

CML 100-Minor 1: 2014-2015 - Semester I

29th August 2014

Marks: 100

Time: 1 hour

Fundamental Equations: $dU = TdS - pdV$; $dH = TdS + Vdp$; $dA = -SdT - pdV$; $dG = -SdT + Vdp$

Maxwell Relations: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$; $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$; $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$; $-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$

Fundamental Equations of State: $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$; $\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V$

Gas Constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 82 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

1) Show that

a. $C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\left(\frac{\partial(-\partial G/\partial T)_p}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

b. $H = A - V\left(\frac{\partial A}{\partial V}\right)_T - T\left(\frac{\partial A}{\partial T}\right)_V$

From the fundamental equation for dA , $\left(\frac{\partial A}{\partial V}\right)_T = -p$; $\left(\frac{\partial A}{\partial T}\right)_V = -S \therefore H = A + Vp + TS$

Or, $A = H - pV - TS = U - TS = A$

c. $\left(\frac{\partial U}{\partial p}\right)_T = V[p\kappa - T\alpha]$

From the fundamental equation for dU , $\left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T$

$= -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T$ (used the 4th Maxwell relation)

$= -TV\alpha + pV\kappa$

d. $\left(\frac{\partial U}{\partial V}\right)_S = \frac{1}{\kappa}$ (For an ideal gas) ($4 \times 7 = 28$ marks)

From the fundamental equation for dU , $\left(\frac{\partial U}{\partial V}\right)_S = -p$ and $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

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

$$\therefore \left(\frac{\partial U}{\partial V}\right)_S = -\frac{1}{\kappa}$$

2) The sublimation pressures of solid Cl_2 are 352 Pa at -112°C and 35 Pa at -126.5°C . The vapour pressures of liquid Cl_2 are 1590 Pa at -100°C and 7830 Pa at -80°C . Calculate ΔH_{sub} , ΔH_{vap} , ΔH_{fus} and the triple point. ($4 \times 6 = 24$ marks)

Use the integrated form for the Clausius Clapeyron equation

$$p = p^* \exp -\chi \quad \text{where} \quad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

For the two equilibrium curves, put the two values of p, T . Get ΔH values of vaporization and sublimation. Fusion is the difference of the two. For triple point equate the two equations to get the value of Temperature. Remember to use the Kelvin scale.

- 3) An operator \hat{A} has normalized eigenfunctions $\phi_1(x), \phi_2(x), \phi_3(x)$ and $\phi_4(x)$ with corresponding eigenvalues $a_1, 4a_1$ and $9a_1$ and $16a_1$. The state of a system is described by a normalized wavefunction Ψ given by $\Psi = \frac{\sqrt{11}}{4} \phi_1(x) + \frac{1}{4} \phi_2(x) + \frac{1}{2} \phi_3(x)$

- a. Is Ψ an eigenfunction of the operator \hat{A} ? Explain.

No. First, Ψ is a linear combination of the eigenfunctions. See $\int \Psi^* \hat{A} \Psi dx$ is not equal to any eigenvalue.

- b. Show that Ψ is normalized.

$$\int \Psi^* \Psi dx = 1$$

$$\Rightarrow \int \left[\frac{\sqrt{11}}{4} \phi_1^*(x) + \frac{1}{4} \phi_2^*(x) + \frac{1}{2} \phi_3^*(x) \right] \left[\frac{\sqrt{11}}{4} \phi_1(x) + \frac{1}{4} \phi_2(x) + \frac{1}{2} \phi_3(x) \right] dx = 1$$

$$\Rightarrow \frac{11}{16} + \frac{1}{16} + \frac{4}{16} = 1, \text{ since } \phi_i \text{'s are orthonormalized.}$$

- c. What are the different eigenvalues that can be obtained from different measurements?
 $a_1, 4a_1$ and $9a_1$. $16a_1$ will never be observed since $\phi_4(x)$ is not a part of Ψ

- d. What are the probabilities of obtaining the different eigenvalues?

Probabilities are square of the coefficients. $\frac{11}{16}, \frac{1}{16}$, and $\frac{4}{16}$ for ϕ_1, ϕ_2 and ϕ_3 , respectively.

- e. What is the average value of the observable ' a ' that one can obtain from a large number of measurements. **(3+3+3+3+6 = 18 marks)**

$\langle a \rangle = \int \Psi^* \hat{A} \Psi dx = \sum_i |c_i|^2 a_i$ when the ϕ_i 's are orthonormal. By virtue of being eigenfunctions, they are orthogonal and the question describes them as normalized.

$$\therefore \sum_i |c_i|^2 a_i = \frac{11}{16} (a_1) + \frac{1}{16} (4a_1) + \frac{4}{16} (9a_1) + 0(16a_1) = \frac{11 + 4 + 36}{16} a_1 = \frac{51}{16} a_1$$

- 4) Short answers: A one line explanation is needed **(5+5+5+5+10 = 30 marks)**

- a. True/False: Entropy change of the system when 1 mol of an ideal gas is expanded irreversibly from 1 L to 2L in an adiabatic process is same as entropy change when 1 mol of same gas is expanded reversibly from 1 L to 2L in an adiabatic process.

False: $\Delta S = C_p \ln T_2/T_1$. For adiabatic expansions between the same initial and final volume the temperature change is maximum for reversible process.

- b. True/False: Gibbs free energy is always constant at constant Temperature and Pressure.

False: This is true only for a closed system. If the number of moles change, that must be taken into account as well.

- c. True/False: Operators A and B commute, where $A = x(\partial/\partial x)$ and $B = x^2(\partial^2/\partial x^2)$

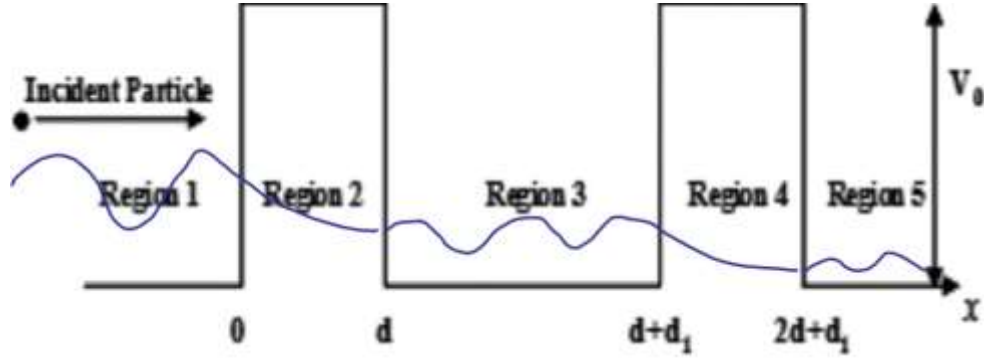
$$\hat{A}^2 f = x \frac{d}{dx} \cdot \left(x \frac{df}{dx} \right) = x \left[x \frac{d^2 f}{dx^2} + \frac{df}{dx} \right] = x^2 \left(\frac{d^2}{dx^2} \right) f + x \frac{df}{dx} = \hat{B} f + \hat{A} f$$

This gives, $\hat{B} = \hat{A}^2 - \hat{A}$, which commutes with \hat{A} . Statement is **true**.

- d. True/False: The wavefunction ψ for a particle in a 1-D box is dimensionless

False: $\int \psi^* \psi dx = 1$. So the dimension of the wavefunction must be $L^{-1/2}$

- a. Shown below is a symmetric double well potential along the x-axis. Draw neatly the wavefunction from region 1 to region 5 and write the expressions for the wavefunctions in the five regions. (No need to match the boundaries or solve the problem)



The amplitudes of the waves must be shown to decrease.

$$\psi_I(x) = A e^{ik_1x} + B e^{-ik_1x} \quad x < 0 \quad k_1 \hbar = \sqrt{2mE}$$

$$\psi_{II}(x) = C e^{k_2x} + B e^{-k_2x} \quad 0 < x < d \quad k_2 \hbar = \sqrt{2m(V_0 - E)}$$

$$\psi_{III}(x) = E e^{ik_1x} + F e^{-ik_1x} \quad d < x < d + d_1 \quad k_1 \hbar = \sqrt{2mE}$$

$$\psi_{IV}(x) = G e^{k_2x} + H e^{-k_2x} \quad d + d_1 < x < 2d + d_1 \quad k_2 \hbar = \sqrt{2m(V_0 - E)}$$

$$\psi_V(x) = J e^{ik_1x} \quad x > 2d + d_1 \quad k_1 \hbar = \sqrt{2mE}$$