

1. One mole of an ideal monatomic gas, initially at 0 °C and 1 bar, is put through each of the reversible steps below (in each case starting at 0 °C and 1 bar). Calculate w , q , ΔU , ΔH , and ΔS for each case.
- (a) Cooling at constant volume to -100 °C.
 - (b) Isothermal compression to 100 bar.
 - (c) Constant pressure heating to 100 °C.
 - (d) Adiabatic expansion to 0.1 bar. (16%)

2. The equilibrium constant K_p for the reaction
- $$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) = 2 \text{NO}$$
- varies with temperature over the range of 1900 to 2600 K according to the equation
- $$\ln(K_p) = 3.13 - 21900/T \quad (\text{unit of } T : \text{K})$$
- Calculate K_p , ΔG° , ΔH° , and ΔS° at 2000 K. (12%)

3. Benzene and toluene form very nearly ideal solutions. At 80 °C, the vapor pressures of benzene and toluene are 100.4 kPa and 38.7 kPa, respectively. For a solution containing 0.5 mole fraction of benzene and 0.5 mole fraction of toluene, what are the composition of the vapor and the total vapor pressure at 80 °C? (12%)

4. (a) For a gas system that PV work is the only type of work involved, show that
- $$C_p - C_v = [P + (\frac{\partial U}{\partial V})_T] (\frac{\partial V}{\partial T})_P$$
- and explain the meanings of the three terms $(\frac{\partial U}{\partial V})_T$, $P(\frac{\partial V}{\partial T})_P$, and $(\frac{\partial U}{\partial V})_T(\frac{\partial V}{\partial T})_P$
- (b) Starting from the definition of Helmholtz energy, $A=U-TS$, show that
- $$(\frac{\partial U}{\partial V})_T = T(\frac{\partial P}{\partial T})_V - P$$
- (c) For a van der Waals gas, show that $(\frac{\partial \bar{U}}{\partial V})_T = \frac{a}{V^2}$ (15%)

5. The standard electromotive force (E°) of the cell
- $$\text{Zn(S)} | \text{ZnCl}_2(0.05 \text{ mol kg}^{-1}) | \text{AgCl(S)} | \text{Ag}$$
- is 0.9854 volts at 25 °C. (a) Write the half-cell reactions and the cell reaction. (b) Estimate the mean ionic activity coefficient of 0.05 mol kg⁻¹ ZnCl₂ using Debye-Hückel theory. (c) Calculate the electromotive force (E) and the reaction Gibbs energy ($\Delta_r G$) of the cell. (15%)

6. The collision diameter of H₂ at 25 °C and 1 bar is 0.247 nm. Calculate the average number of collisions experienced by one molecule in unit time (collision frequency, $z_{1(1)}$), the average number of collisions per unit time and unit volume (collision density, Z_{11}), and the mean free path. (15%)

7. Consider the series of first-order irreversible reactions
- $$\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$$
- The initial concentration of A is $[A]_0$. Neither B nor C are present initially.
- (a) Derive the expression for the variation of $[B]$ with time.
 - (b) At what time does the concentration of B reach a maximum? (15%)