3.9-5 ① $C_p = C_v + \frac{TV\alpha^2}{NK_T}$

② $K_T = K_S + \frac{TV\alpha^2}{NC_p}$

① × K_T − ② × C_p ⇒

$C_p K_T - C_v K_T = K_T C_p - K_S C_p$

$\therefore C_p/C_v = K_T/K_S$

3.9-6. $u = A e^{b(v-v_0)^2} s^{4/3} e^{s/3R}$

(a) Nernst theorem

$$\boxed{T = \left(\frac{\partial u}{\partial s}\right)_v \to 0 \text{ as } s \to 0}$$

Differentiate u w.r.t s at const v

$$T = \left(\frac{\partial u}{\partial s}\right)_v = A e^{b(v-v_0)^2}\left(\frac{4}{3}s^{1/3} + \frac{1}{3R}s^{4/3}\right)e^{s/3R} \to 0 \text{ as } s \to 0$$

Therefore, Nernst theorem is satisfied.

(b) $C_v = T\left(\frac{\partial s}{\partial T}\right)_v$

Since we already know $T(s)$ from (a), we can get C_v^{-1} expression by differentiating T w.r.t s and divide by T.

$$\left(\frac{\partial T}{\partial s}\right)_v = \frac{\partial}{\partial s}\left[A e^{b(v-v_0)^2}\left(\frac{4}{3}s^{1/3} + \frac{1}{3R}s^{4/3}\right)e^{s/3R}\right]_v$$

$$= A e^{b(v-v_0)^2}\left[\left(\frac{4}{9}s^{-2/3} + \frac{4}{9R}s^{1/3}\right) + \left(\frac{4}{9R}s^{1/3} + \frac{1}{9R^2}s^{4/3}\right)\right]e^{s/3R}$$

$$\therefore C_v^{-1} = \frac{1}{T}\left(\frac{\partial T}{\partial s}\right)_v$$

$$= \left[\frac{\frac{4}{9}s^{-2/3} + \frac{4}{9R^2}s^{1/3}}{\frac{4}{3}s^{1/3} + \frac{1}{3R}s^{4/3}} + 1/3R\right]$$

when $T \to 0$ (i.e. $s \to 0$ from (a))

$C_v \sim 3s \sim T^3$

↳ from (a) when $s \to 0$ $T \sim s^{1/3}$

(c) when $T \to \infty$ ($s \to \infty$)

From (b)

$$C_v^{-1} \sim \left[\frac{1}{3R} s^{-1} + \frac{1}{3R} \right] \sim \frac{1}{3R}$$

$$\therefore C_v \sim 3R \sim 3Nk_B$$

Therefore the molar heat capacity $\underline{C_v \sim 3k_B}$ at $T \to \infty$

(d)

Thermal expansion coefficient

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \, ? \quad \text{as } p \to 0$$

From $u = Ae^{b(v-v_0)^2} s^{4/3} e^{s/3R}$

$$-p = \left(\frac{\partial u}{\partial v}\right)_s = 2Ab(v-v_0)\, e^{b(v-v_0)^2} s^{4/3} e^{s/3R} = 2b(v-v_0)u$$

as $p \to 0$ $v \to v_0$ (i.e. v becomes constant) as the pressure approaches to zero value.

$$-p = 2b(v-v_0)u$$

differentiate with respect to T at constant p

$$0 = 2b\left(\frac{\partial v}{\partial T}\right)_p u + 2b(v-v_0)\left(\frac{\partial u}{\partial T}\right)_p$$

$$\therefore \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{(v-v_0)}{uv}\left(\frac{\partial u}{\partial T}\right)_p = \frac{(v-v_0)}{uv} C_p \longrightarrow 0$$

as $p \to 0$ ($\because v \to v_0$)

3.9-8.

$v(T, p)$ on the vicinity of (T_0, p_0)

$$dv \equiv v(T, p) - v(T_0, p_0) = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$$

$$= v\alpha\, dT - v\kappa_T\, dp \qquad dT \equiv \tau = T - T_0$$

$$dp = p = p - p_0$$

near $T = T_0$, $p = p_0$

$$= v_0 \alpha \tau - v_0 \kappa_T p$$

$$= v_0 \tau \left[\alpha^0 + A_\alpha \tau + B_\alpha \tau^2 + D_\alpha p + E_\alpha p^2 + F_\alpha \tau p\right]$$

$$\cancel{v_0 p [} - v_0 p \left[\kappa^0 + A_\kappa \tau + B_\kappa \tau^2 + D_\kappa p + E_\kappa p^2 + F_\kappa \tau p\right]$$

$$v = v_0 + \left[v_0 \alpha^0 \tau - v_0 \kappa^0 p\right] + \left[v_0 A_\alpha \tau^2 - v_0 D_\kappa p^2 + (v_0 D_\alpha - v_0 A_\kappa)\tau p\right] + \left[v_0 B_\alpha \tau^3 - v_0 E_\kappa p^3 + v_0 E_\alpha \tau p^2 + v_0 F_\alpha \tau^2 p - v_0 B_\kappa \tau^2 p - v_0 F_\kappa \tau p^2\right]$$

$$\cancel{= v_0 + (v_0 \alpha^0 - v_0 \kappa^0)}$$

$$\boxed{\begin{aligned} v = v_0 &+ \{v_0 \alpha^0 \tau - v_0 \kappa^0 p\} \\ &+ \{v_0 A_\alpha \tau^2 + v_0 (D_\alpha - A_\kappa)\tau p - v_0 D_\kappa p^2\} \\ &+ \{v_0 B_\alpha \tau^3 + v_0 (F_\alpha - B_\kappa)\tau^2 p + v_0 (E_\alpha - F_\kappa)\tau p^2 - v_0 E_\kappa p^3\} \end{aligned}}$$

3.9-9

$S(T, p_0) \qquad ds = \left(\frac{\partial s}{\partial T}\right)_p dT$

$$S(T, p_0) - S(T_0, p_0) = \frac{1}{T} C_p \tau$$

$$\therefore S(T, p_0) = S(T_0, p_0) + \frac{1}{T_0+\tau}\left[C_p^0 + A_c\tau + B_c\tau^2 + D_c p_0 + E_c p_0^2 + F_c \tau p_0\right]$$

$\xrightarrow{\tau \text{ is small}}$

$$\therefore S(T, p_0) = S(T_0, p_0) \cancel{+ \frac{1}{T_0}\{C_p^0 + A_c\tau + B_c\tau^2 +}$$

$$+ \frac{1}{T_0}\left[C_p^0 + (A_c + F_c p_0)\tau + B_c\tau^2 + D_c p_0 + E_c p_0^2\right\}$$

4.4.1. $\quad C = A + BT \quad (A = 8\,J/K,\ B = 2\times10^{-2}\,J/K^2,\ T_{10} = 400\,K,\ T_{20} = 200\,K)$

$$\Delta U = \int_{T_{10}}^{T_f} C(T)\,dT + \int_{T_{20}}^{T_f} C(T)\,dT = 0$$

$$= \int_{T_{10}}^{T_f} (A+BT)\,dT + \int_{T_{20}}^{T_f} (A+BT)\,dT$$

$$= A(T_f - T_{10}) + \frac{1}{2}B(T_f^2 - T_{10}^2) + A(T_f - T_{20}) + \frac{1}{2}B(T_f^2 - T_{20}^2)$$

$= 0$

$$BT_f^2 + 2AT_f - A(T_{10}+T_{20}) - \frac{B}{2}(T_{10}^2 + T_{20}^2) = 0$$

$$T_f = \frac{-A + \sqrt{A^2 + B\{A(T_{10}+T_{20}) + \frac{B}{2}(T_{10}^2+T_{20}^2)\}}}{B}$$

$$\Delta S = \int_{T_{10}}^{T_f} \frac{C(T)}{T}\,dT + \int_{T_{20}}^{T_f} \frac{C(T)}{T}\,dT \qquad \cong 307K.$$

$\therefore$

$$\Delta S = A\log\frac{T_f}{T_{10}} + B(T_f - T_{10}) + A\log\frac{T_f}{T_{20}} + B(T_f - T_{20})$$

$\Longrightarrow$ $\Delta U =$

$\Delta S =$

4.4.2. $C_3 = BT$ — T_{20} : initial temperature of the body 2.

$$\Delta U = \int_{T_f}^{T_{20}} (A + BT)\,dT + \int_{T_{30}}^{T_{20}} (BT)\,dT = 0$$

$$= A(T_{20} - T_f) + \frac{1}{2}B(T_{20}^2 - T_f^2) + \frac{1}{2}B(T_{20}^2 - T_{30}^2) = 0$$

$$\Delta S_{tot} = A\log\frac{T_{20}}{T_f} + B(T_{20} - T_f) + B(T_{20} - T_{30})$$

$$= \Delta S_2 + \Delta S_3$$

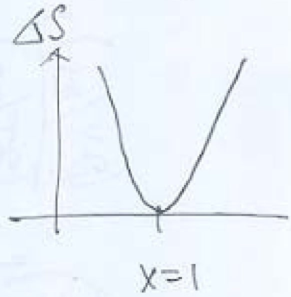
$$\hookrightarrow T_{30} = \left[\frac{2A(T_{20}-T_f) + B(T_{20}^2 - T_f^2)}{B} + T_{20}^2\right]^{1/2} =$$

$$\Delta S_2 = A\log\frac{T_{20}}{T_f} + B(T_{20} - T_f)$$

4.4.-3

$$\Delta S = C_1\log\left(\frac{T_f}{T_{10}}\right) + C_2\log\left(\frac{T_f}{T_{20}}\right)$$

$$= C_1\log\left(\frac{C_1 + C_2X}{C_1 + C_2}\right) + C_2\log\left(\frac{C_1/X + C_2}{C_1 + C_2}\right)$$



$$\left(\frac{\partial\Delta S}{\partial X}\right) = \frac{C_1C_2}{C_1 + C_2X} - \frac{\frac{C_1C_2}{X^2}}{C_1/X + C_2} = \frac{C_1C_2}{C_1 + C_2X}\left(1 - \frac{1}{X}\right)$$

$$= \frac{C_1C_2}{C_1 + C_2X}\left(\frac{1 - X}{X}\right)\begin{cases} > 0 & \text{for } X < 1 \\ < 0 & \text{for } X > 1 \end{cases}$$

& $\Delta S = 0$ when $X = 1$

$\Longrightarrow \therefore\ \Delta S \geq 0$ for $\forall X$