frac{R T_{in}}{V_p} \right) \left[1 + \frac{\rho_2}{\rho_1} \left(\frac{T_1}{T_{in}} - 1 \right) \right] \left[n_o + \left(\frac{Y_{ke} V_f}{\Omega} \right) \beta_1 f(\beta_1) \right]$$

$$\therefore \boxed{(p_g)_{1-2} = \left[1 + \frac{\rho_2}{\rho_1} \left(\frac{T_1}{T_{in}} - 1 \right) \right] \left[\frac{(p_g)_{0-1}}{(T_1/T_{in})} + \left(\frac{Y_{ke} R T_{in}}{\Omega} \frac{V_f}{V_p} \right) \beta_1 f(\beta_1) \right]} \quad \text{--- (7)}$$

$$\beta_2 \leq \beta \leq \beta_3, \quad \rho = \rho_3, \quad n_g = n_g(\beta_2), \quad [\text{Eq. (2)}]$$

$$(p_g)_{2-3} = \left(\frac{RT_{in}}{V_p} \right) \left[1 + \frac{p_3}{p_1} \left(\frac{T_i}{T_{in}} - 1 \right) \right] \left\{ n_0 + \left(\frac{y_{Xe} V_f}{\Omega} \right) [p_1 \bar{f}(p_1) + (p_2 - p_1) \bar{f}(p_2)] \right\}$$

$$\text{or } (p_g)_{2-3} = \left[1 + \frac{p_3}{p_1} \left(\frac{T_i}{T_{in}} - 1 \right) \right] \left\{ \frac{(p_g)_{0-1}}{(T_i/T_{in})} + \left[\frac{y_{Xe} RT_{in}}{\Omega} \frac{V_f}{V_p} \right] [p_1 \bar{f}(p_1) + (p_2 - p_1) \bar{f}(p_2)] \right\}$$

$$\underline{p > p_3}$$

---(8)

$$(p_g)_{3-} = \left[1 + \frac{p_4}{p_1} \left(\frac{T_i}{T_{in}} - 1 \right) \right] \left\{ \frac{(p_g)_{0-1}}{(T_i/T_{in})} + \left(\frac{y_{Xe} RT_{in}}{\Omega} \frac{V_f}{V_p} \right) [p_1 \bar{f}(p_1) + (p_3 - p_1) \bar{f}(p_3)] \right\}$$

---(9)

- c) According to the "life-fraction rule", failure occurs when:

$$\frac{t_1}{t_R(p_{g_{0-1}})} + \frac{t_2 - t_1}{t_R(p_{g_{1-2}})} + \frac{t_3 - t_2}{t_R(p_{g_{2-3}})} + \frac{t_f - t_3}{t_R(p_{g_{3-f}})} = 1 \quad \text{--- (10)}$$

where t_1 , t_2 and t_3 are the times corresponding to burnups β_1 , β_2 and β_3 and t_f is the time at which cladding failure occurs.

Using $t_R = \frac{k}{p_g^n}$, eq. (10) becomes:

$$t_1 p_{g_{0-1}}^n + (t_2 - t_1) p_{g_{1-2}}^n + (t_3 - t_2) p_{g_{2-3}}^n + (t_f - t_3) p_{g_{3-f}}^n = k \quad \text{--- (11)}$$

$p_{g_{0-1}}$, $p_{g_{1-2}}$, $p_{g_{2-3}}$ and $p_{g_{3-f}}$ are given by eqs (6) through (9) in problem 15.5 b). There remains to calculate t_1 , t_2 and t_3 : The burnup is given by:

$$\beta = \dot{F} \Omega t$$

where $\dot{F}$ = fissions/cm³-sec (average over fuel cross section)

Ω = volume per uranium atom, cm³

and the fission density is related to the linear power by:

$$\frac{P}{\pi R^2} = 3.07 \times 10^{-11} \dot{F}$$

$$\therefore \beta = K \rho t \quad \text{--- (12)}$$

where $K = \frac{\Omega}{3.07 \times 10^{-11} \pi R^2}$

$$\therefore t_1 = \frac{1}{K} \frac{\beta_1}{\rho_1} \quad \text{--- (13a)}$$

$$t_2 - t_1 = \frac{1}{K} \frac{\beta_2 - \beta_1}{\rho_2} \quad \text{--- (13b)}$$

$$t_3 - t_2 = \frac{1}{K} \frac{\beta_3 - \beta_2}{\rho_3} \quad \text{--- (13c)}$$

$$t_f - t_3 = \frac{1}{K} \frac{\beta_f - \beta_3}{\rho_4} \quad \text{--- (13d)}$$

Substituting eqs(13) into eq.(11) yields:

$$\boxed{\frac{\beta_1 \rho_{g0-1}^n}{\rho_1} + \frac{(\beta_2 - \beta_1) \rho_{g1-2}^n}{\rho_2} + \frac{(\beta_3 - \beta_2) \rho_{g2-3}^n}{\rho_3} + \frac{(\beta_f - \beta_3) \rho_{g3-f}^n}{\rho_4} = K k}$$

This can be solved for β_f

Problem 15.6

$$\frac{\partial C}{\partial t} = D \nabla^2 C + S = 0 \quad \text{in steady state}$$

$$\therefore D \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) - \lambda C = -Y\dot{F}$$

$$\text{Let } \frac{1}{L^2} = \frac{\lambda}{D}, \text{ then}$$

$$\text{a particular solution is: } C_p = \frac{Y\dot{F}}{\lambda}$$

$$\text{for homogeneous equation: } C = \frac{A}{r} \sinh \frac{r}{L} + \frac{B}{r} \cosh \frac{r}{L}$$

Boundary Conditions: (1) $C(0)$ is finite.

This gives $B=0$

$$(2) \quad C(a) = 0$$

$$\text{This gives } \frac{Y\dot{F}}{\lambda} + \frac{A}{a} \sinh \frac{a}{L} = 0$$

$$\therefore A = -\frac{Y\dot{F}}{\lambda} \frac{a}{\sinh \frac{a}{L}}$$

$$\therefore \boxed{C(r) = \frac{Y\dot{F}}{\lambda} \left(1 - \frac{a}{r} \frac{\sinh \frac{r}{L}}{\sinh \frac{a}{L}} \right)}$$

$$f = \frac{R}{P} = \frac{\text{total rate of release}}{\text{total rate of production}} = \frac{4\pi a^2 j(a)}{\frac{4}{3}\pi a^3 Y\dot{F}}$$

$$= -\frac{3D}{aY\dot{F}} \left. \frac{dC}{dr} \right|_{r=a}$$

$$\therefore f = -\frac{3D}{aY\dot{F}} \cdot \frac{Y\dot{F}}{\lambda} \left(\frac{a}{r^2} \frac{\sinh \frac{r}{L}}{\sinh \frac{a}{L}} - \frac{a}{rL} \frac{\cosh \frac{r}{L}}{\sinh \frac{a}{L}} \right)_{r=a}$$

$$= -\frac{3D}{\lambda} \left(\frac{1}{a^2} - \frac{1}{aL} \coth \frac{a}{L} \right)$$

$$\therefore f = \frac{3D}{\lambda a^2} \left(-1 + \sqrt{\frac{a^2 \lambda}{D}} \coth \sqrt{\frac{a^2 \lambda}{D}} \right)$$

Using the radioactive half life $z_{1/2} = \frac{\ln 2}{\lambda}$, or for simplicity, the radioactive mean life $z = \frac{1}{\lambda}$ and the diffusion mean life $z_D = \frac{a^2}{D}$, we get:

$$f = 3 \frac{z}{z_D} \left(\sqrt{\frac{z_D}{z}} \coth \sqrt{\frac{z_D}{z}} - 1 \right) = \frac{3}{x^2} (x \coth x - 1)$$

where $x^2 = \frac{z_D}{z}$

For $z_D \gg z$, i.e. $x \gg 1$

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} \cong 1 \quad \text{as } x \rightarrow \infty$$

$$\therefore f = \frac{3}{x^2} (x - 1) \cong \frac{3}{x^2} \cdot x = \frac{3}{x} = 3 \sqrt{\frac{z}{z_D}} = \frac{3}{a} \sqrt{\frac{D}{\lambda}}$$

For $z_D \ll z$, i.e. $x \ll 1$

This means that the decay rate is much smaller than the rate of release by diffusion; in this case we can approximate the diffusion equation by:

$$D \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dc}{dr} \right) = -Y\dot{F}$$

$$\therefore r^2 \frac{dc}{dr} = -\frac{Y\dot{F}}{D} \left[\frac{r^3}{3} + C_1 \right]$$

$$\therefore \frac{dc}{dr} = -\frac{Y\dot{F}}{3D} \left[r + \frac{3C_1}{r^2} \right]$$

$$C_1 = 0, \quad \text{since } \left. \frac{dc}{dr} \right|_{r=0} = 0$$

$$\therefore C = -\frac{\gamma \dot{F}}{6D} r^2 + C_2$$

$$\text{Since } C(a) = -\frac{\gamma \dot{F} a^2}{6D} + C_2 = 0,$$

$$\text{we get } C_2 = \frac{\gamma \dot{F} a^2}{6D}$$

$$\therefore C = \frac{\gamma \dot{F} a^2}{6D} \left(1 - \frac{r^2}{a^2}\right)$$

$$\text{and } f = -\frac{3D}{\gamma \dot{F} a} \left. \frac{dc}{dr} \right|_{r=a} = \frac{3D}{a \gamma \dot{F}} \frac{\gamma \dot{F} a}{3D} = 1$$

$$\therefore \underline{f = 1}$$

Problem 15.7

a) Diffusion in coating

$$-D \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) + \lambda C = S(r) \quad \text{--- (1)}$$

where $S(r)$ = fission fragments from fuel pellet deposited in coating at r per cc per sec

B.C. (1) $\left(\frac{dC}{dr} \right)_{a_p} = 0$ (No transfer back to pellet)

(2) $C(a_c) = 0$

To solve the eq. (1) for arbitrary $S(r)$,

let $u = rC$, then (1) becomes

$$D \frac{d^2 u}{dr^2} - \lambda u = -rS(r) \quad \text{--- (1')}$$

B.C. (1) $a_p \left(\frac{du}{dr} \right)_{a_p} = u(a_p)$

$$u(a_c) = 0$$

Then, the general solution to (1') is given by

$$u(r) = A e^{-\sqrt{\lambda/D} r} + B e^{\sqrt{\lambda/D} r} + u_p(r)$$

where $u_p(r)$ is a particular solution to (1')

But, by method of variation of constants, we can assume the trial function is as

$$u_p(r) = v(r) e^{-\sqrt{\lambda_0} r} + w(r) e^{\sqrt{\lambda_0} r} \quad \text{--- (2)}$$

For simplicity let $y_1(r) = e^{-\sqrt{\lambda_0} r}$ and $y_2(r) = e^{\sqrt{\lambda_0} r}$ and since $y_1(r)$ and $y_2(r)$ satisfy the homogeneous equation,

$$D \frac{d^2 u}{dr^2} - \lambda u = 0$$

First taking a derivative of $u_p(r)$ w.r.t. r

$$u_p(r) = v(r) y_1(r) + w(r) y_2(r) \quad \text{--- (3)}$$

$$\therefore \frac{du_p}{dr} = \left(y_1 \frac{dv(r)}{dr} + y_2 \frac{dw(r)}{dr} \right) + \left(v(r) \frac{dy_1(r)}{dr} + w(r) \frac{dy_2(r)}{dr} \right)$$

$$\text{So, assume } y_1 v' + y_2 w' = 0 \quad \text{--- (4)}$$

$$\begin{aligned} \text{Then } \frac{d^2 u_p}{dr^2} &= \left(v(r) \frac{d^2 y_1(r)}{dr^2} + w(r) \frac{d^2 y_2(r)}{dr^2} \right) \\ &\quad + \left(\frac{dv(r)}{dr} \cdot \frac{dy_1(r)}{dr} + \frac{dw(r)}{dr} \cdot \frac{dy_2(r)}{dr} \right) \end{aligned} \quad \text{--- (5)}$$

Substituting (2) and (5) into (1') and using the fact that $y_1(r)$, $y_2(r)$ satisfy

$$Du'' - \lambda u = 0, \text{ then we have}$$

$$v' \cdot y_1' + w' \cdot y_2' = -r S(r)$$

Substituting for $y_1(r)$ and $y_2(r)$ into (4) and (6)

$$e^{-\sqrt{\lambda_0} r} v' + e^{\sqrt{\lambda_0} r} w' = 0 \quad \text{--- (4')}$$

and
$$-e^{-\sqrt{\lambda_0} r} v' + e^{\sqrt{\lambda_0} r} \omega' = -\sqrt{D/\lambda} r S(r) \quad \text{---(6')}$$

Solving (4') and (6') for v' and ω'

$$v' = \frac{dv}{dr} = \frac{1}{2} \sqrt{\frac{D}{\lambda}} r S(r) e^{\sqrt{\lambda_0} r}$$

and
$$\omega' = \frac{d\omega}{dr} = -\frac{1}{2} \sqrt{\frac{D}{\lambda}} r S(r) e^{-\sqrt{\lambda_0} r}$$

$$\therefore v(r) = \frac{1}{2} \sqrt{\frac{D}{\lambda}} \int_{a_p}^r s S(s) e^{\sqrt{\lambda_0} s} ds$$

$$\omega(r) = -\frac{1}{2} \sqrt{\frac{D}{\lambda}} \int_{a_p}^r s S(s) e^{-\sqrt{\lambda_0} s} ds$$

$$\therefore u(r) = [A + v(r)] e^{-\sqrt{\lambda_0} r} + [B + \omega(r)] e^{\sqrt{\lambda_0} r}$$

A and B can be determined from B.C. (1) and (2)

Then the general solution to eq.(1) is given by,

$$C(r) = \frac{1}{r} [A + v(r)] e^{-\sqrt{\lambda_0} r} + \frac{1}{r} [B + \omega(r)] e^{\sqrt{\lambda_0} r} \quad \text{---(7)}$$

Rate of release from the surface of the coating $= -4\pi a_c^2 D \left(\frac{dC}{dr} \right)_{a_c}$

Rate of production in the pellet $= \frac{4}{3} \pi a_p^3 Y_i \dot{F}$

$$\therefore \text{fractional release : } f = - \left(\frac{3 a_c^2 D}{a_p^3 Y_i \dot{F}} \right) \left(\frac{dC}{dr} \right)_{a_c}$$

---(8)

b) (i)

Current through unit area at r (point A) comes from material in pellet which is contained within a spherical cap of radius μ with its center at point A, at which the current is normal.

Consider a volume element dv in pellet at polar angle θ from the vertical axis and a distance s from point A. ($s < \mu$)

Rate of "emission" of fission product "i" from dv is :

$$y_i \dot{F} dv$$

Solid angle subtended by unit area perpendicular to the vertical axis at dv is :

$$\frac{\cos \theta}{4\pi s^2}$$

Then dJ = rate at which ff's from dv cross the unit area at point A

$$= y_i \dot{F} dv \frac{\cos \theta}{4\pi s^2} = -y_i \dot{F} s^2 d\phi ds d(\cos \theta) \cdot \frac{\cos \theta}{4\pi s^2}$$

$$\boxed{dJ = -\frac{1}{4\pi} y_i \dot{F} \cos \theta d\phi ds d(\cos \theta)} \quad \text{--- (9)}$$

To get $J(r)$, integrate s from s_0 to s_1 , θ from 0 to θ_f , ϕ from 0 to 2π . These limits differ depending upon r .

Now define r_c and θ_c such that

$$r_c = \sqrt{a_p^2 + \mu^2} \quad \text{--- (10)}$$

$$\cos \theta_c = \mu / r_c \quad \text{--- (11)}$$

Then we have 3 distinct regions of $J(r)$

I) $a_p < r \leq r_c$

Define θ_f and θ_i such that

$$\sin \theta_f = \frac{a_p}{r}$$

$$\text{or } \cos \theta_f = \sqrt{1 - \left(\frac{a_p}{r}\right)^2} \quad \text{--- (12)}$$

$$\text{and } a_p^2 = \mu^2 + r^2 - 2\mu r \cos \theta_i$$

$$\text{or } \cos \theta_i = \frac{\mu^2 + r^2 - a_p^2}{2\mu r} \quad \text{--- (13)}$$

Then, for $\theta_i \leq \theta \leq \theta_f$

Limits of ξ integration:

$$a_p^2 = r^2 + \xi^2 - 2r\xi \cos \theta$$

$$\text{or } \xi_0 = r \cos \theta - \sqrt{(r \cos \theta)^2 - (r^2 - a_p^2)} \quad \text{--- (14)}$$

$$\text{and } \xi_1 = r \cos \theta + \sqrt{(r \cos \theta)^2 - (r^2 - a_p^2)} \quad \text{--- (15)}$$

for $0 \leq \theta \leq \theta_i$

$$\xi_0 = r \cos \theta - \sqrt{(r \cos \theta)^2 - (r^2 - a_p^2)} \quad (\text{same as before})$$

$$\text{and } \xi_1 = \mu$$

Now let $\eta = \cos\theta$ --- (16)

Then for $a_p \leq r \leq r_c$

$$\begin{aligned} J(r) &= \int_V dV = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_{s_0}^{s_1} ds \int_1^{\cos\theta_f} y_i \dot{F} \cos\theta d(\cos\theta) \\ &= -\frac{1}{2} y_i \dot{F} \left[\int_1^{\cos\theta_i} d\eta \eta \int_{s_0}^{\mu} ds + \int_{\cos\theta_i}^{\cos\theta_f} \eta d\eta \int_{s_0}^{s_1} ds \right] \\ &= -\frac{1}{2} y_i \dot{F} \left[\int_1^{\cos\theta_i} (\mu - s_0) \eta d\eta + \int_{\cos\theta_i}^{\cos\theta_f} (s_1 - s_0) \eta d\eta \right] \end{aligned}$$

Substituting (12) through (16) we get,

$$\begin{aligned} J_I(r) &= y_i \dot{F} \left[\int_{\frac{r^2 + \mu^2 - a_p^2}{2\mu r}}^1 \eta \left[\mu - r\eta + \sqrt{(r\eta)^2 - (r^2 - a_p^2)} \right] d\eta \right. \\ &\quad \left. + 2 \int_{\frac{r^2 + \mu^2 - a_p^2}{2r\mu}}^{\frac{r^2 + \mu^2 - a_p^2}{2\mu r}} \eta \sqrt{(r\eta)^2 - (r^2 - a_p^2)} d\eta \right] \end{aligned} \quad \text{--- (17)}$$

II) $r_c < r \leq a_p + \mu$

In this region only the first term in (17) remains.

$$J_{II}(r) = \frac{1}{2} y_i \dot{F} \int_{\frac{r^2 + \mu^2 - a_p^2}{2\mu r}}^1 \eta \left[\mu - r\eta + \sqrt{(r\eta)^2 - (r^2 - a_p^2)} \right] d\eta \quad \text{--- (18)}$$

III) $r > a_p + \mu$

Since this is beyond the range of the ff's,

$$J_{III}(r) \equiv 0$$

(ii) Evaluation of $S(r)$ due to Recoil from pellet

Since $\mu < (a_c - a_p)$, fragments can not recoil completely out of particle and since μ is of the order of a_p , spherical coordinates must be used.

Let $J(r)$ = fission fragment current at location r , $a_p < r < a_p + \mu$

i.e. $J(r)$ = number of fission fragments crossing unit area $\perp$ to radius at r per sec.

Then $N(r)$ = number of ff's crossing spherical surface at $r = 4\pi r^2 J(r)$

and $4\pi r^2 dr$ = volume of spherical element between r and $r + dr$

$$\therefore S(r) = \frac{N(r) - N(r+dr)}{4\pi r^2 dr} = - \frac{\frac{dN(r)}{dr}}{4\pi r^2}$$

$$= - \frac{1}{r^2} \frac{d}{dr} [r^2 J(r)]$$

Problem 15.8

Stable isotope: atoms/cm³ of fuel produced = $y\dot{F}t$

Radioactive isotope: atoms/cm³-sec produced = $y^*\dot{F}$

fractional release of stable isotope

$$f = \frac{4}{\sqrt{\pi}} \sqrt{D't} \quad \text{--- [Eq. (15.89)]}$$

fractional release rate of radioactive

$$\text{isotope} = 3\sqrt{\frac{D'}{\lambda}} \quad \text{--- [Eq. (15.92)]}$$

Stable isotope at time t,

N = number of atoms of stable fission gas released

$$N = \left[\frac{4}{\sqrt{\pi}} \sqrt{D't} \right] y\dot{F}t$$

Radioactive isotope:

R = rate of release of isotope

$$= \left[3\sqrt{\frac{D'}{\lambda}} \right] y^*\dot{F}$$

Nuclear Balance on radioactive species:

N^* = atoms of radioactive gas in plenum

$$\frac{dN^*}{dt} = R - \lambda N^*$$

$$\therefore N^*(t) = \frac{R}{\lambda} (1 - e^{-\lambda t}) \cong \frac{R}{\lambda} \quad (\text{for large } t)$$

$$N^* = 3\sqrt{\frac{D'}{\lambda}} \frac{y^*\dot{F}}{\lambda}$$

Isotopic ratio

$$\frac{N^*}{N} = \frac{3\sqrt{D'} y^* \dot{F}}{\lambda^{3/2}} \frac{\sqrt{\pi}}{4} \frac{1}{\sqrt{D'} y^* \dot{F} t^{3/2}}$$

$$\therefore \boxed{\frac{N^*}{N} = \frac{3\sqrt{\pi}}{4} \frac{y^*}{y} \frac{1}{(\lambda t)^{3/2}}}$$

Problem 15.9

Let L_f = length of fuel (cm)
 Total power of fuel element = PL_f watts
 (neglecting axial power variations)

$$\text{Total fissions in fuel rod in time } t = \frac{PL_f \text{ watts} \times t \text{ sec}}{3.2 \times 10^{-11} \text{ watt/fissions/sec}}$$

$$\left(\begin{array}{c} \text{Total number of stable} \\ \text{fission gas atoms produced} \\ \text{in fuel rod} \end{array} \right) = \frac{Y_{Xe} PL_f t}{3.2 \times 10^{-11}} \quad \left(\begin{array}{c} Y_{Xe} = 0.25 = \text{yield of} \\ \text{stable Xe-Kr} \end{array} \right)$$

$\bar{f}$ = radially-averaged fractional release from fuel

n_g = gm-atoms fission gases released

$$= \frac{\bar{f} Y_{Xe} PL_f t}{(3.2 \times 10^{-11})(6.023 \times 10^{23})}$$

plenum volume = $V_p = L_p A$ ↖ Cross sectional area of fuel
(table 10.2)

$$\boxed{P_g = \frac{n_g R T_p}{V_p} = \frac{\bar{f} Y_{Xe} P (L_f/L_p) R T_p t}{A (3.2 \times 10^{-11})(6.023 \times 10^{23})}$$

$$A = \frac{\pi}{4} (1.07 - 2 \times 0.061)^2 = 0.71 \text{ cm}^2$$

(a) Empirical diffusion coefficient method:

For $P = 500 \text{ watt/cm}$

Fig. 15.16 gives $\bar{D}' = \bar{D} \approx 5 \times 10^{-10} \text{ sec}^{-1}$

$$\text{for } t = 3 \text{ yrs} = 9.4 \times 10^7 \text{ sec}$$

$$\bar{f} = \frac{4}{\sqrt{\pi}} \sqrt{(5 \times 10^{-10})(9.4 \times 10^7)} = 0.49$$

$$\therefore P_g = \frac{(0.49)(0.25)(500)(4)(82)(320+273)(9.4 \times 10^7)}{(0.71)(3.2 \times 10^{-11})(6.023 \times 10^{23})}$$

$$= \underline{\underline{82 \text{ atm}}}$$

(b) Engineering fission gas release method :

$$T_0 - T_s = \frac{500}{4\pi(0.03)} = 1326^\circ \text{C}$$

$$T_s = 400^\circ \text{C}$$

$$T_0 = 1726^\circ \text{C}$$

$$\therefore \bar{f} = \frac{0.3(1400-400) + 0.5(1726-1400)}{1326} = 0.35$$

$$P_g = \frac{0.35}{0.49} \times 82 = \underline{\underline{58 \text{ atm}}}$$

CHAPTER 16

Problem 16.1

- a) The notation for an edge dislocation means:

When the tensile stress is normal to the extra sheet of atoms, the vacancy concentration at the core increases to the value given in b) below.

This concentration is greater than that in the bulk, so that the dislocation emits vacancies and therefore moves perpendicular to the slip plane (climb) in a manner that will increase the size of the extra sheet of atoms.

- b) See the derivation leading to Eq. (13.175).
Replace p in the formula by $-\sigma$ and set $r=0$.
Divide by Ω to give proper units,

$$C_v(R_d) = C_v^{eq} \exp\left(\frac{\sigma\Omega}{kT}\right) \quad \text{--- (1)}$$

- c) For 1 cm. length along dislocations, the volume of solid associated with 1 cm. of dislocation line = πR^2

$$\text{or } S_d = \frac{1}{\pi R^2}$$

$$\text{or } R = \frac{1}{\sqrt{\pi S_d}} \quad \text{--- (2) [Eq. (13.79)]}$$

- d) Diffusion Equation in Cylindrical Coordinates:

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dC_v}{dr} \right) = 0 \quad \text{[Eq. (13.85)]}$$

Solution is given by Eq. (13.87), flux by Eq. (13.88).

Use $C_v(R) = C_v^{eq}$ and C_{R_d} given by eq. (1), then

$$2\pi R_d J = \frac{2\pi D_v \left[C_v^{eq} \exp\left(\frac{\sigma \Omega}{kT}\right) - C_v^{eq} \right]}{\ln(R/R_d)}$$

Since $\frac{\sigma \Omega}{kT} \ll 1$, the above equation reduces to

$$2\pi R_d J = \frac{2\pi D_v C_v^{eq} \sigma \Omega}{kT \ln(R/R_d)} \quad \frac{\text{vacancies}}{\text{sec-cm. of line}} \quad \text{--- (3)}$$

- e) volume / vacancy = Ω

Flow of volume away from 1 cm.

$$\text{of line} = (2\pi R_d J) \Omega$$

But the sheet of atoms has thickness = b ,

(the Burgers vector)

$\therefore$ Flow of volume away from line = $(b)(1)(v)$

$$\therefore v = \frac{2\pi R_d J \Omega}{b} = 2\pi R_d J b^2 \quad \text{--- (4)}$$

(where $\Omega = b^3$)

Use (3) in (4) to get,

$$\nu = \frac{2\pi D_v C_v^{eq} \sigma \Omega b^2}{kT \ln(R/R_d)} \quad \text{--- (5)}$$

Also note that $D_{vol} = D_v C_v^{eq} \Omega$ --- (6)

- f) Consider a block of solid of volume $V = XYZ$, which consists $\rho_d XY$ dislocations, half of which climb when the tensile stress is applied in the x -direction.

In time Δt , each properly oriented edge dislocation climbs a distance $\nu_c \Delta t$ in the y -direction. For each dislocation, the area swept out is $(\nu_c \Delta t) Z$. Since $\frac{1}{2} \rho_d (XY)$ dislocations climb like this, the total area added to planes perpendicular to the x -axis is:

$$(\nu_c \Delta t) Z \frac{1}{2} \rho_d (XY) \text{ cm}^2$$

or the equivalent of $\frac{(\nu_c \Delta t) Z (\frac{1}{2} \rho_d XY)}{YZ}$ complete

planes of atoms have been added to the surface perpendicular to the x -direction.

Since each plane has a thickness b , the strain in the x -direction is:

$$\Delta x = \frac{(v_c \Delta t) \frac{1}{2} s_d \gamma b}{\gamma z}$$

The creep (or strain) rate in the direction of the applied stress is:

$$\dot{\epsilon} = \frac{1}{x} \frac{\Delta x}{\Delta t} = \frac{1}{2} s_d v_c b \quad \text{--- (7)}$$

The above equation is the same as Eq. (8.21) except for a factor of $\frac{1}{2}$, which corrects from total dislocation density to the density of mobile dislocations. Use (5), (6) and $b^3 = \Omega$ in (7) to get

$$\dot{\epsilon} = \frac{\pi s_d D_{vol} \Omega \sigma}{kT \ln(R/R_d)} \quad \text{--- (8)}$$

This is a form of Nabarro-Herring creep.

Problem 16.2Fission Gas Swelling Law using continuum creep

$$N_b = \text{bubble density}, \quad v = \frac{1}{N_b}$$

Mechanical balance at bubble surface: [Eq. (13.6)]

$$p = \frac{2\gamma}{R_b} + \sigma_i \quad (\sigma_i \text{ positive if directed radially inward})$$

---(1)

Ideal gas law:

$$pV_b = mkT \quad \text{---(2)}$$

Gas atoms/bubble

Assume all gas in v goes to bubble.

$$m = \gamma_{Xe} \dot{F} t (v - V_b) = \text{gas atoms generated in time } t \text{ in volume } V_b$$

---(3)

Combining (1) to (3)

$$\sigma_i = p - \frac{2\gamma}{R_b} = \frac{mkT}{V_b} - \frac{2\gamma}{R_b}$$

$$\therefore \sigma_i = \gamma_{xe} \dot{F} t \left(\frac{V}{V_b} - 1 \right) kT - \frac{2\gamma}{R_b} \quad \text{--- (4)}$$

where $V_b = \frac{4}{3} \pi R_b^3 =$ volume of bubble

External work: (by both inner and outer surfaces) replace Eq. (16.183) by

$(p - \frac{2\gamma}{R_b}) \dot{V}_b =$ rate of work done in solid by internal gas pressure (less surface tension)

$-\sigma \dot{V} =$ work done on solid by applied

Add and use (1) and note that $\dot{V}_b = \dot{V}$

$$\therefore \dot{W} = (\sigma_i - \sigma) \dot{V} \quad \text{--- (5)}$$

σ_i is a function of V_b and t by eq. (4)

Rest of derivation is same as in text except Eq. (16.183) replaced by eq. (5) above.

Eq. (16.185) becomes:

$$(\sigma_i - \sigma) \dot{V} = \frac{2}{3} |\dot{V}| \int_{V_b}^V \sigma^* \frac{dV}{V} \quad \text{--- (6)}$$

Eq. (16.190) becomes:

(replacing $\dot{P}$ by $\dot{s} =$ gas swelling rate
and P by $s = \frac{V_b}{V}$)

$$\dot{s} = \frac{q}{4} \alpha (\sigma_i - \sigma) s \quad \text{--- (7)}$$

Eq. (4) becomes,

$$\sigma_i = \gamma_{xe} \dot{F} kT \left(\frac{1}{s} - 1 \right) t - 2\gamma \left(\frac{4\pi N_b}{3} \right)^{1/3} / s^{1/3}$$

since $R_b = \left(\frac{3V_b}{4\pi} \right)^{1/3} = \left(\frac{3V}{4\pi} \right)^{1/3} s^{1/3} = \left(\frac{3}{4\pi N_b} \right)^{1/3} s^{1/3}$

Eq. (7) becomes:

$$\dot{s} = \frac{9}{4} \alpha \sigma \left\{ \frac{\gamma_{ke} \dot{F} k T}{\sigma} \left(\frac{1-s}{s} \right) t - \frac{2\gamma \left(\frac{4\pi N_b}{3} \right)^{1/3}}{\sigma} s^{-1/3} - 1 \right\} \quad \text{--- (8)}$$

(swelling law) $\nearrow$

When the fuel is weak, $\alpha \rightarrow \infty$, that is the creep rate becomes very large for any non-zero deviatoric stress. For $\dot{s}$ to be finite, $\{ \}$ in eq. (8) must go to zero. (Neglecting s compared to unity in (8))

or :

$$\frac{\gamma_{ke} \dot{F} k T t}{s} - \frac{2\gamma \left(\frac{4\pi N_b}{3} \right)^{1/3}}{s^{1/3}} - \sigma = 0$$

or, with $\sigma = 0$,

$$s = \left(\frac{\gamma_{ke} \dot{F} t k T}{2\gamma} \right)^{3/2} \left(\frac{3}{4\pi N_b} \right)^{1/2} \quad \text{--- (9)}$$

This is Eq. (13.146).

Problem 16.3Power Law Creep

$$\dot{\epsilon}_g = A S_g^n$$

$$\sigma = \frac{2}{3} \int_{V_p}^V \left[-\frac{2}{3S} \frac{V}{V} \frac{\dot{P}}{1-P} \right]^{\frac{1}{n}} \frac{dV}{V}$$

$$\frac{3}{2} \sigma = \left(\frac{2}{3S} \right)^{\frac{1}{n}} \left(\frac{-\dot{P}}{1-P} \right)^{\frac{1}{n}} \int_P^1 \frac{dx}{x^{\frac{1}{n}+1}}$$

$$\int_P^1 \frac{dx}{x^{\frac{1}{n}+1}} = - \left[\frac{n}{x^{\frac{1}{n}}} \right]_P^1 = \left[\frac{n}{x^{\frac{1}{n}}} \right]_1^P = \frac{n}{P^{\frac{1}{n}}} - n$$

$$\therefore \left(\frac{3}{2} \sigma \right) = \left(\frac{2}{3S} \right)^{\frac{1}{n}} \left(\frac{-\dot{P}}{1-P} \right)^{\frac{1}{n}} n \left(\frac{1}{P^{\frac{1}{n}}} - 1 \right)$$

$$\begin{aligned} \text{or } \frac{3\sigma}{2n} &= \left(\frac{2}{3S} \right)^{\frac{1}{n}} \left(\frac{-\dot{P}}{1-P} \right)^{\frac{1}{n}} \left(\frac{1}{P^{\frac{1}{n}}} - 1 \right) \\ &= \left(\frac{2}{3S} \right)^{\frac{1}{n}} \left(\frac{-\dot{P}}{1-P} \right)^{\frac{1}{n}} \frac{1}{P^{\frac{1}{n}}} (1 - P^{\frac{1}{n}}) \end{aligned}$$

$$\therefore \left(\frac{3\sigma}{2n} \right)^n = \left(\frac{2}{3S} \right) \left(\frac{-\dot{P}}{1-P} \right) \frac{1}{P} (1 - P^{\frac{1}{n}})^n$$

$$\text{or } \boxed{\dot{P} = - \left(\frac{3\sigma}{2n} \right)^n \left(\frac{3S}{2} \right) \frac{(1-P)P}{(1-P^{\frac{1}{n}})^n}}$$

Problem 16.4

- a) From problem 13.10, the number of fission fragments intersecting a spherical pore of radius R_p per sec. is:

$4\pi R_p^3 G(\mu/R_p) \dot{F}$, where $\dot{F}$ is the fission density and G is the function plotted in the solution to problem 13.10. For $\mu/R_p \ll 1$, the limiting form of G is μ/R_p and the rate at which a pore is pierced by fission fragments is:

$$4\pi R_p^2 \mu \dot{F} \text{ sec}^{-1}$$

$$\therefore \frac{\text{vacancies redissolved}}{\text{sec} - \text{pore}} = 4\pi R_p^2 \mu \Delta m_v \dot{F}$$

$$\frac{\text{vacancies}}{\text{pore}} = \left(\frac{4}{3}\pi R_p^3\right)/\Omega \quad \text{where } \Omega = \text{volume of a vacancy}$$

dividing:

$$b = \frac{4\pi R_p^2 \mu \Delta m_v \dot{F}}{(4/3\pi R_p^3)/\Omega} = \frac{3\Omega \Delta m_v \mu \dot{F}}{R_p} \text{ sec}^{-1}$$

b)

$$\text{Let } b = b_0 \left(\frac{R_{p0}}{R_p}\right)$$

$$\text{where } b_0 = \frac{3\Omega \Delta m_v \mu \dot{F}}{R_{p0}} \quad \text{and } R_{p0} \text{ is the}$$

initial pore radius.

Eq. (16.143), neglecting vacancy emission from surface, is:

$$4\pi R_p^2 \frac{dR_p}{dt} = - \frac{Q_v^{\text{resol}} \Omega}{N_p} \quad [\text{Eq. (16.143)}]$$

Eq. (16.146) is:

$$\frac{Q_v^{\text{resol}} \Omega}{N_p} = \left(\frac{4}{3}\pi R_p^3\right) b \quad [\text{Eq. (16.146)}]$$

$$\therefore 4\pi R_p^2 \frac{dR_p}{dt} = -\frac{4}{3}\pi R_p^3 b$$

or using the expression for b :

$$\frac{dR_p}{dt} = -\frac{1}{3} R_{p0} b_0$$

using $y = \frac{R_p}{R_{p0}}$

$$\frac{dy}{dt} = -\frac{1}{3} b_0$$

Integrating: $y = 1 - \frac{1}{3} b_0 t$

Using this expression for y in Eq. (16.166):

$$\dot{P} = \frac{dP}{dt} = -b P_0 y^3 = -b_0 P_0 y^2 \quad [\text{since } b = \frac{b_0}{y}]$$

But $\frac{d}{dt} = \frac{dy}{dt} \frac{d}{dy} = -\frac{1}{3} b_0 \frac{d}{dy}$

or $\frac{dP}{dy} = 3P_0 y^2$

Integrating with $P = P_0$ at $y = 1$, we get,

$$P_0 - P = P_0 (1 - y^3)$$

or

$$P_0 - P = P_0 \left[1 - \left(1 - \frac{1}{3} b_0 t \right)^3 \right]$$

Problem 16.5

For parabolic temperature profile in fuel:

$$T_0 - T_s = \frac{\dot{Q}}{4\pi k} \quad \text{---(1)}$$

Therefore thermal stress may be expressed in terms of linear power. In addition, cracking occurs when $\sigma_\theta = -\sigma_f$. Therefore the crack root r_c is given by

$$-\sigma_f = \frac{\alpha E \dot{Q}}{16\pi k (1-\nu)} \left[1 - 3\left(\frac{r_c}{R}\right)^2 \right] \quad \text{---(2)}$$

σ_f = fracture strength (in tension)

Cracking first begins at the surface,

$$\text{or } \frac{r_c}{R} = 1$$

Eq. (2) becomes

$$\frac{\alpha E (100)}{16\pi k (1-\nu)} [-2] = -\sigma_f \quad \text{---(3)}$$

At 500 W/cm, eq. (2) is:

$$\frac{\alpha E (500)}{16\pi k (1-\nu)} \left[1 - 3\left(\frac{r_c}{R}\right)^2 \right] = -\sigma_f \quad \text{---(4)}$$

Equating left hand sides of (3) and (4) (neglect change in σ_f with T):

$$-2(100) = 500 \left[1 - 3\left(\frac{r_c}{R}\right)^2 \right]$$

$$-0.4 = 1 - 3\left(\frac{r_c}{R}\right)^2$$

$$\therefore \frac{r_c}{R} = \sqrt{\frac{1}{3}(1+0.4)}$$

$$= \underline{0.68}$$

T_c = Temperature at the root of crack. For parabolic temperature distribution:

$$\frac{T_c - T_s}{T_0 - T_s} = 1 - \left(\frac{r_c}{R}\right)^2$$

$$\therefore T_c = T_s + (T_0 - T_s) \left[1 - \left(\frac{r_c}{R}\right)^2\right]$$

$$= T_s + \frac{\rho}{4\pi k} \left[1 - \left(\frac{r_c}{R}\right)^2\right]$$

where $\bar{k} = 0.03$ watts/cm-°C. = thermal conductivity of UO_2

$$\therefore T_c = 700 + \frac{500}{4\pi(0.03)} (0.53)$$

$$= \underline{1403^\circ\text{C}}$$

CHAPTER 17

PROBLEM 17.1

$$a) (\bar{Z}_1)_{\text{eff}} = \bar{Z}_1^{2/3} \frac{\hbar}{e^2} \left(\frac{2E}{M_1} \right)^{1/2} \quad (E_f. 17.46)$$

where $M_1 = 100$, $\bar{Z}_1 = 42$, $E = 100 \text{ MeV}$.

$$\hbar = 1.05 \times 10^{-27} \text{ erg-sec}, \quad e = 4.8 \times 10^{-10} \text{ esu}$$

$$\Rightarrow (\bar{Z}_1)_{\text{eff}} = 22.6$$

b)

Considering the quantum mechanical correction factor of z , Bethe's formula becomes,

$$\frac{dE}{dx} = \frac{2\pi N (\bar{Z}_1)_{\text{eff}}^2 \bar{Z}_2 e^4 (M_1/m_e)}{E} \ln \left[\frac{4E}{(M_1/m_e) \bar{I}} \right]$$

Inserting $(\bar{Z}_1)_{\text{eff}}$ from part a) gives,

$$\left(\frac{dE}{dx} \right)_0 = 4\pi \bar{Z}_1^{2/3} \frac{\hbar^2}{m_e} N_0 \bar{Z}_0 \ln \left[\frac{4m_e E}{M_1 \bar{I}_0} \right]$$

$$\text{Let } K = 4\pi \bar{Z}_1^{2/3} \frac{\hbar^2}{m_e} N_0 \bar{Z}_0$$

$$\gamma = \frac{2 \bar{Z}_0}{\bar{Z}_1} \quad \text{and} \quad E_0^* = \frac{M_1}{4m_e} \bar{I}_0$$

then

$$\left(\frac{dE}{dx} \right)_{\text{tot}} = 2K (\bar{Z}_0/\bar{Z}_1) \ln \left[\frac{4m_e E}{M_1 \bar{I}_0} \right] + K \ln \left[\frac{4m_e E}{M_1 \bar{I}_0} \right]$$

or

$$\left(\frac{dE}{dx} \right)_{\text{tot}} = K \left[\gamma \ln \left(\frac{E}{E_0^*} \right) + \ln \left(\frac{E}{E_0^*} \right) \right] = K \ln \left[\frac{E^{\gamma+1}}{(E_0^*)^\gamma E_0^*} \right]$$

$$\text{Let } A = [(E_0^*)^\gamma (E_0^*)]^{-1}$$

$$\text{So that } \left(\frac{dE}{dx} \right)_{\text{tot}} = K \ln [A E^{\gamma+1}]$$

$$\text{Where } A = \left(\frac{4m_e}{M_1} \right)^{\gamma+1} \left(\frac{1}{\bar{I}_0} \right)^\gamma \left(\frac{1}{\bar{I}_0} \right) = 1.32 \times 10^5$$

$$\text{and } N_0 = \frac{10.98 \text{ g/cm}^3}{23.8 \text{ g/mole}} \times 6.02 \times 10^{23} \text{ atoms/mole} = 2.8 \times 10^{22} \text{ atoms/cm}^3$$

$$\gamma = \frac{2 \times 8}{92} = 0.174$$

$\bar{I}$ is the average ionization energy for the orbital electrons of the respective atom

$$\bar{I} = 8.8 \text{ eV}$$

$$\Rightarrow \bar{I}_0 = 8.8 \times 8 = 70.4 \text{ eV} \quad I_0 = 8.8 \times 92 \approx 810 \text{ eV}$$

$$K = 4\pi (42)^{\frac{2}{3}} \frac{(1.05 \times 10^{-27})^2}{0.911 \times 10^{-27}} \times 2.8 \times 10^{22} \times 92$$

$$= 0.428$$

$$\left(\frac{dE}{dx}\right)_{\text{tot}} = K \ln A + K(\gamma+1) \ln E = 2.19 + 0.503 \ln E$$

i) Numerical evaluation

the total distance traveled before a Rutherford collision is $X_c = 2 \times 10^{-4} \text{ cm}$

Let's divide X_c into four equal intervals of each $0.5 \times 10^{-4} \text{ cm} = \Delta X$

$$\Delta E = \left(\frac{dE}{dx}\right)_{\text{tot}} \cdot \Delta X = 1.095 \times 10^{-4} + 0.260 \times 10^{-4} \ln E$$

$$E_0 = 10^8 \text{ eV} = 1.6 \times 10^{-4} \text{ erg}$$

$$\begin{aligned}
 \Delta E_1 &= 1.095 \times 10^{-4} + 0.260 \times 10^{-4} \ln(1.6 \times 10^{-4}) = 0.11 \times 10^{-4} \text{ erg} \\
 E_1 &= (1.60 - 0.11) \times 10^{-4} \text{ erg} = 1.49 \times 10^{-4} \text{ erg} \\
 \Delta E_2 &= 1.095 \times 10^{-4} + 0.26 \times 10^{-4} \ln(1.49 \times 10^{-4}) = 0.101 \times 10^{-4} \\
 E_2 &= (1.49 - 0.101) \times 10^{-4} = 1.389 \times 10^{-4} \text{ erg} \\
 \Delta E_3 &= 0.095 \times 10^{-4} \text{ erg} \\
 E_3 &= 1.294 \times 10^{-4} \text{ erg} \\
 \Delta E_4 &= 0.085 \times 10^{-4} \text{ erg} \\
 E_4 &= E_c = 1.209 \times 10^{-4} \text{ erg} = 75.6 \text{ MeV} \\
 \therefore E_c &\cong 75.6 \text{ MeV}
 \end{aligned}$$

ii) Analytic solution

$$\left(\frac{dE}{dx}\right)_{\text{tot}} = K \ln [A E^{r+1}]$$

$$\text{Integrate} \Rightarrow K X_c = \int_{E_c}^{E_0} \frac{dE}{\ln [A E^{r+1}]}$$

$$\text{Let } u = A E^{r+1} \quad \text{or} \quad E = \frac{1}{A^{1/(r+1)}} u^{1/(r+1)}$$

$$\text{then } du = A(r+1) E^r dE = (r+1) A^{1/(r+1)} u^{r/(r+1)} dE$$

$$u_c = A E_c^{r+1}$$

$$\text{So } K X_c = \int \frac{du}{(r+1) A^{1/(r+1)} u^{r/(r+1)} \ln u}$$

$$\text{Let } \alpha = \frac{r}{r+1}$$

$$K(r+1) A^{1/(r+1)} X_c = \int_{u_c}^{u_0} \frac{du}{u^\alpha \ln u} = \text{Li}\left(\frac{1}{u_c^{\alpha-1}}\right) - \text{Li}\left(\frac{1}{u_0^{\alpha-1}}\right)$$

$$K(r+1) A^{1/(r+1)} X_c = 2.24 = \text{Li}(u_c^{0.252}) - \text{Li}(u_0^{0.252})$$

$$u_0 = 37.73 \quad u_0^{0.252} = 22$$

$$\text{Thus } \text{Li}(u_c^{0.252}) = 2.24 + \text{Li}(22)$$

u_c and E_c can be solved for from graph of Li functions.

6

$$c) T = \frac{1}{2} \Lambda E (1 - \cos \theta), \quad \Lambda = \frac{4 M_1 M_2}{(M_1 + M_2)^2}$$

$$\tan \phi_1 = \frac{(M_2/M_1) \sin \theta}{1 + (M_2/M_1) \cos \theta}$$

Assuming ϕ_1 and θ to be sufficiently small
We have

$$\phi_1 \approx \frac{(M_2/M_1)}{1 + (M_2/M_1)} \theta \Rightarrow \theta \approx \left(1 + \frac{M_1}{M_2}\right) \phi_1$$

$$\text{also } \cos \theta \approx 1 - \frac{\theta^2}{2}$$

$$\therefore T \approx \frac{1}{2} \Lambda E \left[1 - \left(1 - \frac{\theta^2}{2}\right)\right] = \frac{1}{4} \Lambda E \left(1 + \frac{M_1}{M_2}\right)^2 \phi_1^2$$

$$T \approx \frac{M_1}{M_2} E \phi_1^2$$

$$i) T_0 \approx E_0 \left(\frac{M_1}{M_0}\right) \phi_1^2 = \frac{100}{16} \left(\frac{5}{360} \times 2\pi\right)^2 \times 75.6$$

$$= 3.57 \text{ MeV}$$

$$ii) T_u \approx E_u \left(\frac{M_1}{M_u}\right) \phi_1^2$$

$$= 0.156 \text{ MeV}$$

PROBLEM 17.2

From Eq (17.37) $\sigma(E, T) = \pi z_1^2 z_2^2 e^4 \left(\frac{M_1}{M_2} \right) \frac{1}{E T^2} \dots (1)$

From Eq (17.22) $\sigma(E, \theta) = \frac{1}{2\pi} \sigma(E, T) \left| \frac{dT}{d \cos \theta} \right| \dots (2)$

From Eq (17.9) $T = \frac{1}{2} \Lambda E (1 - \cos \theta) \dots (3)$

$\left| \frac{dT}{d \cos \theta} \right| = \frac{1}{2} \Lambda E = \frac{1}{2} \frac{4 M_1 M_2}{(M_1 + M_2)^2} E \dots (4)$

Substitute (1) and (4) into (3)

$\sigma(E, \theta) = z_1^2 z_2^2 e^4 \left(\frac{M_1}{M_1 + M_2} \right)^2 \frac{1}{T^2} \dots (5)$

From (3) $T = \frac{2 M_1 M_2}{(M_1 + M_2)^2} \times 2 \pi^2 \frac{E}{2} \dots (6)$

Substitute (6) into (5)

$\sigma(E, \theta) = \frac{z_1^2 z_2^2 e^4}{16} \left(\frac{M_1 + M_2}{M_2} \right)^2 \frac{1}{E^2 \pi^4 \left(\frac{E}{2} \right)}$

PROBLEM 17.3

Screened Coulomb potential $V_{sc}(r) = \frac{Z_1 Z_2 e^2}{r} e^{-r/a}$
 Inverse power potential $V_p(r) = A/r^2$

At the distance of closest approach

$$V_p(r_m) = \frac{A}{r_m^2} = \frac{E^*}{2} \Rightarrow r_m = \left(\frac{2A}{E^*} \right)^{1/2}$$

$$\text{and } V_{sc}(r_m) = \frac{Z_1 Z_2 e^2}{r_m} e^{-r_m/a}$$

$$= \frac{Z_1 Z_2 e^2}{\left(\frac{2A}{E^*} \right)^{1/2}} \exp \left[- \left(\frac{2A}{E^*} \right)^{1/2} / a \right] = \frac{E^*}{2}$$

So,

$$\exp \left[- \left(\frac{2A}{E^*} \right)^{1/2} / a \right] = \frac{E^*}{2 Z_1 Z_2 e^2} \left(\frac{2A}{E^*} \right)^{1/2}$$

$$\text{or } - \left(\frac{2A}{E^*} \right)^{1/2} = a \ln \left[\left(\frac{2A}{E^*} \right)^{1/2} \frac{E^*}{2 Z_1 Z_2 e^2} \right] \dots (1)$$

The intersection of the plots of both sides of (1) gives E^* , where

$$a = \frac{\sqrt{2} \lambda a_B}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}$$

where a_B is the Bohr radius

PROBLEM 17.4

a) Each atom has 8 nearest neighbors in the b.c.c. structure

$$\Delta E_{\text{sub}} (\text{at } 0^\circ \text{K}) = \frac{1}{2} \times 8 \Phi_B = 4 \Phi_B$$

$$\Phi_B = \frac{8.1}{4} = 2.02 \text{ eV}$$

b) It was shown in Chapter 4, that the compressibility is related to the second derivative of the crystal energy by.

$$\frac{1}{\beta} = V_{\text{eq}} \left(\frac{d^2 U}{dV^2} \right)_{\text{eq}} \quad \text{--- (1)}$$

where V_{eq} is the specific volume $= \frac{a_0^3}{2}$ for bcc
 a_0 is the lattice constant

Let r_{eq} be the distance between nearest neighbor $= \frac{\sqrt{3}}{2} a_0$ For bcc structure.

$$\Rightarrow a_0 = \frac{2}{\sqrt{3}} r_{\text{eq}}$$

$$\therefore V_{\text{eq}} = \frac{a_0^3}{2} = \frac{4}{3\sqrt{3}} r_{\text{eq}}^3 \quad \text{--- (2)}$$

$$\frac{dU}{dV} = \frac{dU}{dr} \frac{dr}{dV}$$

$$\frac{d^2 U}{dV^2} = \frac{d}{dV} \left(\frac{dU}{dV} \right) = \frac{d^2 r}{dV^2} \cdot \frac{dU}{dr} + \frac{d^2 U}{dr^2} \left(\frac{dr}{dV} \right)^2 \quad \text{--- (3)}$$

The first term on the right hand side of (3) is zero, since $\left. \frac{dU}{dr} \right|_{r=r_{\text{eq}}} = 0$ --- (4)

Substitute (3), (4), (2) into (1)

$$\frac{1}{\beta} = \frac{1}{4\sqrt{3} r_{\text{eq}}} \left(\frac{d^2 U}{dr^2} \right)_{\text{eq}} \quad \text{--- (5)}$$

$$U(r) = \frac{1}{2} \times 8 \times V(r) = 4V(r)$$

$$\begin{aligned} \therefore \frac{1}{\beta} &= \frac{1}{4\sqrt{3} r_{eq}} \times 4 \frac{d^2 V}{dr^2} = \frac{k}{\sqrt{3} r_{eq}} \\ &= \frac{k}{\sqrt{3} \cdot \frac{\sqrt{3}}{2} a_0} = \frac{2k}{3a_0} = \frac{k a_0^2}{\frac{3}{2} a_0^3} \\ &= \frac{k a_0^2}{3 \cdot V_{eq}} \end{aligned}$$

$$\therefore k a_0^2 = \frac{3 V_{eq}}{\beta}$$

$$\begin{aligned} &= 3 \times \frac{1}{16.6 \text{ g cm}^{-3}} \times \frac{181 \text{ g/mole}}{6.02 \times 10^{23} \text{ atom/mole}} \\ &\times \frac{1}{0.52 \times 10^{-12} \text{ cm}^2 \text{ dyne}^{-2}} \end{aligned}$$

$$\approx 65 \text{ eV}$$

c) The Miller indices of direction of displacement are $\langle 0, 2, \bar{1} \rangle$

- d) The energy is maximum when the PKA passes through the triangle formed by atoms 1, 2 and 3. (see the drawing in part c)
- $$V(r) = -D + \frac{1}{2} k (r_{eq} - r)^2$$

The planar configuration for the saddle point is:

$$\begin{aligned} E^* &: \text{potential energy at the saddle point} \\ &= 2 \left[-D + \frac{1}{2} k \left(r_{eq} - \frac{\sqrt{11}}{6} a_0 \right)^2 \right] + \left[-D + \frac{1}{2} k \left(r_{eq} - \frac{\sqrt{3}}{3} a_0 \right)^2 \right] \\ &= -3D + 0.178 k a_0^2 \\ &= -3\Phi_B + 0.178 k a_0^2 \end{aligned}$$

$$\begin{aligned} E_{eq} &: \text{potential energy in the equilibrium} \\ &= -8\Phi_B \end{aligned}$$

$$E_d: \text{displacement energy}$$

$$\begin{aligned} &= E^* - E = 5\Phi_B + 0.178 k a_0^2 \\ &= 21.5 \text{ eV} \end{aligned}$$

e)

Octahedral site

$$E_{\text{oct}} = 4 \left[-\phi_B + \frac{1}{2} k \left(\frac{\sqrt{3}}{2} - \frac{\sqrt{2}}{2} \right)^2 a_0^2 \right]$$

$$+ 2 \left[-\phi_B + \frac{1}{2} k \left(\frac{1}{2} - \frac{\sqrt{3}}{2} \right)^2 a_0^2 \right]$$

$$= -6\phi_B + 0.150 k a_0^2$$

$$E_{\text{oct}} - E_{\text{ef}} = 2\phi_B + 0.150 k a_0^2 = 13.69 \text{ eV}$$

f)

PROBLEM 17.5

- a) Since A_1, A_2 and a B atom lie on a (111) plane, they form an equilateral triangle with the sides equal to $D = \frac{a_0}{\sqrt{3}}$

$x = A_1 - B$ distance at collision. Apply the Law of Cosines to triangle $(A_1' A_2 B)$:

$$\begin{aligned} x^2 &= D^2 + (2r_0)^2 - 2(2r_0)D \cos 60^\circ = D^2 + 4r_0^2 - 2r_0 D \\ &= D^2 \left[1 + 4\left(\frac{r_0}{D}\right)^2 - 2\left(\frac{r_0}{D}\right) \right] = D^2 \left[\frac{3}{4} + \frac{1}{4} \left(4\frac{r_0}{D} - 1 \right)^2 \right] \quad (1) \end{aligned}$$

But, from equation (17.41), r_0 is defined by,

$$r_0 = \frac{1}{2} \rho \ln \left(\frac{2A}{E} \right) \quad (2)$$

where ρ and A are the constants of the Born-Mayer potential function

D may be expressed in terms of E_f by eq. (17.95)

$$D = \frac{1}{2} \rho \ln \left(\frac{2A}{E_f} \right) \quad (3)$$

Use (2) and (3) to eliminate the ratio $\frac{r_0}{D}$ in (1)

$$\Rightarrow \frac{r_0}{D} = \frac{1}{4} \frac{\ln \left(\frac{2A}{E} \right)}{\ln \left(\frac{2A}{E_f} \right)} = \frac{1}{4} \frac{\ln \left(\frac{2A}{E_f} \right) + \ln \left(\frac{E_f}{E} \right)}{\ln \left(\frac{2A}{E_f} \right)}$$

$$= \frac{1}{4} \left[1 + \frac{\ln(E_f/E)}{(D/\rho)} \right]$$

OR (1) becomes

$$x = D \left\{ \frac{3}{4} + \left[\left(\frac{\rho}{D} \right) \ln \left(\frac{E_f}{E} \right) \right]^2 \right\}^{1/2} \text{----- (4)}$$

b) $\Delta E = A_1 - 4B$ interaction energy change.
 $= 4[V(x) - V(D)]$

where $V(D)$ is the $A_1 - B$ interaction energy at equilibrium

Using Born - Mayer Potential

$$\Delta E = 4A [\exp(-x/\rho) - \exp(-D/\rho)] \text{----- (5)}$$

ΔE is a function of energy, since x is

c) at the n^{th} collision, the energy loss is $\Delta E(E)$.

If ΔE is small compared to E , the energy loss process may be considered continuous, and:

$$\frac{dE}{dn} = -\Delta E(E) \text{----- (6)}$$

When E decreases to $\frac{1}{4} E_f$, the replacement process ceases. Call the number of collision at this point n_f . From (6)

$$\int_{E_1}^{\frac{1}{4} E_f} \frac{dE}{\Delta E(E)} = - \int_1^{n_f} dn = -(n_f - 1)$$

$$\text{or } n_f = 1 + \int_{\frac{1}{4} E_f}^{E_1} \frac{dE}{\Delta E(E)}$$

$$\text{Let } y = \frac{E}{E_f}$$

$$\eta_f = 1 + E_f \int_{1/4}^{E_f/E_f} \frac{dy}{\Delta E(y)} \quad \text{----- (7)}$$

Using (4) and (5) in (7)

$$\eta_f = 1 + \left(\frac{E_f}{4A} \right) \int_{1/4}^{E_f/E_f} \frac{dy}{\exp \left[-\left(\frac{D}{J} \right) \left[\frac{3}{4} + \left(\frac{J}{D} \ln \frac{1}{y} \right)^2 \right]^{1/2} \right] - \exp \left(-\frac{D}{J} \right)} \quad \text{----- (8)}$$

Note: Denominator of (8) $\rightarrow 0$ as the term in the square bracket $\rightarrow 1$, this determines a minimum value of y ($y_{\min}$) which must be $< 1/4$ for the integral to be valid. $y_{\min}$ may be found from

$$\frac{J}{D} \ln \left(\frac{1}{y_{\min}} \right) = \frac{1}{2},$$

$$\text{or } \ln \left(\frac{1}{y_{\min}} \right) = \frac{D}{2J} = \ln \left(\frac{2A}{E_f} \right) \quad (\text{using (3)})$$

$$\text{or } y_{\min} = \frac{E_f}{2A} \quad \text{----- (9)}$$

From Fig 17.5 $A \approx 2 \times 10^4 \text{ eV}$ and $E_f \approx 10^2 \text{ eV}$

$$y_{\min} = 2.5 \times 10^{-3}, \text{ which is } < 1/4$$

PROBLEM 17.6

Lindhard stopping formula =

$$\left(\frac{dE}{dx}\right)_e = k \sqrt{E} \quad \text{Eq (17.52)}$$

$$k = 0.3 N Z^{2/3}, \text{ eV}^{1/2}/\text{\AA} \quad \text{Eq (17.53a)}$$

Let x be the distance before dechanneling.

$$\int_{E_0}^{E_{ch}} \frac{dE'}{\sqrt{E'}} = k x = 2 \left[\sqrt{E'} \right]_{E_{ch}}^{E_0} = 2(\sqrt{E_0} - \sqrt{E_{ch}})$$

$$x = \frac{2 \left(1 - \sqrt{E_{ch}/E_0} \right)}{k/\sqrt{E_0}}$$

$$E_{ch} = 300 \text{ eV}, \quad Z = 29, \quad N = 0.085 \text{ \AA}^{-3}$$

$$E_0 = 30 \text{ KeV}$$

$$\sqrt{\frac{E_{ch}}{E_0}} = 0.1$$

$$\therefore k = 0.24$$

$$x = \frac{2(1 - 0.1)}{0.24 / \sqrt{3 \times 10^4}} = 1.3 \times 10^3 \text{ \AA}$$

PROBLEM 17.7

a) Assume neutron is at rest initially.

Momentum conservation requires that after the reaction: $\frac{E_r}{c} = p_r = p_{57}$

$$\Rightarrow E_{57} = \frac{(p_{57})^2}{2M} = \frac{E_r^2}{2Mc^2}$$

$$\therefore E_{57} = \frac{7^2}{2 \times 56.9354 \times 9.3148 \times 10^2} = 4.62 \text{ eV}$$

b) ν_{KP} = number of displacement calculated by Kinchin - Pease formula

$$\nu_{KP} = \frac{E}{2E_d} - \text{mod}(1) \frac{E}{2E_d} = 9.42 - 0.42 = 9$$

ν_L = number of displacement calculated by Lindhard's model

$$= \xi(E) \nu_{KP} = \frac{\nu_{KP}}{1 + 0.13(3.4 \epsilon^{1/6} + 0.4 \epsilon^{3/4} + \epsilon)}$$

where $\epsilon = \frac{E}{\left(\frac{ZZe^2}{a}\right)}$, $a = \frac{0.88 a_0}{Z^{1/3}}$

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.53 \times 10^{-8} \text{ cm}, \quad Z = 26$$

$$\therefore a = \frac{0.88 \times 0.53 \times 10^{-8}}{26^{1/3}} = 1.97 \times 10^{-9} \text{ cm}$$

$$\epsilon = 4.62 \times 1.6 \times 10^{-12} \times \frac{1.97 \times 10^{-9}}{2 \times 26 \times (4.8 \times 10^{-10})^2} = 0.122$$

$$\Rightarrow \nu_L = \frac{9.42}{1 + 0.13[3.4 \times (0.122)^{1/6} + 0.4(0.122)^{3/4} + 0.122]} = 7$$

$$c) N_{56} = \left(\frac{\rho_{Fe} N_{Av}}{\bar{M}_{Fe}} \right) \times \text{isotope fraction of Fe-56}$$

$$(R_d)_g = \frac{99.6}{100} N_{56} \Phi_{th} \bar{\sigma}_{56} \gamma_{kp}$$

where $\bar{\sigma}_{56}$ is the absorption cross section for Fe-56 in thermal flux

$$\Rightarrow (R_d)_g = \frac{99.6}{100} \times \frac{7.2 \times 6.02 \times 10^{23}}{56 \times 9354} \times 10^{13} \times 2.5 \times 10^{-24} \times 9$$

$$= 1.73 \times 10^{13} \text{ displacements/sec.}$$

$$d) \Phi_f(E_n) = 10^5 \delta(E_n - 0.5)$$

$$(R_d)_f = N_{Fe} \int_{E_d/\Lambda}^{\infty} \sigma_d(E_n) \Phi_f(E_n) dE_n$$

$$= N_{Fe} \sigma_d(0.5 \text{ MeV}) \times 10^{15}$$

For elastic and isotropic scattering

$$\sigma(E_n, E) = \frac{\sigma_{el}}{\Lambda E_n}, \quad \Lambda = \frac{4 M_n \bar{M}_{Fe}}{(M_{Fe} + 1)^2} \approx 0.069$$

$$\text{and } \sigma_d(E_n) = \int_{E_d}^{\Lambda E_n} \frac{\sigma_{el}}{\Lambda E_n} \frac{E}{2E_d} dE = \frac{\Lambda E_n}{4 E_s} \sigma_{el}$$

From BNL-325, the cross section for iron at 0.5 MeV is ~ 3 barns

$$\text{So } \sigma_d(0.5 \text{ MeV}) = \frac{0.069 \times 0.5 \times 10^6 \times 3 \times 10^{-24}}{4 \times 25} = 1.15 \times 10^{-21} \text{ cm}^2$$

$$= 1150 \text{ barns}$$

$$(R_d)_f = 10^{15} N_{Fe} \cdot \sigma_d(0.5 \text{ MeV})$$

$$= 10^{15} \times \left(\frac{7.2}{56} \times 6.02 \times 10^{23} \right) \times 1.15 \times 10^{-21}$$

$$= 8 \times 10^{16} \text{ displacements/sec}$$

PROBLEM 17.8

$$dpa = \frac{(R_d \frac{\text{displacements}}{\text{cm}^3 \text{ sec}}) \times (t_{\text{irr sec}})}{(N \frac{\text{atoms}}{\text{cm}^3})} = \frac{R_d t_{\text{irr}}}{N}$$

$$\text{From eq (17.115)} \quad R_d = N \int_{E_d/\Lambda}^{\infty} \sigma_d(E_n) \phi(E_n) dE_n$$

$$dpa = t_{\text{irr}} \int \sigma_d(E_n) \phi(E_n) dE_n = \Phi t_{\text{irr}} \int \sigma_d(E_n) f(E_n - 0.5) dE_n$$

$$\approx [\Phi t_{\text{irr}}] \sigma_d(0.5 \text{ MeV})$$

$$\text{From problem 17.7} \quad \sigma_d(0.5 \text{ MeV}) = 1150 \text{ barns}$$

$$\Rightarrow dpa = 10^{22} \times 1.15 \times 10^{-21} \approx 12$$

PROBLEM 17.9

For isotropic (in the C.M. system), elastic scattering, the energy transfer cross section is

$$\sigma(E_n, E) = \frac{\sigma(E_n)}{\Lambda E_n} \quad \text{--- (1)}$$

where $\Lambda = \frac{4A}{(A+1)^2} \quad \text{--- (2)}$

For a neutron of energy E_n , the average PKA energy is

$$\bar{E}(E_n) = \frac{\int_0^{\Lambda E_n} E \sigma(E_n, E) dE}{\int_0^{\Lambda E_n} \sigma(E_n, E) dE} \quad \text{--- (3)}$$

Using (1) in (3)

$$\bar{E}(E_n) = \frac{1}{2} \Lambda E_n \quad \text{--- (4)}$$

In a neutron flux spectrum $\phi(E_n)$, the average PKA energy is obtained by weighting $\bar{E}(E_n)$ given by (4) with the scattering rate $\sigma(E_n)\phi(E_n)$

$$\bar{\bar{E}} = \frac{\int_0^{\infty} \sigma(E_n) \phi(E_n) \bar{E}(E_n) dE_n}{\int_0^{\infty} \sigma(E_n) \phi(E_n) dE_n} \quad \text{--- (5)}$$

Using Eq (1), (4) and the fission neutron spectrum $\phi(E_n)$ in eq (5)

$$\bar{\bar{E}} = \frac{1}{2} \Lambda \frac{\int_0^{\infty} e^{-E_n} \sinh \sqrt{2E_n} dE_n}{\int_0^{\infty} \frac{1}{E_n} e^{-E_n} \sinh \sqrt{2E_n} dE_n} \quad \text{--- (6)}$$

Evaluating the above integrals numerically, $\bar{E}$ for iron ($\Lambda = 0.065$) is found to be,

$$\bar{E} = 0.33 \text{ MeV} \text{ --- (7)}$$

The average neutron energy in the fission spectrum is

$$\begin{aligned} \bar{E}_n &= \frac{\int_0^\infty \phi(E_n) E_n dE_n}{\int_0^\infty \phi(E_n) dE_n} = \frac{\int_0^\infty E_n e^{-E_n} \sinh \sqrt{2E_n} dE_n}{\int_0^\infty e^{-E_n} \sinh \sqrt{2E_n} dE_n} \\ &= 2.0 \text{ MeV} \text{ --- (8)} \end{aligned}$$

The average PKA energy of the average neutron is obtained by using (8) in (4).

$$\bar{E} = \frac{1}{2} \Lambda \bar{E}_n = 0.065 \text{ MeV} \text{ --- (9)}$$

Note: The correct result is Eq (7), NOT Eq (9).

PROBLEM 17.10

Atom displacements per neutron

$$= \frac{\text{displacements/cm}^3\text{-sec}}{\text{neutron collision/cm}^2\text{-sec}}$$

From Eq (17.115)

$$R_d = \frac{\text{displacements}}{\text{cm}^3\text{-sec}} = N \int_{E_d/\Lambda}^{\infty} \sigma_d(E_n) \phi(E_n) dE_n$$

For monoenergetic neutron flux

$$R_d = N \sigma_d(E_n) \Phi, \Phi \text{ is the total neutron flux}$$

$$\text{Neutron collision rate} = N \sigma_{\text{scat}}(E_n) \Phi$$

where σ_{scat} includes both elastic and inelastic scattering cross section

$$\therefore \frac{\text{displacements}}{\text{neutron collision}} = \frac{\sigma_d(E_n)}{\sigma_{\text{scat}}(E_n)} = \frac{3200}{2.3} \approx 1400$$

E_n (MeV)	σ_d (barn) (Fig 17.17)	σ_{scat} (barns) (BNL-325, Fe)	$\frac{\text{displacements}}{\text{neutron collision}}$
0.5	600	3	200
14	3200	2.3	1400

PROBLEM 17.11

a) Maximum energy transfer to an atom by elastic collision with electron of energy E_e

$$= 4 \frac{m_e}{M} E_e (1 + E_e), \quad E_e \text{ in MeV}$$

In order to displace an atom, the energy received must be at least E_d , the atom displacement energy. A lower limit on E_e which can cause

$$E_d = 4 \left(\frac{m_e}{M} \right) E_{e_{min}} (1 + E_{e_{min}}) \quad \text{all energy in MeV}$$

then $E_{e_{min}}$ can be determined by the above equation

or, if E_d in eV $E_{e_{min}}$ can be solved by

$$E_{e_{min}} (1 + E_{e_{min}}) = \left(\frac{M}{4 m_e} E_d \times 10^{-6} \right) \quad \text{--- (2)}$$

b) Total nuclear cross section $\sigma(E_e) = \int_0^{E_{pmax}} \frac{d\sigma}{dE_p} dE_p$

But if collision is to transfer enough energy to displace lattice atom, the minimum energy transfer is E_d

$$\sigma_d(E_e) = \int_{E_d}^{E_{pmax}} \frac{d\sigma}{dE_p} dE_p$$

$$\sigma_d = \left(\frac{Z e^2}{m_e c^2} \right)^2 \pi (1 - \beta^2) \left\{ \left(\frac{E_d}{E_{pmax}} - 1 \right) - \beta^2 \ln \left(\frac{E_p}{E_d} \right) + \pi \left(\frac{Z}{137} \right) \beta \left[2 \times \left(\sqrt{\frac{E_p}{E_{pmax}}} - 1 \right) - \ln \left(\frac{E_p}{E_d} \right) \right] \right\}$$

Number of primary knock ons.

$P_d(x) dx =$ probability of displacement collision in (x, dx)

$x =$ path length

$$P_d(x) dx = \sigma_d N dx$$

but E_e and x are related by stopping power

$$dx = \frac{dE_e}{\left(\frac{dE_e}{dx}\right)_e}$$

$P_d(E_e) dE_e$ probability of displacement collision during slowing down from E_e to $E_e - dE_e$

$$P_d(E_e) dE_e = \frac{N \sigma_d}{\left(dE_e/dx\right)_e} dE_e$$

also $P_d(E_e) =$ average number of displacement collision per unit energy loss

total number of displacement collision

$$= \int_{E_{e, \min}}^{E_e} P_d(E_e') dE_e'$$

$$\frac{\text{total number of PKA}}{\text{incident electron}} = N \int_{E_{e, \min}}^{E_e} \frac{\sigma_d(E_e')}{\left(-dE_e'/dx\right)} dE_e'$$

Total number of displaced atoms

But, the formula gives the total number of atoms displaced by the electron under consideration, NOT the total number of displaced atoms - i.e. it gives the number of PKA's

Each PKA of energy E_p gives $\nu(E_p)$ displaced atoms.
Re-do calculations for probabilities of PKA
in (E_p, dE_p) yields.

$P_d(E_e, E_p) dE_p$: average number of displacement
collision per unit energy loss with the
energy of PKA (E_p, dE_p)

$$P_d(E_e, E_p) = \frac{N \left(\frac{d\sigma}{dE_p} \right)}{(dE_e/dx)}$$

average number of displaced atoms per unit energy
loss produced by PKA in $(E_p, dE_p) = P_d(E_e, E_p) \nu(E_p) dE_p$

$$\bar{n}(E_e) = \frac{\text{total number of displaced atoms}}{\text{incident electron}}$$

$$= N \int_{E_e^{\min}}^{E_e} \frac{1}{-(dE_e'/dx)_{E_e'}} \left[\int_{E_d}^{E_p^{\max}(E_e')} \left(\frac{d\sigma}{dE_p} \right) \nu(E_p) dE_p \right] dE_e'$$

$\uparrow$ $\bar{e}-\bar{e}$ collision $\uparrow$ e^- -nucleus collision

c) Special case

$\left(\frac{E_p^{\max}}{E_d} \right)$ just slightly greater than unity

or $\left(\frac{E_e}{E_e^{\min}} \right)$ just slightly larger than 1

Since $E_d < E_p^{max} < 2E_d$, $P(E_p) = 1$

$$\therefore \int_{E_d}^{E_p^{max}} \left(\frac{d\sigma}{dE_p} \right) P(E_p) dE_p = \sigma_d(E_e)$$

$$\approx \left(\frac{ze^2}{m_e c^2} \right)^2 \frac{\pi(1-\beta^2)}{\beta^4} \left[\frac{E_p^{max}}{E_d} - 1 \right]$$

Since $E_e \approx E_e^{min}$ $\frac{dE_e}{dx} = \text{constant at all } E_e \text{ value}$

$$\Rightarrow \bar{n}(E_e) = \frac{N(E_e - E_e^{min})}{(-dE/dx)_{E_e}} \left(\frac{ze^2}{m_e c^2} \right)^2 \frac{\pi}{\beta^4(1-\beta^2)} \left[\frac{E_p^{max}(E_e)}{E_d} - 1 \right]$$

PROBLEM 17.12

a) number of Compton electrons produced/cm³-sec in energy range (E_e, dE_e) by photons in energy range (E_r, dE_r)

$$= (ZN) \phi(E_r) dE_r \sigma_c(E_r, E_e) dE_e$$

multiply by $\bar{n}(E_e)$ = number of displaced atoms per electron of energy E_e and integrate over all energies (For γ -Ray and electron)

$$R_d = ZN \int_{E_r^{\min}}^{E_r^0} \phi(E_r) \left\{ \int_{E_e^{\min}}^{E_e^{\max}} \sigma_c(E_r, E_e) \bar{n}(E_e) dE_e \right\} dE_r \quad (1)$$

Since the Compton electrons are of energy ~ 1 MeV, we must use relativistic kinematics.

$E_e^{\min}$ calculated in problem 17.11 as a

solution of
$$E_e^{\min} (1 + E_e^{\min}) = \left(\frac{M}{4m_e} E_d \times 10^{-6} \right) \quad (2)$$

Where $E_e^{\min}$ in MeV and E_d in eV

$E_e^{\max}$ = the maximum energy of a Compton electron produced by a photon of energy E_r is

$E_e^{\max} = E_r - E_r'$, where E_r' is the energy of the backscattered ($\theta = 180^\circ$) photons.

$$E_r' = \frac{E_r}{1 + 2 \frac{E_r}{m_e c^2}} = \frac{E_r}{1 + 4 E_r}, \quad E_r \text{ in MeV}$$

$$\therefore E_e^{\max} = \frac{4 E_r^2}{1 + 4 E_r} \quad (3)$$

$$\underline{E_r^{\min}}$$

The photon must be sufficient enough so that when a backscattered γ -e collision occurred the secondary electron energy is $E_e^{\min}$ or $E_r^{\min}$ is determined by:

$$\frac{4(E_r^{\min})^2}{1 + 4(E_r^{\min})} = E_e^{\min} = \frac{1}{2} \left[\sqrt{1 + 4\left(\frac{M}{m_e} E_d \times 10^6\right)} - 1 \right] \quad \text{---(4)}$$

b) No damage will occur if E_r is less than or equal to $E_r^{\min}$, as determined by (4)

$$\text{Let } \boxed{E^* = \frac{M}{4m_e} E_d \times 10^{-6}} \text{ , MeV}$$

$$x = E_r^{\min}$$

$$\frac{4x^2}{1 + 4x} = \frac{1}{2} (\sqrt{1 + 4E^*} - 1) = A$$

$$4x^2 - 4Ax - 1 = 0$$

$$x = E_r^{\min} = \frac{A + \sqrt{A^2 + \frac{1}{4}}}{2}$$

$$= \frac{1}{2} \left[\frac{1}{2} (\sqrt{1 + 4E^*} - 1) + \sqrt{\frac{1}{4} (\sqrt{1 + 4E^*} - 1)^2 + \frac{1}{4}} \right]$$

$$\text{ii } \boxed{E_r^{\min} = \frac{1}{4} \left[(\sqrt{1 + 4E^*} - 1) + 2 \sqrt{(\sqrt{1 + 4E^*} - 1)^2 + 1} \right]}$$

PROBLEM 17.13

From Eq. (17.151)

$$b = \int_{T_{\min}/\Lambda}^{\infty} dE_n \phi(E_n) \int_{T_{\min}}^{\Lambda E_n} \sigma(E_n, T) dT$$

Where ΛE_n is the maximum energy transfer to a lattice atom by a neutron of energy E_n

and $\Lambda = \frac{4A}{(A+1)^2}$

$\sigma(E_n, T)$ is the energy transfer cross section for neutron scattering

Since this is a monoenergetic neutron flux

$$\phi(E_n) = \Phi \delta(E_n - 0.5), \quad E_n \text{ in MeV}$$

Assume the scattering process is elastic and isotropic in C.M. system and $\sigma_{el} = 10 \times 10^{-24} \text{ cm}^2$

$$\Rightarrow \sigma(E_n, T) = \frac{\sigma_{el}}{\Lambda E_n}$$

$$\therefore b = \Phi \int_{T_{\min}}^{\Lambda E_n} \frac{\sigma_{el}}{\Lambda E_n} dT = \Phi \sigma_{el} \left(1 - \frac{T_{\min}}{\Lambda E_n}\right)$$

$$\Rightarrow b = \Phi \sigma_{el} \left(1 - \frac{T_{\min}}{\Lambda E_n}\right)$$

$$T_{\min} \approx 25 \text{ eV}$$

$$\therefore b = 10^{-8} \text{ sec}^{-1}$$

Resolution by fission fragment recoils

$$b = 1.7 \times 10^{-17} \dot{F} \text{ sec}^{-1}$$

From Eq (10.1)

$$\dot{F} = \eta \sigma_f N_f \phi$$

where η is the enrichment, $= 0.15$

σ_f : the effective fission cross section for the fissile species in the appropriate neutron energy spectrum. for a fast reactor

$$\sigma_f = 1.8 \text{ barns} = 1.8 \times 10^{-24} \text{ cm}^2$$

N_f : total number density of the heavy metal atom, In TBR this number is about the same as the uranium atom density in pure UO_2 , which is $\approx 2.4 \times 10^{22} \text{ atoms/cm}^3$

$$\phi = 10^{15} \text{ g}(E_n - 0.5)$$

$$\therefore \dot{F} = 0.15 \times 1.8 \times 10^{-24} \times 2.4 \times 10^{22} \times 10^{15} = 0.65 \times 10^{13} \frac{\text{cm}^{-3}}{\text{sec}}$$

$$b = 1.7 \times 10^{-17} \times \dot{F} = 1.10 \times 10^{-4} \text{ sec}^{-1}$$

$$b_{\text{fast neutron}} = 10^{-8} \text{ sec}^{-1}$$

$$b_{\text{recoil}} = 1.1 \times 10^{-4} \text{ sec}^{-1}$$

The magnitude of b_{recoil} is four orders of magnitude larger than $b_{\text{fast neutron}}$, i.e.

the resolution effect is more important for the fission fragment than that for fast neutron.

PROBLEM 17.14

- a) Resolution due to direct neutron collisions:
Similar to Eq (13.116) for He bubbles in
a neutron flux is

$$b_{\text{direct}} = \int_{T_{\min}}^{\infty} dE_n \phi(E_n) \int_{T_{\min}}^{\Lambda_{\text{He}} E_n} \sigma_{\text{He-n}}(E_n, T) dT$$

For elastic, isotropic scattering of neutron on He atoms,

$$\sigma_{\text{He-n}}(E_n, T) = \frac{\sigma_{\text{He-n}}}{\Lambda_{\text{He}} E_n}$$

$$\Lambda_{\text{He}} = \frac{4(4)}{(1+4)^2} = 0.64$$

$$b_{\text{direct}} = \sigma_{\text{He-n}} \int_{T_{\min}}^{\infty} \phi(E_n) \left(1 - \frac{T_{\min}}{\Lambda_{\text{He}} E_n}\right) dE_n$$

For monoenergetic flux

$$b_{\text{direct}} = \sigma_{\text{He-n}} \Phi \left(1 - \frac{T_{\min}}{\Lambda_{\text{He}} E_n}\right)$$

$$\text{where } \frac{T_{\min}}{\Lambda_{\text{He}} E_n} \approx 0$$

$$\sigma_{\text{He-n}} \approx 1 \times 10^{-24} \text{ cm}^2$$

$$\Phi = 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$$

$$\therefore b_{\text{direct}} = (10^{-24})(10^{15}) = 10^{-9} \text{ sec}^{-1}$$

- b) Resolution of He in stainless steel due to recoil
 $\phi(E_r)$ flux spectrum of iron recoils

E_r recoil atom energy

$\sigma_{\text{Fe-He}}(E, T)$ energy transfer cross section
for iron-Helium interaction

Following Eq (17.151)

$$\text{brecoil} = \int_{T_{\min}/\Lambda}^{\infty} dE_r \phi(E_r) \int_{T_{\min}}^{\Lambda E_r} \sigma_{\text{Fe-He}}(E_r, T) dT \quad \text{--- (1)}$$

$$\Lambda = \frac{4 M_{\text{Fe}} M_{\text{He}}}{(M_{\text{Fe}} + M_{\text{He}})^2} = 0.25 \quad \text{--- (2)}$$

$T_{\min}$: minimum energy of He atom for resolution

Following Eq (17.156) - (17.157)

$$\sigma_{\text{Fe-He}}(E_r, T) = \frac{K}{E_r^2} \quad \text{--- (3)}$$

where

$$K = \frac{\sqrt{Z} \pi Z_{\text{Fe}} Z_{\text{He}} a_B e^2 \exp(-1)}{\Lambda (Z_{\text{Fe}}^{2/3} + Z_{\text{He}}^{2/3})^{1/2}} \left(\frac{M_{\text{Fe}} + M_{\text{He}}}{M_{\text{He}}} \right) \quad \text{--- (4)}$$

$$Z_{\text{Fe}} = 26$$

$$Z_{\text{He}} = 2$$

$$a_B e^2 = 7.5 \times 10^{-16} \text{ eV-cm}^2$$

$$\left. \begin{array}{l} Z_{\text{Fe}} = 26 \\ Z_{\text{He}} = 2 \\ a_B e^2 = 7.5 \times 10^{-16} \text{ eV-cm}^2 \end{array} \right\} \Rightarrow K = 1.2 \times 10^{-12} \text{ eV-cm}^2$$

The recoil flux spectrum is given by Eq (17.166) with appropriate changes from ff to n and W to Fe

$$\phi(E_r) = \frac{4}{E_r^2 \sigma_{\text{Fe-Fe}}(E_r)} \int_{E_r/\Lambda_n}^{\infty} dE_n \phi(E_n) \int_{E_r}^{\Lambda_n E_n} E \sigma_{\text{Fe}}(E_n, E) dE \quad \text{--- (5)}$$

$$\text{Where } \Lambda_n = \frac{4 \times 56}{(1 + 56)^2} = 0.069 \quad \text{--- (6)}$$

$\sigma_{\text{Fe-Fe}}$: cm - iron atomic scattering cross sections

$\sigma_{\text{Fe}}(E_n, E)$: energy transfer cross section for neutrons on iron

$\Phi(E_n)$ = neutron flux spectrum
 For isotropic, elastic neutron scattering

$$\sigma_{Fe}(E_n, E) = \frac{\sigma_{Fe-n}(E_n)}{\Lambda_n E_n} \quad \text{--- (7)}$$

$\sigma_{Fe-n}(E_n)$: elastic scattering cross section for iron
 Using (7) in (5) :

$$\Phi(E_r) = \frac{2}{\Lambda_n E_r^2 \sigma_{Fe-Fe}} \int_{E_r/\Lambda_n}^{\infty} \frac{\sigma_{Fe-n}(E_n) \Phi(E_n) (\Lambda_n^2 E_n^2 - E_r^2)}{E_n} dE_n \quad \text{--- (8)}$$

Assuming an energy dependent scattering cross section and a monoenergetic flux at E_n , $\Phi(E_n) = \Phi \delta(E_n - E_n)$

$$\Rightarrow \Phi(E_r) = 2 \left(\frac{\Lambda_n^2 E_n^2 - E_r^2}{\Lambda_n E_n E_r^2} \right) \left(\frac{\sigma_{Fe-n}}{\sigma_{Fe-Fe}} \right) \Phi \quad \text{--- (9)}$$

where E_n is given

Using (2), (3), (4), (6), and (9) in (1)

$$b_{recoil} = 2K\Phi \left(\frac{\sigma_{Fe-n}}{\sigma_{Fe-Fe}} \right) \int_{T_{min}/\Lambda}^{\Lambda_n E_n} \left(\frac{\Lambda_n^2 E_n^2 - E_r^2}{\Lambda_n E_n E_r^2} \right) \left(\frac{1}{T_{min}} - \frac{1}{\Lambda E_r} \right) dE_r \quad \text{--- (10)}$$

Where $\Lambda_n E_n$ is the maximum recoil energy in monoenergetic neutron flux

$$\begin{aligned} \therefore b_{recoil} = 2K \left(\frac{\sigma_{Fe-n}}{\sigma_{Fe-Fe}} \right) \Phi & \left[\left(\frac{\Lambda_n E_n}{T_{min}} \right) \left(\frac{\Lambda}{T_{min}} - \frac{1}{\Lambda_n E_n} \right) \right. \\ & - \left(\frac{1}{\Lambda_n E_n T_{min}} \right) \left(\Lambda_n E_n - \frac{T_{min}}{\Lambda} \right) - \left(\frac{\Lambda_n E_n}{2\Lambda} \right) \left(\frac{\Lambda^2}{T_{min}^2} - \frac{1}{\Lambda_n^2 E_n^2} \right) \\ & \left. + \frac{1}{\Lambda \Lambda_n E_n} \ln \left(\frac{\Lambda_n \Lambda E_n}{T_{min}} \right) \right] \end{aligned}$$

where $\sigma_{\text{Fe-n}} \approx 3 \times 10^{-24} \text{ cm}^2$

$\sigma_{\text{Fe-Fe}} \approx 5 \text{ Å}^2 = 5 \times 10^{-16} \text{ cm}^2$

$K = 1.2 \times 10^{-12} \text{ eV-cm}^2$

$\Phi = 10^{15} \text{ neutrons/cm}^2/\text{sec}$

$\Lambda_n E_n = (0.069) \times (0.5 \times 10^6) = 3 \times 10^4 \text{ eV}$

$T_{\text{min}} \approx 200 \text{ eV}$

$T_{\text{min}}/\lambda = 800 \text{ eV}$

$$\therefore b_{\text{breuil}} = 2 \times (1.2 \times 10^{-12}) \left(\frac{3 \times 10^{-24}}{5 \times 10^{-16}} \right) (10^{15}) \left[\frac{3 \times 10^4}{2 \times 10^3} \frac{1}{8 \times 10^2} \right. \\ \left. - \frac{1}{2 \times 10^3} - \frac{3 \times 10^4}{0.5} \times \frac{1}{(8 \times 10^2)^2} + \frac{1}{1.25 \times 3 \times 10^4} \ln \left(\frac{3 \times 10^4}{8 \times 10^2} \right) \right] \\ = 1.3 \times 10^{-6} \text{ sec}^{-1}$$

$\Rightarrow b_{\text{breuil}} = 1.3 \times 10^{-6} \text{ sec}^{-1}$

CHAPTER 18Problem 18.1

(A)

boundary conditions :

$$1) \text{ at void } C_v(R) = C_v^e \exp\left[\frac{2\gamma \Omega}{R kT}\right]$$

$$2) \text{ in bulk } C_v(\infty) = C_v^e$$

Diffusion equation for vacancies, source free, r dependence only, becomes:

$$\frac{d}{dr}\left(r^2 \frac{dC_v}{dr}\right) = 0 \Rightarrow \frac{dC_v}{dr} = \frac{C_1}{r^2}$$

$$\therefore C_v(r) = -\frac{C_1}{r} + C_2$$

Apply boundary conditions:

$$r \rightarrow \infty$$

$$C_v(\infty) = C_2 = C_v^e$$

$$r = R$$

$$C_v(R) = -\frac{C_1}{R} + C_v^e = C_v^e \exp\left[\frac{2\gamma \Omega}{R kT}\right]$$

$$\therefore C_1 = R C_v^e \left[1 - \exp\left(\frac{2\gamma \Omega}{R kT}\right)\right]$$

Thus,

$$\left.\frac{dC_v(r)}{dr}\right|_R = \frac{C_1}{R^2} = \frac{C_v^e}{R} \left[1 - \exp\left(\frac{2\gamma \Omega}{R kT}\right)\right]$$

For $\frac{2\gamma \Omega}{R kT} \ll 1$, we may expand exponent

$$\therefore \left.\frac{dC_v}{dr}\right|_R \approx -\frac{C_v^e}{R^2} \frac{2\gamma \Omega}{kT}$$

Equating the volumetric loss rate of the void with the outward current of volume carried by diffusing vacancies, obtain:

$$\begin{aligned}
 -\frac{d}{dt} \left(\frac{4\pi}{3} R^3 \right) &= -D_v \left(\frac{dc_v}{dr} \right)_R 4\pi R^2 \\
 &= 4\pi D_v c_v^e \frac{2\gamma \Omega^2}{kT}
 \end{aligned}$$

∴ integrating, obtain

$$R^3 = -3 D_v c_v^e \frac{2\gamma \Omega^2}{kT} t + (\text{constant})$$

but, constant = R_0^3 , since $R(t=0) = R_0$

$$\therefore R_0^3 - R^3 = 3 D_v \Omega^2 c_v^e \left(\frac{2\gamma}{kT} \right) t$$

or

$$R(R_0, t) = \left\{ R_0^3 - Qt \right\}^{1/3} \quad \text{where } Q = 3 D_v c_v^e \left(\frac{2\gamma}{kT} \right) \Omega^2$$

(B)

All voids in the range R to $(R+dR)$ at time t are due to those present at $t=0$ in the range R_0 to (R_0+dR_0) , thus:

$$N(R, t) dR = N_0(R_0) dR_0$$

or

$$N(R, t) = N_0(R_0) \left(\frac{\partial R_0}{\partial R} \right) \quad \leftarrow \text{Jacobian of transformation}$$

From part (A) solve for $R_0(R, t)$:

$$R_0(R, t) = (R^3 + Qt)^{1/3}$$

$$\therefore \frac{\partial R_0}{\partial R} = R^2 (R^3 + Qt)^{-2/3}$$

$$\therefore N(R, t) = N_0(R_0(R, t)) \cdot R^2 (R^3 + Qt)^{-2/3}$$

(C)

Gaussian distribution is given by

$$N_0(R_0) = K \exp\left(-\frac{(R_0 - \bar{R}_0)^2}{2\sigma^2}\right)$$

Symmetric "bell-shaped" curve

To find K , use normalizing condition:

$$\begin{aligned} N_T^0 &= \int_0^\infty N_0(R_0) dR_0 \\ &= K \int_0^\infty \exp\left(-\frac{(R_0 - \bar{R}_0)^2}{2\sigma^2}\right) dR_0 \end{aligned}$$

$$\text{let } x = \frac{R_0 - \bar{R}_0}{\sqrt{2}\sigma} \rightarrow dx = \frac{dR_0}{\sqrt{2}\sigma}$$

Thus,

$$N_T^0 = \sqrt{2}K\sigma \int_{-\bar{R}_0/\sqrt{2}\sigma}^{\infty} e^{-x^2} dx$$

$$= \sqrt{2}K\sigma \left\{ \int_0^\infty e^{-x^2} dx + \int_0^{\bar{R}_0/\sqrt{2}\sigma} e^{-x^2} dx \right\}$$

$$= \sqrt{2}K\sigma \left\{ \frac{\sqrt{\pi}}{2} + \frac{\sqrt{\pi}}{2} \operatorname{erf}\left(\frac{\bar{R}_0}{\sqrt{2}\sigma}\right) \right\}$$

$$\therefore K = \frac{\sqrt{\frac{2}{\pi}} N_T^0}{\sigma [1 + \operatorname{erf}(\bar{R}_0/\sqrt{2}\sigma)]} \approx \frac{\sqrt{\frac{2}{\pi}} \times 10^{15}}{50 [1 + \operatorname{erf}(5.61)]}$$

$$\approx \sqrt{\frac{2}{\pi}} \times \frac{10^{15}}{50(1+1)}$$

$$\approx 7.95 \times 10^{12} \text{ voids/cm}^3\text{-}\bar{A}$$

When average void disappears,

$$R(\bar{R}_0, t) = 0 \Rightarrow \bar{R}_0^3 = Q t_{d(\text{Ave})} \quad (\text{from part A})$$

$$\text{or } Q = \frac{(400)^3}{3 \times (60)^2} \approx 5.9 \times 10^3 \text{ sec}^{-1}$$

Thus,

$$N(R, t) = K \exp \left\{ - \frac{[(R^3 + Qt)^{1/3} - R_0]^2}{2\sigma^2} \right\} \cdot R^2 (R^3 + Qt)^{-2/3}$$

$$\text{for } t = 2 \text{ hrs} = 2 \times 60^2 \text{ sec}$$

$$Qt = 2 \times 60^2 \times 5.9 \times 10^3 \approx 4.25 \times 10^7$$

$$\therefore N(R, 2 \text{ hrs}) = 7.95 \times 10^{12} \exp \left\{ - \frac{[(R^3 + 4.25 \times 10^7)^{1/3} - 400]^2}{2 \cdot (50)^2} \right\} \cdot R^2 (R^3 + 4.25 \times 10^7)^{-2/3}$$

and

$$N_0(R_0) = 7.95 \times 10^{12} \exp \left\{ - \frac{(R_0 - 400)^2}{2 \cdot (50)^2} \right\}$$

in units of $\left[\frac{\text{voids}}{\text{cm}^3 \cdot \text{\AA}} \right]$

Problem 18.2

$$\frac{d\sigma}{d\epsilon} = \sigma \quad \text{at onset of plastic instability} \quad (\text{Egn 18.7})$$

With $\sigma = k\epsilon^n$, obtain

$$kn\epsilon^{n-1} = k\epsilon^n$$

or

$$n = \epsilon_{UTS}$$

$$\therefore \Delta\epsilon_{UTS} = (\epsilon_{UTS})_{unirr} - (\epsilon_{UTS})_{irrad} = \Delta n$$

ie, reduction in uniform elongation due to irradiation = Δn .

Problem 18.3

(A)

Each corner shared by 4 unit cells; center point belongs to unit cell shown

$\therefore$ area a^2 has $(4 \times \frac{1}{4} + 1) = 2$ pinning points

$$\therefore \frac{\text{obstacles}}{\text{area}} = \frac{2}{a^2} = \frac{1}{l^2}$$

$$\therefore l = \frac{a}{\sqrt{2}}$$

case 1

dislocation motion

for case 1:

$$l_0 = a$$

$$h = a/2$$

$$\therefore h l_0 = \left(\frac{a}{2}\right)(a) = \frac{a^2}{2} = l^2 \checkmark$$

case 2: for case 2

$$l_0 = \frac{a}{\sqrt{2}}$$

$$h = \frac{a}{\sqrt{2}}$$

$$\therefore h l_0 = \left(\frac{a}{\sqrt{2}}\right)\left(\frac{a}{\sqrt{2}}\right) = \frac{a^2}{2} = l^2 \checkmark$$

(B)

$$Y = 1 - \frac{1}{1+e^\eta} - A\eta + \text{constant}$$

where $\eta = \frac{x}{r'}$ & $A = \frac{\sigma b \text{ for } r'}{U_0}$

(i)

Y reaches maximum (barrier exists) only if

$$\frac{dY}{d\eta} = 0$$

$$-\frac{d}{d\eta} \left(\frac{1}{1+e^\eta} \right) - A = 0$$

$$\left(\frac{1}{1+e^\eta} \right)^2 e^\eta - A = 0$$

let $z = e^\eta$, $z \in \{\text{Reals} > 0\}$

$$\frac{z}{(1+z)^2} - A = 0$$

Solve for z

$$z - A - 2Az - Az^2 = 0$$

$$z^2 + (2 - \frac{1}{A})z + 1 = 0$$

$$\therefore z = \frac{(\frac{1}{A} - 2) \pm \sqrt{(\frac{1}{A} - 2)^2 - 4}}{2}$$

$$= (\frac{1}{2A} - 1) \pm \sqrt{(\frac{1}{2A} - 1)^2 - 1}$$

Since $|\frac{1}{2A} - 1| > \sqrt{(\frac{1}{2A} - 1)^2 - 1}$,
 $(\frac{1}{2A} - 1) > 0$ for $z > 0$

For $z \in \{\text{Reals}\}$,

$$(\frac{1}{2A} - 1)^2 - 1 > 0$$

$$\left(\frac{1}{2A} - 1\right)^2 > 1$$

$$\frac{1}{2A} - 1 > 1 \quad (\text{positive root taken since } (\frac{1}{2A} - 1) > 0)$$

$$\therefore \frac{1}{4} > A, \text{ if barrier exists.}$$

$$\therefore \text{if } A \geq \frac{1}{4}, \text{ barrier height disappears (barrier does not exist)}$$

(ii)

$$\epsilon = 1 - 4A$$

$$\epsilon - 1 = -4A$$

$$\therefore \frac{1}{2A} = \frac{2}{1-\epsilon}$$

$$\therefore \left(\frac{1}{2A} - 1\right) = \frac{2}{1-\epsilon} - 1 = \frac{1+\epsilon}{1-\epsilon}$$

Thus,

$$\begin{aligned} z &= \left(\frac{1+\epsilon}{1-\epsilon}\right) \pm \sqrt{\left(\frac{1+\epsilon}{1-\epsilon}\right)^2 - 1} \\ &= \frac{1+\epsilon}{1-\epsilon} \left[1 \pm \sqrt{1 - \left(\frac{1-\epsilon}{1+\epsilon}\right)^2} \right] \end{aligned}$$

expand for small ϵ

$$z \approx (1+\epsilon)(1+\epsilon) \left[1 \pm \sqrt{1 - [(1-\epsilon)(1-\epsilon)]^2} \right]$$

$$\approx (1+2\epsilon) \left[1 \pm \sqrt{1 - (1-\epsilon)^4} \right]$$

$$\approx (1+2\epsilon) \left[1 \pm \sqrt{1 - (1-4\epsilon)} \right]$$

$$\approx (1+2\epsilon) \left[1 \pm 2\sqrt{\epsilon} \right]$$

$$\approx 1 \pm 2\sqrt{\epsilon} + 2\epsilon \quad \text{to first order in } \epsilon$$

$$\therefore e^{\eta_{\pm}} \approx 1 \pm 2\sqrt{\epsilon} + 2\epsilon$$

$$\therefore \eta_{\pm} \approx \ln(1 \pm 2\sqrt{\epsilon} + 2\epsilon)$$

using $\ln(1+x) \approx x - \frac{1}{2}x^2 + \dots$ for $|x| < 1$

obtain,

$$\eta_{\pm} \approx \pm 2\sqrt{\epsilon} \quad \text{to lowest order in } \epsilon$$

(iii)

$$Y(\eta_+) = 1 - \left(\frac{1}{1+e^{\eta_+}} \right) - A\eta_+ + \text{const}$$

$$Y(\eta_-) = 1 - \left(\frac{1}{1+e^{\eta_-}} \right) - A\eta_- + \text{const}$$

where

$$A = \frac{1-\epsilon}{4}$$

$$\Delta Y = Y(\eta_+) - Y(\eta_-)$$

$$= - \left(\frac{1}{1+e^{\eta_+}} \right) + \left(\frac{1}{1+e^{\eta_-}} \right) - A\eta_+ + A\eta_-$$

$$\approx - \left(\frac{1}{1+(1+2\sqrt{\epsilon})} \right) + \left(\frac{1}{1+(1-2\sqrt{\epsilon})} \right) + \frac{1-\epsilon}{4} (-2\sqrt{\epsilon} - 2\sqrt{\epsilon})$$

$$\approx \frac{1}{2} \left\{ \frac{1}{1-\sqrt{\epsilon}} - \frac{1}{1+\sqrt{\epsilon}} \right\} + \frac{(\epsilon-1)\sqrt{\epsilon}}{2}$$

$$\approx \frac{\epsilon^{1/2}}{1-\epsilon} + \epsilon^{3/2} - \epsilon^{1/2}$$

$$\approx \epsilon^{1/2}(1+\epsilon) + \epsilon^{3/2} - \epsilon^{1/2}$$

$$\approx 2\epsilon^{3/2}$$

Problem 18.4

Egn 18.39 may be written as

$$\overline{J}_S^{2/3} = (\overline{J}_S^0)^{2/3} - \left(\frac{\overline{J}_S^0}{T_c} \right)^{2/3} T^{2/3}$$

For the Ni data of Fig 18.20:

$$(\overline{J}_S^0)_A \approx 8200^{3/2} \quad \& \quad (\overline{J}_S^0)_B \approx (6750)^{3/2}$$

$$\therefore \frac{(\overline{J}_S^0)_A}{(\overline{J}_S^0)_B} \approx \left(\frac{8200}{6750} \right)^{3/2} \approx 1.34$$

Also,

$$\left(\frac{\overline{J}_S^0}{T_c} \right)_A \approx 66^{3/2} \quad \& \quad \left(\frac{\overline{J}_S^0}{T_c} \right)_B \approx 28^{3/2}$$

$$\therefore \frac{(T_c)_A}{(T_c)_B} = \frac{(\overline{J}_S^0/T_c)_B (\overline{J}_S^0)_A}{(\overline{J}_S^0/T_c)_A (\overline{J}_S^0)_B} \\ \approx (1.34) \left(\frac{28}{66} \right)^{3/2} \\ \approx 0.37$$

From Egn 18.39, $T_c \propto U_0$ or

$$\frac{(U_0)_A}{(U_0)_B} = \frac{(T_c)_A}{(T_c)_B} \approx 0.37$$

but $U_0 \propto r^2$ (see text)

$$\therefore \frac{r_A}{r_B} = \sqrt{\frac{(U_0)_A}{(U_0)_B}} \\ \approx \sqrt{0.37} \\ \approx 0.61$$

From Egn 18.37,

$$N \propto \left[\frac{\overline{J}_S^0}{(U_0)^{3/2}} \right]^2$$

Thus,

$$\begin{aligned}
 \frac{N_A}{N_B} &= \frac{r_A^2}{r_B^2} \left[\frac{(U_o)_B}{(U_o)_A} \right]^3 \left[\frac{(\sigma_s)_A}{(\sigma_s)_B} \right]^2 \\
 &= \left[\frac{(U_o)_B}{(U_o)_A} \right]^2 \left[\frac{(\sigma_s)_A}{(\sigma_s)_B} \right]^2 \\
 &\approx \left(\frac{1.34}{0.37} \right)^2 \\
 &\approx 13.1
 \end{aligned}$$

Problem 18.5

(A)

$$R = \frac{Gb}{\sigma_{xy}} \quad (\text{Egn. 8.15})$$

When $R = l/2$, dislocation line pinches off and leaves bubble.

$$\therefore (\sigma_{xy})_{\text{critical}} = \frac{2Gb}{l} \quad (\text{Egn 8.16 or Egn 18.53})$$

For sweeping,

$$\sigma_{xy} < (\sigma_{xy})_{\text{critical}}.$$

Since bubble spacing along line is given by

$$l = \frac{1}{\sqrt{2RN}} \quad (\text{Egn 18.25})$$

we have:

$$\sigma_{xy} < 2^{3/2} Gb \sqrt{RN}$$

for bubble sweeping by dislocation line.

(B)

Let v_b = velocity of dislocation line with bubbles
then,

v_b = velocity of bubbles due to force F_b

$$v_b = \Gamma_b F_b, \quad F_b = 2\gamma_d \cos \phi \quad (\text{Egn 13.276})$$

$$\Gamma_b = \frac{D_b}{KT} \quad (\text{Nernst - Einstein relation})$$

also,

$$D_b = \frac{3 a_0^4 D_s}{2\pi R^4}$$

(Egn 13.214)

$$\& \cos \phi = \frac{(l/2)}{R} = \frac{l}{2R} = \frac{l \sigma_{xy}}{2Gb}$$

thus,

$$V_b = \frac{3 a_0^4 D_s}{2\pi R^4 kT} \cdot 2\gamma_d \cdot \frac{l \sigma_{xy}}{2Gb}$$

Initially,

$$l = \frac{1}{\sqrt{2RN}}$$

(Egn 18.25)

and

$$\gamma_d = Gb^2$$

(Egn 8.10)

$$\therefore (V_b)_0 = \frac{3 a_0^4 D_s b \sigma_{xy}}{2 \pi R^2 \sqrt{N} kT}$$

(C)

The density of bubbles on the slip plane is $2RN$. After the dislocation line has moved a distance x , each unit length of line has swept up all bubbles in the area $x \cdot l$ behind it.

Number of bubbles per unit length of dislocation line at x is the original number, $\sqrt{2RN}$, plus the number swept up, $(2RN)x$.

$\therefore$ average bubble spacing $l(x)$ is

$$l(x) = \frac{1}{\sqrt{2RN} + 2RNx} = \frac{1}{\sqrt{2RN}} \left\{ \frac{1}{1 + x\sqrt{2RN}} \right\}$$

The velocity at x is therefore (since $v_b \propto l$):

$$v_b(x) = \frac{(v_b)_0}{1 + x\sqrt{2RN}}$$

$$\left(\text{ie } \frac{v_b(x)}{(v_b)_0} = \frac{l(x)}{l_0} \right)$$

Problem 18.6

(A)

Force balances: (independent of assumptions of elasticity theory.)

Axial:

$$t_c \ll R$$

$$2\pi R t_c \sigma_z = \pi R^2 p$$

$$\therefore \boxed{\sigma_z = \frac{R p}{2 t_c}} \quad (1)$$

Azimuthal: pressure force is in $\hat{r}$ direction
 $\hat{y}$ component of pressure force
on $dA = p \sin \theta dA$
 $\therefore$ total $\hat{y}$ pressure force over $1/2$ of tube is
given by:

$$PR \int_0^{\pi} \sin \theta d\theta = 2PR$$

$$\therefore 2PR = 2\sigma_\theta t_c \quad (\text{force balance})$$

$$\therefore \boxed{\sigma_\theta = \frac{R p}{t_c}} \quad (2)$$

(B)

From appendix to Ch B:

$$\epsilon_r = \frac{1}{E} [\sigma_r - \nu(\sigma_\theta + \sigma_z)] \quad (3)$$

$$\epsilon_\theta = \frac{1}{E} [\sigma_\theta - \nu(\sigma_r + \sigma_z)] \quad (4)$$

$$\epsilon_z = \frac{1}{E} [\sigma_z - \nu(\sigma_r + \sigma_\theta)] \quad (5)$$

Equilibrium conditions:

$$\frac{d\sigma_r}{dr} + \frac{\sigma_r - \sigma_\theta}{r} = 0 \quad (6)$$

$$\frac{d\sigma_z}{dz} = 0 \quad (7)$$

Strain-displacement:

$$\epsilon_r = \frac{du}{dr} \quad (8)$$

$$\epsilon_\theta = \frac{u}{r} \quad (9)$$

Plane strain:

$$\epsilon_z = \text{constant} \quad (10)$$

from (8) & (9) obtain,

$$\frac{d\epsilon_\theta}{dr} + \frac{\epsilon_\theta - \epsilon_r}{r} = 0 \quad (11)$$

(compatibility condition)

solve (5) for σ_z

$$\sigma_z = \nu(\sigma_r + \sigma_\theta) + E\epsilon_z \quad (12)$$

substitute into (3) & (4):

$$E\epsilon_r = (1-\nu^2)\sigma_r - \nu(1+\nu)\sigma_\theta - \nu E\epsilon_z \quad (13)$$

$$E\epsilon_\theta = (1-\nu^2)\sigma_\theta - \nu(1+\nu)\sigma_r - \nu E\epsilon_z \quad (14)$$

substitute into (11), recalling plane strain $\rightarrow \frac{\partial \epsilon_z}{\partial r} = 0$

$$(1-\nu) \frac{d\sigma_\theta}{dr} - \nu \frac{d\sigma_r}{dr} + \frac{\sigma_r - \sigma_\theta}{r} = 0$$

eliminate σ_θ by (6):

$$\frac{d^2\sigma_r}{dr^2} + \frac{3}{r} \frac{d\sigma_r}{dr} = \frac{1}{r^3} \frac{d}{dr} \left(r^3 \frac{d\sigma_r}{dr} \right) = 0 \quad (15)$$

integrate twice

$$\sigma_r = -\frac{C_1}{r^2} + C_2$$

Boundary conditions:

$$\sigma_r(R_i) = -P$$

$$\sigma_r(R_o) = 0$$

R_i = inner radius

R_o = outer radius

} (16)

$$\therefore \sigma_r(r) = -\frac{P}{\left(\frac{R_o^2}{R_i^2} - 1\right)} \left(\frac{R_o^2}{r^2} - 1 \right) \quad (17)$$

Use (17) in (6) to obtain:

$$\sigma_\theta = \sigma_r + r \frac{d\sigma_r}{dr}$$

$$\sigma_\theta = \left[\frac{P}{\left(\frac{R_o^2}{R_i^2} - 1\right)} \cdot \left(\frac{R_o^2}{r^2} + 1 \right) \right] \quad (18)$$

Then wall approx:

$$\frac{R_o^2}{r^2} \approx 1$$

(in σ_θ only)

$$\begin{aligned}\frac{R_o^2}{R_i^2} - 1 &\approx \frac{1}{R_i^2} (R_o^2 - R_i^2) \approx \frac{R_o + R_i}{R_i^2} (R_o - R_i) \\ &\approx \frac{2}{R} t_c\end{aligned}$$

$$\sigma_\theta = \frac{R_p}{t_c} \quad \& \quad \sigma_r = -p \left(\frac{R_o - r}{t_c} \right) \quad (19)$$

$\hookrightarrow$ ✓ with (2)

(c)

Strain components:

substitute (17) & (18) into (13) & (19)

$$\epsilon_r = - \frac{p(1+\nu)}{E(R_o^2/R_i^2 - 1)} \left[\frac{R_o^2}{r^2} - (1-2\nu) \right] - \nu \epsilon_z \quad (20)$$

$$\epsilon_\theta = \frac{p(1+\nu)}{E(R_o^2/R_i^2 - 1)} \left[\frac{R_o^2}{r^2} + (1-2\nu) \right] - \nu \epsilon_z \quad (21)$$

thin wall:

$$\epsilon_\theta = \frac{(1-\nu^2) R p}{E t_c} - \nu \epsilon_z \quad (22)$$

axial strain: use (5) with $\sigma_z + \sigma_\theta$
from force balance (eg (1)-(2)) noting
that $\sigma_r \ll \sigma_\theta$

$$\epsilon_z = \frac{1}{E} (\sigma_z - \nu \sigma_\theta) = \frac{R p (1-2\nu)}{2 E t_c} \quad (23)$$

(D)

Eliminate strains by combining (3)-(5) with
(8) & (9). Solve for stress components:

$$\sigma_r = \frac{E}{1+\nu} \left\{ \frac{du}{dr} + \frac{\nu}{1-2\nu} \left(\frac{du}{dr} + \frac{u}{r} + \epsilon_z \right) \right\} \quad (24)$$

$$\sigma_\theta = \frac{E}{1+\nu} \left\{ \frac{u}{r} + \frac{\nu}{1-2\nu} \left(\frac{du}{dr} + \frac{u}{r} + \epsilon_z \right) \right\} \quad (25)$$

$$\sigma_z = \frac{E}{(1+\nu)} \left\{ \epsilon_z + \frac{\nu}{1-2\nu} \left(\frac{du}{dr} + \frac{u}{r} + \epsilon_z \right) \right\} \quad (26)$$

substitute (24) & (25) into (6):

$$\frac{d}{dr} \left(\frac{1}{r} \frac{d(ru)}{dr} \right) = 0 \quad (27)$$

solution:

$$u(r) = \frac{C_1}{r} + C_2 \quad (28)$$

Constants C_1 & C_2 may be determined by substituting (28) into (24) & applying BC's (1b). $u(r)$, however, is most easily determined by (9) & (21)

$$u(r) = r\epsilon_\theta = \frac{p(1+\nu)r}{E(R_o^2/R_i^2 - 1)} \left[\frac{R_o^2}{r^2} + (1-2\nu) \right] - \nu\epsilon_z r \quad (29)$$

(E)

$$\Delta t_c = u(R_o) - u(R_i)$$

but in thin-wall approx:

$$\Delta t_c = u(R_o) - u(R_i) \approx \left(\frac{du}{dr} \right) t_c$$

Using (8) obtain,

$$\therefore \epsilon_r = \frac{\Delta t_c}{t_c}$$

Problem 18.7

The yield stress is the sum of the long-range stresses due to the dislocation network and the stresses due to voids & unfaulted loops

$$\sigma_y = \sigma_{LR} + \sigma_{loop} + \sigma_{void}$$

From (Egn 18.23) & (Egn 18.24)

$$\sigma_{LR} = \frac{Gb}{2\pi l} = \frac{Gb\sqrt{\rho_d}}{2\sqrt{3}\pi}$$

From (Egn 18.62), with $\beta \sim 3$

$$\sigma_{loop} = \frac{\sqrt{2}Gb}{3} \sqrt{R_e N_e}$$

Before unfauling:

$$\sigma_y = Gb \left[\frac{\sqrt{\rho_d}}{2\sqrt{3}\pi} + \frac{\sqrt{2}}{3} \sqrt{R_e N_e} \right] + \sigma_{void}$$

After unfauling, loops join dislocation network

$$\rho_d' = \rho_d + 2\pi R_e N_e$$

$$\therefore \sigma_y' = Gb \left[\frac{\sqrt{\rho_d + 2\pi R_e N_e}}{2\sqrt{3}\pi} \right] + \sigma_{void}$$

$$\therefore (\Delta\sigma_y)_{unfauling} = \sigma_y' - \sigma_y$$

$$= Gb \left\{ \frac{\sqrt{\rho_d}}{2\sqrt{3}\pi} \left[\sqrt{1 + \frac{2\pi R_e N_e}{\rho_d}} - 1 \right] - \frac{\sqrt{2}}{3} \sqrt{R_e N_e} \right\}$$

Problem 18.8

σ_{xy} acts $\perp$ to $\vec{b}_l$, $\therefore$ no force.
 σ_{xx} acts in direction which
 gives force = $b_l \sigma_{xx}$ (see Fig 8.10b)

total force on loop by edge dislocation = $\sigma_{xx} b_l (2\pi R_e)$
 let, dW_l = work done by dislocation as loop
 expands by dR_e

$$dW = \sigma_{xx} b_l (2\pi R_e) dR_e$$

Integrate to obtain,

$$W = \sigma_{xx} b_l \pi R_e^2$$

Stress field of edge dislocation at center of loop (position (x, y)) given by

$$\sigma_{xx} = \sigma_{rr} - 2 \sin \theta \cos \theta \sigma_{re} \quad (\text{Egn 8.22a})$$

where

$$\left. \begin{aligned} \sigma_{rr} &= \frac{\mu \sin \theta}{r} \\ \sigma_{re} &= -\frac{\mu \cos \theta}{r} \end{aligned} \right\} \quad (\text{see Fig 8.8})$$

& where $\mu = \frac{G b_e}{2\pi(1-\nu)}$

Converting to cartesian coordinates
 $y = r \sin \theta$; $x = r \cos \theta$

$$\therefore \sigma_{rr} = \mu \frac{y}{x^2 + y^2}$$

$$\sigma_{re} = -\mu \frac{x}{x^2 + y^2}$$

$$\begin{aligned} \therefore \sigma_{xx} &= \mu \left[\frac{y}{x^2 + y^2} + \frac{2xy}{x^2 + y^2} \cdot \frac{x}{x^2 + y^2} \right] \\ &= \frac{\mu}{(x^2 + y^2)^2} \left[y(x^2 + y^2) + 2x^2y \right] \\ &= \frac{\mu y (3x^2 + y^2)}{(x^2 + y^2)^2} \end{aligned}$$

$$\mu = \frac{G b_e}{2\pi(1-\nu)}$$

Thus,

$$W = \pi R_e^2 b_e \mu \frac{y (3x^2 + y^2)}{(x^2 + y^2)^2}$$

Now,

$$\begin{aligned}
 F_x &= \frac{dW}{dx} \\
 &= \pi R_e^2 b_e y \left[\frac{6x}{(x^2+y^2)^2} - \frac{4x(3x^2+y^2)}{(x^2+y^2)^3} \right] \\
 &= \pi R_e^2 b_e y \frac{2xy(-3x^2+y^2)}{(x^2+y^2)^3}
 \end{aligned}$$

or

$$\frac{F_x}{\pi b_e y} = \frac{2\eta \xi (-3\eta^2 + \xi^2)}{\eta^2 + \xi^2} \equiv f(\eta)$$

where $\eta = \frac{x}{R_e}$, $\xi = \frac{y}{R_e}$

Problem 18.9

(A)

There are 36 edges where helium collects.
 Each edge is shared between 3 grains.
 $\therefore$ There are 12 edges per tetrakaidecahedron
 to accept the $M(8\sqrt{2}l^3)$ atoms of helium
 $\therefore$ Each edge contains:

$$m = \frac{M(8\sqrt{2}l^3)}{12} = \frac{2\sqrt{2}}{3} Ml^3 \text{ atoms He}$$

(B)

Work to form crack given by Egn 18.68
 with σ replaced by $(\sigma+p)$, plus the $p-v$
 work of expanding He in the crack:

$$W = -\frac{\pi(1-\nu)C^2(\sigma+p)^2l}{8G} + 2C\sigma l +$$

$$+ \frac{G(nb)^2l}{4\pi(1-\nu)} \ln\left(\frac{4R}{c}\right) - (\sigma+p)V_c - \int_{V_0}^{V_c} p dV_c$$

← extra term due
to gas ($p-v$ work)

$$\text{where } V_c = \frac{1}{2} nbcl$$

Use ideal gas law

$$pV_c = mRT$$

$$\therefore p = \frac{2mRT}{nbcl}$$

since

$$dV_c = \frac{1}{2} nbldc$$

$$pdV_c = \frac{2mRT}{nbcl} \cdot \frac{1}{2} nbldc = mRT \frac{dc}{c}$$

$$\int_{v_0}^{v_c} p dv_c = mRT \ln\left(\frac{C}{C_0}\right)$$

where C_0 = initial crack length.

Thus,

$$W = \left\{ -\frac{\pi(1-\nu)\sigma^2 l}{8G} \left[1 + \left(\frac{2mRT}{nb\sigma} \right) \frac{1}{C} \right]^2 C^2 + 2\gamma l C + \frac{lG(nb)^2}{4\pi(1-\nu)} \ln\left(\frac{4R}{C}\right) - \frac{1}{2} nb\sigma \left[1 + \left(\frac{2mRT}{nb\sigma} \right) \frac{1}{C} \right] C + \left(-mRT \ln \frac{C}{C_0} \right) \right\}$$

(C)

$$\text{Set } \frac{dW}{dC} = 0$$

$$0 = -\frac{\pi(1-\nu)\sigma^2 l}{8G} \left\{ 2 \left[1 + \left(\frac{2mRT}{nb\sigma} \right) \frac{1}{C} \right]^2 C - \left(\frac{2mRT}{nb\sigma} \right) \frac{1}{C^2} \left[1 + \left(\frac{2mRT}{nb\sigma} \right) \frac{1}{C} \right]^2 C \right\} +$$

$$+ 2\gamma l - \frac{G(nb)^2 l}{4\pi(1-\nu)} \frac{1}{C} - \frac{1}{2} nb\sigma - mRT \frac{1}{C}$$

$$0 = -\frac{2\pi(1-\nu)\sigma^2 l}{8G} C^2 - \frac{3\pi(1-\nu)\sigma^2 l}{8G} aC + \frac{\pi(1-\nu)\sigma^2 l}{8G} a^2 +$$

$$+ 2\gamma l C - \frac{G(nb)^2 l}{4\pi(1-\nu)} - \frac{1}{2} nb\sigma C - \frac{1}{2} nb\sigma a$$

where

$$a \equiv \left(\frac{2mRT}{nb\sigma} \right)$$

Divide by l & collect coefficients of powers of C :

$$0 = \left[\frac{2\pi(1-\nu)\sigma^2}{8G} \right] C^2 - \left[-\frac{1}{2} nb\sigma + 2\gamma - \frac{3\pi(1-\nu)\sigma^2}{8G} a \right] C + \left[\frac{G(nb)^2}{4\pi(1-\nu)} - \frac{\pi(1-\nu)\sigma^2}{8G} a^2 + \frac{1}{2} nb\sigma a \right]$$

Multiply by $\left(\frac{8G}{2\pi(1-\nu)\sigma^2}\right)$ to obtain:

$$0 = c^2 - \frac{8\gamma G}{\pi(1-\nu)\sigma^2} \left[1 - \frac{nb\sigma}{4\gamma} - \frac{3\pi(1-\nu)\sigma^2}{16\gamma G} a \right] +$$

$$+ \frac{8\gamma G}{\pi(1-\nu)\sigma^2} \cdot \frac{G(nb)^2}{8\pi\gamma(1-\nu)} \left[1 + \frac{\sigma 4\pi(1-\nu)}{2G(nb)} a + \right.$$

$$\left. + \left(-\frac{\pi(1-\nu)\sigma^2}{8G\gamma} \right) \left(\frac{8\pi(1-\nu)\gamma}{G(nb)^2} \right) \frac{a^2}{2} \right]$$

By defining

$$A \equiv \frac{G(nb)^2}{8\pi\gamma(1-\nu)} ; B \equiv \frac{8\gamma G}{\pi(1-\nu)\sigma^2}$$

we may rewrite the above equation as

$$0 = c^2 - B \left[1 - 2\sqrt{\frac{A}{B}} - \frac{3a}{2B} \right] c + AB \left[1 + \frac{2a}{\sqrt{AB}} - \frac{a^2}{2AB} \right]$$

Condition for neutral stability is obtained by setting discriminant of quadratic formula for c equal to 0. (See text) i.e:

$$B^2 \left(1 - 2\sqrt{\frac{A}{B}} - \frac{3a}{2B} \right)^2 = 4AB \left(1 + \frac{2a}{\sqrt{AB}} - \frac{a^2}{2AB} \right)$$

$$\left(1 - 4\sqrt{\frac{A}{B}} + 4\frac{A}{B} \right) - \left(\frac{3}{B} - \frac{6\sqrt{A}}{B^{3/2}} \right) a + \frac{9}{4B^2} a^2 = \frac{4A}{B} +$$

$$+ \frac{8\sqrt{A}}{B^{3/2}} a - \frac{2}{B^2} a^2$$

Thus,

$$0 = 1 - 4\sqrt{\frac{A}{B}} - \left(3 + 2\sqrt{\frac{A}{B}} \right) \left(\frac{a}{B} \right) + \frac{17}{4} \left(\frac{a}{B} \right)^2$$

Upon substitution for $a, A, & B$ in the above equation, one obtains a quadratic in σ which may be solved algebraically for σ . Since the result yields little physical insight, we will make a low pressure approximation, i.e. $(\frac{a}{B}) \ll 1$

first order approx:

① neglect $(\frac{a}{B})^2$

② when $(\frac{a}{B}) = 0$ result is

$$\left(\frac{A}{B}\right)_0 = \frac{1}{16}$$

③ use ② in coefficient of $\frac{a}{B}$

$$3 + 2\sqrt{\frac{A}{B}} \approx 3 + 2 \cdot \frac{1}{4} \approx \frac{7}{2}$$

$$\therefore 1 \approx 4\sqrt{\frac{A}{B}} + \frac{7}{2}\left(\frac{a}{B}\right)$$

$$1 \approx 4\sqrt{\frac{A}{B}} \left(1 + \frac{7(\frac{a}{B})}{8(\sqrt{\frac{A}{B}})}\right) \leftarrow \approx \frac{1}{4}$$

$$1 \approx 16 \frac{A}{B} \left(1 + \frac{7}{2}\left(\frac{a}{B}\right)\right)^2$$

$$\therefore B \approx 16A \left(1 + 7\left(\frac{a}{B}\right)\right)$$

Using definitions of A & B in above,

$$\frac{8\gamma G}{\pi(1-\nu)\sigma^2} = \frac{G(nb)^2/16}{8\pi\gamma(1-\nu)} \left(1 + 7\frac{a}{B}\right)$$

$$\frac{8^2\gamma^2}{4^2} = \sigma^2(nb)^2 \left(1 + 7\left(\frac{a}{B}\right)\right)$$

Taking $\sqrt{\quad}$ & using nb from Egn 18.74 obtain:

$$\sigma_{crit}(\sigma_{xy} - \sigma_i) \approx \frac{2G\gamma}{d} \left(1 + 7\frac{a}{B}\right)^{-1/2} \approx \frac{2G\gamma}{d} \left(1 - \frac{7}{2}\frac{a}{B}\right)$$

Now,

$$\left(\frac{a}{b}\right) = \frac{2mRT\pi(1-\nu)\sigma_{crit}^2}{nb l \sigma_{crit} \text{ BKG}} = \frac{mRT\pi(1-\nu)\sigma_{crit}}{4(\sigma_{xy}-\sigma_x) d/6 \text{ BKG}}$$

& assuming

$$\sigma_{crit} \approx 2(\sigma_{xy}-\sigma_x) ; \text{ i.e. } \sigma_x \approx 0, 2\sigma_{xy} \approx \sigma$$

$$\left(\frac{a}{b}\right) \approx \frac{\pi(1-\nu)mRT}{2l d}$$

Substituting for m from part (a)

$$\left(\frac{a}{b}\right) \approx \frac{\pi(1-\nu)2\sqrt{2}M d^3 RT}{6l d}$$

& taking $l \approx d$, obtain

$$\left(\frac{a}{b}\right) \approx \frac{\pi\sqrt{2}(1-\nu)M d^2 RT}{3l}$$

Thus with

$$(\sigma_{xy}-\sigma_x) \approx \frac{1}{2} \sigma_{crit}$$

$$\therefore \sigma_{crit} = \left(\frac{4Gd}{D}\right)^{1/2} \left(1 - \frac{7}{2}\left(\frac{a}{b}\right)\right)$$

$$= (\sigma_{crit})_{no \text{ gas}} \left(1 - \frac{7\sqrt{2}\pi(1-\nu)M d^2 RT}{12d}\right)$$

pressure of gas reduces initial stress

Problem 18.10

(A)

cylindrical coordinates

Vacancy diffusion equation in cylindrical coordinates is.

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_v}{\partial r} \right) + \frac{\partial^2 C_v}{\partial z^2} = 0$$

← {source free ($G_v = 0$)
no ϕ dependence}

let

$$\Theta = \frac{C_v - C_v^{\text{eq}} \exp\left(\frac{2\gamma}{R} \frac{z}{KT}\right)}{C_v^{\text{eq}} \exp\left(\frac{\sigma R}{KT}\right) - C_v^{\text{eq}} \exp\left(\frac{2\gamma}{R} \frac{z}{KT}\right)}$$

then,

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Theta}{\partial r} \right) + \frac{\partial^2 \Theta}{\partial z^2} = 0$$

with boundary conditions:

$$(1) C_v(R, z) = C_v^{\text{eq}} \exp\left(\frac{2\gamma}{R} \frac{z}{KT}\right)$$

(Egn 18.80)

$$(2) \left. \frac{\partial C_v(r, z)}{\partial r} \right|_{r=R} = 0$$

(Egn 18.81)

$$(3) \left. \frac{\partial C_v(r, z)}{\partial z} \right|_{z=0} = 0$$

$$(4) C_v\left(r, \pm \frac{W}{2}\right) = C_v^{\text{eq}} \exp\left(\frac{\sigma R}{KT}\right)$$

Transforming to Θ , these B.C.'s become

$$(1)' \Theta(R, z) = 0$$

$$(2)' \left. \frac{\partial \Theta}{\partial r} \right|_{r=R} = 0$$

$$(3) \quad \left. \frac{\partial \Theta}{\partial z} \right|_{z=0} = 0$$

$$(4) \quad \Theta(r, \pm \frac{W}{2}) = 1$$

(B)

$$\text{Let } \Theta(r, z) = P(r) Y(z)$$

Insert into diffusion equation & divide by Θ :

$$\frac{1}{Pr} \frac{d}{dr} \left(r \frac{dP}{dr} \right) = - \frac{1}{Y} \frac{d^2 Y}{dz^2} = -\alpha^2$$

Thus,

$$\frac{d^2 Y}{dz^2} - \alpha^2 Y = 0 \quad \Rightarrow \quad \text{soln } Y(z) = A \sinh \alpha z + B \cosh \alpha z$$

Apply BC # (3)' to obtain

$$A = 0 \quad \Rightarrow \quad Y(z) = B \cosh \alpha z$$

Also,

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dP}{dr} \right) + \alpha^2 P = 0 \quad \leftarrow \text{(Bessel's equation of order 0)}$$

which has solution

$$P(r) = E J_0(\alpha r) + G N_0(\alpha r)$$

where J_0 & N_0 are Bessel functions of first and second kind, respectively.

Apply BC # (2)' to obtain:

$$E J_0'(\alpha R) + G N_0'(\alpha R) = 0$$

$$\text{Since } J_0'(z) = J_1(z)$$

$$\& N_0'(z) = N_1(z)$$

we obtain

$$E J_1(\alpha R) + G N_1(\alpha R) = 0$$

Thus,

$$P(r) = E \left[J_0(\alpha r) - \frac{J_1(\alpha R)}{N_1(\alpha R)} N_0(\alpha r) \right]$$

Applying BC # (1)' we find

$$P(R) = 0 \Rightarrow J_0(\alpha R) N_1(\alpha R) = J_1(\alpha R) N_0(\alpha R) \quad (1)$$

The roots satisfying the above equation provide α_n such that:

$$\Theta(r, z) = \sum_{n=0}^{\infty} A_n \cosh(\alpha_n z) \left\{ J_0(\alpha_n r) - \frac{J_1(\alpha_n R)}{N_1(\alpha_n R)} N_0(\alpha_n r) \right\} \quad (2)$$

Finally, applying BC # (u)',

$$\Theta(r, \pm \frac{w}{2}) = 1 = \sum_{n=0}^{\infty} A_n \cosh(\alpha_n \frac{w}{2}) \left\{ J_0(\alpha_n r) - \frac{J_1(\alpha_n R)}{N_1(\alpha_n R)} N_0(\alpha_n r) \right\}$$

define $\{M_0(\alpha_n r)\}$

$$1 = \sum_{n=0}^{\infty} A_n \cosh(\alpha_n \frac{w}{2}) \{M_0(\alpha_n r)\} \quad (3)$$

To find coefficients A_n , multiply both sides of above equation by $r M_0(\alpha_m r)$ & integrate from R to R

By orthogonality property obtain

$$\begin{aligned} \boxed{m \neq n}: \quad I &\equiv \int_R^R r M_0(\alpha_n r) M_0(\alpha_m r) dr = \frac{1}{(\alpha_n^2 - \alpha_m^2)} \left\{ \alpha_m r M_0(\alpha_n r) M_1'(\alpha_m r) + \right. \\ &\quad \left. + (-\alpha_n r) M_1(\alpha_n r) M_0(\alpha_m r) \right\} \Big|_R \\ &= \frac{1}{(\alpha_n^2 - \alpha_m^2)} \left\{ \alpha_m [R M_0(\alpha_n R) M_1(\alpha_m R)] - \alpha_m [R M_0(\alpha_n R) \right. \\ &\quad \cdot M_1(\alpha_m R)] - \alpha_n [R M_1(\alpha_n R) M_0(\alpha_m R)] + \alpha_n [R M_1(\alpha_n R) \cdot \\ &\quad \cdot M_0(\alpha_m R)] \Big\} \end{aligned}$$

Noting that

$$M_{-n}(\alpha_n R) = (-1)^n M_n(\alpha_n R)$$

$$\& M_1(\alpha_n R) = J_1(\alpha_n R) - \frac{J_1(\alpha_n R)}{N_1(\alpha_n R)} N_1(\alpha_n R) = 0$$

obtain,

$$\begin{aligned} I &= \frac{1}{(\alpha_n^2 - \alpha_m^2)} \left\{ \alpha_m [-R M_0(\alpha_n R) M_1(\alpha_m R)] + \alpha_n [R M_1(\alpha_n R) M_0(\alpha_m R)] \right\} \\ &= \frac{1}{(\alpha_n^2 - \alpha_m^2)} \left\{ R [\alpha_n M_1(\alpha_n R) M_0(\alpha_m R) - \alpha_m M_0(\alpha_n R) M_1(\alpha_m R)] \right\} \end{aligned}$$

Finally note that

$$M_0(\alpha_n R) = J_0(\alpha_n R) - \frac{J_1(\alpha_n R)}{N_1(\alpha_n R)} N_0(\alpha_n R) = 0$$

because of Egn (1)

Thus,

$$I = 0 \quad \text{for } m \neq n$$

For $m=n$:

$$\begin{aligned} I &= \int_R^{\infty} r M_0^2(\alpha_n r) dr = \frac{1}{2} r^2 [M_0^2(\alpha_n r) + M_1^2(\alpha_n r)] \Big|_R^{\infty} \\ &= \frac{1}{2} \left\{ \infty^2 [M_0^2(\alpha_n \infty) + M_1^2(\alpha_n \infty)] - R^2 [M_0^2(\alpha_n R) + M_1^2(\alpha_n R)] \right\} \quad (4) \end{aligned}$$

where

$$M_1(\alpha_n r) = - \frac{dM_0(\alpha_n r)}{d(\alpha_n r)} = J_1(\alpha_n r) - \frac{J_1(\alpha_n R)}{N_1(\alpha_n R)} N_1(\alpha_n r)$$

Thus, using Egn (3),

$$\int_R^{\infty} r M_0(\alpha_n r) dr = A_n \cosh\left(\alpha_n \frac{W}{2}\right) I_{(n=m)} + \underbrace{0}_{\substack{n_1 \\ n=m \text{ term}}} \quad \underbrace{\uparrow}_{\text{all other terms}}$$

$$A_n = \frac{\int_R^{\infty} r M_0(\alpha_n r) dr}{\cosh\left(\alpha_n \frac{W}{2}\right) I_{(n=m)}}$$

Now,
$$\int_R^R r M_0(\alpha_n r) dr = - \frac{1}{\alpha_n^2} (\alpha_n r) M_1(\alpha_n r) \Big|_R^R$$

$$= \frac{1}{\alpha_n} [R M_1(\alpha_n R) - R M_1(\alpha_n R)]$$

So
$$A_n = \frac{\frac{1}{\alpha_n} [R M_1(\alpha_n R) - R M_1(\alpha_n R)]}{\cosh(\alpha_n \frac{W}{2}) I_{n=m}}$$

where $I_{n=m}$ is given by Egn (4)

&
$$\Theta(r, z) = \sum_{n=0}^{\infty} A_n \cosh(\alpha_n z) M_0(\alpha_n r) \quad (\text{Egn 2})$$

(C)

Rate of void growth is obtained by a "volume balance"

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = 2R \int_0^{W/2} J(z) dz$$

current of "volume" to annulus

$$4\pi R^2 \frac{dR}{dt} = 2R \int_0^{W/2} (2\pi R) \left\{ D_{vgb} \frac{\partial C_v}{\partial r} \right\}_R dz$$

$$\therefore \frac{dR}{dt} = \frac{D_{vgb} R C_v^{\infty}}{R} \left[\exp\left(\frac{\sigma R}{kT}\right) - \exp\left(\frac{2\gamma' R}{R kT}\right) \right] \int_0^{W/2} \left(\frac{\partial \Theta}{\partial r} \right)_R dz$$

Since $\sigma R \ll kT$ & $\frac{2\gamma' R}{R} \ll kT$ after nucleation,

we can write:

$$\frac{dR}{dt} \approx \frac{D_{vgb} R}{R kT} \left(\sigma - \frac{2\gamma'}{R} \right) \int_0^{W/2} \left(\frac{\partial \Theta}{\partial r} \right)_R dz$$

Since $\left(\frac{\partial \Theta}{\partial r} \right)_R = - \sum_{n=0}^{\infty} A_n \cosh(\alpha_n z) \alpha_n M_1(\alpha_n R)$

$$\therefore \frac{dR}{dt} = - \frac{D_{vgb} R}{R kT} \left(\sigma - \frac{2\gamma'}{R} \right) \sum_{n=0}^{\infty} A_n \sinh\left(\frac{\alpha_n W}{2}\right) M_1(\alpha_n R)$$

Problem 18.11

$$\sigma = \sigma_a \times \frac{1}{\left(\text{fraction of initial grain boundary area not occupied by bubbles} \right)}$$

where

σ_a = applied stress.

$$\therefore \sigma = \sigma_a \times \left(\frac{1}{1 - f_b} \right)$$

where

f_b = fraction of grain boundary occupied by bubbles.

$$\text{Now, } f_b \approx \left(\frac{R}{\bar{R}} \right)^2$$

$$\therefore \sigma \approx \frac{\sigma_a}{1 - \left(\frac{R}{\bar{R}} \right)^2}$$

← use in Egn 18.85

Problem 18.12Major He^4 production reactions in Type 304 s.s.Thermal flux $\text{B}^{10}(n, \alpha)$ Fast flux $\text{B}^{10}(n, \alpha)$ $\text{Ni}(n, \alpha)$ $\text{Fe}(n, \alpha)$ $\text{Cr}(n, \alpha)$

let

 N = number density of atoms ϕ_T = thermal flux ϕ_F = fast flux

Atom balance differential equations:

$$\frac{dN_{\text{Fe}}}{dt} = -N_{\text{Fe}} \sigma_F^{\text{Fe}} \phi_F \quad (1)$$

$$\frac{dN_{\text{Cr}}}{dt} = -N_{\text{Cr}} \sigma_F^{\text{Cr}} \phi_F \quad (2)$$

$$\left. \begin{aligned} \frac{dN_{\text{B}^{10}}}{dt} &= -N_{\text{B}^{10}} \sigma_T^{\text{B}^{10}} \phi_T - N_{\text{B}^{10}} \sigma_F^{\text{B}^{10}} \phi_F \\ &= -N_{\text{B}^{10}} (\sigma_T^{\text{B}^{10}} \phi_T + \sigma_F^{\text{B}^{10}} \phi_F) \end{aligned} \right\} \quad (3)$$

For Ni we can decouple fast & thermal components if we assume only small fraction of Ni will be consumed ($N_{\text{Ni}}(t) \cong N_{\text{Ni}}^0$), i.e. write separate equations for fast & thermal He production, then add to obtain total He production by Ni. Thus, for fast component

$$\begin{aligned} \frac{dN_{\text{Ni}}^{(F)}}{dt} &= -N_{\text{Ni}} \sigma_F^{\text{Ni}} \phi_F \\ &\cong -N_{\text{Ni}}^{(F)} \sigma_F^{\text{Ni}} \phi_F \end{aligned} \quad (4)$$

where

 $N_{\text{Ni}}^{(F)}$ = number of Ni atoms if $\phi_T = 0$

$$N_2 = \left(\frac{\lambda_1}{\lambda_2 - \lambda_1} \right) N_1^0 \left(e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) + N_2^0 e^{-\lambda_2 t} \quad (14)$$

$$\text{where } \lambda_1 = \sigma_T^{N_{58}} \phi_T$$

$$\lambda_2 = \sigma_T^{N_{59}} \phi_T$$

Now,

$$N_1 + N_2 + N_3 = N_1^0 + N_2^0$$

$$\therefore N_3 = N_1^0 + N_2^0 - N_1 - N_2 \quad (15)$$

Similarly, for equations 7, 8, 9, 10, the number of He atoms/cm³ from X(n, α) reactions = the number of X atoms/cm³ "burnt" = $N_X^0 - N_X(t)$

Thus,

$$N_{He} = N_{Fe}^0 (1 - e^{-\sigma_F^{Fe} \phi_F t}) + N_{Cr}^0 (1 - e^{-\sigma_F^{Cr} \phi_F t}) +$$

$$+ N_{B^{10}}^0 (1 - e^{-(\sigma_T^{B^{10}} \phi_T + \sigma_F^{B^{10}} \phi_F) t}) + N_{Ni}^0 (1 - e^{-\sigma_F^{Ni} \phi_F t}) +$$

$$+ \left[N_{N_{58}}^0 (1 - e^{-\sigma_T^{N_{58}} \phi_T t}) + N_{N_{59}}^0 (1 - e^{-\sigma_T^{N_{59}} \phi_T t}) + \right.$$

$$\left. + \left(\frac{-\lambda_1}{\lambda_2 - \lambda_1} \right) N_{N_{58}}^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \right] \quad (16)$$

Now,

$$\phi_F = 10^{15} \text{ n/cm}^2\text{-sec} \quad t \approx 3.15 \times 10^7 \text{ sec.}$$

$$\phi_T = 10^{13} \text{ n/cm}^2\text{-sec}$$

$$\sigma_F^{Fe} = 0.23 \times 10^{-27} \text{ cm}^2 \rightarrow t\lambda^{Fe} = \sigma_F^{Fe} \phi_F t = 7.24 \times 10^6$$

$$\sigma_F^{Cr} = 0.2 \times 10^{-27} \text{ cm}^2 \rightarrow t\lambda^{Cr} = \sigma_F^{Cr} \phi_F t = 6.3 \times 10^6$$

$$\sigma_F^{Ni} = 4.2 \times 10^{-27} \text{ cm}^2 \rightarrow t\lambda^{Ni} = \sigma_F^{Ni} \phi_F t = 1.32 \times 10^4$$

$$\sigma_F^{B^{10}} = 623 \times 10^{-27} \text{ cm}^2 \rightarrow t\lambda^{B^{10}} = \sigma_F^{B^{10}} \phi_F t = 1.96 \times 10^2$$

$$\sigma_T^{B^{10}} = 3840 \times 10^{-24} \text{ cm}^2 \rightarrow t\lambda_T^{B^{10}} = \sigma_T^{B^{10}} \phi_T t = 1.21$$

$$\sigma_T^{N_{58}} = 464 \times 10^{-24} \text{ cm}^2 \rightarrow t\lambda_1 = 1.39 \times 10^{-3}$$

$$\sigma_T^{N_{59}} = 13.0 \times 10^{-24} \text{ cm}^2 \rightarrow t\lambda_2 = 4.1 \times 10^{-3}$$

Also,

$$N_i^0 = f_i \cdot \frac{\rho_{ss}}{A_i} \times 6.02 \times 10^{23} \frac{\text{atoms}}{\text{mole}} \times I_i$$

where

 $f_i = \text{weight fraction of element } i = (\text{weight } \%) / 100$
 $\rho_{ss} = \text{mass density of stainless steel} \approx 8.32 \text{ gm/cm}^3$
 $A_i = \text{atomic weight of element } i$
 $I_i = \text{natural isotope fraction of isotope } i$

Therefore,

$$N_{Fe}^0 = \left(\frac{70}{100}\right) \cdot \frac{8.32}{55.85} \times 6.02 \times 10^{23} = 6.28 \times 10^{22} \left[\frac{\text{atoms}}{\text{cm}^3}\right]$$

$$N_{Cr}^0 = \left(\frac{19}{100}\right) \cdot \frac{8.32}{52.0} \times 6.02 \times 10^{23} = 1.83 \times 10^{22}$$

$$N_{Ni}^0 = \left(\frac{0.005}{100}\right) \cdot \frac{8.32}{10.01} \times 6.02 \times 10^{23} \times 0.196 = 4.90 \times 10^{17}$$

$$N_{Ni}^0 = \left(\frac{9}{100}\right) \cdot \frac{8.32}{58.71} \times 6.02 \times 10^{23} = 7.68 \times 10^{21}$$

$$N_{Ni}^0 = \left(\frac{9}{100}\right) \cdot \frac{8.32}{58.71} \times 6.02 \times 10^{23} \times 0.679 = 5.21 \times 10^{21}$$

$$N_{Ni}^0 = \left(\frac{9}{100}\right) \cdot \frac{8.32}{59} \times 6.02 \times 10^{23} \times 0 = 0$$

$$N_{Mn}^0 = \left(\frac{0.8}{100}\right) \cdot \frac{8.32}{54.94} \times 6.02 \times 10^{23} = 7.29 \times 10^{20}$$

$$N_{Si}^0 = \left(\frac{0.5}{100}\right) \cdot \frac{8.32}{28.09} \times 6.02 \times 10^{23} = 8.92 \times 10^{20}$$

$$N_{Mo}^0 = \left(\frac{0.2}{100}\right) \cdot \frac{8.32}{95.94} \times 6.02 \times 10^{23} = 1.04 \times 10^{20}$$

$$N_C^0 = \left(\frac{0.06}{100}\right) \cdot \frac{8.32}{12.01} \times 6.02 \times 10^{23} = 2.50 \times 10^{20}$$

$$N^0 \approx \sum N_i^0 \times \left(\frac{100\%}{99.5605\%}\right) \approx 9.08 \times 10^{22} \times \frac{100}{99.5605}$$

$$\approx 9.12 \times 10^{22} / \text{cm}^3$$

where

 $N^0 = \text{initial number of atoms in } 1 \text{ cm}^3 \text{ s.s.}$

& where factor $\sim \left(\frac{100}{99.5605}\right)$ compensates for "minor elements" not counted in sum by assuming they are of same "average atomic mass" as "major elements".

Approximating,

$$e^{-\lambda t} \approx 1 - \lambda t + \frac{(\lambda t)^2}{2} \dots \quad \text{for } |\lambda t| \ll 1$$

obtain, using Eqn (16):

$$\begin{aligned} N_{He} &\approx (6.28 \times 10^{22})(7.24 \times 10^{-6}) + \\ &+ (1.83 \times 10^{22})(6.3 \times 10^{-6}) + (4.90 \times 10^{17}) \left(1 - e^{-(1.21 + 1.96 \times 10^{-2})} \right) + \\ &+ (7.68 \times 10^{21})(1.32 \times 10^{-4}) + (5.21 \times 10^{21}) \left[1 - 1 + \lambda_1 t - \frac{\lambda_1 t^2}{2} + \right. \\ &\quad \left. + \left(\frac{-\lambda_1}{\lambda_2 - \lambda_1} \right) \left(1 - \lambda_1 t + \frac{(\lambda_1 t)^2}{2} - 1 + \lambda_2 t - \frac{(\lambda_2 t)^2}{2} \right) \right] \\ &\approx 4.55 \times 10^{17} + 1.15 \times 10^{17} + (4.90 \times 10^{17})(1 - 0.292) + \\ &\quad + (1.01 \times 10^{18}) + (5.21 \times 10^{21}) \underbrace{\left[\frac{\lambda_1 t (\lambda_2 t)}{2} \right]}_{\approx 2.85 \times 10^{-6}} \\ \therefore N_{He} &\approx 1.95 \times 10^{18} \text{ /cm}^3 \end{aligned}$$

$$\therefore \frac{N_{He}}{N^0} \times 10^6 = \frac{1.95 \times 10^{18}}{9.12 \times 10^{22}} \times 10^6 \approx 21.4 \text{ ppm He}^4$$

Note: Thermal nickel term makes only small addition to N_{He} relative to other terms & may be neglected in less exacting analysis.

Problem 18.13

$$\sigma = \frac{1}{2} \sigma_{crit} = \frac{1}{2} \left(\frac{4}{3\sqrt{3}} \frac{\gamma}{R_0} \right) = \frac{2}{3\sqrt{3}} \frac{\gamma}{R_0}$$

where σ_{crit} is given by Egn 18.98.

Substitute for σ in Egn 18.97:

$$\frac{2}{3\sqrt{3}} \frac{\gamma}{R_0} = \frac{2\gamma}{R} \left(1 - \frac{R_0^2}{R^2} \right)$$

or

$$R^3 - R_0 3\sqrt{3} R^2 + 3\sqrt{3} R_0^3 = 0, \text{ where } R_0 = 1000 \text{ \AA}.$$

The above cubic equation in R may be solved numerically or analytically (by general cubic formula) to yield real > 0 root:

$$R = \sqrt{3} (1 + (2 \cos 20^\circ)) R_0 \cong 4.987 R_0$$

$$\therefore R \cong 4987 \text{ \AA}$$

When 2 bubbles coalesce, the stress-free radius, R_0' , is (from Egn 18.44)

$$\left. \begin{array}{l} R_0^2 \propto m \\ R_0'^2 \propto 2m \end{array} \right\} \Rightarrow R_0' = \sqrt{2} R_0$$

The stress remains the same & applying Egn 18.97 to the coalesced bubble of radius R' , obtain:

$$\sigma = \frac{2\gamma}{3\sqrt{3} R_0} = \frac{2\gamma}{R'} \left(1 - \frac{R_0'^2}{R'^2} \right) = \frac{2\gamma}{R'} \left(1 - 2 \frac{R_0^2}{R'^2} \right)$$

or

$$R'^3 - R_0 3\sqrt{3} R'^2 + 6\sqrt{3} R_0^3 = 0; R_0 = 1000 \text{ \AA}$$

Numerical or analytical solution yields

$$R' = \sqrt{3} R_0$$

$$\cong 1732 \text{ \AA}$$

Note for this example, $R' < R$

Problem 18.14

- (A) Equilibrium conditions (no stress):
at bubble surface

$$p = \frac{2\gamma}{r} \quad (1)$$

at intersection with grain boundary,

$$\gamma_{gb} = 2\gamma \cos \theta \quad (2)$$

ideal gas law

$$pV = mRT$$

To find volume of top half of lenticular bubble,
integrate $dV = \pi (\rho \sin \theta')^2 dz'$ from $z' = \rho \cos \theta$ to $z' = \rho$:

$$\frac{1}{2} V = \int_{\rho \cos \theta}^{\rho} \pi \rho^2 \sin^2 \theta' dz' \quad ; \quad \text{let } \begin{cases} \mu = \cos \theta \\ \mu' = \cos \theta' \end{cases}$$

$$= \int_{\rho \mu}^{\rho} \pi \rho^2 (1 - \mu'^2) dz'$$

$$= \pi \rho^2 \int_{\rho \mu}^{\rho} \left(1 - \frac{z'^2}{\rho^2}\right) dz'$$

$$= \pi \rho^3 \left[(1 - \mu) - \frac{(1 - \mu^3)}{3} \right] = \frac{\pi \rho^3}{3} (3 - 3\mu - 1 + \mu^3)$$

$$\therefore V = \frac{2\pi \rho^3}{3} (1 - \mu)^2 (2 + \mu) \quad (4)$$

Eliminating p from (1)&(3) obtain,

$$\frac{2\gamma}{\rho} = \frac{mkT}{v}$$

Using (4),

$$\frac{2\gamma}{\rho} = \frac{3mkT}{2\pi\rho^3(1-\mu)^2(2+\mu)}$$

$$\therefore \rho = \left[\frac{3mkT}{4\pi\gamma(1-\mu)^2(2+\mu)} \right]^{1/2} \quad (5)$$

↖ when $\gamma_{gb}=0, \mu=0$, (5) reduces to Eqn 18.94.

(B)

With tensile stress (hydrostatic), Eq (1) becomes

$$p + \sigma = \frac{2\gamma}{\rho}$$

where ρ = new radius of curvature.

Eqn(3) & (4) imply

$$p = \frac{mkT}{v} = \frac{3mkT}{2\pi\rho^3(1-\mu)^2(2+\mu)} \quad (\mu \text{ unchanged})$$

$$\therefore \sigma = \frac{2\gamma}{\rho} - \frac{3mkT}{2\pi\rho^3(1-\mu)^2(2+\mu)} \quad \leftarrow \text{analog of Eqn 18.97} \quad (6)$$

If we plot $\sigma(\rho)$ for fixed m, μ , we obtain curves similar to those in Fig 18.41.

$$\sigma = \frac{2\gamma}{\rho} - \frac{a}{\rho^3} \quad (6a)$$

$$\text{where } a = \frac{3mkT}{2\pi(1-\mu)^2(2+\mu)}$$

(C)

Critical stress condition:

$$\frac{d\sigma}{d\rho} = 0$$

$$\frac{d\sigma}{dp} = -\frac{2\gamma}{p^2} + \frac{3a}{p^4} = 0$$

$$\therefore p = \sqrt{\frac{3a}{2\gamma}} \quad \text{at } \sigma = \sigma_{\text{crit.}}$$

Substitute into (6a):

$$\sigma_{\text{crit}} = 2\gamma \sqrt{\frac{2\gamma}{3a}} - a \left(\frac{2\gamma}{3a} \right)^{3/2}$$

or

$$\sigma_{\text{crit}} = \frac{2}{3} \frac{(2\gamma)^{3/2}}{\sqrt{3a}} \quad (7)$$

Now, for spherical bubble,

$$\mu = 0; a = a^* = \frac{3mkT}{4\pi}$$

$$\text{Thus } \sigma_{\text{crit}}^* = \frac{2}{3} \frac{(2\gamma)^{3/2}}{\sqrt{3a^*}}$$

$$\therefore \frac{\sigma_{\text{crit}}}{\sigma_{\text{crit}}^*} = \sqrt{\frac{a^*}{a}} = \frac{(1-\mu)\sqrt{2+\mu}}{\sqrt{2}} \quad (8)$$

$$\text{When } \frac{\gamma_{gb}}{\gamma} = 0.4, \mu = 0.2 \quad (\text{using Egn 2})$$

Thus

$$\frac{\sigma_{\text{crit}}}{\sigma_{\text{crit}}^*} \approx 0.84 \quad \leftarrow 16\% \text{ reduction of critical stress}$$

See G.W. Lewthwaite, J. Nucl. Mater. 42, 235 (1972) for additional details.

Problem 18.15

$$\epsilon_f = \left(\frac{\pi^2}{12Nd^3} \right)^{1/2}$$

(Egn 18.103)

$$\therefore N = \frac{\pi^2}{\epsilon_f^2 12d^3} \quad (1)$$

Also

$$R_{\text{crit}} \approx 0.77 \frac{\gamma}{\sigma}$$

(Egn 18.98) (2)

Using Egn 18.99,

$$M = \frac{4}{3} \pi R_{\text{crit}}^2 \left(\frac{2\gamma}{kT} \right) N \quad (3)$$

Substituting (1) & (2) into (3) obtain:

$$\begin{aligned} M &= \frac{4}{3} \pi (0.77)^2 \frac{\gamma^2}{\sigma^2} \frac{2\gamma}{kT} \frac{\pi^2}{\epsilon_f^2 12d^3} \\ &= \frac{4\pi^3 (0.77)^2 (1500)^3}{18 \left(2 \times 10^5 \frac{\text{N}}{\text{m}^2} \times 10^4 \frac{\text{J}}{\text{m}^2} \right)^2 (1.38 \times 10^{-6}) (1273) (0.01)^2 (15 \times 10^{-4} \text{m})^3} \\ &\approx 5.81 \times 10^{16} \text{ /cm}^3 \end{aligned}$$

$$\text{fraction He} = \frac{M}{N_s} = \frac{M}{(1/2)} = \frac{M a_0^3}{4}$$

for fcc steel, $a_0 \approx 3.52 \times 10^{-8} \text{ m}$

$$\therefore \text{ppm He} = \frac{(5.81 \times 10^{16}) (3.52 \times 10^{-8})^3}{4} \times 10^6$$

$$= 0.63 \text{ ppm}$$

Problem 18.16

(A)

Assuming cubic shape for grain
He production rate / grain = $Gd^3 \frac{\text{He atoms}}{\text{sec}}$

Number of bubble sites per grain = $\frac{N_{gb} 6d^2}{2}$

← each face shared by 2 grains.

∴ rate of He atom capture / site $\equiv Q = \frac{Gd^3}{3d^2 N_{gb}}$

$$Q = \frac{Gd}{3N_{gb}} \quad \begin{array}{l} \text{He atoms} \\ \text{site-sec} \end{array}$$

(B)

Since bubble is at equilibrium for $t \leq t_c$,

$$\sigma + p - \frac{2\gamma}{R} = 0$$

By ideal gas law,

$$p\left(\frac{4}{3}\pi R^3\right) = mKT$$

where $m = Qt = \text{He atoms in the bubble at time } t$

Combining the preceding 3 equations,

$$\sigma + \left[\frac{QKT}{\frac{4}{3}\pi} \right] \frac{t}{R^3} - \frac{2\gamma}{R} = 0$$

This equation is equivalent to Egn 18.97 & a plot of the formula would look like Fig. 18.41 except that the parameter would be t , not R_0 .

The specified stress intersects each curve at a unique value of R , so that the curve $R(t)$ for $t < t_c$ can be obtained. When the stress line is tangent to the peak of the curve, $t = t_c$. At this point,

$$\left. \frac{d\sigma}{dR} \right|_{R_c} = 0$$

But the equilibrium condition must also hold at t_c :

$$\sigma + \left[\frac{QKT}{\frac{4}{3}\pi} \right] \frac{t_c}{R_c^3} - \frac{2\gamma}{R_c} = 0$$

Combining above 2 equations yields:

$$t_c = \frac{4\pi}{3} \left(\frac{2\gamma}{KT} \right) \frac{1}{Q} \left(\frac{4}{3\sqrt{3}} \frac{\gamma}{\sigma} \right)^2$$

The bubble radius at t_c may also be determined:

$$R_c = \frac{4}{3} \frac{\gamma}{\sigma}$$

(C)

For $t > t_c$, growth is given by Egn 18.102, with $p = p(R, t)$ known, i.e.

$$\frac{dR}{dt} = \frac{wDgbR}{Q^2KT} \left[\sigma - \frac{2\gamma}{R} + \left(\frac{QKT}{\frac{4}{3}\pi} \right) \frac{t}{R^3} \right] \frac{(R/R_c)^2 - 1}{2\ln(R/R_c) - 1 + (R/R_c)^2}$$

The rupture time is obtained by numerical integration of the above formula, starting at $R = R_c$ at $t = t_c$ & stopping at $t = t_R$ at which $R = R_f = \sqrt{\frac{\pi}{4}} R$. Note that Eq 18.88 does not apply in this case because (dR/dt) is not separable in R & t .

(D)

Elongation at fracture given by Egn 18.89

$$\epsilon_F = \frac{\pi}{6d\sqrt{Ngb}}$$

Problem 18.17

Assuming steady state creep,

$$t_R = \frac{\epsilon_F}{\dot{\epsilon}}$$

Also,

$$\dot{\epsilon} = A \sigma^n \quad (\text{from Egn 8.46})$$

where A, n can be obtained from Fig 10.29

Additionally, from Fig 18.30.

$$\epsilon_F = B(\phi t)^m$$

where B & m can be obtained from Fig 18.30

Thus,

$$t_R = \frac{B(\phi t)^m}{A \sigma^n}$$

Using hoop stress-fission gas pressure relation,

$$\sigma = \frac{pD}{2t_{cl}} \quad (\text{Egn 18.8a})$$

& from statement of problem

$$p = ct$$

$$\therefore t_R = \frac{B(\phi t)^m}{A} \left(\frac{2t_{cl}}{ctD} \right)^n$$

Using life fraction approach, (Egn 18.106), obtain:

$$\sum_{k=1}^{t_F/\Delta t} \frac{\Delta t}{t_R(k\Delta t)} = 1 \Rightarrow \int_1^{t_F/\Delta t} \frac{\Delta t dk}{t_R(k\Delta t)} = 1$$

where t_F is divided into equal intervals of Δt

Let

$$k\Delta t = t \quad \& \therefore dk = \frac{dt}{\Delta t}$$

Thus,

$$\int_1^{t_F/\Delta t} \frac{\Delta t dK}{t_R(K\Delta t)} = \int_0^{t_F} \frac{dt}{t_R(t)} = 1$$

$$\int_0^{t_F} dt A \left(\frac{CD}{2t_{cl}} \right)^n \frac{t^n}{B\phi^m t^m} = 1$$

$$\int_0^{t_F} t^{n-m} dt = \left(\frac{2t_{cl}}{CD} \right)^n \frac{B\phi^m}{A}$$

$$\frac{t^{n-m+1}}{(n-m+1)} \Big|_0^{t_F} = \left(\frac{2t_{cl}}{CD} \right)^n \frac{B\phi^m}{A} \quad \text{for } n-m \neq -1$$

or

$$t_F = \left[\left(\frac{2t_{cl}}{CD} \right)^n \frac{B\phi^m}{A} (n-m+1) \right]^{\frac{1}{n-m+1}}$$

valid for $n-m+1 > 0$

For $n-m+1 \leq 0$, $t_F = \infty$

PROBLEM 19.1

Since $\frac{\Delta V}{V} = \frac{\text{volume of voids}}{\text{volume of metal}}$

The number of vacancies in the voids is $\frac{(\Delta V/V)}{\Omega}$ per unit volume of metal.

The total number of vacancy created at fluence Φt is $\rho \Sigma_s \Phi t$ (per unit volume of metal)

$\therefore$ Fraction of vacancies created which are in voids = $\frac{(\Delta V/V)}{\rho \Sigma_s \Omega \Phi t}$

At a fluence of 5×10^{22} Fig 19.4 shows that

the swelling is $\sim 3\%$, Take $\rho = 30$, $\Sigma_s = 0.2 \text{ cm}^{-1}$
 $\Omega = 12 \text{ \AA}^3$

$$\Rightarrow \frac{(\Delta V/V)}{\rho \Sigma_s \Omega \Phi t} = \frac{3 \times 10^{-2}}{(30) \times (0.2) \times (12 \times 10^{-24}) (5 \times 10^{22})}$$

$$= 0.8 \%$$

PROBLEM 19.2

Eq (19-43) is;
$$\frac{h(m)}{h(m+1)} = \frac{N^{eq}(m)}{N^{eq}(m+1)} + \frac{\beta_i}{\beta_v} = F(m)$$

then
$$\frac{h(m+1)}{h(m)} = [F(m)]^{-1}$$

Taking log of both sides,
$$\ln \left[\frac{h(m+1)}{h(m)} \right] = -\ln F(m)$$

Summing from $m'=0$ to $m'=m-1$

$$\sum_{m'=0}^{m-1} \ln \left[\frac{h(m'+1)}{h(m')} \right] = \ln \prod_{m'=0}^{m-1} \frac{h(m'+1)}{h(m')} = \ln \frac{h(m)}{h(0)} = -\sum_{m'=0}^{m-1} \ln F(m')$$

From Eq (19-36) it is seen that;

$$\lim_{m \rightarrow \infty} \frac{N^{eq}(m)}{N^{eq}(m+1)} = \lim_{m \rightarrow \infty} \frac{1}{\gamma_v} \exp \left[\frac{2}{3} \gamma m^{-1/3} \right] \rightarrow \infty$$

However
$$\frac{\beta_i}{\beta_v} \leq 1$$

thus
$$\lim_{m \rightarrow \infty} \frac{h(m+1)}{h(m)} = \frac{N^{eq}(m+1)}{N^{eq}(m)}$$

Clearly, $h(0)$ can be chosen as $N^{eq}(0) = N_s$

So,
$$\ln \left[\frac{h(m)}{N_s} \right] = -\sum_{m'=0}^{m-1} \ln \left[\frac{N^{eq}(m')}{N^{eq}(m'+1)} + \frac{\beta_i}{\beta_v} \right]$$

Which is eq (19.44)

PROBLEM 19.3

Classical Nucleation Theory:

$$h(m) = N^{\text{st}}(m) = N_s \exp [m \ln s_v - \frac{2}{3} \xi m^{2/3}]$$

$$\text{where } \xi = (36 \pi \Omega^2)^{1/3} \frac{\gamma}{kT}$$

$$I = \frac{\beta_v(m_c)}{\int_0^\infty \frac{dm}{N^{\text{st}}(m)}} \quad \text{Eq (19.47)}$$

$$\text{Let } f(m) = m \ln s_v - \frac{2}{3} \xi m^{2/3}$$

f has a maximum value at $m_c = \left(\frac{2\xi}{3 \ln s_v}\right)^3$ which is the critical cluster size.
Expand $f(m)$ about m_c :

$$f(m) = f(m_c) + \left(\frac{df}{dm}\right)_{m_c} (m - m_c) + \frac{1}{2} \left(\frac{d^2f}{dm^2}\right)_{m_c} (m - m_c)^2 + \dots$$

$$\frac{df}{dm} = \ln s_v - \frac{2}{3} \xi m^{-1/3}$$

$$\frac{d^2f}{dm^2} = \frac{2}{9} \xi m^{-4/3}$$

$$\left(\frac{d^2f}{dm^2}\right)_{m_c} = \frac{2}{9} \xi \left(\frac{3 \ln s_v}{2\xi}\right)^4 = \frac{9}{8} \frac{(\ln s_v)^4}{\xi^3}$$

$$\begin{aligned} f(m_c) &= \left(\frac{2\xi}{3 \ln s_v}\right)^3 \ln s_v - \frac{2}{3} \xi \left(\frac{2\xi}{3 \ln s_v}\right)^2 \\ &= \left(\frac{2}{3}\right)^3 \frac{\xi^3}{(\ln s_v)^3} - \left(\frac{2}{3}\right)^2 \frac{\xi^3}{(\ln s_v)^2} = -\frac{4}{27} \frac{\xi^3}{(\ln s_v)^3} \end{aligned}$$

$$N^{\text{st}}(m) = N_s \exp \left[f(m_c) + \frac{9}{16} \frac{(\ln s_v)^4}{\xi^3} (m - m_c)^2 \right]$$

$$\text{But } N_s e^{f(m_c)} = N^{\text{st}}(m_c)$$

$$\Rightarrow N^{eq}(m) = N^{eq}(m_c) \exp \left[\frac{q}{16} \frac{(\ln S_v)^4}{\xi^3} (m - m_c)^2 \right]$$

$$I = \frac{\beta_v(m_c) N^{eq}(m_c)}{\int_1^\infty e^{-k(m-m_c)^2} dm} ; k = \frac{q}{16} \frac{(\ln S_v)^4}{\xi^3}$$

Let $t = m - m_c$

when $m = 1$

$$t = 1 - m_c = -(m_c - 1)$$

when $m = \infty$

$$t = \infty$$

$$\int_1^\infty e^{-k(m-m_c)^2} dm = \int_{-(m_c-1)}^\infty e^{-kt^2} dt = \int_{-(m_c-1)}^0 e^{-kt^2} dt$$

$$+ \int_0^\infty e^{-kt^2} dt$$

But $(m_c - 1) \gg 1$, $\int_{-\infty}^0 e^{-kt^2} dt = \int_0^\infty e^{-kt^2} dt$

$$\begin{aligned} \Rightarrow \int_1^\infty e^{-k(m-m_c)^2} dm &= \int_0^\infty e^{-kt^2} dt = \frac{2}{\sqrt{k}} \int_0^\infty e^{-w^2} dw \\ &= \frac{2}{\sqrt{k}} \cdot \frac{\sqrt{\pi}}{2} = \left(\frac{\pi}{k}\right)^{1/2} = \sqrt{\pi} \cdot \frac{4}{3} \times \frac{\xi^{3/2}}{(\ln S_v)^2} \end{aligned}$$

where $w = \sqrt{k} t$

$$\Rightarrow I = \frac{3}{4\sqrt{\pi}} \frac{(\ln S_v)^2}{\xi^{3/2}} \beta_v(m_c) N^{eq}(m_c)$$

$$N^{eq}(m_c) = N_0 \exp \left[m_c \ln S_v - \xi m_c^{2/3} \right]$$

$$= N_0 \exp \left[\left(\frac{2\xi}{3 \ln S_v} \right)^3 \ln S_v - \xi \left(\frac{2\xi}{3 \ln S_v} \right)^2 \right]$$

$$\Rightarrow N^{eq}(m_c) = N_0 \exp \left[-\frac{4}{27} \frac{\xi^3}{(\ln S_v)^2} \right]$$

In a gas-liquid system, N_s is interpreted as the total number of molecules in the system. In the present case, N_s is the total number of lattice sites.

$$\beta_V(m_c) = 4\pi R_c D_V C_V \text{ (diffusion limited)}$$

$$C_V = S_V C_V^{eq}$$

$$m_c = \frac{(\frac{4}{3}\pi R_c^3)}{\Omega}$$

$$R_c = \left(\frac{3\Omega}{4\pi}\right)^{1/3} \quad m_c^{1/3} = \left(\frac{3\Omega}{4\pi}\right)^{1/3} \left(\frac{2^3}{3 \ln S_V}\right)$$

$$\beta_V(m_c) = (4\pi)^{2/3} (3\Omega)^{1/4} \frac{2^3}{3} \frac{S_V}{\ln S_V} D_V C_V^{eq}$$

$$I = \frac{3}{2\sqrt{4\pi}} \frac{(\ln S_V)^2}{3^{3/2}} (4\pi)^{2/3} (3\Omega)^{1/3} \frac{2^3}{3} \frac{S_V}{\ln S_V} D_V C_V^{eq} \times$$

$$N_s \exp\left[-\frac{4}{27} \frac{3^3}{(\ln S_V)^3}\right]$$

$$\Rightarrow I = \frac{(4\pi)^{1/6} (3\Omega)^{1/3}}{3^{1/2}} N_s D_V C_V^{eq} S_V \ln S_V \exp\left[-\frac{4}{27} \frac{3^3}{(\ln S_V)^3}\right]$$

PROBLEM 19.4

Eq (19.45) is $\frac{d(N/h)}{dm} = - \frac{I}{\beta_V(m) h(m)}$

which implies: $\int_1^{(N/h)_m} d\left(\frac{N}{h}\right) = -I \int_1^m \frac{dm'}{\beta_V(m') h(m')}$

Since $h(m')$ has a sharp minimum at $m' = m_c$, the main contribution to the integrals comes from this neighborhood. Thus, expanding $\ln h(m')$ about m_c gives

$$\ln h(m') = \ln h(m_c) + \frac{1}{2} \left[\frac{d^2 \ln h}{d m'^2} \right]_{m_c} (m' - m_c)^2 \\ = \ln h(m_c) + k(m' - m_c)^2$$

where $k = \frac{1}{2} \left[\frac{d^2 \ln h}{d m'^2} \right]_{m_c}$
or $h(m') = h(m_c) e^{k(m' - m_c)^2}$

Substituting into the above integral with $\beta_V(m') \cong \beta_V(m_c)$, we obtain:

$$\frac{N(m)}{h(m)} - 1 = - \frac{I}{\beta_V(m_c) h(m_c)} \int_1^m e^{-k(m' - m_c)^2} dm'$$

From eq (19.47) and (19.48) it is clear that:

$$\left[\frac{I}{\beta_V(m_c) h(m_c)} \right]^{-1} = \int_1^\infty e^{-k(m' - m_c)^2} dm'$$

So, $\frac{N(m)}{h(m)} = 1 - \frac{\int_1^m e^{-k(m' - m_c)^2} dm'}{\int_1^\infty e^{-k(m' - m_c)^2} dm'}$

Let $Q(m) = \int_1^m e^{-k(m' - m_c)^2} dm'$

$$\begin{aligned} \text{let } x &= \sqrt{k} (m' - m_c) \\ dx &= \sqrt{k} dm' & dm' &= \frac{1}{\sqrt{k}} dx \\ \text{when } m' &= 1 & x &= -\sqrt{k} (m_c - 1) \\ m' &= m & x &= \sqrt{k} (m - m_c) \end{aligned}$$

$$Q(m) = \frac{1}{\sqrt{k}} \int_{-\sqrt{k}(m_c-1)}^{\sqrt{k}(m-m_c)} e^{-x^2} dx = \frac{1}{\sqrt{k}} \left[\int_0^{\sqrt{k}(m_c-1)} e^{-x^2} dx + \int_0^{\sqrt{k}(m-m_c)} e^{-x^2} dx \right]$$

$$\text{But } \operatorname{erf}(Y) = \frac{2}{\sqrt{\pi}} \int_0^Y e^{-x^2} dx$$

$$Q(m) = \frac{\sqrt{\pi}}{2\sqrt{k}} \left\{ \operatorname{erf}[\sqrt{k}(m-m_c)] + \operatorname{erf}[\sqrt{k}(m_c-1)] \right\}$$

$$Q(\infty) = \frac{\sqrt{\pi}}{2\sqrt{k}} \left\{ 1 + \operatorname{erfc}[\sqrt{k}(m_c-1)] \right\}$$

$$\text{Assume } \sqrt{k}(m_c-1) > 3, \operatorname{erf}[\sqrt{k}(m_c-1)] \rightarrow 1$$

$$Q(\infty) = \left(\frac{\pi}{k} \right)^{\frac{1}{2}}$$

$$\Rightarrow \frac{Q(m)}{Q(\infty)} = \frac{1}{2} \left\{ 1 + \operatorname{erf}[\sqrt{k}(m-m_c)] \right\}$$

$$\therefore \frac{N(m)}{h(m)} = 1 - \frac{Q(m)}{Q(\infty)}$$

$$\frac{N(m)}{h(m)} = 1 - \frac{1}{2} \left\{ 1 + \operatorname{erf}[\sqrt{k}(m-m_c)] \right\}$$

$$\Rightarrow N(m) = \frac{1}{2} h(m) \operatorname{erfc}[\sqrt{k}(m-m_c)]$$

PROBLEM 19.5

Point defect balance at beginning of irradiation,

$$N=0$$

$$f_e = 0$$

$$f_N = f_d = 10^{-1} \text{ cm}^{-2}$$

$$V = 30 \quad (\text{Eq (19.94)})$$

$$\Sigma_d \approx 0.2 \text{ cm}^{-1}$$

$$\Phi = 10^{14} \text{ neutrons/cm}^2 \cdot \text{sec}$$

$$\left. \begin{array}{l} V \Sigma_d \Phi = 30 \times 0.2 \times 10^{14} \\ = 6 \times 10^{14} \text{ cm}^{-3} \text{ sec}^{-1} \end{array} \right\}$$

$$Z_v \approx \frac{2\pi}{\ln\left(\frac{R}{R_1}\right)} = \frac{6.28}{\ln\left(\frac{1.8 \times 10^{-5}}{3}\right)} = 0.98$$

$$Z_i = 1.02 Z_v \approx 1.01$$

Dislocation capture radius R

$$(\pi R^2) f_d = 1$$

$$R = \frac{1}{\sqrt{\pi f_d}} = 1.8 \times 10^{-5} \text{ cm} = 1.8 \times 10^3 \text{ \AA}$$

Since $D_i \gg D_v$

$$k_{iv} = \frac{Z_{iv} D_i \Omega}{a_0^2} \quad [\text{eq (13.42)}]$$

For iron $\Omega = 12 \text{ \AA}^3$

$$a_0^2 \approx \Omega^{2/3} = 5.24 \text{ \AA}^2$$

For interstitial $D_i = a_0^2 \gamma \exp(-E_i^*/kT)$

(From problem (19.11)) $\gamma \approx 10^{13} \text{ sec}^{-1}$, $E_i^* \approx 13 \text{ kJ/mole}$

$$D_i = (5.24 \times 10^{-16}) \times (10^{13}) \exp\left(-\frac{13}{8.31 \times 0.773}\right) = 6.9 \times 10^{-4} \frac{\text{cm}^2}{\text{sec}}$$

$$Z_{iv} \approx 100$$

$$k_{iv} = (10^2)(6.9 \times 10^{-4}) \times \frac{12}{5.24} \times 10^{-8} = 1.6 \times 10^{-9} \frac{\text{cm}^3}{\text{sec}}$$

For Vacancy $D_v = a_0^2 \gamma \exp(-E_v^*/kT)$

From problem 19.11, $E_v^* = 125 \text{ KJ/mole}$

$$D_v = (5.24 \times 10^{-16}) \times 10^{13} \exp\left(-\frac{125}{8.31 \times 0.773}\right) = 1.85 \times 10^{-11} \frac{\text{cm}^2}{\text{sec}}$$

A. Equations (19.136) and (19.137) (neglect C_v^{eq})

$$V \Sigma_3 \Phi = Z_v \int_N D_v C_v + k_{iv} C_i C_v \quad \text{--- (1)}$$

$$V \Sigma_3 \Phi = Z_i \int_N D_i C_i + k_{iv} C_i C_v \quad \text{--- (2)}$$

$$\text{or } \frac{V \Sigma_3 \Phi}{\int_A} = Z_v (D_v C_v) + \left(\frac{k_{iv}}{\int_A D_i D_v}\right) (D_i C_i) (D_v C_v) \quad \text{--- (1a)}$$

$$\frac{V \Sigma_3 \Phi}{\int_A} = Z_i (D_i C_i) + \left(\frac{k_{iv}}{\int_A D_i D_v}\right) (D_i C_i) (D_v C_v) \quad \text{--- (2a)}$$

$$\frac{V \Sigma_3 \Phi}{\int_A} = \frac{6 \times 10^{14}}{10^4} = 6 \times 10^5 \text{ cm}^{-1} \text{ sec}^{-1}$$

$$\frac{k_{iv}}{\int_A D_i D_v} = \frac{1.6 \times 10^{-9}}{(10^4)(6.9 \times 10^{-4})(1.85 \times 10^{-11})} = 1.25 \times 10^{-4} \text{ cm}^{-1} \text{ sec}$$

Subtract (1a) from (2a)

$$Z_v (D_v C_v) = Z_i (D_i C_i) \quad \text{--- (3)}$$

Use (3) in (1a)

$$6 \times 10^5 = 0.98 (D_v C_v) + (1.25 \times 10^{-4}) \left(\frac{0.98}{1.0}\right) (D_v C_v)^2$$

$\uparrow \frac{Z_v}{Z_i}$

$$\Rightarrow 1.25 \times 10^{-4} (D_v C_v)^2 + (D_v C_v) - 6 \times 10^5 = 0$$

solve the above equation $D_v C_v = 6.54 \times 10^4$

$$\Rightarrow C_v = \frac{6.54 \times 10^4}{1.85 \times 10^{-11}} = 3.53 \times 10^{15}$$

this number was obtained from problem (19.11)

$$C_v^{eq} = \frac{1}{2} \exp\left(-\frac{160}{8.31 \times 0.773}\right) = 1.27 \times 10^{12}$$

$$S_v = \frac{C_v}{C_v^{eq}} = \frac{3.53 \times 10^{15}}{1.27 \times 10^{12}} = 2780$$

$$D_i C_i = (0.98)(6.54 \times 10^4) = 6.41 \times 10^4$$

$$C_i = \frac{6.41 \times 10^4}{6.9 \times 10^{-4}} = 9.3 \times 10^7$$

$$C_v^{eq} = \frac{1}{\Omega} \exp\left(-\frac{420}{8.31 \times 773}\right) \quad \leftarrow \text{from problem (19.11)} = 3.35 \times 10^{-6}$$

$$S_i = \frac{C_i}{C_i^{eq}} = \frac{9.3 \times 10^7}{3.35 \times 10^{-6}} = 2.8 \times 10^{13}$$

B. From Equations (19.136) and (19.137) the ratio the ratio of the terms representing vacancy and interstitial absorption by voids (the first term on the right) is

$$\left(\frac{\beta_i}{\beta_v}\right)_{\text{void}} = \frac{4\pi R N D_i C_i}{4\pi R N D_v [C_v - C_v^{eq} \exp(\frac{2\gamma\Omega}{RkT})]}$$

Since $\frac{C_v}{C_v^{eq}} \gg 1$ and the surface tension term is $\sim$ unity

$$\left(\frac{\beta_i}{\beta_v}\right)_{\text{void}} = \frac{D_i C_i}{D_v C_v} \underset{\substack{\uparrow \\ \text{eq (3)}}}{=} \frac{Z_v}{Z_i} = 0.98$$

For dislocation, the terms on right of equations (1) and (2) gives

$$\left(\frac{\beta_v}{\beta_i}\right)_{\text{disl}} = \frac{Z_v \int N D_v C_v}{Z_i \int N D_i C_i} = \frac{Z_v D_v C_v}{Z_i D_i C_i} \underset{\substack{\uparrow \\ \text{Eq (3)}}}{=} 1$$

The ratio is exactly unity because when dislocations are the only sink for point defects (i.e. before voids have been nucleated), the

dislocations must absorb vacancies and interstitials at the same rate.

C. Void nucleation

From Fig (19.10.), For $S_v = 2780$, $T = 773^\circ K$
interpolation yields $I_{void} \cong 10^7 \text{ voids/cm}^3\text{-sec}$

At startup $(\frac{\beta_v}{\beta_i})_{disl} \cong 1$ $I_{loop} = 0$

D. If the steel contained a concentration N_p of incoherent precipitate particles of radius R_p , a term $4\pi R_p N_p D_v C_v$ would be added to the right hand side of eq (1) and a comparable term $4\pi R_p N_p D_i C_i$ to eq (2) and eq (3) would be replaced by

$$Z_v \int d D_v C_v + 4\pi R_p N_p D_v C_v = Z_i \int d D_i C_i + 4\pi R_p N_p D_i C_i$$

$$\text{or } (D_v C_v)(1+x) = D_i C_i \left(\frac{Z_i}{Z_v} + x \right) \text{ --- (3a)}$$

$$\text{where } x = \frac{4\pi R_p N_p}{Z_v \int d} = \frac{4 \times (6.28)(10^{-6})(4 \times 10^{12})}{(0.98)(109)} \cong 0.1$$

$$\text{Then } \left(\frac{\beta_i}{\beta_v} \right)_{void} = \frac{1+x}{\frac{Z_i}{Z_v} + x}$$

$$\text{If } x \ll 1, \left(\frac{\beta_i}{\beta_v} \right)_{void} = \frac{Z_v}{Z_i} \left[1 + \left(\frac{Z_i - Z_v}{Z_i} \right) x \right]$$

$$\left(\frac{\beta_v}{\beta_i} \right)_{disl} = \frac{\frac{Z_v}{Z_i}}{\left(\frac{Z_v}{Z_i} \right) \left[1 + \left(\frac{Z_i - Z_v}{Z_i} \right) x \right]} \cong 1 - \left(\frac{Z_i - Z_v}{Z_i} \right) x$$

For $\alpha = 0.1$

$$\left(\frac{\beta_i}{\beta_v}\right)_{\text{void}} = 0.98 [1 + (0.02)(0.1)] = 0.982$$

$$\left(\frac{\beta_v}{\beta_i}\right)_{\text{void}} = 1 - (0.02)(0.1) = 0.998$$

The void nucleation rate is NOT significantly changed when $\left(\frac{\beta_i}{\beta_v}\right)_{\text{void}}$ increase from 0.98 to 0.982. However the loop nucleation rate is given by (19.92)

$$I_{\text{loop}} = (2 \times 10^{37}) (2 \times 10^{-3}) (2.8 \times 10^{13})^3 \exp\left(-\frac{1150}{8.31 \times 1733}\right)$$

$$= 2 \times 10^{-3} \frac{\text{nuclei}}{\text{cm}^3\text{-sec}}$$

which is still negligibly small

PROBLEM 19.6

Let P be the helium production rate
From Fig (18.40) the production rate for a
fluence of 10^{15} is

$$P = \frac{1}{8} \frac{8.5 \text{ PPM}}{500 \text{ days}} \times \frac{1 \text{ day}}{3600 \times 24 \text{ sec}} \times 10^{-6} \frac{\text{atoms He/atom Fe}}{\text{PPM}} \\ \times 0.85 \times 10^{23} \text{ atoms Fe/cm}^3 \\ = 2 \times 10^{10} \frac{\text{atoms He}}{\text{cm}^3 \cdot \text{sec}}$$

The P replaces $\gamma_{\text{He}} \dot{F}$ in fusion gas bubble
nucleation in UO_2 .

$$k_{11} = \frac{\beta_{11} \Omega D_{\text{He}}}{a^2} \quad [\text{Eq (13.44)}]$$

where k_{11} is the He-He interaction rate constant

$$\beta_{11} \approx 84$$

$$\Omega = 12 \times 10^{-24} \text{ cm}^3$$

$$a = 3 \text{ \AA}$$

$$k_{12} = \frac{\beta_{12} \Omega D_{\text{He}}}{a^2}, \quad \beta_{12} \approx 12$$

$$k_{11} = \frac{(84)(12 \times 10^{-24})(10^{-16})}{9 \times 10^{-16}} = 1.1 \times 10^{-22} \text{ cm}^3/\text{sec}$$

$$k_{12} = 2.7 \times 10^{-23} \text{ cm}^3/\text{sec}$$

$$\left(\frac{P}{3k_{11}} \right) \left(\frac{k_{12}}{2b} \right)^2 = \frac{2 \times 10^{10}}{3(1.1 \times 10^{-22})} \left[\frac{2.7 \times 10^{-23}}{2 \times 10^{-6}} \right]^2$$

According to Fig 13.13, the resolution-dominated
limit is applicable, and C_c is given by

$$\text{Eq (13.142)} \quad C_c = \left(\frac{2b \gamma_{\text{He}} \dot{F}}{3k_{11} k_{12}} \right)^{1/3}$$

$$\Rightarrow C_c = \left[\frac{(2)(10^{-6})(2 \times 10^{10})}{(3)(1.1 \times 10^{-22})(2.7 \times 10^{-23})} \right]^{1/3} = 1.65 \times 10^{16} \frac{\text{atoms He}}{\text{cm}^3}$$

$$C_{>c} = \left(\frac{1.1 \times 10^{-22}}{2 \times 10^{-6}} \right)^{1/3} \left(\frac{2 \times 10^{10}}{3 \times 2.7 \times 10^{-23}} \right)^{2/3}$$

$$= 1.5 \times 10^{16} \frac{\text{diatoms}}{\text{cm}^3}$$

$$\tau_c = \frac{1.65 \times 10^{16} + 2(1.5 \times 10^{16})}{2 \times 10^{10}} = 2.3 \times 10^6 \text{ sec}$$

$$\Phi \tau_c = (10^{15}) (2.3 \times 10^6) = 0.23 \times 10^{22} \text{ neutrons/cm}^2 \approx 1 \text{ month}$$

He bubble nucleation is complete at about $\frac{1}{4}$ of the fluence required for void nucleation

PROBLEM 19.7

Neglecting vacancies in di-interstitial balance

$$R_{if} = \beta_i(1) C_i \text{ ----- (3)}$$

$$R_{ir} = \alpha_i(2) N_2 + 2b N_2 \text{ ----- (4)}$$

where $2b N_2$ is resolution term, there is 2 in this term, because there are 2 interstitial per di-interstitial

N_2 = concentration of di-interstitials.

Assuming reaction (1) in equilibrium, because of low interaction rate of (2)

$$\beta_i(1) C_i = [\alpha_i(2) + 2b] N_2$$

$$\therefore N_2 = \frac{\beta_i(1) C_i}{\alpha_i(2) + 2b}$$

Using (19.69) for $\beta_i(1)$ and (19.72) for $\alpha_i(2)$

$$N_2 = \frac{\frac{3i_i \Omega D_i C_i^2}{a_0^2}}{\frac{3i_i D_i}{a_0^2} e^{-B/kT} + 2b} = \frac{\Omega e^{B/kT} C_i^2}{1 + \frac{2a_0^2 b}{3i_i D_i} e^{B/kT}} \text{ --- (5)}$$

The tri-interstitial balance becomes

$$I_2 = I_3 \text{ ----- (6)}$$

$$\text{Eq (19.85) is } I_2 = \beta_i(2) N_2 - \beta_v(3) N_3 - 3b N_3 \text{ --- (7)}$$

$(i_2 + i \rightarrow i_3) \quad (i_3 + v \rightarrow i_2) \quad (i_3 \xrightarrow{\text{resol}} i + i_2)$

and

$$I_3 = \beta_i(3)N_3 - \beta_v(4)N_4 - 4bN_4 \quad \text{--- (8)}$$

$(i_3 + i \rightarrow i_4) \quad (i_4 + v \rightarrow i_3) \quad (i_4 \xrightarrow{\text{resol}} i + i_3)$

or

$$(\beta_i(3) + \beta_v(3) + 3b)N_3 = \beta_i(2)N_2 + (\beta_v(4) + 4b)N_4 \quad \text{--- (9)}$$

Similarly

$$(\beta_i(4) + \beta_v(4) + 4b)N_4 = \beta_i(3)N_3 + (\beta_v(5) + 5b)N_5 \quad \text{--- (10)}$$

⋮

$$\text{Now } \beta_i(n) = \sum n_i \frac{\Omega}{a_0^2} D_i C_i \quad \text{--- (11a)}$$

$$\beta_v(n) = \sum n_v \frac{\Omega}{a_0^2} D_v C_v \quad \text{--- (11b)}$$

Assume $\sum n_i \approx \sum n_v = 10n$, i.e. the combinatorial number is proportional to the number of point defects in the cluster

$$\text{Let } \frac{\beta_i(2)}{\beta_v(2)} = \frac{\beta_i(3)}{\beta_v(3)} = \frac{\beta_i(4)}{\beta_v(4)} = \frac{\beta_i}{\beta_v} = \frac{D_i C_i}{D_v C_v} \quad \text{--- (12)}$$

= constant determined from point defect balance

And

$$\frac{nb}{\beta_v(n)} = \frac{nb}{10n \frac{\Omega}{a_0^2} D_v C_v} = \frac{a_0^2 b}{10\Omega D_v C_v} = f, \text{ a constant --- (13)}$$

Divide eq (9) by $\beta(3)$ and eq (10) by $\beta(4)$

then

$$(1 + \frac{\beta_i}{\beta_v} + f)N_3 = \frac{2}{3} \frac{\beta_i}{\beta_v} N_2 + \frac{4}{3} (1 + f)N_4 \quad \text{--- (14)}$$

$$(1 + \frac{\beta_i}{\beta_v} + f)N_4 = \frac{3}{4} \frac{\beta_i}{\beta_v} N_3 + \frac{5}{4} (1 + f)N_5 \quad \text{--- (15)}$$

In general

$$\left(1 + \frac{\beta_i}{\beta_v} + f\right) n N_n = \frac{\beta_i(n-1)}{\beta_v} N_n + (1+f)(n+1) N_{n+1} \quad \text{--- (16)}$$

Let $g_n = n N_n$

then eq (16) becomes $\left(1 + \frac{\beta_i}{\beta_v} + f\right) g_n = \frac{\beta_i}{\beta_v} g_{n-1} + (1+f) g_{n+1}$ --- (17)

Eq (17) is a second order difference eq there should be 2 solutions.

When $f = 0$ and $\beta_i/\beta_v = 1$, the two solutions are

$$g_n^{(1)} = K_1 \quad (N_n = K_1/n)$$

$$g_n^{(2)} = K_2 n \quad (N_n = K_2)$$

The solution $g_n = K_1$, also satisfies eq (17). We have NOT been able to find the second solution. However, we shall assume that this second solution gives N_n which increases with n , and so can be discarded. Therefore from the first solution ($g_n = K_1$) we have $n N_n = \text{constant} = 2 N_2$

$$N_n = \frac{2 N_2}{n}$$

$$\text{or } N_3 = \frac{2 N_2}{3} \quad \text{--- (18)}$$

Use (18) in (7)

$$I_2 = I_{\text{loop}} = \beta_i(2) N_2 - \frac{2}{3} [\beta_v(3) + 3b] N_2$$

$$\text{But } \frac{2}{3} \beta_v(3) = \beta_v(2), \quad \frac{2b}{\beta_v(2)} = f$$

$$I_{\text{loop}} = \beta_i(2) N_2 - \beta_v(2) (1+f) N_2$$

$$= \left[1 - \frac{\beta_v}{\beta_i} (1+f)\right] \beta_i(2) N_2$$

Substitute eq (5), (13) and (19.75)

$$I_{loop} = \left[1 - \frac{\beta_v}{\beta_i} \left(1 + \frac{a_o^2 b}{10 \Omega D_{VCV}} \right) \right] \frac{I_{loop}^*}{\left[1 + \frac{2 a_o^2 b}{\beta_{ic} D_i} e^{B/kT} \right]^0} \quad \text{--- (19)}$$

Where $I_{loop}^* = \frac{Z_{di} \Omega^2 D_i C_i^3}{a_o^2} \exp(B/kT) \quad \text{Eq (19.77)}$

When $b \rightarrow 0$, eq (19) reduces to eq (19.90)

PROBLEM 19.8

Volume contraction

Free energy of the system:

$$G = G_0 + g(m_v) + n_v \mu_v + n_i \mu_i \quad \text{--- (1)}$$

where G_0 is free energy of defect-free stress-free solid $g(m_v)$ is the reversible work required to create a void containing m_v vacancies against external pressure σ with constant internal gas pressure P in the cavity.

$$g(m_v) = E(m_v) + \Delta V_{\text{ext}} \sigma - \Delta V_{\text{void}} P \quad \text{--- (2)}$$

$$\Delta V_{\text{ext}} = \Delta V_{\text{void}} = m_v \Omega \quad \text{--- (3)}$$

$$E(m_v) = 4\pi R^2 \gamma \quad \text{--- (4)}$$

$$m_v = \frac{4/3 \pi R^3}{\Omega} \quad \text{--- (5)}$$

$$G = G_0 + E(m_v) + m_v \Omega (\sigma - P) + n_v \mu_v + n_i \mu_i$$

$$\delta G = \frac{dE}{dm_v} \delta m_v + \Omega (\sigma - P) \delta m_v + \mu_v \delta n_v + \mu_i \delta n_i = 0$$

$$\delta m_v = \delta n_i - \delta n_v$$

$$\delta G = \left[\frac{d\epsilon}{dm_v} + \Omega(\sigma - P) \right] (\delta n_i - \delta n_v) + \mu_v \delta n_v + \mu_i \delta n_i = 0$$

$$\frac{d\epsilon}{dm_v} = \frac{d\epsilon}{dR} \frac{dR}{dm_v} = (8\pi R\gamma) \left(\frac{\Omega}{4\pi R^2} \right) = \left(\frac{2\gamma}{R} \right) \Omega$$

$$\left(\frac{2\gamma}{R} - P + \sigma \right) \Omega - \mu_v = 0 \quad \text{--- (6)}$$

$$\left(\frac{2\gamma}{R} - P + \sigma \right) \Omega + \mu_i = 0 \quad \text{--- (7)}$$

$$\text{But } \mu_i = -\mu_v \quad \text{--- (8)}$$

Chemical potential of vacancy.

$$\mu_v = kT \ln \left(\frac{C_v}{C_v^{\text{eq}}} \right) \quad \text{--- (9)}$$

C_v^{eq} equilibrium concentration of vacancy in a solid subject to external pressure σ

$$C_v^{\text{eq}} = (C_v^{\text{eq}})_0 \exp \left(- \frac{\sigma \Omega}{kT} \right) \quad \text{--- (10)}$$

where $(C_v^{\text{eq}})_0$ is the equilibrium - vacancy concentration in stress - free solid.

Ω : volume change of solid when an atom move from interior to surface

1) Volume of solid initially $= V$

2) Remove an atom to surface, NOT allowing contraction of the lattice around vacancy
Volume $= V + \Omega$

3) Contract solid around vacant site by ψ_v
Volume $= V + \Omega - \psi_v$

$$\therefore \Omega = \Omega - \psi_v \quad \text{--- (11)}$$

$$C_v^{\text{eq}} = (C_v^{\text{eq}})_0 \exp \left[- \frac{\sigma(\Omega - \psi_v)}{kT} \right] \quad \text{--- (12)}$$

Substitute (12) into (9)

$$\mu_v = kT \ln \left(\frac{C_v}{C_v^{eq}} \right) = kT \ln \left[\frac{C_v}{(C_v^{eq})_0} \right] + kT \ln \left[\frac{(C_v^{eq})_0}{C_v^{eq}} \right]$$

$$\text{But, } \ln \left[\frac{(C_v^{eq})_0}{C_v^{eq}} \right] = \frac{\sigma(\Omega - \psi_v)}{kT}$$

$$\therefore \mu_v = kT \ln \left[\frac{C_v}{(C_v^{eq})_0} \right] + \sigma(\Omega - \psi_v) \quad \text{--- (13)}$$

Insert (13) into (6)

$$\left(\frac{\sigma}{R} - P \right) \Omega + \sigma \Omega = kT \ln \left[\frac{C_v}{(C_v^{eq})_0} \right] + \sigma \Omega - \sigma \psi_v$$

$$C_v = (C_v^{eq})_0 \exp \left[\frac{(\sigma/R - P) \Omega + \sigma \psi_v}{kT} \right]$$

This is the equilibrium vacancy concentration in the solid adjacent to a void of radius R , with internal gas pressure P and in a hydrostatic (compressive) stress field σ

PROBLEM 19.9

A. The diffusion eq is

$$D_v \nabla^2 C_v + G' = k^2 D_v C_v$$

where $k^2 = Z_v f_a + 4\pi R_N + 4\pi R_P N_P$
and $G' = \gamma \Sigma_s \phi - k_{iv} C_i C_v$

Under the assumption of semi-infinite medium,

$$\frac{d^2 C_v}{dz^2} - k^2 C_v = - \frac{G'}{D_v} = -G$$

B.C 1) $C_v(0) = 0$

2) $C_v(\infty)$ is finite

⇒ the solution is $C_v(z) = A e^{-kz} + B e^{kz} + \frac{G}{k^2}$

$C_v(\infty)$ is finite ⇒ $B = 0$

$C_v(0) = 0 \Rightarrow A + \frac{G}{k^2} = 0 \Rightarrow A = - \frac{G}{k^2}$

$$C_v(z) = \frac{G}{k^2} (1 - e^{-kz})$$

$$\text{so } J_v = -D_v \left(\frac{dC_v}{dz} \right)_{z=0} = - \frac{D_v G}{k}$$

B. Total absorption by grain boundary = $4\pi\left(\frac{d}{2}\right)^2 J_v$

$$Q_v^{gb} = \frac{4\pi\left(\frac{d}{2}\right)^2 J_v}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3} = \frac{6 J_v}{d} = \frac{6 D_v G}{k d} \frac{\text{vacancies}}{\text{cm}^2\text{-sec}}$$

Since $Q_v^{gb} = k_{gb}^2 D_v C_v(\infty)$

$$= k_{gb}^2 D_v \cdot \frac{G}{k^2} = \frac{6 D_v G}{k d}$$

$$\text{Thus } k_{gb}^2 = \frac{6 k}{d}$$

the above equation is the grain boundary sink efficiency for use in point defect balance

PROBLEM 19.10

From Eq (19.139):

$$\frac{\dot{R}}{\dot{R}_0} = F(\gamma) + \frac{\dot{R}_e}{\dot{R}_0} \quad \text{----- (1)}$$

Eq (19.142):

$$F(\gamma) = \frac{2}{\gamma} [\sqrt{1+\gamma} - 1] \quad \text{----- (2)}$$

Eq (19.143 b) with $N = N_p = 0$

$$\gamma = \frac{4 \beta_{iv} \nu \Sigma_s \Phi \Omega}{D_v a_0^2 (Z_v f_d)^2} \quad \text{----- (3)}$$

$$D_v = 10^{13} a_0^2 \exp(-E_v^*/kT)$$

$$a_0 \approx \Omega^{1/3}; \quad Z_v \approx 1, \quad \Omega \approx 11 \text{ \AA}^3 \text{ (For Mo)}$$

From (3)

$$\gamma = \frac{4 \beta_{iv} \nu \Sigma_s \Phi}{10^{13} \Omega^{1/3} f_d^2} \exp(E_v^*/kT) \quad \text{----- (4)}$$

$$\begin{aligned} \gamma &= \frac{4 \times (30)(100)(0.3)(10^{14})}{10^{13} (2.2 \times 10^{-8}) (10^{10})^2} \exp\left(\frac{190}{8.31(T_m/10^3)} - \frac{1}{T/T_m}\right) \\ &= 1.6 \times 10^{-8} \exp\left[\frac{7.88}{T/T_m}\right] \quad \text{----- (5)} \end{aligned}$$

From Eq (19.140) with $N = N_p = 0$

$$\dot{R}_0 = \frac{\nu \Sigma_s \Phi (Z_i - Z_v) \Omega}{R Z_v Z_i f_d} \quad \text{----- (6)}$$

From Eq (19.144) ($R_p = f_L = 0$, $f_N = f_d$)

$$\dot{R}_e = - \frac{D_v C_v^i \Omega Z_v f_d \left(\frac{\gamma}{R} - \frac{\Omega}{kT}\right)}{R Z_v f_d} \quad \text{----- (7)}$$

From (6) and (7)

$$\frac{\dot{R}_e}{\dot{R}_0} = - \frac{D_v C_v^i \Omega \left(\frac{\gamma}{R} - \frac{\Omega}{kT}\right) Z_i Z_v f_d}{R \nu \Sigma_s \Phi (Z_i - Z_v)}$$

where $\frac{kT}{\gamma} \approx 1 \text{ \AA}^2$

$$D_v C_v^0 \Omega = 10^{13} a_0^2 \exp\left(-\frac{E_v^*}{kT}\right) \exp\left(-\frac{E_v}{kT}\right)$$

$$= 10^{13} \Omega^{2/3} \exp\left(-\frac{E_v^* + E_v}{kT}\right)$$

$$\frac{R_e}{R_0} = - \frac{(10^{13})(11^{2/3} \times 10^{-16})(1.02)(10^{10}) \exp\left[-\frac{190+190}{(8.31)(T_m/10^3)} \frac{1}{(T/T_m)}\right]}{(10^{-16})(300 \times 10^{-8})(100)(10.3)(10^{14})(0.02)}$$

$$\frac{R_e}{R_0} = - 2.8 \times 10^{15} \exp\left(-\frac{15.8}{T/T_m}\right)$$

T/T_m	γ	$F(\gamma)$	R_e/R_0	R/R_0
0.1	2.7×10^{26}	1.22×10^{-13}	-7×10^{-54}	1.22×10^{-13}
0.2	2.1×10^9	4.4×10^{-5}	-1.4×10^{-19}	4.4×10^{-5}
0.3	4.09×10^3	0.031	-3.8×10^{-8}	0.031
0.35	95.9	0.184	-7×10^{-5}	0.184
0.4	5.75	0.56	-0.020	0.54
0.41	3.56	0.64	-0.051	0.59
0.42	2.25	0.80	-0.129	0.67
0.43	1.46	0.78	-0.309	0.47
0.44	0.96	0.83	-0.711	0.12
0.45	0.64	0.88	-1.06	-0.18

From the above table, peak void swelling for Mo should be at $\frac{T}{T_m} = 0.42$, i.e. at $\sim 945^\circ\text{C}$

At the coagulating temperature of 500°C
 $\frac{T}{T_m}$ of stainless steel is $0.44 \Rightarrow R/R_0 = 1$
 $\frac{T}{T_m}$ of molybdenum is $0.27 \Rightarrow R/R_0 = 0.01$
 the replacement of stainless steel by molybdenum as the cladding material would avoid the swelling problem to a large extent.

PROBLEM 19.11

$$\frac{D_v C_v^{eq}}{D_i C_i^{eq}} = \frac{e^{-(\epsilon_v^* + \epsilon_v)/kT}}{e^{-(\epsilon_i^* + \epsilon_i)/kT}} = \exp \left[\frac{(\epsilon_i^* + \epsilon_i) - (\epsilon_v^* + \epsilon_v)}{kT} \right]$$

$$\epsilon_i^* + \epsilon_i = 433 \text{ KJ/mole}$$

$$\epsilon_v^* + \epsilon_v = 285 \text{ KJ/mole}$$

$$\text{at } T = 773^\circ \text{K}$$

$$\frac{D_v C_v^{eq}}{D_i C_i^{eq}} = \exp \left[\frac{148 \times 10^3}{8.31 \times 773} \right] \approx 1 \times 10^{10}$$

Since $\frac{D_v C_v^{eq}}{D_i C_i^{eq}}$ is large, γ^* is large compared

to unity and the solution would be located in the region of Fig 19.17 with $\theta_i \approx 0$, $\theta_v \rightarrow 1$. In this case, γ_v from eq (19.130) has the limiting behavior (assuming $a_0/R_p \ll 1$):

$$\gamma_i \approx 1$$

$$\text{and from Eq (19.131): } \gamma_v = \frac{D_i C_i^{eq}}{D_v C_v^{eq}} \approx 10^{-10}$$

$\therefore$ Vacancy absorption by coherent precipitates

is negligible at thermal equilibrium

PROBLEM 19.12

In the absence of thermal emission, Eq (19.95) becomes:

$$Q_v^{\text{void}} = 4\pi R N D_v C_v W_v \text{ --- (1)}$$

and for interstitials:

$$Q_v^{\text{void}} = 4\pi R N D_i C_i W_i \text{ --- (2)}$$

Point defect balance becomes (Eq (19.136) and Eq (19.138)) neglect recombination and coherent precipitates)

$$\gamma \Sigma_s \Phi = 4\pi R N D_v C_v W_v + Z_v f_d D_v C_v \text{ --- (3)}$$

$$\gamma \Sigma_s \Phi = 4\pi R N D_i C_i W_i + Z_i f_d D_i C_i \text{ --- (4)}$$

from (3) $D_v C_v = \frac{\gamma \Sigma_s \Phi}{4\pi R N W_v + Z_v f_d} \text{ --- (3a)}$

from (4) $D_i C_i = \frac{\gamma \Sigma_s \Phi}{4\pi R N W_i + Z_i f_d} \text{ --- (4a)}$

The void growth law, Eq (19.138) becomes (with void bias factors included):

$$\dot{R}_c = \frac{\Omega}{R} (D_v C_v W_v - D_i C_i W_i) \text{ --- (5)}$$

Using (3a) and (4a) in (5)

$$\dot{R}_c = \frac{\gamma \Sigma_s \Phi \Omega}{R} \left[\frac{W_v}{4\pi R N W_v + Z_v f_d} - \frac{W_i}{4\pi R N W_i + Z_i f_d} \right] \text{ --- (6)}$$

$$= \frac{\gamma \Sigma_s \Phi \Omega}{R} \frac{[4\pi R N W_i W_v + f_d Z_i W_v - 4\pi R N W_v W_i - f_d Z_v W_i]}{(4\pi R N W_v + Z_v f_d)(4\pi R N W_i + Z_i f_d)}$$

$$= \frac{\gamma \Sigma_s \Phi \Omega f_d (Z_i W_v - Z_v W_i)}{R (4\pi R N W_v + Z_v f_d)(4\pi R N W_i + Z_i f_d)}$$

In denominator, let $W_v = W_i$, $Z_i = Z_v$ (NOT in numerator, though)

$$\dot{R}_o = \frac{\mathcal{V} \Sigma_s \Phi \Omega f_d W_v (Z_i - Z_v \frac{W_i}{W_v})}{R (4 \pi R N W_v + Z_v f_d)^2}$$

$$= \frac{\mathcal{V} \Sigma_s \Phi \Omega f_d W_v (Z_i - Z_v \frac{W_i}{W_v})}{R Z_v^2 f_d^2 \left[1 + \frac{4 \pi R N W_v}{Z_v f_d} \right]^2} \times \frac{4 \pi R N}{4 \pi R N}$$

$$\dot{R}_o = \frac{\mathcal{V} \Sigma_s \Phi \Omega (Z_i - Z_v \frac{W_i}{W_v})}{4 \pi R^2 N Z_v} \times \frac{4 \pi R N W_v / Z_v f_d}{\left[1 + \frac{4 \pi R N W_v}{Z_v f_d} \right]^2}$$

Let $X = \frac{4 \pi R N W_v}{Z_v f_d}$ (Replace Eq (19.146))

$$\Rightarrow \dot{R}_o = \frac{\mathcal{V} \Sigma_s \Phi \Omega}{4 \pi R^2 N} \left(\frac{Z_i - Z_v \frac{W_i}{W_v}}{Z_v} \right) \frac{X}{(1+X)^2} \quad \text{--- (8)}$$

(8) replaces Eq (19.145)

PROBLEM 19.13

A.

Q_v^{void} = source of vacancies from void

From Eq (19.95)

$$Q_v^{\text{void}} = 4\pi R N D_v [C_v^{\text{eq}} \exp(\frac{2\gamma\Omega}{RkT}) - C_v] \quad \text{--- (1)}$$

Q_v^d = sink of vacancies to dislocations, From Eq (19.101)

$$Q_v^d = Z_v D_v \rho_d (C_v - C_v^{\text{eq}}) \quad \text{--- (2)}$$

Pure annealing $Q_v^d = Q_v^{\text{void}} \quad \text{--- (3)}$

or

$$4\pi R N D_v [C_v^{\text{eq}} \exp(\frac{2\gamma\Omega}{RkT}) - C_v] = Z_v \rho_d D_v (C_v - C_v^{\text{eq}}) \quad \text{--- (4)}$$

Solve (4) for C_v

$$C_v = C_v^{\text{eq}} \left[\frac{1 + \frac{Z_v \rho_d}{4\pi R N} + \frac{2\gamma\Omega}{RkT}}{1 + \frac{Z_v \rho_d}{4\pi R N}} \right] \quad \text{--- (5)}$$

Substitute into (1)

$$Q_v^{\text{void}} = 4\pi R N D_v C_v^{\text{eq}} \frac{\frac{2\gamma\Omega}{RkT}}{1 + \frac{Z_v \rho_d}{4\pi R N}} \quad \text{--- (6)}$$

$\frac{Q_v^{\text{void}}}{N}$: rate of loss of vacancies from a single void

$(\frac{Q_v^{\text{void}}}{N}) \Omega$: rate of volume loss from void

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = - \frac{Q_v^{\text{void}}}{N} \Omega$$

Using (6)

$$\frac{dR}{dt} = - \frac{\gamma D_v C_v^{\text{eq}} \Omega^2}{R^2 k T} \frac{1}{1 + \frac{4 \pi R N}{z_v f_d}} \quad \text{--- (7)}$$

Integrate (7)

$$\int_{R_0}^R R^2 \left(1 + \frac{4 \pi N}{z_v f_d} R \right) dR = - \frac{\gamma D_v C_v^{\text{eq}} \Omega^2}{k T} t$$

$$R_0^3 - R^3 + \frac{3}{4} \left(\frac{4 \pi N}{z_v f_d} \right) (R_0^4 - R^4) = 3 D_v C_v^{\text{eq}} \Omega^2 \left(\frac{\gamma}{k T} \right) t \quad \text{--- (8)}$$

When $\frac{4 \pi N}{z_v f_d} \rightarrow 0$, Recover solution of problem (18.1a)

B. Only vacancy concentration at void surface is changed

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = - \frac{Q_v^{\text{void}} \Omega}{N} = - 4 \pi R D_v \Omega \left[C_v^{\text{eq}} \exp \left(\frac{-P + \frac{\gamma}{R} \Omega}{k T} \right) \right.$$

$\left. - C_v^{\text{eq}} \right]$

$$\text{But } P \left(\frac{4}{3} \pi R^3 \right) = \gamma k T$$

$$\therefore \frac{dR}{dt} = - \frac{D_v C_v^{\text{eq}} \Omega}{R} \left[\frac{\gamma}{R} - \frac{\gamma k T}{\frac{4}{3} \pi R^3} \right] \frac{\Omega}{k T}$$

$$\frac{dR}{dt} = -D_v C_v^{\infty} \Omega^2 \left(\frac{\gamma}{kT} \right) \frac{1}{R^2} \left[1 - \frac{1}{\frac{4}{3}\pi} \left(\frac{kT}{\gamma} \right) \frac{1}{R^3} \right]$$

$$\text{Let } a = \frac{1 \cdot kT}{\frac{4}{3}\pi \cdot \gamma}$$

$$\therefore \frac{R^2 dR}{1 - a/R^2} = -D_v C_v^{\infty} \Omega^2 \left(\frac{\gamma}{kT} \right) dt$$

$$\int_R^{R_0} \frac{R^2 dR}{1 - a/R^2} = D_v C_v^{\infty} \Omega^2 \left(\frac{\gamma}{kT} \right) \tau$$

PROBLEM 19.14

(A).

the area per atom is $(\sqrt{2})^{2/3} = a_0^2$ area per loop is πR_L^2

m = number of atoms in a loop

$$m = \frac{\pi R_L^2}{a_0^2}$$

$$\frac{dm}{dt} = (J_i - J_v) 2\pi R_L = \frac{d}{dt} \left(\frac{\pi R_L^2}{a_0^2} \right)$$

$$= \frac{2\pi R_L}{a_0^2} \frac{dR_L}{dt}$$

$$\therefore \frac{dR_L}{dt} = a_0^2 [z_i D_i (C_i - C_i^l) - z_v D_v (C_v - C_v^l)]$$

(B). Setting $C_v^l = K_{iv} = N_p = 0$, in Eq (19.136) and (19.137) gives:

$$\partial \Sigma_s \Phi = [4\pi R_N + z_v (\beta_N + \beta_L)] C_v D_v$$

$$\partial \Sigma_s \Phi = [4\pi R_N + z_i (\beta_N + \beta_L)] C_i D_i$$

Solving for C_i, C_v

$$C_v = \frac{\partial \Sigma_s \Phi}{D_v [4\pi R_N + z_v (\beta_N + \beta_L)]}$$

$$C_i = \frac{\partial \Sigma_s \Phi}{D_i [4\pi R_N + z_i (\beta_N + \beta_L)]}$$

Insert C_v, C_i into the loop growth law of part (A), and let $\beta_d = \beta_N + \beta_L$

$$\therefore \frac{dR_L}{dt} = a_0^2 \partial \Sigma_s \Phi \left[\frac{z_i}{4\pi R_N + z_i \beta_d} - \frac{z_v}{4\pi R_N + z_v \beta_d} \right]$$

$$(C) \rho_d = \rho_d^0 + 2\pi R_e N_e$$

$$\frac{d\rho_d}{dt} = 2\pi N_e \frac{dR_e}{dt}$$

Use result of part (B) for $\frac{dR_e}{dt}$

$$\therefore \frac{d\rho_d}{dt} = 2\pi N_e a_0^2 \rho \Sigma_s \Phi \left[\frac{Z_i}{4\pi R N + Z_i \rho_d} - \frac{Z_v}{4\pi R N + Z_v \rho_d} \right]$$

$$\text{If } Z_i \approx Z_v$$

$$\frac{d\rho_d}{dt} = \frac{2\pi N_e \frac{\Omega}{a_0} \rho \Sigma_s \Phi}{4\pi R N + Z_v \rho_d} (Z_i - Z_v)$$

(D) Eq. (19.140) can be written as

$$R \frac{dR}{dt} = \frac{(\rho \Sigma_s \Phi \Omega) \left(\frac{Z_i - Z_v}{Z_v} \right) Z_v \rho_d}{(4\pi R N + Z_v \rho_d)^2}, \text{ Since } N_p = 0 \text{ and } Z_i \approx Z_v$$

$$\text{Let } x = \frac{4\pi R N}{Z_v \rho_d^0} \quad \text{dimensionless void size}$$

$$Y = \frac{Z_v \rho_d}{Z_v \rho_d^0} \quad \text{dimensionless dislocation density}$$

$$\theta = \frac{(4\pi N)^2}{(Z_v \rho_d^0)^3} (\rho \Sigma_s \Phi \Omega) \left(\frac{Z_i - Z_v}{Z_v} \right) (t - t_0)$$

= dimensionless time.

then equation (19.140) becomes

$$\frac{dx}{d\theta} = \frac{Y}{x(x+Y)^2}$$

Assuming $\rho_d \approx \text{constant} \Rightarrow Y \approx \text{constant}$

$$\text{or } \int_{x(0)}^{x(10)} (x^3 + Yx^2 + Y^2x) dx = \int_0^{\theta} Y d\theta$$

$$\therefore Y\theta = \frac{1}{4}(X^4 - X_0^4) + \frac{2}{3}Y(X^3 - X_0^3) + \frac{1}{2}Y^2(X^2 - X_0^2) \dots (1)$$

$$\text{where } X_0 = \frac{4\pi R_c N}{Z_v \rho_a^0}$$

$$Y = \frac{\rho_a(t_0)}{\rho_a^0} = \frac{\rho_a^0 + 2\pi R_c N_e}{\rho_a^0}$$

$$= 1 + \frac{2\pi R_c N_e}{\rho_a^0}$$

From (1) $X(\theta)$ can be solved

(E) From part (c)

$$\frac{d\rho_a}{dt} = \frac{2\pi N_e \Omega \rho_s \Phi}{(4\pi R N + Z_v \rho_a) a_0} (Z_i - Z_v) \dots (2)$$

$$\text{Let } X = \frac{4\pi R N}{Z_v \rho_a^0}$$

$$Y = \frac{Z_v \rho_a}{Z_v \rho_a^0}$$

$$\theta = \frac{(4\pi N)^2}{(Z_v \rho_a^0)^3} (\rho_s \Phi \Omega) \left(\frac{Z_i - Z_v}{Z_v} \right) (t - t_0)$$

$$\text{and } A = \frac{N_e Z_v^3 \rho_a^0}{8\pi a_0 N^2} = \text{a constant}$$

then eq (2) becomes

$$\frac{dY}{d\theta} = \frac{A}{X + Y} \dots (3)$$

At time t_0 , the number of vacancies in the void nuclei is equal to the number of interstitials in the embryo loops

$$\frac{\pi R_c^2 N_e}{a_0^2} = \frac{\frac{4}{3} \pi R_c^3 N}{\Omega}$$

$$\therefore R_c = \left[\frac{4}{3} R_c^3 \frac{N}{N_e} \frac{a_0^2}{\Omega} \right]^{1/2}$$

$$J_d(10) = J_d^0 + 2\pi R_{ec} N_e$$

$$Y(10) = \frac{Z_v J_d(10)}{Z_v J_d^0} = 1 + \frac{2\pi R_{ec} N_e}{J_d^0}$$

given

$$R_c = 10 \text{ \AA} = 10^{-7} \text{ cm}$$

$$N = 10^{14} \text{ voids/cm}^3$$

$$N_e = 10^{15} \text{ loops/cm}^3$$

$$J_d^0 = 10^9 \text{ cm}^{-2}$$

$$\Omega = 12 \text{ \AA}^3$$

$$X_0 = \frac{4\pi R_c N}{Z_v J_d^0} = 0.126$$

$$R_{ec} = \left[\frac{4}{3} R_c^3 - \frac{N}{N_e} \frac{a_0^3}{\Omega} \right]^{1/2} = 0.76 \times 10^{-7} \text{ cm}$$

$$Y(10) = 1 + \frac{2\pi R_{ec} N_e}{J_d^0} = 1.48$$

$$A = \frac{N_e Z_v^3 J_d^0}{8\pi a_0 N^2} = 1.73 \times 10^2$$

Now. solve the differential equations numerically

$$\begin{cases} \frac{dx}{d\theta} = \frac{Y}{X(X+Y)^2} \\ \frac{dY}{d\theta} = \frac{A}{X+Y} \end{cases}$$

with the initial conditions

$$X_0 = 0.126$$

$$Y_0 = Y(10) = 1.48$$

and $X_{i+1} = X_i + \frac{Y_i(\Delta\theta)}{X_i(X_i+Y_i)^2}$

$$Y_{i+1} = Y_i + \frac{1.73(\Delta\theta)}{X_i + Y_i}$$

With $\Delta\theta = 0.001$ the results are plotted on the next page.

(F)

at a fluence 5×10^{22} , $\theta = 91$

From the above plot, $x = 1.418$ when $\theta = 91$

$$x = 1.418 \Rightarrow R = 112 \text{ \AA}$$

$$\frac{\Delta V}{V} = \left(\frac{4}{3} \pi R^3 \right) \times N = 0.06\%$$

when Y is assumed constant at $Y_0 = 1.48$, the plot shows that $x \approx 4$ at $\theta = 91$. Or, $R = 316 \text{ \AA}$. In this case, $\Delta V/V = 1.35\%$. The increased sink efficiency due to loop growth markedly reduces void growth.

PROBLEM 19.15

Diffusion-limited growth law with constant matrix concentration of point defects:

$$\dot{R} = \frac{A}{R} \quad \text{--- (1)}$$

$$A = \Omega (D_v C_v - D_i C_i) = \text{Constant} \quad \text{--- (2)}$$

(A.) For a uniform initial distribution, the radius of voids at time $t > t_0$ is obtained by integrating Eq (1)

$$R^2 = R_0^2 + 2A(t - t_0) \quad \text{--- (3)}$$

and the swelling at time $t > t_0$ is:

$$\left(\frac{\Delta V}{V}\right)_t = \left(\frac{4}{3}\pi R^3\right)N = \frac{4}{3}\pi [R_0^2 + 2A(t - t_0)]^{\frac{3}{2}} N$$

For $R_0^2 \ll 2A(t - t_0)$

$$\left(\frac{\Delta V}{V}\right)_t = \frac{4}{3}\pi (2A)^{\frac{3}{2}} (t - t_0)^{\frac{3}{2}} N \quad \text{--- (4)}$$

(B.) General initial distribution $N_0(R_0)$ and distribution at time t $N(R, t)$

$$N = \text{constant} = \int_0^\infty N_0(R_0) dR_0 = \int_0^\infty N(R, t) dR$$

by growth law (3). R_0 and R are related by

$$R_0(R, t) = [R^2 - 2A(t - t_0)]^{\frac{1}{2}} \quad \text{--- (5)}$$

$R_0(R, t)$ is what the radius of void must have been at t_0 if radius at t is R

$$N(R, t) = N_0(R_0) \left| \frac{\partial R_0}{\partial R} \right| \quad \text{--- (6)}$$

$$\text{From (5)} \quad \left| \frac{\partial R_0}{\partial R} \right|_t = \frac{R}{[R^2 - 2A(t-t_0)]^{1/2}}$$

$$\therefore N(R, t) = \frac{R N_0[R_0(R, t)]}{[R^2 - 2A(t-t_0)]^{1/2}} \quad \text{--- (7)}$$

$R_0(R, t)$ is given by eq (5)

$$\therefore \text{swelling } \left(\frac{\Delta V}{V} \right)_t = \int_0^\infty \frac{4}{3} \pi R^3 N(R, t) dR \quad \text{--- (8)}$$

Use (7) in (8)

$$\frac{\Delta V}{V} = \frac{4\pi}{3} \int_0^\infty \frac{R^4 N_0[R_0(R, t)]}{[R^2 - 2A(t-t_0)]^{1/2}} dR \quad \text{--- (9)}$$

(c) If the initial distribution is

$$\begin{aligned} N_0[R_0(R, t)] &= \delta [R_0(R, t) - R_0] N \\ &= \delta [\sqrt{R^2 - 2A(t-t_0)} - R_0] N \end{aligned}$$

$$\frac{\Delta V}{V} = \frac{4}{3} \pi N \int_0^\infty \frac{R^4 \delta [\sqrt{R^2 - 2A(t-t_0)} - R_0]}{[R^2 - 2A(t-t_0)]^{1/2}} dR$$

$$\text{Let } u^2 = R^2 - 2A(t-t_0)$$

$$R^4 dR = \frac{1}{2} R^3 dR^2 = u [u^2 + 2A(t-t_0)]^{3/2} du$$

$$dR^2 = 2u du$$

$$R^3 = [u^2 + 2A(t-t_0)]^{3/2}$$

$$\frac{\Delta V}{V} = \frac{4}{3} \pi N \int_0^\infty \frac{u [u^2 + 2A(t-t_0)]^{3/2} \delta(u - R_0) du}{u} = \frac{4}{3} \pi N [R_0^2 + 2A(t-t_0)]^{3/2}$$

Neglecting R_0^2 , this is the result of part (A).

PROBLEM 19.16

(A)

$$L = R\theta \quad \text{--- (1)}$$

$$A = \frac{R^2}{2} (\theta - \sin\theta) \quad \text{--- (2)}$$

$$\frac{L}{2} = R \sin\left(\frac{\theta}{2}\right) = \text{constant} \quad \text{--- (3)}$$

$$\text{From (3)} \quad R = \frac{L/2}{\sin \frac{\theta}{2}} \quad \text{--- (4)}$$

Insert (4) into (2)

$$A = \frac{L^2}{8} \left(\frac{\theta - \sin\theta}{\sin^2 \frac{\theta}{2}} \right) = \frac{L^2}{4} \left(\frac{\theta - \sin\theta}{1 - \cos\theta} \right)$$

$$\frac{dA}{d\theta} = \frac{L^2}{4} \left[1 - \frac{(\theta - \sin\theta) \sin\theta}{(1 - \cos\theta)^2} \right]$$

Insert (4) into (1)

$$L = \frac{l}{2} \left(\frac{\theta}{\sin \frac{\theta}{2}} \right)$$

$$\frac{dL}{d\theta} = \frac{l}{2} \left[\frac{\sin(\frac{\theta}{2}) - (\frac{\theta}{2}) \cos(\frac{\theta}{2})}{\sin^2 \frac{\theta}{2}} \right]$$

$$\frac{dL}{dA} = \frac{dL/d\theta}{dA/d\theta} = \frac{(l/2) [\sin \frac{\theta}{2} - \frac{\theta}{2} \cos(\frac{\theta}{2})] (1 - \cos\theta)^2}{(l/2)^2 \sin^2 \frac{\theta}{2} (1 - \cos\theta)^2 - (\theta - \sin\theta) \sin\theta}$$

$$= \frac{\sin \frac{\theta}{2}}{(l/2)} \left[4 \times \frac{\sin^2(\frac{\theta}{2}) - (\frac{\theta}{2}) \sin(\frac{\theta}{2}) \cos(\frac{\theta}{2})}{(1 - \cos\theta)^2 - (\theta - \sin\theta) \sin\theta} \right]$$

$$= \frac{1}{R} \left[4 \times \frac{\frac{1}{2}(1 - \cos\theta) - (\frac{\theta}{2}) \frac{1}{2} \sin\theta}{1 - 2\cos\theta + \cos^2\theta - \theta \sin\theta + \sin^2\theta} \right]$$

$$= \frac{1}{R} \cdot 2 \times \frac{1 - \cos\theta - \frac{1}{2}\theta \sin\theta}{2 - 2\cos\theta - \theta \sin\theta}$$

$$= \frac{1}{R} \cdot \frac{1 - \cos\theta - \frac{1}{2}\theta \sin\theta}{1 - \cos\theta - \frac{1}{2}\theta \sin\theta} = \frac{1}{R} \times 1 = \frac{1}{R}$$

$$\therefore \frac{dL}{dA} = \frac{1}{R} \quad \text{for all } \theta$$

$$(B) \quad A = \frac{1}{2} R^2 (\theta - \sin \theta)$$

$$R = \frac{l/2}{\sin(\theta/2)}$$

$$\text{Let } f = \frac{1}{R}$$

$$A = \frac{1}{2} \frac{\theta - \sin \theta}{f^2}$$

$$= \frac{l^2}{8} \frac{\theta - \sin \theta}{\sin^2 \theta/2}$$

$$\frac{dA}{df} = \frac{dA}{d\theta} \cdot \frac{d\theta}{df} = \frac{dA/d\theta}{df/d\theta}$$

$$\frac{dA}{d\theta} = \frac{l^2}{4} \left[\frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{\sin^4(\theta/2)} \right]$$

$$\frac{df}{d\theta} = \frac{1}{(l/2)} \cdot \frac{1}{2} \cos(\theta/2)$$

$$\frac{dA}{d(1/R)} = \frac{l^3}{8} \cdot \frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{\sin^4(\theta/2) \cos(\theta/2)}$$

Eliminate θ in the above equation by using

$$R = \frac{l/2}{\sin(\theta/2)}$$

When $\theta \rightarrow 0$

$$\cos \theta \approx 1 - \frac{\theta^2}{2} + \frac{\theta^4}{4!}$$

$$1 - \cos \theta = \frac{\theta^2}{2} - \frac{\theta^4}{4!}$$

$$\frac{1}{2} \theta \sin \theta = \frac{1}{2} \theta^2 - \frac{\theta^4}{2 \times 3!}$$

$$1 - \cos \theta - \frac{1}{2} \theta \sin \theta = \frac{\theta^2}{2} - \frac{\theta^4}{4!} - \frac{\theta^2}{2} + \frac{\theta^4}{2 \times 3!} = \theta^4 \left(\frac{1}{2 \times 3!} - \frac{1}{4!} \right)$$

$$= \frac{\theta^4}{4!}$$

$$\sin^4\left(\frac{\theta}{2}\right) \approx \frac{\theta^4}{16}$$

$$\therefore \frac{dA}{d(1/R)} \approx \frac{l^3}{8} \times \frac{16}{4!} = \frac{l^3}{12}$$

When $\theta \rightarrow \pi$

$$\cos \theta \rightarrow -1, \quad \sin \theta \rightarrow 0$$

$$\sin\left(\frac{\theta}{2}\right) \rightarrow 1, \quad \cos\left(\frac{\theta}{2}\right) \rightarrow 0$$

$$\frac{dA}{d(1/R)} \rightarrow \infty$$

(c) Evaluation of $\left(\frac{\partial \mathcal{L}}{\partial A}\right)_R$ for end connected to void.

$$A + A' = \frac{1}{2} R^2 (\theta - \sin \theta) \quad \text{----- (1)}$$

Assume length of line in void $\approx R$

$$l + 2R = R\theta \quad \text{----- (2)}$$

$$R = \frac{l/2}{\sin(\theta/2)} \quad \text{----- (3)}$$

$$\alpha = \frac{\theta}{2}$$

$$A' = (\pi R^2) \frac{\alpha}{2\pi} = \frac{R^2 \theta}{4} \quad \text{----- (4)}$$

$$(4) \text{ in (1) } A = \frac{1}{2} R^2 (\theta - \sin \theta) - \frac{1}{4} R^2 \theta \quad \text{----- (5)}$$

Insert (3) into (2) $\mathcal{L} = \frac{l}{2} \left[\frac{\theta}{\sin(\frac{\theta}{2})} \right] - 2R \dots (6)$

$$\left(\frac{\partial \mathcal{L}}{\partial \theta} \right)_R = \frac{l}{2} \left\{ \frac{\sin(\frac{\theta}{2}) - (\frac{\theta}{2}) \cos(\frac{\theta}{2})}{\sin^2(\frac{\theta}{2})} \right\} = \frac{l}{2} \left\{ \frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{2 \sin^3(\frac{\theta}{2})} \right\} \dots (7)$$

(3) into (5)
 $A = \frac{l^2}{4} \left(\frac{\theta - \sin \theta}{1 - \cos \theta} \right) - \frac{1}{2} R^2 \theta \dots (8)$

$$\begin{aligned} \left(\frac{\partial A}{\partial \theta} \right)_R &= \frac{l^2}{4} \left[1 - \frac{(\theta - \sin \theta) \sin \theta}{(1 - \cos \theta)^2} \right] - \frac{1}{2} R^2 \\ &= \frac{l^2}{4} \left[\frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{2 \sin^4(\frac{\theta}{2})} \right] - \frac{1}{2} R^2 \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial \mathcal{L}}{\partial A} \right)_R &= \frac{\left(\frac{\partial \mathcal{L}}{\partial \theta} \right)_R}{\left(\frac{\partial A}{\partial \theta} \right)_R} \\ &= \frac{\frac{l}{2} \left\{ \frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{2 \sin^3(\frac{\theta}{2})} \right\}}{\left(\frac{l}{2} \right)^2 \left\{ \frac{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}{2 \sin^4(\frac{\theta}{2})} \right\} - \frac{1}{2} R^2} \\ &= \frac{\sin(\frac{\theta}{2})}{\frac{l}{2}} \left\{ \frac{1}{1 - \frac{\frac{1}{2} R^2}{(\frac{l}{2})^2} \frac{2 \sin^4(\frac{\theta}{2})}{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}} \right\} \\ &= \frac{1}{R} \left\{ \frac{1}{1 - \frac{\frac{1}{2} R^2}{(\frac{l}{2})^2} \times \frac{2 \sin^4(\frac{\theta}{2})}{1 - \cos \theta - \frac{1}{2} \theta \sin \theta}} \right\} \\ &= \frac{1}{R f(R, l, R)} \end{aligned}$$

$$\left(\frac{\partial \mathcal{L}}{\partial A} \right)_R = \frac{1}{R} \frac{1}{f(R, l, R)}$$

PROBLEM 19.17

$$A_{\perp} = A + \frac{dA}{d(1/R)} \left(\frac{1}{R_{\perp}} - \frac{1}{R} \right) \quad \text{--- (1)}$$

$$A_{\parallel} = A + \frac{dA}{d(1/R)} \left(\frac{1}{R_{\parallel}} - \frac{1}{R} \right) \quad \text{--- (2)}$$

$$C_i' = C_i + \delta C_i \quad \text{--- (3)}$$

where $\frac{dA}{d(1/R)} = P$

$$(1) \times \frac{1}{3} + (2) \times \frac{2}{3}$$

$$\frac{1}{3} A_{\perp} + \frac{2}{3} A_{\parallel} = A + \frac{1}{3} P \left(\frac{1}{R_{\perp}} - \frac{1}{R} \right) + \frac{2}{3} P \left(\frac{1}{R_{\parallel}} - \frac{1}{R} \right)$$

$$C_i + \delta + \frac{b f d A}{l \Omega} + \frac{b f d P}{l \Omega} \left[\frac{1}{3} \left(\frac{1}{R_{\perp}} - \frac{1}{R} \right) + \frac{2}{3} \left(\frac{1}{R_{\parallel}} - \frac{1}{R} \right) \right]$$

$$= \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i + \delta}$$

$$= \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i \left(1 + \frac{\delta}{C_i} \right)}$$

$$\approx \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i} \left(1 - \frac{\delta}{C_i} \right)$$

$$= \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i} - \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{\delta}{C_i^2}$$

$$\Rightarrow \delta + \frac{b f d P}{l \Omega} \left[\frac{1}{3} \left(\frac{1}{R_{\perp}} - \frac{1}{R} \right) + \frac{2}{3} \left(\frac{1}{R_{\parallel}} - \frac{1}{R} \right) \right]$$

$$= \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{\delta}{C_i^2} \quad \text{--- (4)}$$

$$\ln \left(\frac{C_i'}{C_i^0} \right) = \ln \left(\frac{C_i + \delta}{C_i^0} \right) = \ln \left[\frac{C_i}{C_i^0} \left(1 + \frac{\delta}{C_i} \right) \right]$$

$$= \ln \left(\frac{C_i}{C_i^0} \right) + \ln \left(1 + \frac{\delta}{C_i} \right) \approx \ln \left(\frac{C_i}{C_i^0} \right) + \frac{\delta}{C_i}$$

$$\frac{T}{bR_1} - \sigma = \frac{kT}{\Omega} \ln\left(\frac{C_i}{C_i^{\text{ref}}}\right) + \frac{kT}{\Omega} \frac{\delta}{C_i}$$

$$\frac{T_a}{bR_1} - \sigma = \frac{T_a}{bR} + \frac{kT}{\Omega} \frac{\delta}{C_i}$$

$$\frac{T_a}{b} \left(\frac{1}{R_1} - \frac{1}{R} \right) = \sigma + \frac{kT}{\Omega} \frac{\delta}{C_i} \quad \text{--- (5)}$$

$$\frac{T_a}{b} \left(\frac{1}{R_1} - \frac{1}{R} \right) = \frac{kT}{\Omega} \frac{\delta}{C_i} \quad \text{--- (6)}$$

Substitute (5) and (6) into (4)

$$\delta + \frac{b^2 \rho_a P}{l \Omega} - \frac{b}{T_a} \left[\frac{1}{3} \left(\sigma + \frac{kT}{\Omega} \frac{\delta}{C_i} \right) + \frac{2}{3} \left(\frac{kT}{\Omega} \frac{\delta}{C_i} \right) \right]$$

$$= \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{\delta}{C_i^2}$$

$$\delta + \frac{b^2 \rho_a P}{l \Omega T_a} \left[\frac{1}{3} \sigma + \frac{kT}{\Omega} \frac{\delta}{C_i} \right] = \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{\delta}{C_i^2}$$

$$\frac{b^2 \rho_a P \sigma}{3 l \Omega T_a} = \left\{ \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i^2} - 1 - \frac{b^2 \rho_a P kT}{l \Omega^2 T_a C_i} \right\} \delta$$

$$\therefore \delta = \frac{b^2 \rho_a P \sigma}{3 l \Omega T_a \left\{ \left[\frac{\gamma_V \Sigma_3 \Phi}{k_{iv}} + \frac{4\pi}{15} \frac{\Sigma_3 \Phi R_0^5}{\Omega^2 D_i} \right] \frac{1}{C_i^2} - 1 - \frac{b^2 \rho_a P kT}{l \Omega^2 T_a C_i} \right\}} \quad \text{--- (7)}$$

Substitute (7) into (5) and solve for $\frac{1}{R_1} - \frac{1}{R}$,
then into (1) to get $A_1 - A$

PROBLEM 19.18

number of uncollapsed disks in (m, dm) per PKA
 $= N(m) dm = \frac{V}{\ln V} \frac{dm}{m^2}$

Rate of formation of uncollapsed disks in (m, dm) / cm
 $= \left(\frac{V}{\ln V} \right) \Sigma_s \Phi \frac{dm}{m^2}$

Volume increase
 uncollapsed disk of size $m = m \Omega$

$$\frac{d\left(\frac{\Delta V}{V}\right)}{dt} = \int_1^{m_c} \frac{V}{\ln V} \Sigma_s \Phi m \Omega \frac{dm}{m^2} = \Sigma_s \Phi \Omega \left(\frac{V}{\ln V} \right) \ln m_c$$

$$\therefore \frac{\Delta V}{V} = \Sigma_s \Phi \Omega \left(\frac{V}{\ln V} \right) \ln m_c \times t$$

$$= \Omega \Sigma_s (\Phi t) \left(\frac{V}{\ln V} \right) \ln m_c$$

$$\Omega = 12 \times 10^{-24} \text{ cm}^3$$

$$\Sigma_s = 0.2 \text{ cm}^{-1}$$

$$\Phi t = 10^{20} \text{ neutrons/cm}^2$$

$$m_c \approx 200$$

$$V = 500$$

$$\therefore \frac{\Delta V}{V} = (12 \times 10^{-24}) \times (0.2) (10^{20}) \left(\frac{500}{\ln 500} \right) \ln 200$$

$$\approx 10 \%$$

PROBLEM 19.19

(A.) Let $\Omega [D_v C_v - D_i C_i] = A(t)$, then Eq (19.175) (with $R_c \approx 0$) may be written as:

$$\frac{1}{2} R^2 = \int_{\tau}^t A(t') dt'$$

Take derivative with respect to τ at constant t

$$\frac{\partial}{\partial \tau} \left(\frac{1}{2} R^2 \right) = R \left(\frac{\partial R}{\partial \tau} \right)_t = - \frac{R}{\left(\frac{\partial \tau}{\partial R} \right)_t}$$

$$\frac{\partial}{\partial \tau} \int_{\tau}^t A(t') dt' = -A(\tau)$$

$$\therefore \left(\frac{\partial \tau}{\partial R} \right)_t = - \frac{R}{A(\tau)}$$

In Eq (19.173)

$$N(R, t) = \frac{R I_{\text{nucl}} [T(R, t)]}{\Omega \{ D_v C_v [T(R, t)] - D_i C_i [T(R, t)] \}}$$

It is assumed that C_v and C_i are constant and $I_{\text{nucl}} = \text{constant}$

$$N(R, t) = \begin{cases} \frac{R I_{\text{nucl}}}{\Omega (D_v C_v - D_i C_i)} & \text{for } 0 \leq R \leq [2\Omega (D_v C_v - D_i C_i)]^{1/2} \sqrt{t} \\ 0 & \text{for } R > [2\Omega (D_v C_v - D_i C_i)]^{1/2} \sqrt{t} \end{cases}$$

(B.) $A = \Omega (D_v C_v - D_i C_i)$

$$\frac{\Delta V}{V} = \int_0^{R_{\text{max}}} \frac{4}{3} \pi R^3 N(R, t) dR$$

$$N(R) = \frac{R I_{\text{nuc}}}{A}, \text{ up to } R_{\text{max}} = \sqrt{2At}$$

$$\frac{\Delta V}{V} = \frac{4}{3} \pi \frac{I_{\text{nuc}}}{A} \int_0^{\sqrt{2At}} R^4 dR$$

$$= \frac{4 \pi \times 2^{5/2}}{15} I_{\text{nuc}} A^{3/2} t^{5/2}$$

$$= \frac{2^{9/2}}{15} \pi I_{\text{nuc}} \Omega^{3/2} (D_V C_V - D_i C_i)^{3/2} t^{5/2}$$

This model neglects the sinks of vacancies and interstitials introduced by the void themselves and by the loops.
At constant flux Φ :

$$\frac{\Delta V}{V} \sim (\Phi t)^{5/2}$$

CHAPTER 20PROBLEM 20.1

A.

Balance over slice dx in one leg of loop of Fig 20.7

Cross sectional area $A = \pi \frac{d^2}{4}$

Input $= v c A$

output $= v (c + \frac{dc}{dx} dx) A$

$\therefore$ Net input from wall $= v \frac{dc}{dx} dx A$

$= K_d (C_{sat} - c) P dx$

$$\therefore \frac{dc}{dx} = \frac{K_d (C_{sat} - c) P}{v A} = \frac{4 K_d}{d v} (C_{sat} - c)$$

which is equation (20.12)

$$\text{Let } \gamma = \frac{x}{L}$$

$$\frac{dc}{d\gamma} = \frac{4 K_d L}{v d} (C_{sat} - c)$$

$$\text{Let } \frac{4 K_d L}{v d} = \gamma$$

$$\frac{dc}{d\gamma} + \gamma c = \gamma C_{sat}$$

$$\text{Integrating } c = A e^{-\gamma} + C_{sat}$$

$$\text{When } \gamma = 0, c = c(0) = A + C_{sat}$$

$$\therefore A = c(0) - C_{sat}$$

at Hot leg

$$\frac{C_{ant}^h - C(7)}{C_{ant}^h - C(10)} = e^{-Y_h \tau} \quad \text{--- (1)}$$

(1) is equation (20.14a) in the text

at cold leg

$$\frac{C(7) - C_{ant}^c}{C(1) - C_{ant}^c} = e^{-Y_c \tau} \quad \text{--- (2)}$$

which is equation (20.14b) in the text

B. at $x = L$

From (1) $\frac{C_{ant}^h - C(1)}{C_{ant}^h - C(10)} = e^{-Y_h} \approx 1 - Y_h \quad \text{--- (3)}$

at $x = 0$

From (2) $\frac{C(10) - C_{ant}^c}{C(1) - C_{ant}^c} = e^{-Y_c} \approx 1 - Y_c \quad \text{--- (4)}$

Let $\beta = \frac{C_{ant}^c}{C_{ant}^h} < 1$

$X_c = \frac{C(1)}{C_{ant}^h} \quad X_h = \frac{C(10)}{C_{ant}^h} \quad (\text{see Fig 20.3})$

From (3) $\frac{1 - X_c}{1 - X_h} = 1 - Y_h$

or $X_c = Y_h + (1 - Y_h) X_h \quad \text{--- (5)}$

From (4) $\frac{X_h - \beta}{X_c - \beta} = 1 - Y_c$

or $X_h = (1 - Y_c) X_c + \beta Y_c \quad \text{--- (6)}$

solving (5) and (6)

$$X_h = \frac{\beta Y_c + (1 - Y_c) Y_h}{1 - (1 - Y_c)(1 - Y_h)} \quad \text{--- (7)}$$

as $\beta \rightarrow 1$, $X_h \rightarrow 1$ and as $Y_c \rightarrow 0$, $X_h \rightarrow 1$

$$X_c = \frac{Y_h + \beta Y_c (1 - Y_h)}{1 - (1 - Y_c)(1 - Y_h)} \quad \text{--- (8)}$$

As $\beta \rightarrow 1$ $X_c \rightarrow 1$ and As $Y_c \rightarrow 0$ $X_c \rightarrow 1$

C. Expand to first order in Y_c
denominator of (7) :

$$\begin{aligned} 1 - (1 - Y_c)(1 - Y_h) &= 1 - [1 - (Y_c + Y_h) + Y_c Y_h] \\ &= Y_c + Y_h - Y_c Y_h = Y_h + (1 - Y_h) Y_c \\ &= Y_h \left[1 + \left(\frac{1 - Y_h}{Y_h} \right) Y_c \right] \end{aligned}$$

Numerator of equation (7)

$$\begin{aligned} \beta Y_c + (1 - Y_c) Y_h &= Y_h \left[1 - Y_c + \frac{\beta}{Y_h} Y_c \right] \\ &= Y_h \left[1 + \left(\frac{\beta - Y_h}{Y_h} \right) Y_c \right] \end{aligned}$$

$$X_h = \frac{1 + \left(\frac{\beta - Y_h}{Y_h} \right) Y_c}{1 + \left(\frac{1 - Y_h}{Y_h} \right) Y_c} \quad \text{--- (9)}$$

For $Y_c \rightarrow 0$ (9) becomes

$$\begin{aligned} X_h &\rightarrow 1 - \left[\frac{1 - Y_h}{Y_h} - \frac{\beta - Y_h}{Y_h} \right] Y_c \\ &= 1 - \left(\frac{1 - Y_h - \beta + Y_h}{Y_h} \right) Y_c \end{aligned}$$

$$X_h = 1 - (1 - \beta) \frac{Y_c}{Y_h}$$

$$1 - X_h = (1 - \beta) \frac{Y_c}{Y_h} \quad \text{--- (10)}$$

Using (10) in (5)

$$X_c = X_h + (1 - Y_h) \left[1 - \frac{Y_c}{Y_h} (1 - \beta) \right]$$

$$\text{or } X_c = 1 - \left(\frac{1 - Y_h}{Y_h} \right) (1 - \beta) Y_c \quad \text{--- (11)}$$

Rate of removal of metal from hot leg = rate
of metal deposition in cold leg
= flow rate $\times [C(1) - C(0)]$ gms/sec

$$\begin{aligned}\text{flow rate} &= VA \text{ cm}^3/\text{sec} \\ \text{rate of metal transport} &= VA [C(L) - C(0)] \\ &= VA C_{\text{sat}}^h (X_c - X_h)\end{aligned}$$

Using (10) and (11)

$$\begin{aligned}\text{rate of metal transport} &= VA C_{\text{sat}}^h Y_c (1 - \beta) \\ &= V \frac{\pi d^2}{4} [C_{\text{sat}}^h - C_{\text{sat}}^c] \left(\frac{4 K_{dc} L}{V d} \right) \\ &= \pi d L K_{dc} (C_{\text{sat}}^h - C_{\text{sat}}^c)\end{aligned}$$

This is just the deposition rate over entire cold leg (area = $\pi d L$) with a driving force equal to the saturation concentration difference between the hot and cold legs. If $C_{\text{sat}}^c \ll C_{\text{sat}}^h$, transport rate is independent of $T_h - T_c$.

PROBLEM 20.2

Type 316 steel contains 0.3 wt% silicon
($X_{Si} \approx 0.006$ atom fraction)

The reaction is

Since the silicon forms ideal solution in steel, the activity of silicon in steel is equal to its atom fraction X_{Si} , the law of mass is

$$\frac{1}{a_{O^*} X_{Si}^{1/3}} = \exp\left(-\frac{\Delta G_1^0}{RT}\right) \quad \text{--- (2)}$$

where a_{O^*} : critical oxygen activity for Na_2SiO_3 precipitation

ΔG_1^0 : standard state free energy change of reaction (1)

$$\Delta G_{f, Na_2O}^0 = -397 + 118(T/10^3) \text{ kJ/mole} \quad \text{Equation (20.16)}$$

Formation of Na_2SiO_3 from the elements:

$$\Delta G_{f, Na_2SiO_3}^0 = -511 + 95(T/10^3) \text{ kJ/mole}$$

$$\Delta G_1^0 = \Delta G_{f, Na_2SiO_3}^0 - \Delta G_{f, Na_2O}^0 = -114 - 23(T/10^3)$$

$$\text{at } T = 700^\circ C = 973^\circ K \quad \Delta G_1^0 = -136.4 \text{ kJ/mole}$$

$$\begin{aligned}
 a_o^* &= X_{Si}^{-\frac{1}{3}} \exp(\Delta G_i^0 / RT) \\
 &= (0.006)^{\frac{1}{3}} \exp \left[\frac{-136.4}{(8.314)(0.973)} \right] \\
 &= 2.6 \times 10^{-7}
 \end{aligned}$$

From Eq (20-18), $C_{sat} = 5680 \text{ ppm @ } 700^\circ\text{C}$

$\therefore$ The critical oxygen concentration in sodium is $(2.6 \times 10^{-7})(5680) = 1.5 \times 10^{-3} \text{ ppm by weight Na}_2\text{SiO}_3$ should form in all sodium loops. Since the oxygen content is greater than this

PROBLEM 20.3

Let $C_{int}(0)$ = interface concentration of O in Sodium

Diffusion rate of oxygen to surface from bulk sodium = $k_d (C_o - C_{int}(0))$ gms O/cm²-sec --- (1)

The reaction proceeds at the interface according to Eq (20.24) as long as $C_{int}(0)$ is greater than the critical oxygen concentration

$$a_o^* = \exp(\Delta G^\circ/RT) \text{ --- (2)}$$

where ΔG° is the standard free energy of the reaction given by equation (20.23). In this problem, ΔG° is assumed to be more negative than the value calculated in the text, so that a_o^* is also small. The standard oxygen concentration is given by

$$C_o^* = a_o^* C_{sat}(0)$$

where $C_{sat}(0)$ is the saturation concentration of

oxygen in Na (Eq (20.18))

The rate of this reaction

is proportional to the difference between $C_{\text{int(o)}}$ and C_o^* .

The rate of reaction of Na_2O with iron = $k_r(C_{\text{int(o)}} - C_o^*)$ --- (4)

Since the diffusion and reaction steps are in series, we may equate (1) and (4) and eliminate $C_{\text{int(o)}}$

$$k_d(C_o - C_{\text{int(o)}}) = k_r(C_{\text{int(o)}} - C_o^*) \text{ --- (5)}$$

$$\text{or } C_{\text{int(o)}} = \frac{\left(\frac{k_d}{k_r}\right) C_o + C_o^*}{1 + \frac{k_d}{k_r}} \text{ --- (6)}$$

Substituting (6) into (1) gives the oxygen transport rate to the surface:

$$\text{Rate of oxygen transport} = K_d(C_o - C_o^*) \text{ --- (7)}$$

Where K_d is the overall transfer coefficient including the chemical reaction step represented by k_r :

$$\frac{1}{K_d} = \frac{1}{k_d} + \frac{1}{k_r} \text{ --- (8)}$$

Eq (7) gives the rate of oxygen transport to the surface. To get the corrosion rate,

each gram atom of O removes $\frac{1}{3}$ gram atom of Fe
therefore

$$\dot{m} = \frac{1}{3} \times \frac{56}{16} \times \text{oxygen transport rate in } \frac{\text{gm O}}{\text{cm}^2 \cdot \text{sec}} \quad (9)$$

Using (7) and (8) in (9)

$$\dot{m} = \frac{56}{48} \left[\frac{1}{\frac{1}{k_d} + \frac{1}{k_R}} \right] (C_o - C_o^*) \frac{\text{gm Fe}}{\text{cm}^2 \cdot \text{sec}} \quad (10)$$

No corrosion occurs if $C_o \leq C_o^*$. In this calculation based upon Eq (20.25) in the text C_o^* was estimated to be ~ 130 ppm @ 450°C and 1650 ppm @ 700°C . Generally, $C_o \leq 5$ ppm. However, if $\Delta G_{\text{Na ferrite}}$ is more negative than indicated by Eq (20.21), ΔG° of equation (20.23) is also more negative. Hence, equations (2) and (3) show that C_o^* becomes smaller if $C_{\text{sat}(O)}$ is less than ~ 1 ppm. Corrosion by formation of sodium ferrite could occur and its rate would be given by equation (10).

PROBLEM 20.4

$$\Omega = 12 \text{ \AA}^3 = 12 \times 10^{-24} \text{ cm}^3$$

$$(3\Omega)^{1/3} = (36 \times 10^{-24})^{1/3} = 3.3 \times 10^{-8} \text{ cm}$$

$$\gamma = 100 \text{ dynes/cm (interfacial tension)}$$

$$kT = (1.38 \times 10^{-16}) (1.8 \times 10^3) = 1.1 \times 10^{-13} \text{ dyne-cm}$$

$$\frac{\gamma}{kT} = \frac{10^2 \text{ dyne/cm}}{1.1 \times 10^{-13} \text{ dyne-cm}} = 10^{15} \text{ cm}^{-2}$$

$$(36\pi\Omega^2)^{1/3} = (4\pi)^{1/3} (3\Omega)^{2/3} = 2.5 \times 10^{-15} \text{ cm}^2$$

$$\xi = 2.5$$

$$(4\pi)^{1/6} \frac{(3\Omega)^{1/3}}{\xi^{1/2}} = \frac{1.5 \times 3.3 \times 10^{-8}}{\sqrt{2.5}} = 3 \times 10^{-8} \text{ cm}$$

In nucleation formula, $N_s = \text{Iron atoms/c.c.}$

$$\approx C = 5 \text{ } C_{\text{sat}}^{\text{hot}}(\text{Fe})$$

(i.e. the number of nucleation sites = number of atoms in solution)

$$\therefore I = 3 \times 10^{-8} D (C_{\text{sat}}^{\text{hot}}(\text{Fe}) 5)^2 \ln S \exp \left[-\frac{4}{27} \frac{\xi^3}{(\ln S)^2} \right]$$

$$S = \frac{C_{\text{sat}}^{\text{hot}}(\text{Fe})}{C_{\text{sat}}^{\text{cold}}(\text{Fe})}$$

$$T_{\text{hot}} \approx 700^\circ\text{C}, \quad C_{\text{sat}}^{\text{hot}}(\text{Fe}) = 6 \text{ ppm}$$

$$T_{\text{cold}} \approx 500^\circ\text{C}, \quad C_{\text{sat}}^{\text{cold}} = 0.3 \text{ ppm (wt)}$$

$$C_{\text{sat}}^{\text{hot}}(\text{Fe}) = 3 \times 10^{-7} \frac{\text{gm Fe}}{\text{gm Na}} \times 0.8 \frac{\text{gm Na}}{\text{cm}^3} \times \frac{\text{gm atom Fe}}{56 \text{ gm Fe}}$$

$$\times 6.02 \times 10^{23} \frac{\text{atoms Fe}}{\text{gm. atom Fe}} = 3 \times 10^{15} \frac{\text{atoms Fe}}{\text{cm}^3}$$

When the hot leg solution is cooled to 500°C , Initial $S = \frac{6}{0.3} = 20$, $\ln S = 3$

$(C_{\text{ant } S})^2 = [(3 \times 10^{15}) (20)]^2 = 3.6 \times 10^{33} \text{ cm}^{-6}$
 the diffusivity of iron in sodium is
 $D = 10^{-5} \text{ cm}^2/\text{sec}$

$$\frac{4}{27} \frac{S^3}{(\ln S)^2} = \frac{4}{27} \times \frac{(2.5)^3}{(3)^2} = 0.26$$

$$e^{-0.26} \approx 1$$

The nucleation rate is

$$I = (3 \times 10^{-8}) (1 \times 10^{-5}) (3.6 \times 10^{33}) (3 \times 10^1) \\ = 4 \times 10^{21} \text{ cm}^{-3} \text{ sec}$$

The size of the critical nucleus is

$$m_c = \left(\frac{2.3}{3 \ln S} \right)^3 = \left(\frac{5}{9} \right)^3 < 1$$

This means that classical nucleation theory is probably NOT valid

PROBLEM 20.5

A

Axial variation of linear power

$$P(z) = P_0 \cos\left(\frac{\pi z}{z'}\right)$$

where z' is determined by the axial power peaking factor.

$$\frac{P(z=0)}{P(z=\frac{z}{2})} = 1.8 = \frac{1}{\cos\left(\frac{\pi z}{2z'}\right)}$$

$$\therefore \frac{\pi z}{2z'} = \cos^{-1}\left(\frac{1}{1.8}\right) = 0.98$$

$$P(z) = P_0 \cos\left(\frac{\pi z}{z'} \cdot \frac{z}{z}\right) = P_0 \cos\left(1.86 \frac{z}{z}\right) \quad \text{--- (1)}$$

Neglecting power generation in blanket:

$$\begin{aligned} \text{Total rod power} &= \int_{-\frac{z}{2}}^{\frac{z}{2}} P(z) dz = P_0 \int_{-\frac{z}{2}}^{\frac{z}{2}} \cos\left(1.86 \frac{z}{z}\right) dz \\ &= \frac{2z P_0}{1.96} \end{aligned}$$

also

$$\text{Total rod power} = \frac{\text{reactor electrical power}}{\text{thermal efficiency} \times \text{number of rod}}$$

$$= \frac{10^9 \text{ Watts}}{0.4 \times 10^5} = 2.5 \times 10^4 \text{ Watts}$$

For $2z = 90 \text{ cm}$

$$P_0 = \frac{2.5 \times 10^4 \times 1.96}{90} = 544 \text{ Watts/cm}$$

Heat Balance in Sodium:

W : Sodium flow/rod

C_p : Sodium heat capacity

$$P = W C_p \frac{dT}{dz} = P_0 \cos\left(1.96 \frac{z}{2}\right)$$

Integrating

$$T(z) - T_{\text{inlet}} = \left(-\frac{P_0}{W C_p}\right) \int_{-\frac{z}{2}}^z \cos\left(1.96 \frac{z}{2}\right) dz$$

$$T_{Na}(z) - T_{\text{inlet}} = \frac{P_0}{W C_p} \frac{z}{1.96} \left[\sin\left(1.96 \frac{z}{2}\right) + \sin(0.98) \right]$$

at $z = \frac{z}{2}$

$$T_{\text{outlet}} - T_{\text{inlet}} = \frac{P_0}{W C_p} \frac{z}{1.96} [2 \sin(0.98)] = 650 - 470$$

$$\therefore T_{Na}(z) = 470 + 180 \left[\frac{\sin\left(1.96 \frac{z}{2}\right) + 0.83}{1.66} \right] \dots (2)$$

T_{cl} : temperature of outside of claddings

h_{Na} : sodium film heat transfer coefficient

Heat flux through clad wall

$$= \frac{P}{2\pi R_a} = h_{Na} (T_{cl} - T_{Na})$$

R_a : fuel rod radius = 0.135 cm (Table 10.2)

$$\therefore T_{cl} = T_{Na} + \frac{P}{2\pi R_a h_{Na}}$$

$$T_{cl} = T_{Na} + \frac{P_0}{2\pi R_a h_{Na}} \cos\left(1.96 \frac{z}{2}\right)$$

From Table 10, $h_{Na} \approx 12 \frac{\text{watts}}{\text{cm}^2 \cdot ^\circ\text{C}}$

$$T_{ce} = T_{Na} + \frac{544}{(6.28)(0.315)(12)} \cos(1.96 \frac{z}{2})$$

$$= T_{Na} + 23^\circ\text{C} \cos(1.96 \frac{z}{2})$$

$$\therefore T_{ce}(z) = 470 + 180 \left[\frac{\sin(1.96 \frac{z}{2}) + 0.83}{1.66} \right] + 23 \cos(1.96 \frac{z}{2}) \quad \text{--- (3)}$$

Corrosion rate from eq (20.55)

$$C_0 = 5 \text{ ppm}$$

$$R = 8.31 \text{ J/mole } ^\circ\text{K}$$

neglect x/d

$$\therefore \dot{m} = (1.1 \times 10^8)(5)^{1.3} \exp\left(-\frac{1.46}{8.31 T_{ce}/10^3}\right)$$

$$\dot{m} = 8.9 \times 10^8 \exp\left(-\frac{17.57}{(T_{ce}/10^3)}\right) \quad \text{--- (4)}$$

Corrosion in fueled portions of core

$z/2$	$T_{ce} (^\circ\text{K})$	$\dot{m} (\mu\text{m/yr})$	$\cos(1.96 \frac{z}{2}) \dot{m}$
-0.5	756	0.07	0.04
-0.4	773	0.12	0.08
-0.3	792	0.21	0.17
-0.2	813	0.37	0.34
-0.1	834	0.63	0.62
0	856	1.08	1.08
0.1	876	1.73	1.70
0.2	896	2.62	2.42
0.3	912	3.82	3.18
0.4	926	5.12	3.63
0.5	936	6.26	3.47

Total core corrosion rate

$$\dot{m} \left(\frac{\text{gms}}{\text{cm}^2 \cdot \text{yr}} \right) = \dot{m} \left(\frac{\mu\text{m}}{\text{yr}} \right) \frac{\text{cm}}{10^4 \mu\text{m}} \times 7.9 \frac{\text{gms}}{\text{cm}^3}$$

$$\therefore \dot{m} \left(\frac{\text{gms}}{\text{cm}^2 \cdot \text{yr}} \right) = \dot{m} \left(\frac{\mu\text{m}}{\text{yr}} \right) \times 7.9 \times 10^{-4}$$

Metal loss rate from one fuel rod
Consider a slice of thickness dz
rate of metal loss in dz

$$= \dot{m} \left(\frac{\text{gms}}{\text{cm}^2 \cdot \text{yr}} \right) \cdot 2\pi R_a dz$$

$$\text{metal loss rate from rod} = \int_{-z/2}^{z/2} \dot{m}(z) 2\pi R_a dz$$

$$= 2\pi R_a z \int_{-1/2}^{1/2} \dot{m}(z/2) d(z/2)$$

$$= (628)(0.315)(90) \int_{-1/2}^{1/2} \dot{m}(z/2) d(z/2)$$

$$= 178 \text{ cm}^2 \times \left[\frac{0.1(0.7)}{2} + 0.1(0.12) \right]$$

$$+ 0.1 \times (5.12) + \frac{0.1(626)}{2}$$

$$= 178 \text{ cm}^2 \times 1.88$$

$$\therefore \text{metal loss rate from fuel rod (fueled portion only)} = (7.9 \times 10^{-4})(178)(1.88)$$

$$= 0.27 \text{ gms/yr}$$

The top axial blanket (30 cm) is at the outlet sodium temperature of 650°C for which the corrosion rate,

$$\dot{m} = 8.9 \times 10^{-8} \exp\left(-\frac{17.57}{0.923}\right) = 4.81 \mu\text{m/yr}$$

The area is $(6.28)(0.315)(30) = 59.3 \text{ cm}^2$
 metal loss rate from upper axial blanket
 section is $(4.81)(7.9 \times 10^{-4})(59.3) = 0.23 \text{ gms/yr}$
 $\therefore$ Total metal loss rate per rod
 $= 0.50 \text{ gms/yr}$

For 40 years operation at a 75% load factor
 the total metal loss $= (0.50) \text{ gms/yr} \times 30 \text{ yr}$
 $\times 10^5 \text{ rods} = 1.5 \times 10^6 \text{ gms}$

[The reaction $\text{Mn}^{55} (n, n) \text{Mn}^{54}$ is negligible]
 at time t activity in type 304 SS cladding
 given by

$$\frac{d\text{Mn}^{54}}{dt} = \sigma_{\text{eff}} N_{\text{Fe}^{54}} \Phi - \lambda N_{\text{Mn}^{54}}$$

$$N_{\text{Mn}^{54}} = \frac{\sigma_{\text{eff}} N_{\text{Fe}^{54}} \Phi}{\lambda} (1 - e^{-\lambda t}) \quad \text{--- (1)}$$

λ decay constant of $\text{Mn}-54 = \frac{0.693}{T_{1/2}} = 0.81 \text{ yr}^{-1}$

Φ total fast flux at the position in question

$$N_{\text{Fe}^{54}} = (0.85 \times 10^{23}) (0.85) (0.058)$$

$\uparrow$ (metal atom density in steel) $\uparrow$ (fraction of Fe in steel) $\uparrow$ (Natural abundance of Fe-54 in iron)

$$= 3.2 \times 10^{21} \frac{\text{atoms Fe}^{54}}{\text{cm}^3 \text{ steel}}$$

$\sigma_{\text{eff}} =$ effective cross section for reaction
 in neutron spectrum $= 16 \text{ mb}$

Mn^{54} release due to the $Fe^{54}(n,p)Mn^{54}$ reaction in the cladding. Consider a slice dz of cladding where the corrosion rate is $\dot{m}$ and the fast flux is Φ . In time dt the amount of steel lost by corrosion is $(2\pi R a dz) \dot{m} dt$ gms. The Mn^{54} content of the steel is given by eq (1) and the number of Mn^{54} atoms lost in dt from the slice is

$$(2\pi R a dz) \dot{m} dt \times \frac{N_{Mn^{54}}}{\rho} \quad \rho = \text{density of steel}$$

or the ratio of Mn^{54} release from the entire fuel pin is

$$\frac{2\pi R a}{\rho} \bar{\sigma}_{eff} N_{Fe^{54}} (1 - e^{-\lambda t}) \int_{-z/2}^{z/2} \Phi(z) \dot{m}(z) dz$$

where the integral is extended into the upper blanket ($z/2$). For all 100000 fuel elements in the core, the rate of Mn^{54} release is

$$Q(t) = 10^5 \frac{2\pi R a}{\rho} \frac{\bar{\sigma}_{eff} N_{Fe^{54}}}{\lambda} (1 - e^{-\lambda t}) \Phi_0 \int_{-z/2}^{z/2} \cos(1.96 \frac{z}{Z}) \dot{m} dz$$

where the flux shape follows the linear power axial distribution and in addition, extends into the axial blankets.

From part A, $\frac{z}{Z} = \frac{\pi}{1.96}$ and $Q(t)$ is

$$Q(t) = 10^{-4} (10^5 2\pi R a Z) \frac{(\bar{\sigma}_{eff} N_{Fe^{54}})}{\lambda} (1 - e^{-\lambda t}) \Phi_0 \times \left[\int_{-1/2}^{1/2} \cos(1.96 \frac{z}{Z}) \dot{m}(\frac{z}{Z}) d(\frac{z}{Z}) + \dot{m}_{BL} \int_{\frac{1}{2}}^{0.80} \cos(1.96 \frac{z}{Z}) d(\frac{z}{Z}) \right]$$

where $\dot{m}$ is now expressed in $\mu\text{m}/\text{yr}$.
 $\dot{m}(\frac{3}{2})$ in fueled region from Table in part A

Assume all Mn^{54} is retained in cold trap

Mn^{54} balance on cold trap
 Input = $Q(t)$ atoms Mn^{54}/yr

decay = λN_{Mn} atoms Mn^{54}/yr

$$\frac{dN_{\text{Mn}}}{dt} = Q(t) - \lambda N_{\text{Mn}}$$

Now write $Q(t)$ as $Q(t) = B(1 - e^{-\lambda t})$

where

$$B = 10^{-4} (10^5 2\pi R a z) \frac{\sigma_{\text{eff}} N_{\text{Fe}}^{54}}{\lambda} \Phi_0 \left[\int_{-1/2}^{1/2} \cos(1.96 \frac{3}{2}) \dot{m} d(\frac{3}{2}) \right. \\ \left. + \dot{m}_{\text{Be}} \int_{1/2}^{0.80} \cos(1.96 \frac{3}{2}) d(\frac{3}{2}) \right]$$

$$\frac{dN_{\text{Mn}}}{dt} = B(1 - e^{-\lambda t}) - \lambda N_{\text{Mn}}$$

Integrating

$$N_{\text{Mn}} = c e^{-\lambda t} + B e^{-\lambda t} \int e^{\lambda t} (1 - e^{-\lambda t}) dt$$

$$= C e^{-\lambda t} + \frac{B}{\lambda} (1 - \lambda t + e^{-\lambda t})$$

Evaluate C from condition $N_{Mn}(0) = 0$

$$\Rightarrow C = -\frac{B}{\lambda}$$

$$\therefore N_{Mn} = \frac{B}{\lambda} [1 - \lambda t + e^{-\lambda t} - e^{-\lambda t}] = \frac{B}{\lambda} [1 - (1 + \lambda t) e^{-\lambda t}]$$

or with A_{Mn} = activity of Mn^{54} in cold trap
 $= \lambda N_{Mn}$

$$A_{Mn} = B [1 - (1 + \lambda t) e^{-\lambda t}] \quad \text{--- (2)}$$

Evaluation of B:

internal area of fueled section of core
 $= 10^5 \cdot 2\pi R a Z = (10^5)(6.28)(0.315)(90) = 1.78 \times 10^7 \text{ cm}^2$

$$\sigma_{\text{eff}} N_{Fe}^{54} = (1.6 \times 10^{-27})(3.2 \times 10^{21}) = 5.12 \times 10^{-5} \text{ cm}^{-1}$$

$$\Phi_0 = 7 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$$

$$\lambda = 0.81 \text{ yr}^{-1} = 2.58 \times 10^{-8} \text{ sec}^{-1}$$

From part A table

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} \cos(1.96 \frac{z}{2}) \sin d(\frac{z}{2}) = 0.1 \left(\frac{0.04}{2} + 0.08 + \dots + \frac{3.47}{2} \right)$$

$$= 1.50 \mu\text{m/yr}$$

$$\dot{m}_{BL} \int_{\frac{1}{2}}^{0.80} \cos(1.96 \frac{z}{2}) d(\frac{z}{2}) = (0.0865)(4.81)$$

$$= 0.42 \mu\text{m/yr}$$

$$\therefore B = (10^{-4})(1.78 \times 10^7) \left(\frac{5.12 \times 10^{-5}}{2.58 \times 10^{-8}} \right) (7 \times 10^{15}) (1.50 + 0.42)$$

$$= 4.75 \times 10^{22} \text{ yr}^{-1}$$

Converting to Curies

$$B = \frac{4.75 \times 10^{22} \text{ yr}^{-1}}{3.14 \times 10^7 \frac{\text{sec}}{\text{yr}} \times 3.7 \times 10^{10} \frac{\text{dis/sec}}{\text{Ci}}} = 4.1 \times 10^4 \text{ Ci}$$

$$\text{at } t = 1 \text{ yr} \quad \lambda t = 0.81$$

$$1 - (1 + \lambda t) e^{-\lambda t} = 1 - 1.81 e^{-0.81} = 0.195$$

$$A_{Mn} = (4.1 \times 10^4)(0.195) = 0.8 \times 10^4 \text{ Ci}$$

PROBLEM 20.6

Substituting Eq (20.59) into Eq (20.63)

$$\ln K_H = \ln C_{\text{NaOH}} - \Delta G_f^\circ \text{NaOH} / RT$$

$$\text{or } \Delta G_f^\circ \text{NaOH} = R \frac{T}{10^3} [\ln C_{\text{NaOH}} - \ln K_H] \text{ ----- (1)}$$

$$= R (T/10^3) \left[\left(14 - \frac{55}{R(T/10^3)} \right) - \left(5.3 - \frac{2.3}{R(T/10^3)} \right) \right]$$

$$\Delta G_f^\circ \text{NaOH} = -52.7 + 8.7 R (T/10^3)$$

$$\Delta G_f^\circ \text{NaOH} = -52.7 + 72 (T/10^3) \text{ KJ/mole}$$

which is ~ 6 Kcal/mole different from value from equation (20.58) at 1000°K.

PROBLEM 20.7

Hydrogen equilibrates between the sodium and the exposed face of the nickel:

$$H(\text{solution in Na}) = H(\text{solution in Ni at } \textcircled{1})$$

Let $P_{H_2}^{eq}$ be the hydrogen pressure in equilibrium with concentration C_H in sodium.

From eq (20.62)

$$(P_{H_2}^{eq})^{1/2} = \frac{C_H}{K_{HNa}} \quad \text{--- (1)}$$

where K_{HNa} is the Sievert's law constant for hydrogen in sodium

Sievert's law for hydrogen in nickel is

$$K_{HNi} = \frac{(C_{H_{Ni}})_1}{(P_{H_2}^{eq})^{1/2}} = \frac{(C_{H_{Ni}})_1}{(C_H / K_{HNa})^{1/2}} \quad \frac{\text{ppm}}{\text{atm}^{1/2}}$$

$$\text{or } (C_{H_{Ni}})_1 = \left(\frac{K_{HNi}}{K_{HNa}} \right) C_H \quad \text{--- (2)}$$

at the opposite face of the Nickel membrane P_{H_2} is in equilibrium with $(CHNi)_2$

$$(CHNi)_2 = K_{HNi} P_{H_2}^{1/2} \quad \text{----- (3)}$$

The flux of H atoms through the membrane is:

$$J = AB \frac{D_{HNi}}{\delta} [(CHNi)_1 - (CHNi)_2], \quad \frac{\text{atoms H}}{\text{sec}}$$

where δ is membrane thickness

A surface area of membrane

Using (2) and (3)

$$B = 6.02 \times 10^{23} \rho_{Ni} \times 10^{-6} \frac{\text{atoms H/cm}^3 \text{ Ni}}{\text{PPM}}$$

ρ_{Ni} = density of nickel

$$J = AB \frac{D_{HNi}}{\delta} \left[\left(\frac{K_{HNi}}{K_{H_2Ni}} \right) C_H - K_{HNi} P_{H_2}^{1/2} \right] \quad \text{----- (4)}$$

The pumping speed S of a vacuum pump is related to the molecular throughput Q (molecules/sec) by the ideal gas law

$$PS = QRT_0$$

where T_0 = temperature of pump operation = 300°K

P = gas pressure in vacuum chamber (torr)

R = gas constant, lit-atm/molecule-°K

For the present case $P = P_{H_2}$

$$Q = \frac{1}{2} J \quad (\text{flux of } H_2 = \frac{1}{2} \text{ flux of H})$$

$$\therefore J = \frac{2 P_{H_2} S}{R T_0} \quad \text{----- (5)}$$

Equate (4) and (5)

$$P_{H_2} = \left[\frac{RT_0 A B D_{H_2} K_{H_2}}{2 \delta S} \right] \left[\frac{C_H}{K_{HNa}} - P_{H_2}^{1/2} \right] \text{--- (6)}$$

If the ^{↑ constant} constant in eq (6) is known measurement of P_{H_2} in the dynamic mode determines C_H by eq (6).

$\left(\frac{C_H}{K_{HNa}} \right)^2 = P_{H_2} = P_{H_2}^{eq}$ which represents the equilibrium mode of operation

Note. The current measured by the ion pump is proportional to the gas pressure.

PROBLEM 20.8at 370°C (643°K)

From equation (20.18) or Fig 20.9 :

$$C_{\text{sat}}(0) = \exp \left[14.4 - \frac{46.5}{(8.31)(0.643)} \right] = 298 \text{ ppm}$$

$$a_o = \frac{C_o}{C_{\text{sat}}(0)} = \frac{5}{298} = 0.017$$

= oxygen activity

From eq (20.16)

$$\Delta G_{f, \text{Na}_2\text{O}}^{\circ} = -397 + 118(0.643) = -321 \text{ KJ/mole}$$

with air as the reference element

$$P_{\text{O}_2} = 0.21 \text{ atm.}$$

From eq (20.67)

$$\Delta \mathcal{E} = \frac{(8.31)(0.643)}{(4)(9648)} \left[\ln(0.21) - 2 \ln(0.017) - 2 \times \frac{(-321)}{(8.31)(0.643)} \right]$$

$$\Delta \mathcal{E} = 1.75 \text{ volts.}$$

PROBLEM 20.9

A. In terms of Sieverts law, constant for the V-O system, eq (20.70) is

$$\frac{C_O^V}{C_O^{Na}} = \frac{K_O^V \exp \left[\frac{\Delta G_f^{Na_2O}}{RT} \right]}{C_{Na}^{(10)}} \quad \text{--- (1)}$$

at 750°C

$$\text{Eq (20.16)} \rightarrow \Delta G_f^{Na_2O} = -397 + 118(1.023) = -276 \text{ kJ/mole}$$

$$\text{Eq (20.18)} \rightarrow C_{Na}^{(10)} = \exp \left[14.4 - \frac{46.5}{(8.31)(1.023)} \right]$$

$$= 7560 \text{ ppm by wt}$$

$$K_O^V = 2 \times 10^{16} \frac{\text{gm atoms O}}{\text{gm atoms V}} \times \frac{\text{gm atom V}}{51 \text{ gms V}} \times \frac{16 \text{ gms O}}{\text{gm atom O}} \times 100 \frac{\text{wt \%}}{\text{wt fraction}}$$

$$= 6.3 \times 10^{17}$$

$$\frac{C_O^V}{C_O^{Na}} = 6.3 \times 10^{17} \frac{\exp \left(-\frac{276}{(8.31)(1.023)} \right)}{7560} = 0.66$$

About a factor of 2 lower than straight line portion of Fig 20.26

$$B. (C_O^{Na})_{\text{MAX}} = (0.66)(2.3) = 1.5 \text{ ppm}$$

C. fractional error in $(C_O^{Na})_{\text{MAX}}$ = fractional error

$$\text{in } \exp \left[\frac{(\Delta G_f^{Na_2O})}{RT} \right] = \exp \left[\frac{\Delta(\Delta G_f^{Na_2O})}{RT} \right]$$

$$= \exp \left(\frac{10}{8.31 \times 1.023} \right) = 3.2$$

i.e. 320 %

PROBLEM 20.10

a_c^{Na} : activity of carbon in sodium (specified)
 W_c^{int} : carbon content of austenite in steel exposed to sodium

Boundary condition at $z=0$ (the sodium steel interface) (Omit T in functional dependence of γ_c)

From eq (20.97)

$$a_c = W_c^{int} \gamma_c [W_{Cr}^{int}, W_{Ni}^{int}] \quad \text{--- (1)}$$

From (20.105) at the interface

$$W_{Ni}^{int} = W_{Ni}^0 \left(\frac{X - W_{Cr}^0}{X - W_{Cr}^{int}} \right) \quad \text{--- (2)}$$

Use in (1)

$$a_c^{Na} = F \left\{ W_{Cr}^{int}, W_{Ni}^0 \left(\frac{X - W_{Cr}^0}{X - W_{Cr}^{int}} \right), W_c^{int} \right\}$$

solve for W_{Cr}^{int}

$$W_{Cr}^{int} = F^{-1} (W_c^{int}, X, W_{Cr}^0, W_{Ni}^0, a_c) \quad \text{--- (3)}$$

From (20.103) $W_{Cr}^{int} = \frac{W_{Cr}^0 - f^{int} X}{1 - f^{int}} \quad \text{--- (4)}$

From (20.139) $f^{int} = \frac{f_e / f_{ss}}{1.058} \left(\frac{R_{int}}{R} \right)^3 \quad \text{--- (5)}$

where R_{int} = radius of carbide particles in steel exposed to sodium

R given by (20.133) in terms of N

Combine (4) and (5) and equate to (3)

$$\frac{W_c^0 - \frac{J_c/p_{ss}}{1.058} \bar{X} \left(\frac{R_{int}}{R} \right)^3}{1 - \frac{J_c/p_{ss}}{1.058} \left(\frac{R_{int}}{R} \right)^3} = F^{-1}(W_c^{int}, \bar{X}, W_c^0, W_{Ni}^0, A_c) \quad \text{---(6)}$$

W_c^{int} can be solved as a function of R_{int}

From (20.136) applied to steel at sodium-steel interface:

$$W_c^{int} - (W_c^R)_{int} = \frac{0.058}{\bar{X}} \frac{D_M}{D_c} \left\{ W_c^{int} - H[(W_c R_{int}, W_c^0, W_{Ni}^0, \bar{X})] \right\} \quad \text{---(7)}$$

Using (3) in (7)

$$W_c^{int} - (W_c^R)_{int} = \frac{0.058}{\bar{X}} \frac{D_M}{D_c} \left\{ F^{-1}(W_c^{int}, \bar{X}, W_c^0, W_{Ni}^0, A_c) - H[(W_c^R)_{int}, W_c^0, W_{Ni}^0, \bar{X}] \right\} \quad \text{---(8)}$$

Solve $(W_c^R)_{int}$ as a function of W_c^{int} from (8)

Combine (6) and (8), $\Rightarrow$ have $(W_c^R)_{int}$ as function of R_{int}

From (20.140)

$$\frac{dR_{int}}{dt} = \left(\frac{1.058}{0.058} \right) \frac{J_{ss}}{J_c} \frac{D_c}{R_{int}} [W_c^{int} - (W_c^R)_{int}] \quad \text{---(9)}$$

Using (6) for W_c^{int} and (6)+(8) for $(W_c^R)_{int}$,
get $\frac{dR_{int}}{dt}$ as a function of R_{int}

Solve (9) for $R_{int}(t)$. Substitute into (6),
gives $W_c^{int}(t)$, this time dependent quantity
is the boundary condition $W_c(0, t)$ for
Eq (20.138)

Boundary condition at $z=0$ (bulk steel)

Here, we neglect diffusion because all concentration gradients vanish. The concentration of carbon in the austenite is governed only by precipitation kinetics of dissolved carbon to the carbide particles. From Eq (20.138) with the concentration gradient omitted:

$$\frac{d}{dt} [(1-f_\infty) W_{c\infty}] = -4\pi R_\infty D_c N (W_{c\infty} - W_{c\infty}^R) \quad (10)$$

where R_∞ = Radius of carbide particles far from sodium-steel interface.

From (20.140)

$$\frac{dR_\infty}{dt} = \left(\frac{1.058}{0.058} \right) \left(\frac{f_{cs}}{f_c} \right) \frac{D_c}{R_\infty} (W_{c\infty} - W_{c\infty}^R) \quad (11)$$

$$\text{From (20.139)} \quad f_\infty = \frac{(f_c/f_{cs})}{1.058} \left(\frac{R_\infty}{R} \right)^3 \quad (12)$$

From (20.137)

$$\frac{D_c}{D_M} \frac{\bar{X}}{0.058} (W_{c\infty} - W_{c\infty}^R) = \frac{W_{c\infty}^R - f_\infty \bar{X}}{1 - f_\infty} - H(W_{c\infty}^R, W_{c\infty}^R, W_{Ni}^R, \bar{X}) \quad (13)$$

Solve for $W_{c\infty}(t)$ and $R_\infty(t)$ by integrating (10) and (11) with f_∞ and $W_{c\infty}^R$ given by (12) and (13). The initial condition for this integration are

$$W_{c\infty}(0) = (W_c^T)_{fab} \quad (14)$$

$$R_\infty(0) = 0 \quad (15)$$

which assumes that all carbon in the as-fabricated steel is present in supersaturated solution in the austenite.

PROBLEM 20.11

A.

Equivalence of the two formulations of the diffusion equations [i.e. Eq (20.123) and Eq (20.128)] can be seen from the $\frac{dR}{dt}$ equation (20.140)

$$D_c (W_c - W_c^R) = \frac{f_c}{f_{ss}} \frac{0.058}{1.058} R \frac{dR}{dt}$$

Substitute this into (20.138)

$$\frac{\partial [W_c(1-f)]}{\partial t} + 4\pi N \frac{f_c}{f_{ss}} \frac{0.058}{1.058} R^2 \frac{dR}{dt} = D_c \frac{\partial^2 W_c}{\partial z^2}$$

or

$$\frac{\partial [W_c(1-f)]}{\partial t} + 4\pi N \frac{f_c}{f_{ss}} \frac{0.058}{1.058} \frac{1}{3} \frac{dR^3}{dt} = D_c \frac{\partial^2 W_c}{\partial z^2}$$

Remove $\frac{\partial}{\partial t}$

$$\frac{\partial}{\partial t} [W_c(1-f) + (\frac{4}{3}\pi R^3) N \frac{f_c}{f_{ss}} \frac{0.058}{1.058}] = D_c \frac{\partial^2 W_c}{\partial z^2}$$

But from (20.133), $\frac{4}{3}\pi R^3 N = (\frac{R}{R_c})^3$ and the second term on the right is 0.058f by Eq (20.139)

$$\therefore \frac{\partial}{\partial t} [W_c(1-f) + 0.058f] = D_c \frac{\partial^2 W_c}{\partial z^2}$$

By eq (20.109) $W_c^T = W_c(1-f) + 0.058f$

$$\therefore \frac{\partial W_c^T}{\partial t} = D_c \frac{\partial^2 W_c}{\partial z^2} \quad \text{which is Eq (20.123)}$$

B

If D_i is very large in Eq (20.134), but J_i is finite then $W_i = W_i^R$ (Basic requirement of the equilibrium model)

But D_c not infinite in Eq (20.123)

PROBLEM 20.12

The specifications $a_c = 0.01$, $W_{Cr}^0 = 0.18$ fix the point (A) on the plot. the carbon concentration of (A) is

$$W_c^T = 1.1 \times 10^{-3} \text{ (1100 ppm)}$$

- B Since both phase of the steel (austenite and carbide) have the same carbon activity, the composition of the austenite phase is given by moving down the $a_c = 0.01$ isoactivity line from (A) to the solubility line at point (B) at (B)
- $$W_{aust}(c) = 3 \times 10^{-4} = 300$$
- $$W_{Cr} = 0.11 = 11\%$$

C. Eliminating f from Eqs (20.103) and (20.109)

$$\frac{W_C^T - W_{\text{sat}}(C)}{0.058 - W_{\text{sat}}(C)} = \frac{W_{Cr}^0 - W_{Cr}}{X - W_{Cr}}$$

or

$$X = W_{Cr} + \left(\frac{0.058 - W_{\text{sat}}(C)}{W_C^T - W_{\text{sat}}(C)} \right) (W_{Cr}^0 - W_{Cr})$$

Using the result of (A) and (B)

$$X = 5.16$$

D. Since $X = \left(\frac{Cr}{Cr + Fe} \right)$ carbide, it cannot be > 1 . Therefore, either Eqs (20.113) or (20.101) or both are incorrect representation of the equilibrium behavior of carbon in stainless steel.

PROBLEM 20.13

The diffusion equation in fuel

$$\frac{\partial X}{\partial t} = D_f \frac{1}{Y} \frac{\partial}{\partial Y} \left(Y \frac{\partial X}{\partial Y} \right) \quad \text{--- (1)}$$

$$\text{I.C. } X(r, 0) = X_0 \quad \text{--- (2)}$$

$$\text{B.C. I } \left(\frac{\partial X}{\partial Y} \right)_0 = 0 \quad \text{--- (3)}$$

equilibrium at interface is maintained
 i.e. $C_0^{\text{int}} = 52 - 750 X^{\text{int}} \quad \text{--- (4)}$

The oxygen flux into sodium

$$J_0 = k_d \frac{p_{\text{Na}}}{16 \times 10^6} [C^{\text{int}} - C_0] = D_0^f \frac{p_f}{270} \left(\frac{\partial X}{\partial Y} \right)_R, \quad \frac{\text{gm atoms}}{\text{cm}^2 \text{ sec}}$$

where $(\Delta G_{O_2})_f$ has become equal to $(\Delta G_{O_2})_{\text{Na}}$ throughout the fuel pin, the stoichiometry would be X_{eq} given by $C_0 = 52 - 750 X_{\text{eq}} \quad \text{--- (5)}$

$$\text{or } \frac{750 k_d p_{\text{Na}}}{16 \times 10^6} (X_{\text{eq}} - X^{\text{int}}) = D_0^f \frac{p_f}{270} \left(\frac{\partial X}{\partial Y} \right)_R \quad \text{--- (6)}$$

(6) is the second B.C

$$\text{Let } \theta = \frac{X^{\text{eq}} - X}{X^{\text{eq}} - X_0} \quad \text{--- (7)}$$

$$\gamma = \frac{Y}{R} \quad \text{--- (8)}$$

$$T = \frac{D_0^f t}{R^2} \quad \text{--- (9)}$$

$$\frac{\partial \theta}{\partial T} = \frac{1}{\gamma} \frac{\partial}{\partial \gamma} \left(\gamma \frac{\partial \theta}{\partial \gamma} \right) \quad \text{--- (10)}$$

$$\text{I.C.} \quad \theta(\gamma, 0) = 1 \quad \text{--- (11)}$$

$$\text{B.C.} \quad \left(\frac{\partial \theta}{\partial \gamma} \right)_{\gamma=0} = 0 \quad \text{--- (12)}$$

$$\frac{750 \text{ ka } J_{Nn}}{16 \times 10^6} [X_{ef} - X_{int}] = \frac{D_0^f J_f}{270R} \left(\frac{\partial X}{\partial \gamma} \right)_R$$

$$= - \frac{D_0^f J_f}{270R} (X_{ef} - X_0) \left(\frac{\partial \theta}{\partial \gamma} \right)_{\gamma=1}$$

$$\text{But} \quad \frac{X_{ef} - X_{int}}{X_{ef} - X_0} = \theta(1, T)$$

$$A \theta(1, T) + \left(\frac{\partial \theta}{\partial \gamma} \right)_{\gamma=1} = 0 \quad \text{--- (13)}$$

$$\text{where} \quad \frac{1}{A} = \frac{D_0^f 16 \times 10^6}{750 \times 270 R \text{ ka}} \frac{J_f}{J_{Nn}} \quad \text{--- (14)}$$

solution of (10) - (13) in Carslaw and Jaeger
"Conduction of Heat in Solid" 2nd edition
P. 202

$$\theta = \sum_{n=1}^{\infty} e^{-\beta_n^2 T} \frac{2 A J_0(\beta_n \gamma)}{(\beta_n^2 + A^2) J_0(\beta_n)} \quad \text{--- (15)}$$

where β_n 's are the roots of $\beta J_1(\beta) = A J_0(\beta)$ --- (16)

For the parameter specified

$$A = \frac{(750)(270)(0.3)(0.75)}{(4 \times 10^{13})(16 \times 10^6)(12)} = 3.6 \times 10^9$$

$\therefore$ the roots $\beta_n \ll A$ (see P. 393 of Carslaw and Jaeger) and (15) reduces to (using (16) too)

$$\theta = 2 \sum_{n=1}^{\infty} e^{-\beta_n^2 T} \frac{J_0(\beta_n \gamma)}{\beta_n J_1(\beta_n)} \quad \text{--- (17)}$$

which is the solution for $X_{eq} = X_{int}$ (i.e. when $A \rightarrow \infty$)
 Eq (13) reduces to $\theta(1, \tau) = 0$ the solution (17)
 is plotted on Fig 24 of Carslaw and Jaeger

For $\theta(0, \tau) = 0.5$, $\tau \approx 0.2$
 from (9) $t = \frac{(0.2)(0.3)^2}{4 \times 10^{-13}} = 4.5 \times 10^{10} \text{ sec}$
 $= 1433 \text{ yrs}$

However, this calculation neglects the strong
 temperature dependence of D_o^f , which would
 make oxygen diffusion much more rapid
 in the center of the fuel than assumed
 here. For addition, D_o^f is NOT known for
 hypostoichiometric oxide fuel

PROBLEM 20.14

Carnot efficiency $\frac{dW}{dQ_1} = \frac{T_1 - T_2}{T_1}$

$$dQ_1 = -m c_p dT_1$$

$$\frac{1}{m c_p} \frac{dW}{dT_1} = - \frac{T_1 - T_2}{T_1} = -1 + \frac{T_2}{T_1}$$

$$\frac{W}{m c_p} = - \int_{T_1}^{T_2} \left(1 - \frac{T_2}{T_1'}\right) dT_1' = \int_{T_2}^{T_1} \left(1 - \frac{T_2}{T_1}\right) dT_1$$

$$\frac{W}{m c_p} = (T_1 - T_2) - T_2 \ln\left(\frac{T_1}{T_2}\right)$$

Q_1 = Total energy lost by particle
 $= m c_p (T_1 - T_2)$

$$\eta = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1 - T_2} \ln\left(\frac{T_1}{T_2}\right) = 1 - \frac{1000}{1500} \ln 2.5$$

$$= 0.39 = 39\%$$

CHAPTER 21

Problem 21.1

(A)

Neglecting swelling & creep, Eq (21.27) becomes,
when applied to the entire cylinder

$$u(r) = C_2 r + \alpha \left(\frac{1+\nu}{1-\nu} \right) \frac{1}{r} \int_0^r T r' dr' \quad (1a)$$

and thus,

$$\frac{du}{dr} = C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) \left\{ T(r) - \frac{1}{r^2} \int_0^r T r' dr' \right\} \quad (1b)$$

where we have used boundary condition
 $u(r)$ bounded at $r=0 \rightarrow C_1 = 0$

$$\therefore \frac{du}{dr} + \frac{u}{r} = 2C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) T(r) \quad (1c)$$

Eq (21.23) becomes:

$$\begin{aligned} \sigma_r(r) = & \frac{E}{1+\nu} \left\{ C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) \left[T(r) - \frac{1}{r^2} \int_0^r T r' dr' \right] + \right. \\ & \left. + \frac{\nu}{1-2\nu} \left[2C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) T(r) + \epsilon_z - 3\alpha T(r) \right] - \alpha T \right\} \end{aligned}$$

Combining coefficients of $T(r)$, we find they sum to 0:

$$\sigma_r(r) = \frac{E}{1+\nu} \left\{ \frac{C_2}{1-2\nu} - \alpha \left(\frac{1+\nu}{1-\nu} \right) \frac{1}{r^2} \int_0^r T r' dr' + \frac{\nu \epsilon_z}{1-2\nu} \right\} \quad (2)$$

No radial stress component at $r=R$ implies

$$\frac{C_2}{1-2\nu} + \frac{\nu \epsilon_z}{1-2\nu} = \alpha \left(\frac{1+\nu}{1-\nu} \right) \frac{1}{R^2} \int_0^R T r' dr' \quad (3)$$

or, σ_r becomes

$$\sigma_r(r) = \frac{\alpha E}{1-\nu} \left\{ \frac{1}{R^2} \int_0^R T r' dr' - \frac{1}{r^2} \int_0^r T r' dr' \right\} \quad (4)$$

Eq (21.24) becomes:

$$\sigma_{\theta}(r) = \frac{E}{1+\nu} \left\{ C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) \frac{1}{r^2} \int_0^r T r' dr' + \right. \\ \left. + \frac{\nu}{1-2\nu} \left[2C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) T(r) + \epsilon_z - 3\alpha T \right] - \alpha T \right\}$$

In this case, the coefficient of T is $-\alpha \left(\frac{1+\nu}{1-\nu} \right)$.

Using C_2 as determined above, Eq (3):

$$\sigma_{\theta}(r) = \frac{\alpha E}{1-\nu} \left\{ \frac{1}{R^2} \int_0^R T r' dr' + \frac{1}{r^2} \int_0^r T r' dr' - T \right\} \quad (5)$$

Assume no axial restraint, i.e.

$$\int_0^R 2\pi r \sigma_z dr = 0 \quad (6)$$

Eq (21.25) becomes using Eq (1C)

$$\sigma_z = \frac{E}{1+\nu} \left\{ \epsilon_z + \frac{\nu}{1-2\nu} \left[2C_2 + \alpha \left(\frac{1+\nu}{1-\nu} \right) T + \epsilon_z - 3\alpha T \right] + \right. \\ \left. + (-\alpha T) \right\}$$

or

$$\sigma_z = \frac{E}{1+\nu} \left\{ \frac{2\nu}{1-2\nu} C_2 + \frac{1-\nu}{1-2\nu} \epsilon_z - \alpha \left(\frac{1+\nu}{1-\nu} \right) T \right\} \quad (7)$$

Apply $\frac{2}{R^2} \int_0^R r dr$ to this equation:

$$\therefore 0 = \frac{E}{1+\nu} \left\{ \frac{2\nu}{1-2\nu} C_2 + \frac{1-\nu}{1+2\nu} \epsilon_z - 2\alpha \left(\frac{1+\nu}{1-\nu} \right) \frac{1}{R^2} \int_0^R T r dr \right\} \quad (8)$$

Combine Eq's (7) & (8)

$$\therefore \sigma_z = \frac{2\alpha E}{1-\nu} \left\{ \frac{1}{R^2} \int_0^R T r dr - \frac{1}{2} T \right\} \quad (9)$$

Parabolic temperature profile:

$$T = T_s + (T_0 - T_s) \left(1 - \frac{r^2}{R^2}\right) \\ = T_0 - \Delta T \frac{r^2}{R^2} \quad \text{where } \Delta T \equiv T_0 - T_s \quad (10)$$

$$\frac{1}{r^2} \int_0^r T r' dr' = \frac{1}{2} T_0 - \frac{1}{4} \Delta T \frac{r^2}{R^2} \quad (11)$$

$$\frac{1}{R^2} \int_0^R T r dr = \frac{1}{2} T_0 - \frac{1}{4} \Delta T \quad (12)$$

Substitute Eqs (10) & (12) into (5)

$$\sigma_\theta = -\frac{\alpha E}{1-\nu} \frac{\Delta T}{4} \left[1 - 3\left(\frac{r}{R}\right)^2\right] \quad (13)$$

Use Eq (15.212)

$$\Delta T = \frac{\rho}{4\pi k} \quad (14)$$

which yields Eq (21.49):

$$\sigma_\theta = -\frac{\alpha E \rho}{16\pi(1-\nu)k} \left[1 - 3\left(\frac{r}{R}\right)^2\right] \quad (15)$$

Substitute Eqs (10) & (12) into (9),

$$\sigma_z = -\frac{\alpha E}{1-\nu} \frac{\Delta T}{2} \left[1 - 2\left(\frac{r}{R}\right)^2\right] \quad (16)$$

(B)

For a hollow cylinder, the analog of Eq (5) is:

$$\sigma_\theta(r) = \frac{\alpha E}{1-\nu} \left\{ \frac{1 + (r_0/r)^2}{R^2 - r_0^2} \int_{r_0}^R T r' dr' + \frac{1}{r^2} \int_{r_0}^r T r' dr' - T \right\} \quad (17)$$

The temperature distribution in the fuel is given by solution of Eq (10.49), subject to Eqn (10.50) & (10.51):

$$T - T_s = \frac{1}{4} \frac{H R^2}{k} \left\{ \left(1 - \frac{r^2}{R^2} \right) + 2 \left(\frac{r_0}{R} \right)^2 \ln \left(\frac{r}{R} \right) \right\} \quad (18)$$

Linear Power is:

$$P = \pi R^2 \left(1 - \frac{r_0^2}{R^2} \right) H \quad (19)$$

Eq (18) & (19) $\rightarrow$

$$T = T_s + \frac{P}{4\pi k} \frac{1}{1 - (r_0/R)^2} \left\{ \left(1 - \frac{r^2}{R^2} \right) + 2 \left(\frac{r_0}{R} \right)^2 \ln \left(\frac{r}{R} \right) \right\} \quad (20)$$

$$\begin{aligned} \int_{r_0}^r T r' dr' &= \frac{P}{4\pi k} \frac{R^2}{(1 - \frac{r_0^2}{R^2})} \left\{ \frac{1}{2} \left[\left(\frac{r}{R} \right)^2 - \left(\frac{r_0}{R} \right)^2 \right] - \frac{1}{4} \left[\left(\frac{r}{R} \right)^4 - \left(\frac{r_0}{R} \right)^4 \right] + \right. \\ &\quad \left. + \left(\frac{r_0}{R} \right)^2 \left[\frac{r^2}{R^2} \ln \left(\frac{r}{R} \right) - \left(\frac{r_0}{R} \right)^2 \ln \left(\frac{r_0}{R} \right) \right] \right\} + \\ &\quad + T_s \frac{1}{2} R^2 \left[\left(\frac{r}{R} \right)^2 - \left(\frac{r_0}{R} \right)^2 \right] \quad (21) \end{aligned}$$

Finally, substitute Eq (20) & (21) into (17), noting that the T_s terms cancel, and obtain:

$$\begin{aligned} \sigma_\theta(r) &= \frac{\alpha E P}{4\pi(1-\nu)k} \frac{1}{1-\eta_0^2} \left\{ \frac{1 + (\eta_0/\eta)^2}{1-\eta_0^2} \left[\frac{1}{2}(1-\eta_0^2) + \right. \right. \\ &\quad \left. \left. - \frac{1}{4}(1-\eta_0^2) - \eta_0^4 \ln \eta_0 \right] + \frac{1}{\eta^2} \left[\frac{1}{2}(\eta^2 - \eta_0^2) + \right. \right. \\ &\quad \left. \left. - \frac{1}{4}(\eta^4 - \eta_0^4) + \eta_0^2(\eta^2 \ln \eta - \eta_0^2 \ln \eta_0) \right] + \right. \\ &\quad \left. - [1 - \eta^2 + 2\eta_0^2 \ln \eta] \right\} \quad (22) \end{aligned}$$

where $\eta \equiv \frac{r}{R}$, $\eta_0 \equiv \frac{r_0}{R}$

For $M_0 \rightarrow 0$, Eq (22) reduces to

$$\sigma_0(r) = \frac{\alpha E P}{4\pi(1-\nu)k} \left(\frac{3}{4} r^2 - \frac{1}{4} \right) \quad (23)$$

↑ this is eqn (15)

$$\begin{aligned} (c) \quad \frac{\alpha E P}{4\pi(1-\nu)k} &= \frac{10^{-5} (1.75 \times 10^8) (500)}{4\pi (0.68) (0.03)} \\ &\approx 34 \times 10^6 \text{ kn/m}^2 \end{aligned}$$

Radius of central void is given by

$$0.97 (R^2 - r_0^2) = 0.85 R^2$$

$$\rightarrow M_0 = 0.35$$

Problem 21.1 (c)

Problem 21.2

(A)

In the thin wall approximation,

$$T \cong T_i - \frac{\Delta T_c x}{t_c} \quad (1)$$

where T_i = inside cladding temperature x = distance from inside of cladding

In Eq. (17) of Prob 21.1 (B)

$$\frac{1 + (r_0/r)^2}{R^2 - r_0^2} = \frac{2}{\underset{2R \uparrow}{(R+r_0)} \underset{\uparrow t_c}{(R-r_0)}} \cong \frac{1}{R t_c}$$

$$\int_{r_0}^r T r' dr' \cong R \int_0^x T dx' = R \left[T_i x - \frac{1}{2} \frac{\Delta T_c}{t_c} x^2 \right]$$

$$\sigma_\theta(x) = \frac{\alpha E}{1-\nu} \left\{ \frac{1}{t_c} \left[T_i t_c - \frac{1}{2} \frac{\Delta T_c}{t_c} t_c^2 \right] + \frac{1}{R} \left[T_i x + \right. \right. \\ \left. \left. - \frac{1}{2} \frac{\Delta T_c}{t_c} x^2 \right] - T_i + \frac{\Delta T_c x}{t_c} \right\}$$

Neglect terms in x/R by thin-wall approximation,

$$\sigma_\theta(x) \cong - \left(\frac{\alpha E}{1-\nu} \right) \frac{\Delta T_c}{2} \left(1 - \frac{2x}{t_c} \right)$$

Maximum occurs at outside ($x/t_c = 1$) of clad:

$$(\sigma_\theta)_{\max} = \frac{\alpha E \Delta T_c}{2(1-\nu)} \quad (2)$$

(B)

$$\text{Heat flux thru cladding} = \frac{P}{2\pi R} = \frac{k \Delta T_c}{t_c}$$

Using above relation in (2):

$$(\sigma_\theta)_{\max} = \frac{\alpha E \beta t_c}{4\pi(1-\nu)RK} \quad (3)$$

$$\text{for } (\sigma_\theta)_{\max} = \sigma_y$$

$$P_{\text{yield}} = \frac{4\pi(1-\nu)RK\sigma_y}{\alpha E t_c}$$

$$= \frac{4\pi(0.68)(0.32 + 0.038)(0.24)(2.1 \times 10^5)}{(1.2 \times 10^{-5})(1.4 \times 10^8)(0.038)}$$

$$P_{\text{yield}} \approx 2400 \text{ Watts/cm}$$

(C)

From prob 18.6(A):

$$\sigma_\theta = \frac{P_{\text{plenum}} R}{t_c} \quad (4)$$

$$\text{for } \sigma_\theta = \sigma_y,$$

$$(P_p)_{\text{yielding}} = \frac{\sigma_y t_c}{R} = \frac{(2.1 \times 10^5)(0.038)}{0.32}$$

$$\approx 2.5 \times 10^4 \frac{\text{KN}}{\text{m}^2}$$

$$\approx 246 \text{ atm}$$

(D)

$$\sigma_\theta = \left(\frac{500}{2400} + \frac{50}{246} \right) (2.1 \times 10^5) \approx 8.6 \times 10^4 \frac{\text{KN}}{\text{m}^2}$$

$\approx \sigma_y$

From Fig. 18.12, $T = 727^\circ\text{C}$,

$$\text{biaxial stress} = 8.6 \times 10^4 \text{ KN/m}^2$$

$$\therefore t_R \approx .600 \text{ hrs.}$$

(E)

Adding Eq (3) & (4),

$$(\sigma_{\theta})_{\max} = \left[\frac{\alpha E \rho}{4\pi (1-\nu) R k} \right] t_c + \frac{P_p R}{t_c} \quad (4)$$

or

$$(\sigma_{\theta})_{\max} = a t_c + \frac{b}{t_c}$$

At minimum of $(\sigma_{\theta})_{\max}$

$$\frac{d(\sigma_{\theta})_{\max}}{d t_c} = 0 = a - \frac{b}{(t_c)_{\text{opt}}^2}$$

$$\therefore (t_c)_{\text{opt}} = \sqrt{\frac{b}{a}}$$

or

$$\begin{aligned} (t_c)_{\text{opt}} &= \left[\frac{4\pi (1-\nu) R^2 k P_p}{\alpha E \rho} \right]^{1/2} \quad (5) \\ &= \left[\frac{4\pi (0.68) (0.32)^2 (0.24) (5.1 \times 10^3)}{(1.2 \times 10^{-5}) (1.4 \times 10^8) (500)} \right]^{1/2} \end{aligned}$$

$$(t_c)_{\text{opt}} \approx 0.036 \text{ cm}$$

Problem 21.3

From prob 18.6(A):

$$\sigma_\theta = \frac{P_p R}{t_c} \quad (1)$$

$$\sigma_z = \frac{P_p R}{2t_c} \quad (2)$$

$$\sigma_r \approx 0$$

From Eq (21.16) & the creep law:

$$\dot{\epsilon}_\theta^c = B (\sigma^*)^{n-1} \left[\sigma_\theta - \frac{1}{2} \sigma_z \right] \quad (3)$$

Eq (21.18) $\rightarrow$

$$\sigma^* = \frac{1}{\sqrt{2}} \left[\sigma_\theta^2 + \sigma_z^2 + (\sigma_\theta - \sigma_z)^2 \right]^{1/2}$$

From Eq (1) & (2) obtain,

$$\sigma_z = \frac{1}{2} \sigma_\theta$$

$$\therefore \sigma^* = \frac{1}{\sqrt{2}} \left[\sigma_\theta^2 + \frac{1}{4} \sigma_\theta^2 + \frac{1}{4} \sigma_\theta^2 \right]^{1/2} = \frac{\sqrt{3}}{2} \sigma_\theta$$

Eq (3) becomes,

$$\dot{\epsilon}_\theta^c = B \left(\frac{\sqrt{3}}{2} \right)^{n-1} \sigma_\theta^{n-1} \frac{3}{4} \sigma_\theta$$

and at time t ,

$$\left(\frac{\Delta R}{R} \right)_{\text{creep}} = \dot{\epsilon}_\theta^c t = \left(\frac{3}{4} \right)^{\frac{n+1}{2}} B \left(\frac{P_p R}{t_c} \right)^n t \quad (4)$$

Elastic deformation:

$$\epsilon_\theta = \frac{u}{r} \xrightarrow[\text{wall}]{\text{thin}} \frac{\Delta R}{R}$$

Combining Eqs (22) & (23) of Prob 18.6(C):

$$\left(\frac{\Delta R}{R} \right)_{\text{elastic}} = \frac{P_p R}{2E t_c} (1-2\nu) \quad (5)$$

Problem 21.4

$$\frac{\Delta R_f}{R_0} = \frac{1}{3} \alpha_f (T - T_0)$$

$$\frac{\Delta R_c}{R_0} = \frac{1}{3} \alpha_c (T - T_0)$$

at $T = T^*$, $\Delta R_f - \Delta R_c = t_g = \frac{1}{3} (\alpha_f - \alpha_c) (T^* - T_0) R_0$

$$\therefore T^* = T_0 + \frac{3 t_g}{(\alpha_f - \alpha_c) R_0}$$

note α = volumetric coef. of thermal expansion.

From thermodynamics,

$$dP = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha_f}{\beta_f}$$

$$\frac{1}{\beta_f} = \text{bulk modulus of fuel}$$

$$\left(\frac{\partial P}{\partial V} \right)_T = - \frac{1}{\beta_f V}$$

Now, dV is due to thermal expansion of clad for $T > T^*$,
(by assumption) $\rightarrow$
or, $dV = \alpha_c V dT$

$$\begin{aligned}\therefore dp &= \frac{\alpha_f}{\beta_f} dT - \frac{\alpha_c}{\beta_f} dT \\ &= \frac{\alpha_f - \alpha_c}{\beta_f} dT\end{aligned}$$

or

$$p = \frac{(\alpha_f - \alpha_c)}{\beta_f} (T - T^*)$$

Problem 21.5

At $T = T^*$, the fuel contacts the cladding. For $T > T^*$, interfacial pressure is generated.

Let,

$$\Delta T \equiv T - T^* \quad (1)$$

The displacement equation is given by Eq (21.26) with $\epsilon_r^c = \epsilon^s = 0$. Since $T \neq$ function of r , we have

$$\frac{d}{dr} \left[\frac{1}{r} \frac{d(ru)}{dr} \right] = 0$$

Integrate:

$$u = C_1 r - \frac{C_2}{r}$$

Because u is bounded at $r=0$, $C_2 = 0$ &

$$\therefore u = C_1 r \quad (2)$$

Boundary condition at $u=R$ is $u=0$, so that

$$C_1 = 0$$

But, we also require

$$\sigma_r(R) = -P_{fc} \quad (3)$$

With $u = \epsilon^s = \epsilon^c = 0$, Egn's (21.23) & (21.25) become:

$$\sigma_r = \frac{E}{1+\nu} \left\{ \frac{\nu}{1-2\nu} \epsilon_z - \frac{1+\nu}{1-2\nu} \alpha T \right\} \quad (4)$$

$$\sigma_z = \frac{E}{1+\nu} \left\{ \frac{1-\nu}{1-2\nu} \epsilon_z - \frac{1+\nu}{1-2\nu} \alpha T \right\} \quad (5)$$

Neither σ_r nor σ_z depend upon r , so σ_r in Eq (4) is equal to $-P_{fc}$ at all r .

(i)

Complete axial restraint $\epsilon_z = 0$ Use $\epsilon_z = 0$ & $\sigma_r = -P_{fc}$ in Eq (4) to obtain:

$$P_{fc} = \frac{E \alpha T}{1-2\nu} \quad (6)$$

According to Eq (A.28) of Appendix to Ch 8, the reciprocal of the compressibility of the fuel (i.e. its bulk modulus) is

$$\frac{1}{3K} = \frac{1-2\nu}{E}$$

So that Eq (4) reduces to the solution to problem 21.4(B), which was obtained from purely thermodynamic considerations.

(ii) No axial restraint condition is

$$\int_0^R \sigma_z r dr = 0,$$

but since $\sigma_z \neq$ function of r . This condition is equivalent to $\sigma_z = 0$. Therefore, ϵ_z is determined from Eq (5) as

$$\epsilon_z = \frac{1+\nu}{1-\nu} \alpha T \quad (7)$$

Substituting Eq (7) into (4) & setting $\sigma_r = -P_{fc}$ as before yields:

$$P_{fc} = \frac{E \alpha T}{1-\nu} \quad (8)$$

For the case of complete loss of fuel strength ($E=0$, $\nu=1/2$), $P_{fc}=0$ & the fuel expands in the clad like a heated liquid in an open tube.

Problem 21.6

(A) Temperature Distribution

Region ①:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT_1}{dr} \right) = -\frac{H}{k_1} \quad (1)$$

Region ②:

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT_2}{dr} \right) = 0 \quad (2)$$

Boundary conditions (assume fuel-clad thermal resistances negligible)

$$T_1(0) = \text{bounded} \quad (3)$$

$$T_1(R) = T_2(R) \quad (4)$$

$$k_1 \left. \frac{dT_1}{dr} \right|_R = k_2 \left. \frac{dT_2}{dr} \right|_R \quad (5)$$

$$T_2(\infty) = 0 \quad (6)$$

The solutions of (1) & (2) subject to (3), (4), (5), & (6) are:

$$T_1(r) = \frac{H}{6k_1} (R^2 - r^2) + \frac{R^2 H}{3k_2} \quad (7)$$

$$T_2(r) = \left[\frac{\left(\frac{4}{3} \pi R^3 \right) H}{4 \pi k_2 r} \right] = \frac{R^3 H}{3k_2 r} \quad (8)$$

(B)

The differential equations of radial stress are
(with spherical symmetry):

$$\text{Region ①: } \frac{1}{r^4} \frac{d}{dr} \left(r^4 \frac{d\sigma_r}{dr} \right) = -\frac{2E_1\alpha_1}{1-\nu_1} \frac{1}{r} \frac{dT_1}{dr} \quad (9)$$

$$\text{Region ②: } \frac{1}{r^4} \frac{d}{dr} \left(r^4 \frac{d\sigma_r}{dr} \right) = -\frac{2E_2\alpha_2}{1-\nu_2} \frac{1}{r} \frac{dT_2}{dr} \quad (10)$$

Boundary conditions:

$$v_1(0) = \text{bounded}$$

$$v_2(\infty) = 0$$

$$v_1(R) = -p_c$$

$$v_2(R) = -p_c$$

(if gap open, $p_c = 0$)

Solving Eqs (9) & (10) using (7) & (8) and subject to (11)-(14), obtain:

$$v_1(r) = -p_c - k_1(R^2 - r^2)$$

$$\text{where } k_1 = \frac{E_1 \alpha_1 H}{15 k_1 (1 - \nu_1)}$$

$$v_2(r) = -p_c \frac{R^3}{r^3} - k_2 R^3 \left(\frac{1}{r} - \frac{R^2}{r^3} \right)$$

$$k_2 = \frac{E_2 \alpha_2 H}{3 k_2 (1 - \nu_2)}$$

Determine whether gap open or closed by comparing displacements of regions ① & ② at $r = R$.
For spherical system (equilibrium conditions):

$$\sigma_r = \sigma_r + \frac{1}{2} r \frac{d\sigma_r}{dr}$$

Strain - displacement relation

Let $u =$ radial displacement

$$e_r = \frac{u}{r}$$

(constitutive relation)

$$e_r = \frac{1}{E} (\sigma_r - \nu(\sigma_r + \sigma_\theta)) + \alpha T$$

equal to σ_ϕ

Combine $E_1(19), (20), (21)$ & obtain $u(r)$ in terms of σ_r & $\frac{d\sigma_r}{dr}$, i.e.:

$$u = \frac{r}{E} \left\{ (1-\nu) \left(\sigma_r + \frac{1}{2} r \frac{d\sigma_r}{dr} \right) - \nu \sigma_r \right\} + \alpha T r \quad (22)$$

Now insert $E_1(7), (8), (15), (17)$ into (22) & evaluate $u_1(R)$ & $u_2(R)$:

Assume gap open:

Set $P_{fc} = 0$. If $u_2(R) > u_1(R)$, assumption is ok.
If not, must assume gap closed. Set $u_1(R) = u_2(R)$ & solve for P_{fc} .

In sphere

$$u_1 = \frac{r}{E_1} \left\{ (1-\nu_1) \left[-P_{fc} - k_1(R^2 - r^2) + k_1 r^2 \right] - \nu_1 (-P_{fc} - k_1(R^2 - r^2)) \right\} + \frac{\alpha_1 H}{6k_1} (R^2 - r^2) + \frac{\alpha_1 R^2 H r}{3k_2}$$

at $r=R$

$$u_1(R) = \frac{R}{E_1} \left\{ (1-\nu_1) (-P_{fc} + k_1 R^2) + \nu_1 P_{fc} \right\} + \frac{\alpha_1 R^3 H}{3k_2}$$

$$\therefore u_1(R) = \frac{R}{E_1} \left\{ (1-\nu_1) k_1 R^2 - (1-2\nu_1) P_{fc} \right\} + \frac{\alpha_1 R^3 H}{3k_2} \quad (23)$$

Outside sphere:

$$u_2 = \frac{r}{E_2} \left\{ (1-\nu_2) \left[-P_{fc} \frac{R^3}{r^3} - k_2 R^3 \left(\frac{1}{r} - \frac{R^2}{r^3} \right) + \frac{3P_{fc}}{2} \frac{R^3}{r^3} + \right. \right. \\ \left. \left. - \frac{k_2 R^3}{2} \left(-\frac{1}{r} + 3 \frac{R^2}{r^3} \right) \right] + \nu_2 \left[P_{fc} \frac{R^3}{r^3} + k_2 R^3 \left(\frac{1}{r} - \frac{R^2}{r^3} \right) \right] \right\} + \\ + \frac{(\frac{4}{3} \pi R) \alpha H r}{4 \pi k_2 r}$$

at $r=R$:

$$\therefore u_2(R) = \frac{R}{E_2} \left\{ \frac{1}{2} (1+\nu_2) P_{fc} - (1-\nu_2) k_2 R^2 \right\} + \frac{\alpha_2 R^3 H}{3k_2} \quad (24)$$

If gap open $P_{fc} = 0$

from (23):

$$u_1(R) = \frac{(1-\nu_1) k_1 R^3}{E_1} + \frac{\alpha_1 R^3 H}{3k_2} = \frac{\alpha_1 R^3 H}{3} \left(\frac{1}{5k_1} + \frac{1}{k_2} \right)$$

from (22):

$$u_2(R) = \frac{-(1-\nu_2) k_2 R^3}{E_2} + \frac{\alpha R^3 H}{3k_2} = 0$$

$$u_1(R) > u_2(R) \Rightarrow \therefore \text{gap closed}$$

Set $u_1(R) = u_2(R)$ from (23) & (24):

$$\frac{R}{E_1} \left[(1-\nu_1) k_1 R^2 - (1-2\nu_1) P_{fc} \right] + \frac{\alpha_1 R^3 H}{3k_2} =$$

$$= \frac{R}{E_2} \left[\frac{1}{2} (1+\nu_2) P_{fc} - (1-\nu_2) k_2 R^2 \right] + \frac{\alpha_2 R^3 H}{3k_2}$$

$$\frac{(1-\nu_1) k_1 R^2}{E_1} + \frac{(1-\nu_2) k_2 R^2}{E_2} + \frac{(\alpha_1 - \alpha_2) R^3 H}{3k_2} =$$

$$= \left[\frac{(1-2\nu_1)}{E_1} + \frac{(1+\nu_2)}{2E_2} \right] P_{fc}$$

$$\frac{\alpha_1 H R^2}{15k_1} + \frac{\alpha_2 H R^2}{3k_2} + \frac{(\alpha_1 - \alpha_2) H R^2}{3k_2} = \left[\frac{1-2\nu_1}{E_1} + \frac{1+\nu_2}{2E_2} \right] P_{fc}$$

Thus

$$P_{fc} = \frac{\frac{\alpha_1 H R^2}{3} \left(\frac{1}{5k_1} + \frac{1}{k_2} \right)}{\frac{1-2\nu_1}{E_1} + \frac{1+\nu_2}{2E_2}} \quad (25)$$

Problem 21.7

For the LMFBR core considered in problem 20.5, the radial reduction of the linear power is neglected and the axial dependence of P is given by:

$$P(z) = 544 \cos(1.96 \frac{z}{z}) \text{ W/cm} \quad (1)$$

where z = core height $(-\frac{z}{2} \leq z \leq \frac{z}{2})$
 With Nu inlet & outlet temperatures of 470°C & 650°C , respectively, and a Nu heat transfer coefficient of $12 \text{ W/cm}^2\text{-}^\circ\text{C}$, the temperature of the outside of the cladding is

$$T_{co} = 470 + 180 \left\{ \frac{\sin(1.96 \frac{z}{z}) + 0.83}{1.66} \right\} + 23 \cos(1.96 \frac{z}{z}) \quad (2)$$

In the thin wall approximation, heat flux through the cladding is:

$$\frac{P}{2\pi R_c} = \frac{k_c \Delta T_c}{t_c} \quad (3)$$

where $\Delta T_c \equiv$ temperature drop thru the cladding.
 The mid-wall (ie average) cladding temperature is:

$$\bar{T}_c = T_{co} + \frac{1}{2} \Delta T_c = T_{co} + \frac{P t_c}{4\pi R_c k_c}$$

Using Eq (1) & the cladding property data

$$\bar{T}_c = T_{co} + 22 \cos(1.96 \frac{z}{z}) \quad (4)$$

⚡
 see table

(B)

Use Eq (10.56) to find initial power density of fuel:

$$H_0 = [3.07 \times 10^{-11} g_0 \sigma_f N_{f_0} \Phi_0] \quad (5)$$

where

$$g_0 = 0.15$$

$$\sigma_f = 2 \text{ barns}$$

$$N_{f_0} \approx 2.2 \times 10^{22} \text{ atoms/cm}^3 \quad (90\% \text{ dense fuel initially})$$

the linear power is

$$\begin{aligned} \mathcal{P} &= \pi R_c^2 H_0 \\ &= \pi R_c^2 (3.07 \times 10^{-11}) g_0 N_{f_0} \sigma_f \Phi_0 \end{aligned}$$

The linear power $\mathcal{P}$ is held constant through irradiation. Despite restructuring & burnup, the product $(\pi R_c^2 g_0 N_{f_0})$, which is the number of Pu atoms per cm. of fuel, remains constant if the breeding ratio is unity. Therefore, the fast flux is also independent of irradiation time

$$\begin{aligned} \Phi &= \frac{\mathcal{P}}{(3.07 \times 10^{-11}) \pi R_c^2 g_0 N_{f_0} \sigma_f} \\ &= \frac{544 \cos(1.96 \pi/2)}{(3.07 \times 10^{-11}) (3.14) (0.315)^2 (0.15) (2.2 \times 10^{22}) (2 \times 10^{-28})} \\ \therefore \Phi(z) &\approx 8.6 \times 10^{15} \cos(1.96 \pi/2) \frac{\text{neutrons}}{\text{cm}^2 \cdot \text{sec}} \quad (6) \end{aligned}$$

⚡

see table

From Prob. 20.5

y/z	T_c (°K)	$\bar{T}_c$ (°K)	$\Phi \times 10^{15}$	$\frac{\Delta V}{V}$
-0.5	756	768	4.8	3.5
-0.4	773	788	6.1	5.2
-0.3	792	810	7.2	6.7
-0.2	813	833	8.0	7.5
-0.1	834	855	8.4	7.5
0	856	878	8.6	6.9
0.1	876	897	8.4	5.9
0.2	896	916	8.0	4.7
0.3	912	930	7.2	3.4
0.4	926	941	6.1	2.2
0.5	936	948	4.8	1.3

← peak swelling below midplane primarily because of decrease of $\Delta V/V$ with increasing temp. dominates the increase due to the slucence.

(C) From Eq (19.120) $\Phi t \times 10^{22} = \frac{\Phi_0 t \times 10^{22}}{10^{23}} \left(\frac{\Phi}{\Phi_0} \right)$

$$\frac{\Delta V}{V} (\%) = \left(10 \frac{\Phi}{\Phi_0} \right)^{g(\theta)} F(T)$$

$$g(\theta) = 2.05 - \frac{27}{\theta} + \frac{7\theta}{\theta^2}, \quad \theta = T - 623$$

$$F(T) = (T - 40) \times 10^{-10} \exp \left\{ 32.6 - \frac{5100}{T} - 0.015T \right\}$$

Problem 21.8

(A) Unrestrained thermal bowing:

from Eq (21.68):

$$v_1^{th}(\eta) = \frac{1}{2} \alpha \nabla T_1 \eta^2$$

$$v_2^{th}(\eta) = \frac{1}{2} \alpha \nabla T_2 \eta^2$$

Elements touch if $v_1^{th}(L) - v_2^{th}(L) \geq \delta$

or

$$\frac{1}{2} \alpha (\nabla T_1 - \nabla T_2) L^2 \geq \delta$$

$$\nabla T_1 - \nabla T_2 \geq \frac{2\delta}{\alpha L^2}$$

(B) When touching

let F = interaction force (negative on ①, positive on ②)

Deflection due to F is:

$$v_1^m = -\frac{F\eta^2}{2EI} \left(L - \frac{\eta}{3}\right)$$

$$v_2^m = \frac{F\eta^2}{2EI} \left(L - \frac{\eta}{3}\right)$$

Total deflections:

$$v_1(\eta) = v_1^{th} + v_1^m = \frac{1}{2} \alpha \nabla T_1 \eta^2 - \frac{F\eta^2}{2EI} \left(L - \frac{\eta}{3}\right)$$

$$v_2(\eta) = v_2^{th} + v_2^m = \frac{1}{2} \alpha \nabla T_2 \eta^2 + \frac{F\eta^2}{2EI} \left(L - \frac{\eta}{3}\right)$$

When just touching at top

$$v_1(L) = v_2(L) + \delta$$

or

$$\frac{1}{2} \alpha (\nabla T_1 - \nabla T_2) L^2 - \frac{2FL^3}{3EI} = \delta$$

$$\therefore F = \frac{3EI}{4L^3} \left\{ \alpha L^2 (\nabla T_1 - \nabla T_2) - 2\delta \right\}$$

Problem 21.9

a) In Eq. 21.79, neglect $\Delta \epsilon^s$ and
 set $F = KV(L, t)$

$$\frac{d^2 v}{dz^2} = - \frac{(L-z)K}{EI} \left[v(L, t) + c\Phi E \int_0^t v(L, t') dt' \right] + \frac{\alpha \Delta T}{2h}$$

Integrating, (noting that $\Delta T \neq \Delta T(z)$)

$$v(z, t) = \frac{\alpha \Delta T}{4h} z^2 - \frac{K \left[v(L, t) + c\Phi E \int_0^t v(L, t') dt' \right]}{2EI} \left(L - \frac{z}{3} \right) z^2$$

Set $z = L$

$$v(L, t) = \frac{\alpha \Delta T}{4h} L^2 - \frac{K}{2EI} \left[v(L, t) + c\Phi E \int_0^t v(L, t') dt' \right] \cdot \frac{2}{3} L^3$$

$$\text{or, } \underbrace{\left(1 + \frac{KL^3}{3EI} \right)}_a v(L, t) + \underbrace{\frac{cKL^3\Phi}{3EI} \int_0^t v(L, t') dt'}_b = \underbrace{\frac{\alpha \Delta T L^3}{4h}}_m$$

Take derivative with respect to t , obtain

$$a \frac{dv}{dt} + bv = 0$$

I.C.: $v(L, 0) = m/a$ (from integral eqn.)

$$\text{Solution: } v(L, t) = (m/a) \cdot e^{-\left(\frac{b}{a}\right)t}$$

or,

$$v(L, t) = \left[\frac{\frac{\alpha \Delta T L^2}{4h}}{\left(1 + \frac{KL^3}{3EI} \right)} \right] \exp \left[- \frac{\frac{cKL^3\Phi}{3EI}}{\left(1 + \frac{KL^3}{3EI} \right)} \cdot t \right]$$

Thus, deflection profile is:

$$v(z,t) = \frac{\alpha \Delta T}{4h} z^2 - \frac{k}{2EI} \frac{m}{a} \left[e^{-\frac{b}{a}t} + \frac{c\Phi E}{b/a} \left(1 - e^{-\frac{b}{a}t} \right) \right] \left(L - \frac{z}{3} \right) z^2$$

b) When $\Delta T = 0$ at $t = t^*$

$$v^*(z,t^*) = -\frac{k}{2EI} \frac{m}{a} \left[e^{-\frac{b}{a}t^*} + \frac{c\Phi E}{b/a} \left(1 - e^{-\frac{b}{a}t^*} \right) \right] \left(L - \frac{z}{3} \right) z^2$$

Note: The flux term is retained because it applies to $0 \leq t \leq t^*$.

When spring is removed as well, the first term in the brackets also disappears, and:

$$v^*(z,t^*) = -\frac{k}{2EI} \frac{m}{b} c\Phi \left(1 - e^{-\frac{b}{a}t^*} \right) \left(L - \frac{z}{3} \right) z^2$$

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