1(a) $dE = T\,dS - p\,dV$ $\qquad dF = -S\,dT - p\,dV$

$\left(\frac{\partial E}{\partial S}\right)_T = \left(\frac{\partial E}{\partial S}\right)_V + \left(\frac{\partial E}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T$ $\qquad$ Maxwell : $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$= T + (-p)\left(\frac{\partial T}{\partial p}\right)_V$ $\qquad$ or $\left(\frac{\partial V}{\partial S}\right)_T = \left(\frac{\partial T}{\partial p}\right)_V$

$= -p^2 \frac{\partial}{\partial p}\left(\frac{T}{p}\right)_V$

(b) $\left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p}$ $\qquad dH = T\,dS + V\,dp$

$= \frac{-1}{C_p}\left[\left(\frac{\partial H}{\partial p}\right)_S + \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T\right]$ $\qquad dG = -S\,dT + V\,dp$

$= \frac{-1}{C_p}\left(V + T\left[-\left(\frac{\partial V}{\partial T}\right)_p\right]\right)$ $\qquad$ Maxwell : $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

$= \frac{T^2}{C_p}\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_p$

2(a) $dE = T\,dS + \tau\,dL$

Internal Energy, Temperature, entropy, tension, length

(b) $\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial T}{\partial L}\right)_S \left(\frac{\partial S}{\partial T}\right)_L < 0$ $\qquad$ Entropy decreases.

(>0 adiabatic elongation temperature increase) $\qquad$ ($\frac{C_L}{T}$ Heat capacity >0)

3(a) $E = N_2 \varepsilon$, $\quad N_1 + N_2 = N$

$\Omega = \binom{N}{N_2} \cdot 4^{N_2} = \frac{N!}{N_2!(N-N_2)!} 4^{N_2}$

$S = k\ln\Omega \approx k\left[N\ln N - N_2 \ln N_2 - (N-N_2)\ln(N-N_2) + N_2 \ln 4\right]$

$= k\left[N\ln N - \frac{E}{\varepsilon}\ln\frac{E}{\varepsilon} - \left(N - \frac{E}{\varepsilon}\right)\ln\left(N - \frac{E}{\varepsilon}\right) + \frac{N}{\varepsilon}\ln 4\right]$

(b) $\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial S/\partial N_2}{\partial E/\partial N_2} = \frac{k}{\varepsilon}\left[-(\ln N_2 + 1) - (-\ln(N-N_2) - 1) + \ln 4\right]$

$= \frac{k}{\varepsilon}\left[\ln 4\,\frac{N-N_2}{N_2}\right]$

$\frac{N_2}{N_1} = \frac{N_2}{N-N_2} = 4\exp\left(-\frac{\varepsilon}{kT}\right)$

4(a) $Z_1 = \frac{1}{h^2}\int e^{-\beta H}\,d^2x\,d^2p$ $\qquad \left[a(x^2+y^2) + 2bxy = (a+b)\left(\frac{x+y}{\sqrt{2}}\right)^2 + (a-b)\left(\frac{x-y}{\sqrt{2}}\right)^2\right]$ (rotation)

$= \frac{1}{h^2}\iint \exp\left(-\frac{\beta}{2m}(p_x^2+p_y^2)\right)dp_x\,dp_y \iint \exp\left(-\frac{\beta m\omega^2}{2}\left[(a+b)q_1^2 + (a-b)q_2^2\right]\right)\overbrace{\frac{\partial(x,y)}{\partial(q_1,q_2)}}^{=1} dq_1\,dq_2$

$= \frac{1}{h^2}\left(\int_{-\infty}^{\infty}\exp\left(-\frac{\beta}{2m}p^2\right)dp\right)^2 \left(\int_{-\infty}^{\infty}\exp\left(-\frac{\beta m\omega^2}{2}(a+b)q_1^2\right)dq_1\right)\left(\int_{-\infty}^{\infty}\exp\left(-\frac{\beta m\omega^2}{2}(a-b)q_2^2\right)dq_2\right)$

$= \frac{1}{h^2}\left(\sqrt{\frac{\pi}{\frac{\beta}{2m}}}\right)^2 \sqrt{\pi\frac{2}{\beta m\omega^2(a+b)}}\sqrt{\pi\frac{2}{\beta m\omega^2(a-b)}} = \left(\frac{kT}{\hbar\omega}\right)^2 \frac{1}{\sqrt{a^2-b^2}}$ $\qquad \int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$ $(a>0)$

$Z = \frac{Z_1^N}{N!} = \frac{(a^2-b^2)^{-\frac{N}{2}}}{N!}\left(\frac{kT}{\hbar\omega}\right)^{2N}$

(b) $E = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\ln\left(\frac{1}{\hbar\omega\beta}\right)^{2N} = \frac{2N}{\beta} = 2NkT$

$C = \frac{dE}{dT} = 2Nk = 4N\left(\frac{1}{2}k\right)$

D.o.F of each particle is 4. N particles. Consistent with classical equipartition theorem.

5(a) Extent of reaction : $d\xi = \frac{dN_i}{\nu_i}$ $\quad$ dN_i are related to one another by stiochiometric ratio of reaction

T, V constant. $dF = -SdT - pdV + \sum_i \mu_i dN_i = -SdT - pdV + \left(\sum_i \mu_i \nu_i\right) d\xi$

Chemical equilibrium : $\left(\frac{\partial F}{\partial \xi}\right)_{T,V} = \sum_i \mu_i \nu_i = 0$

(b) Indistinguishable particles: $Z = f^N/N!$, $\ln Z \approx N(\ln f - \ln N + 1)$

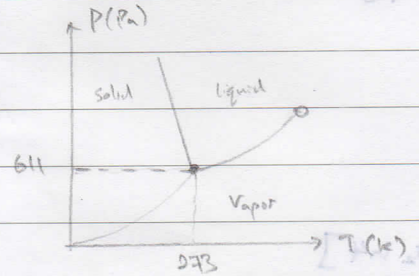
$F = -kT\ln Z = -kTN(\ln f - \ln N + 1)$

$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\left[(\ln f - \ln N + 1) + N\left(-\frac{1}{N}\right)\right] = -kT\ln\frac{f}{N}$

At equilibrium : $0 = \sum_i \nu_i \mu_i = -kT\sum_i \nu_i \ln\frac{f_i}{N_i}$

$\Rightarrow 0 = \sum_i \ln\left(\frac{f_i}{N_i}\right)^{\nu_i} \Rightarrow 1 = \prod_i \left(\frac{f_i}{N_i}\right)^{\nu_i} \Rightarrow \prod_i f_i^{\nu_i} = \prod_i N_i^{\nu_i}$

6(a)



(b) liquid $\rightarrow$ solid $\rightarrow$ Vapor. Using Clausius-Clapeyron,

Melting slope : $\frac{dP}{dT} = \frac{L}{T\Delta V} = -1.02\times10^7 \text{ Pa K}^{-1}$

$\frac{P_{freeze} - 611\text{ pa}}{-1.1k} = \frac{dP}{dT} \Rightarrow P_{freeze} = 1.12\times10^7 \text{ Pa}$

Sublimation : $L = 2845 \text{ J/g}$

$P_{sub} = P_0 \exp\left(-\frac{L}{Nk}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$

$= P_0 \exp\left(-\frac{lM_r}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) = 562 \text{ Pa}$

(c) $\alpha_i = \frac{1}{v_i}\left(\frac{\partial v_i}{\partial T}\right)_P$, $C_{P_i} = T\left(\frac{\partial s_i}{\partial T}\right)_P$ $\quad$ $dG = -SdT + VdP$

Maxwell : $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$l = T\Delta S$

$$\frac{dl}{dT} = \Delta S + T\Delta\frac{dS}{dT}$$

$$= \frac{l}{T} + T\Delta\left[\left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T\frac{dP}{dT}\right]$$

$$= \frac{l}{T} + \Delta\left[T\left(\frac{\partial S}{\partial T}\right)_P\right] - T\left[\Delta\left(\frac{\partial V}{\partial T}\right)_P\right]\frac{dP}{dT}$$

$$= \frac{l}{T} + \Delta C_p - T\Delta(\alpha V)\frac{l}{T\Delta V}$$

$$= \frac{l}{T} + \Delta C_p - \frac{\Delta(\alpha V)}{\Delta V}l$$

NO.: Date:

7(a) $$Z = \sum_{n=0}^{N} e^{-\beta n \epsilon} = \frac{1-\exp(-(N+1)\beta\epsilon)}{1-\exp(-\beta\epsilon)} = \frac{\sinh\left(\frac{N+1}{2}\beta\epsilon\right)}{\sinh\left(\frac{1}{2}\beta\epsilon\right)} \exp\left(-\frac{N}{2}\beta\epsilon\right)$$

(b) $$\ln Z = \ln\sinh\left(\frac{N+1}{2}\beta\epsilon\right) - \ln\sinh\left(\frac{\beta\epsilon}{2}\right) - \frac{N}{2}\beta\epsilon$$

$$\langle n\rangle \epsilon = \langle E\rangle = -\frac{\partial \ln Z}{\partial\beta}$$

$$= -\left[\frac{\cosh\left(\frac{N+1}{2}\beta\epsilon\right)}{\sinh\left(\frac{N+1}{2}\beta\epsilon\right)}\left(\frac{N+1}{2}\epsilon\right) - \frac{\cosh\left(\frac{\beta\epsilon}{2}\right)}{\sinh\left(\frac{\beta\epsilon}{2}\right)}\left(\frac{\epsilon}{2}\right) - \frac{N\epsilon}{2}\right]$$

$$= \frac{\epsilon}{2}\left[-(N+1)\coth\left(\frac{N+1}{2}\beta\epsilon\right) + \coth\left(\frac{1}{2}\beta\epsilon\right) + N\right]$$

$$\langle n\rangle = \frac{1}{2}\left[-(N+1)\coth\left(\frac{N+1}{2}\beta\epsilon\right) + \coth\left(\frac{1}{2}\beta\epsilon\right) + N\right]$$

$$\langle n^2\rangle = \frac{1}{Z}\sum n^2 e^{-\beta n\epsilon} = \frac{1}{\epsilon^2 Z}\frac{\partial^2}{\partial\beta^2}Z$$

$$\langle(\Delta n)^2\rangle = \langle n^2\rangle - \langle n\rangle^2 = \frac{1}{\epsilon^2 Z}\frac{\partial^2}{\partial\beta^2}Z - \left(-\frac{1}{\epsilon Z}\frac{\partial}{\partial\beta}Z\right)^2$$

$$= \frac{1}{\epsilon^2 Z^2}\left(Z\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{\partial Z}{\partial\beta}\right)^2\right) = \frac{1}{\epsilon^2}\frac{\partial}{\partial Z}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) = \frac{1}{\epsilon^2}\frac{\partial^2}{\partial\beta^2}(\ln Z)$$

$$= -\frac{1}{\epsilon}\frac{\partial}{\partial\beta}\langle n\rangle$$

$$= -\frac{1}{2\epsilon}\left[-(N+1)\left[-\operatorname{csch}^2\left(\frac{N+1}{2}\beta\epsilon\right)\left(\frac{N+1}{2}\epsilon\right)\right] - \operatorname{csch}^2\left(\frac{1}{2}\beta\epsilon\right)\left(\frac{1}{2}\epsilon\right)\right]$$

$$= \frac{1}{4}\left[-(N+1)^2\operatorname{csch}^2\left(\frac{N+1}{2}\beta\epsilon\right) + \operatorname{csch}^2\left(\frac{1}{2}\beta\epsilon\right)\right]$$

(c) At low temperature, $\beta\epsilon \gg 1$.

$$\langle n\rangle = \frac{1}{2}\left[N\left(1-\coth\left(\frac{N+1}{2}\beta\epsilon\right)\right) + \left[\coth\left(\frac{\beta\epsilon}{2}\right) - \coth\left(\frac{N+1}{2}\beta\epsilon\right)\right]\right]$$

$$= \frac{1}{2}\left[N\frac{-2}{\exp[(N+1)\beta\epsilon]-1} + \left(\frac{2}{\exp(\beta\epsilon)-1}+1\right) - \left(\frac{2}{\exp[(N+1)\beta\epsilon]-1}+1\right)\right]$$

$$= -\frac{N+1}{\exp[(N+1)\beta\epsilon]-1} + \frac{1}{\exp(\beta\epsilon)-1}$$

$$= \exp(-\beta\epsilon)\left[-\underbrace{\frac{N+1}{\exp(N\beta\epsilon)-\exp(-\beta\epsilon)}}_{\approx 0} + \underbrace{\frac{1}{1-\exp(-\beta\epsilon)}}_{\approx 1}\right] \approx \exp(-\beta\epsilon)$$

$\operatorname{csch} x \sim 2e^{-x}$

$$\langle(\Delta n)^2\rangle = \exp(-\beta\epsilon)\left[-\underbrace{\left(\frac{N+1}{2}\right)^2\exp(\beta\epsilon)\operatorname{csch}^2\left(\frac{N+1}{2}\beta\epsilon\right)}_{\approx 0} + \underbrace{\frac{\exp(\beta\epsilon)}{4}\operatorname{csch}^2\left(\frac{\beta\epsilon}{2}\right)}_{\approx 1}\right] = \exp(-\beta\epsilon)$$

Both expressions are independent of N in the low temperature limit, where the system tends to occupy the lowest energy levels, corresponding to a small number of open sites.

NO.: Date:

8 (a) Gibbs – Duhem : $-SdT + Vdp - Nd\mu = 0 \Rightarrow dp = \frac{S}{V}dT + \frac{N}{V}d\mu$

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial V}{\partial \mu}\right)_{T,N}\left(\frac{\partial N}{\partial V}\right)_{T,\mu} \quad (3)$$

$$= -\left(\frac{\partial V}{\partial p}\right)_{T,N}\left(\frac{\partial p}{\partial \mu}\right)_{T,N}\left(\frac{\partial p}{\partial \mu}\right)_{T,V}$$

$$= -\left(\frac{\partial V}{\partial p}\right)_{T,N}\left(\frac{\partial p}{\partial \mu}\right)^2_{T,V}$$

$$\left(\frac{\partial p}{\partial V}\right)_{\mu,T} = 0 \quad — (1)$$

$$\left(\frac{\partial p}{\partial \mu}\right)_{V,T} = \frac{N}{V} \quad — (2)$$

Grand potential : $\Phi = E - TS - \mu N$

$d\Phi = -SdT - pdV - Nd\mu$

Maxwell : $\left(\frac{\partial N}{\partial V}\right)_{T,\mu} = \left(\frac{\partial p}{\partial \mu}\right)_{T,V}$ — (3)

Note : $\left(\frac{\partial p}{\partial \mu}\right)_{T,N} = \left(\frac{\partial p}{\partial \mu}\right)_{T,V} + \underbrace{\left(\frac{\partial p}{\partial V}\right)_{T,\mu}}_{=0 \text{ from } (1)}\left(\frac{\partial V}{\partial \mu}\right)_{T,N}$

$= \left(\frac{\partial p}{\partial \mu}\right)_{T,V}$

Using grand canonical ensemble,

$$\langle N\rangle = \frac{1}{\Xi}\sum_i n_i \exp\left(\frac{n_i\mu - E_i}{kT}\right) = \frac{kT}{\Xi}\frac{\partial}{\partial \mu}(\Xi)_{T,V}$$

$$\langle N^2\rangle = \frac{1}{\Xi}\sum_i n_i^2 \exp\left(\frac{n_i\mu - E_i}{kT}\right) = \frac{k^2T^2}{\Xi}\frac{\partial^2}{\partial \mu^2}(\Xi)_{T,V}$$

$$\langle (N-\langle N\rangle)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 = \frac{k^2T^2}{\Xi^2}\left[\Xi\frac{\partial^2\Xi}{\partial\mu^2} - \left(\frac{\partial \Xi}{\partial \mu}\right)^2\right] = k^2T^2\frac{\partial}{\partial \mu}\left(\frac{1}{\Xi}\frac{\partial \Xi}{\partial \mu}\right)_{T,V}$$

$$= kT\frac{\partial}{\partial \mu}\langle N\rangle$$

$$\frac{\langle (N-\langle N\rangle)^2\rangle}{\langle N\rangle^2} = \frac{1}{\beta\langle N\rangle^2}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \frac{1}{\beta V}\left(\frac{V}{\langle N\rangle}\right)^2\underbrace{\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\langle N\rangle}\right)}_{\kappa_T}\underbrace{\left(\frac{\partial p}{\partial \mu}\right)^2_{T,V}}_{\frac{N}{V}\text{ from }(2)}$$

$$= \frac{\kappa_T}{\beta V}$$

(b) $Z_1 = \frac{V}{\lambda^3}$, $\lambda = \frac{h}{\sqrt{2\pi mkT}}$, $Z = \frac{Z_1^N}{N!}$

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} Z = \sum_{N=0}^{\infty}\frac{1}{N!}\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)^N = \exp\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)$$

Ideal gas : $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T} = -\frac{1}{V}\frac{\partial}{\partial p}\left(\frac{NkT}{p}\right)_{N,T} = -\frac{NkT}{V}\left(-\frac{1}{p^2}\right) = \frac{1}{p}$

$\langle (N-\langle N\rangle)^2\rangle / \langle N\rangle^2 = \frac{\kappa_T}{\beta V} = \frac{kT}{pV} = \frac{1}{N}$.

Similarly for E : $\langle E\rangle = \frac{1}{Z}\sum_i E_i \exp(-\beta E_i) = -\frac{\partial}{\partial\beta}\ln Z$

$\langle E^2\rangle = \frac{1}{Z}\sum_i E_i^2 \exp(-\beta E_i) = \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}Z$

$\langle (E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Z^2}\left[Z\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{\partial Z}{\partial\beta}\right)^2\right] = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right) = -kT^2\frac{\partial E}{\partial T} = T^2kC_V$

Ideal gas (monoatomic) : $E = \frac{3}{2}NkT$, $C_V = \frac{3}{2}Nk$

$\langle (E-\langle E\rangle)^2\rangle / \langle E\rangle^2 = \left(T^2k\left(\frac{3}{2}Nk\right)\right) / \left(\frac{3}{2}NkT\right)^2 = \frac{2}{3N}$