

Solutions to PC2230 AY0607 Paper

Part I

$$1(i) \quad \frac{1}{T_i} = \left(\frac{\partial S_i}{\partial E_i} \right)_{V_i, N_i}$$

$$1(ii) \quad \frac{P_i}{T_i} = \left(\frac{\partial S_i}{\partial V_i} \right)_{E_i, N_i}$$

2(a) Clausius statement of the 2nd law of thermodynamics is “Heat, by itself, cannot pass from a colder to a hotter body”.

$$2(b) \quad \begin{aligned} dE &= TdS - PdV \\ dF &= -PdV - SdT \\ dG &= VdP - SdT \\ dH &= TdS + VdP \end{aligned}$$

- (i) At constant E and V , entropy is maximum at equilibrium.
- (ii) At constant T and V , Helmholtz free energy is minimum at equilibrium
- (iii) At constant T and P , Gibbs free energy is minimum at equilibrium
- (iv) At constant H and P , entropy is maximum at equilibrium

3 3 possible situations: spin parallel to B , spin anti-parallel to B , spin perpendicular to B
3 possible energies of dipole: μB , $-\mu B$, 0

Partition function of 1 atom,

$$Z_1 = \sum_r e^{-E_r \beta} = e^{-\mu B / kT} + e^{\mu B / kT} + e^0 = 2 \cosh \frac{\mu B}{kT} + 1 = 2 \cosh x + 1$$

Mean magnetic moment of 1 atom,

$$\bar{\mu} = \frac{1}{\beta} \left(\frac{\partial \ln Z_1}{\partial B} \right)_{\beta} = \frac{1}{\beta} \frac{1}{Z_1} \frac{\partial Z_1}{\partial x} \frac{\partial x}{\partial B} = \frac{1}{\beta} \frac{1}{Z_1} (2 \sinh x) \frac{\mu}{kT} = \mu \frac{2 \sinh x}{1 + 2 \cosh x}$$

$$\text{Mean magnetic moment of } N \text{ atoms} = N\bar{\mu} = N\mu \frac{2 \sinh x}{1 + 2 \cosh x} \quad (\text{shown})$$

4 Energy of harmonic oscillator = $\hbar\omega(n + \frac{1}{2})$

$$\begin{aligned} \text{Partition function, } Z &= \sum_n \exp(-\beta\epsilon) = \sum_n \exp(-\beta \hbar\omega(n + \frac{1}{2})) \\ &= \exp(-\frac{1}{2} \beta \hbar\omega) \left(\sum_n \exp(-n\beta \hbar\omega) \right) \\ &= \exp(-\frac{1}{2} \beta \hbar\omega) \frac{1}{1 - \exp(-\beta \hbar\omega)} \end{aligned}$$

$$\text{Let } x = \beta\hbar\omega, Z = \frac{e^{-x/2}}{1 - e^{-x}}, \ln Z = -\frac{1}{2}x - \ln(1 - e^{-x})$$

$$\bar{\epsilon} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial x} \frac{\partial x}{\partial \beta} = -\left(-\frac{1}{2} - \frac{e^{-x}}{1 - e^{-x}}\right)\hbar\omega = \left(\frac{1}{2} + \frac{e^{-x}}{1 - e^{-x}}\right)\hbar\omega$$

$$\text{For } N \text{ molecules, mean energy} = 3N\bar{\epsilon} = 3N\hbar\omega\left(\frac{1}{2} + \frac{e^{-x}}{1 - e^{-x}}\right)$$

$$C_V = \frac{\partial \bar{\epsilon}}{\partial T} = \frac{\partial \bar{\epsilon}}{\partial x} \frac{\partial x}{\partial T} = 3N\hbar\omega\left(\frac{\hbar\omega}{kT^2}\right)\left(\frac{e^{-x}}{(1 - e^{-x})^2}\right) = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^x}{(e^x - 1)^2}$$

$$\therefore C_V = 3Nk\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp\left(\frac{\Theta_E}{T}\right)}{\left[\exp\left(\frac{\Theta_E}{T}\right) - 1\right]^2} \text{ (shown)}$$

5 $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS = \left(\frac{\partial S}{\partial E}\right)_V \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$dS = \frac{1}{T} C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$TdS = C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \text{ (shown)}$$

6 Sum of chemical potentials of LHS = $3(-0.4) + 2(-0.3) + 4(0.2) = -1.0$

Sum of chemical potentials of RHS = $2(0.1) + 3(-0.2) = -0.4$

At equilibrium, the chemical potentials of both sides must be equal, which will be -0.7 .

Hence, the reaction will proceed from right to left spontaneously, so that the chemical potential of LHS will increase to -0.7 , while the RHS can decrease to -0.7 .

Part II

1(a) $F = -kT \ln Z$

$$\left(\frac{\partial F}{\partial V}\right)_T = -kT \left(\frac{\partial \ln Z}{\partial V}\right)_\beta = -kT\beta P$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \text{ (shown)}$$

1(b)(i) For ideal gas, the potential energy of interaction between the molecules is negligible compared to their kinetic energy of motion.

For classical gas, the potential energy of interaction between the molecules is not negligible.

$$1(b)(ii) \quad Z(T, V, N) = \frac{1}{N!} [Z_1(T, V)]^N = \frac{1}{N!} [Z_{tr} Z_{int}]^N = \frac{1}{N!} V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_{int}^N$$

$$Z_{int} = \left[\frac{Z(T, V, N) N!}{V^N} \left(\frac{h^2}{2\pi mkT} \right)^{3N/2} \right]^{\frac{1}{N}} = \frac{1}{V} \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} [Z(T, V, N) N!]^{\frac{1}{N}}$$

$$1(b)(iii) \quad Z = \frac{1}{N!} V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} [Z_{int}]^N$$

For $N \gg 1$, using Stirling's formula, $N! = \left(\frac{N}{e} \right)^N$

$$Z = \left(\frac{e}{N} \right)^N V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} [Z_{int}]^N$$

$$F = -kT \ln Z = -NkT \ln \left[\left(\frac{eV}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{3/2} Z_{int} \right]$$

1(b)(iv) For ideal classical gas, the internal partition function can be ignored as the potential energy of the gas molecules is negligible.

Considering F_{tr} only,

$$F_{tr} = -NkT \ln \left[\frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]$$

Using $P = - \left(\frac{\partial F}{\partial V} \right)_T$,

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = NkT \left(\frac{1}{V} \right)$$

$$\Rightarrow PV = NkT$$

$$2(a)(i) \quad u(T) = \int_0^\infty u(\omega, T) d\omega = \int_0^\infty \frac{\hbar \omega^3}{\pi^2 c^3 [\exp(\hbar \omega / kT) - 1]} d\omega$$

$$\text{Let } x = \frac{\hbar \omega}{kT}, \quad dx = \frac{\hbar}{kT} d\omega, \quad \omega = \frac{kT}{\hbar} x$$

$$u(T) = \int_0^\infty \frac{\hbar \omega^3}{\pi^2 c^3 [\exp(\hbar \omega / kT) - 1]} d\omega = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^3 \frac{kT}{\hbar} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

$$u(T) = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^3 \frac{kT}{\hbar} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^4 \frac{\pi^4}{15} = \frac{\pi^2 k^4}{15 \hbar^3 c^3} T^4$$

$$u(T) = \frac{\pi^2 k^4}{15 \hbar^3 c^3} T^4 = aT^4 \quad (\text{Stefan-Boltzmann law})$$

$$2(a)(ii) \quad f = \frac{c}{\lambda} = \frac{3.0 \times 10^8}{3.0 \times 10^{-2}} = 1.0 \times 10^{10} \text{ Hz}$$

$$P = \sigma e A T^4 = 5.67 \times 10^{-8} (4\pi) (7 \times 10^8)^2 (6000)^4 = 4.52 \times 10^{26} \text{ W}$$

$$\text{Power radiated per megacycle bandwidth} = \frac{4.52 \times 10^{26}}{1.0 \times 10^4 \text{ MHz}} = 4.52 \times 10^{22} \text{ W (MHz)}^{-1}$$

$$2(b)(i) \quad V = V(T, P)$$

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP = \beta V dT - \kappa V dP$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \quad C_P = \left(\frac{\partial E}{\partial T} \right)_P$$

$$S = S(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP = \left(\frac{\partial S}{\partial E} \right)_P \left(\frac{\partial E}{\partial T} \right)_P dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$dS = \frac{1}{T} C_P dT - V \beta dP$$

$$T dS = C_P dT - V \beta T dP \quad (1)$$

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV = \left(\frac{\partial S}{\partial E} \right)_V \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial V} \right)_T dV$$

$$dS = \frac{1}{T} C_V dT - \left(\frac{\partial V}{\partial T} \right)_P \frac{1}{-\kappa V} (\beta V dT - \kappa V dP) = \frac{C_V}{T} dT + \frac{\beta^2 V}{\kappa} dT - V \beta dP$$

$$T dS = \left(C_V + \frac{T \beta^2 V}{\kappa} \right) dT - T V \beta dP \quad (2)$$

Comparing (1) and (2),

$$C_P = C_V + \frac{T \beta^2 V}{\kappa} \Rightarrow C_P - C_V = \frac{T \beta^2 V}{\kappa}$$

2(b)(ii) Since β and κ is always positive, $\frac{T \beta^2 V}{\kappa}$ is always positive, $C_P - C_V$ is always positive, hence $C_P > C_V$

3(a)(i) At equilibrium, the Gibbs free energy per molecule is the same.

$$g_1(T, P) = g_2(T, P)$$

3(a)(ii) $g_1(T, P) = g_2(T, P)$

$$g_1(T + dT, P + dP) = g_2(T + dT, P + dP)$$

By Taylor's series expansion,

$$g_1 + \left(\frac{\partial g_1}{\partial P}\right)_T dP + \left(\frac{\partial g_1}{\partial T}\right)_P dT = g_2 + \left(\frac{\partial g_2}{\partial P}\right)_T dP + \left(\frac{\partial g_2}{\partial T}\right)_P dT$$

$$\text{Since } g_1 = g_2, \left(\frac{\partial g_1}{\partial P}\right)_T dP + \left(\frac{\partial g_1}{\partial T}\right)_P dT = \left(\frac{\partial g_2}{\partial P}\right)_T dP + \left(\frac{\partial g_2}{\partial T}\right)_P dT$$

$$\left(\frac{\partial g_1}{\partial P}\right)_T dP - \left(\frac{\partial g_2}{\partial P}\right)_T dP = \left(\frac{\partial g_2}{\partial T}\right)_P dT - \left(\frac{\partial g_1}{\partial T}\right)_P dT$$

$$-\Delta\left(\frac{\partial g}{\partial P}\right)_T dP = \Delta\left(\frac{\partial g}{\partial T}\right)_P dT$$

$$\frac{dP}{dT} = -\frac{\Delta\left(\frac{\partial g}{\partial T}\right)_P}{\Delta\left(\frac{\partial g}{\partial P}\right)_T}$$

For each phase, $dG_i = -S_i dT + V_i dP + \mu_i dN_i$

For 1-component phase, $\mu_i = g_i$, $G_i = g_i N_i$

$$dG_i = g_i dN_i + N_i dg_i$$

$$g_i dN_i + N_i dg_i = -S_i dT + V_i dP + \mu_i dN_i$$

$$N_i dg_i = -S_i dT + V_i dP$$

$$\left(\frac{\partial g_i}{\partial T}\right)_P = -\frac{S_i}{N_i} \quad \left(\frac{\partial g_i}{\partial P}\right)_T = \frac{V_i}{N_i}$$

$$\frac{dP}{dT} = -\frac{\Delta\left(\frac{\partial g}{\partial T}\right)_P}{\Delta\left(\frac{\partial g}{\partial P}\right)_T} = \frac{\Delta\left(\frac{S}{N}\right)}{\Delta\left(\frac{V}{N}\right)} = \frac{\Delta S}{\Delta V}$$

3(a)(iii) At phase transformation from phase 1 to phase 2, $\Delta S = \frac{L_{12}}{T}$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T\Delta V}$$

3(b) One of the reasons is that because the volume of water contracts when it melts. This is shown in the values given, the specific volume of ice is bigger than that of water at 0°C.

$$\Delta V = V_{\text{water}} - V_{\text{ice}} = (1.00013 - 1.09070) \times 10^{-3} = -0.09057 \times 10^{-3} \text{ m}^3 / \text{kg}$$

$$\frac{dP}{dT} = -\frac{3.35 \times 10^5}{(0.09057 \times 10^{-3})T} = -\frac{3.70 \times 10^9}{T} \text{ Pa/K}$$

Since T is always positive, the gradient of the solid-liquid phase transition curve is always negative for water. As a result, the triple point temperature is higher than the ice point temperature at any pressure.