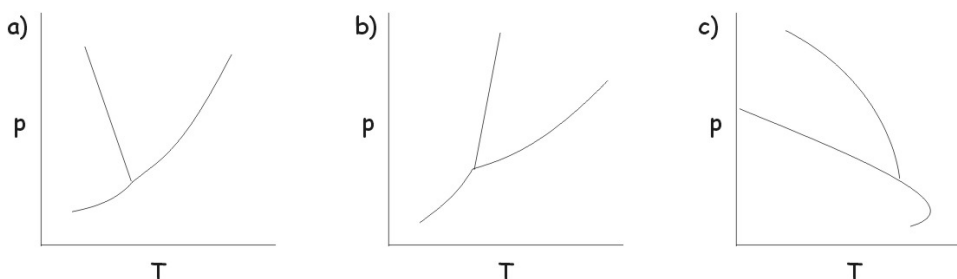


THERMODYNAMICS III

Q1. 1999 General Physical Chemistry I, Q5

- a) Derive the Clapeyron equation for the temperature dependence of the pressure at which two phases are in equilibrium. You may use without proof the relationship $dG = Vdp - SdT$, in which the symbols have their usual meanings. [3]
- b) Develop the result in a) for the case in which one of the phases is gaseous, to establish the Clausius-Clapeyron equation. Identify any assumptions you make. [3]
- c) Many of the higher mountains in the world have altitudes in excess of 25000 feet above sea level. At these altitudes the atmospheric pressure is around 250 Torr. Calculate the changes in
 i) the freezing point; and
 ii) the boiling point
 of water at this pressure relative to normal conditions, given the following data
 density of ice = 0.92 g cm^{-3}
 density of water = 1.00 g cm^{-3}
 enthalpy of fusion of ice = 6.01 kJ mol^{-1}
 enthalpy of vapourisation of water at the normal boiling point = 40.7 kJ mol^{-1}
 normal freezing point of water = 273.15 K
 1 bar = 760 Torr
 relative atomic masses: O = 16, H = 1. [8]
- d) The single-component phase diagrams shown below relate to the following substances: water, carbon dioxide, and carbon. Identify which diagram relates to which substance and label all phases shown. [6]



Q2. 1998 General Physical Chemistry II, Q1

- a) Define the quantities *enthalpy* (H), and *Gibbs Free Energy* (G) and explain why they are widely used in chemistry [4]
- b) Starting from the laws of thermodynamics, derive an expression, suitable for application to solid-liquid or solid-solid equilibrium, for the slope dp/dT of any line in a one-component phase diagram. [4]
- c) A partial phase diagram for sulphur, not to scale, is given below. The triple point, where rhombic sulphur, monoclinic sulphur, and vapour, are in equilibrium is at 5×10^{-7} bar and 368.4 K . At this point the densities of rhombic and monoclinic sulphur are 2070 kg m^{-3} and 1960 kg m^{-3} respectively, and the enthalpy change in the transition is 819 J mol^{-1} . Estimate the temperature of the triple point between rhombic,

monoclinic and liquid sulphur, which occurs at 1288 bar pressure, using each of the following approximations.

i) Assume that the entropy change and volume change in the transition from rhombic to monoclinic are constant.

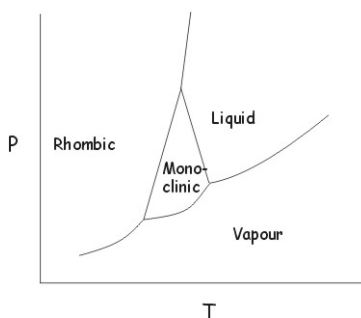
ii) Assume that the enthalpy change is constant, but the volume change varies with pressure according to the equation:

$$\Delta V = \Delta V_0 (1 - aP)$$

where P is the pressure in bar, $a = 1.55 \times 10^{-5} \text{ bar}^{-1}$ and ΔV_0 is the volume change at the lower triple point.

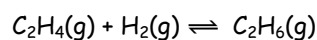
Comment on the validity of the above approximation that the enthalpy change is constant and suggest how higher accuracy might be attained. [12]

[Relative atomic mass of sulphur = 32.06]



Q3 1999 Advanced Physical Chemistry, Q5

A. The reaction enthalpy and entropy of the gas phase reaction

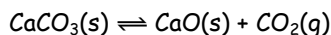


are $\Delta_r H^\circ = -137.0 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = -120.5 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. In the temperature range 298-1000 K, the difference in molar heat capacities of products and reactants is

$$\Delta_r C_p^\circ / (\text{J K}^{-1} \text{ mol}^{-1}) = -27.2 + 0.0256 (T/\text{K})$$

- a) Calculate $\Delta_r H^\circ$ and $\Delta_r S^\circ$ at 1000 K and hence show that the equilibrium constant $K_p = 2.92$ at 1000 K.
- b) 1 mol $\text{C}_2\text{H}_4(\text{g})$ and 1 mol $\text{H}_2(\text{g})$ are mixed at 1 bar total pressure and 1000 K.
 - i) Determine the number of moles of ethane present at equilibrium at 1 bar.
 - ii) What total pressure would be needed for the mole fraction of ethane at equilibrium to be 0.99 at 1000 K? [14]

- B. 10 g of solid CaCO_3 is sealed in an evacuated container (volume 10 dm^3) at 1000 K and allowed to come to equilibrium according to the equation:



- a) What mass of CaCO_3 remains at equilibrium? Assume that CO_2 behaves ideally. $\Delta_r G^\ominus = +23.5 \text{ kJ mol}^{-1}$ at 1000 K. Relative atomic masses: C 12, O 16, Ca 40.
- b) A small quantity of CaO is sealed in a vessel containing a large excess of CO_2 at 1 bar. Discuss the equilibrium composition in the temperature range 1000-1200 K. Assume that $\Delta_r H^\ominus$ (178 kJ mol⁻¹) and $\Delta_r S^\ominus$ are independent of temperature. [10]

- C. a) Give the expression for the chemical potential of a component in an ideal solution.
- b) Two compounds A and B form an ideal solution when liquid, but are totally immiscible as solids. Show that if A and B have identical enthalpies of fusion ($\Delta_{\text{fus}}H^\ominus$), then the mole fraction of A at the eutectic point is given by

$$\ln\left(\frac{x_A}{1-x_A}\right) = \frac{\Delta_{\text{fus}}H^\ominus}{R} \left(\frac{1}{T_A} - \frac{1}{T_B}\right)$$

where T_A and T_B are the melting points of the two compounds.

- c) Determine the composition and temperature of the eutectic mixture from the following data:

$$\Delta_{\text{fus}}H^\ominus = 10.0 \text{ kJ mol}^{-1} \quad T_A = 320 \text{ K} \quad T_B = 370 \text{ K}$$

Sketch the phase diagram. [10]

Q4 2000 Advanced Physical Chemistry, Q1

- a) State the third law of thermodynamics. [2]
- b) What is meant by the third law entropy of a substance, and how can this quantity be determined for a gaseous substance from experimental data? [5]
- c) What is the statistical entropy? Outline briefly how it can be determined from theoretical or experimental (spectroscopic) information. [5]
- d) Explain why the heat capacities of polyatomic gases are functions of temperature. [4]
- e) The constant pressure heat capacity C_p of $\text{CO}_2(\text{g})$ follows the equation

$$C_p = 44.2 + 8.79 \times 10^{-3} T - 8.54 \times 10^5 / T^2$$

where C_p is expressed in $\text{J K}^{-1} \text{ mol}^{-1}$ and T is in K. Low temperature measurements give the third law entropy of solid CO_2 at its sublimation temperature, 194.6 K, as $70.8 \text{ J K}^{-1} \text{ mol}^{-1}$. Its enthalpy of sublimation is $25.23 \text{ kJ mol}^{-1}$.

Calculate the third law entropy of $\text{CO}_2(\text{g})$ at 298 K and compare it with the statistical entropy of $213.7 \text{ J K}^{-1} \text{ mol}^{-1}$. [6]

f) The difference between the third law entropy and the statistical entropy is called *residual entropy*. Comment on, and where possible suggest explanations for the following residual entropies (given in $\text{J K}^{-1} \text{ mol}^{-1}$):

CH_3D 11.6 CO 5.0 H_2O 3.4

[Note that exact agreement with theory is not expected.] [6]

g) The entropies of $\text{H}_2(\text{g})$ and $\text{HD}(\text{g})$ at 298 K are, respectively, $130.68 \text{ J K}^{-1} \text{ mol}^{-1}$ and $143.8 \text{ J K}^{-1} \text{ mol}^{-1}$. Account for the *difference* between the two values.

$$\left[q_{\text{trans}} = \frac{V}{\Lambda^3}, \quad \Lambda = \left(\frac{h^2}{2\pi m k T} \right)^{1/2}, \quad q_{\text{rot}} = \frac{kT}{\sigma B} \right]$$