

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

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

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

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

2) The sublimation pressures of solid Cl₂ are 352 Pa at -112 °C and 35 Pa at -126.5 °C. The vapour pressures of liquid Cl₂ are 1590 Pa at -100 °C and 7830 Pa at -80 °C. Calculate ΔH_{sub} , ΔH_{vap} , ΔH_{fus} and the triple point. (4 × 6 = 24 marks)

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.

b. Show that Ψ is normalized.

c. What are the different eigenvalues that can be obtained from different measurements?

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

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)

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.

b. True/False: Gibb's free energy is always constant at constant Temperature and Pressure.

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

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

e. 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)

