

THERMODYNAMICS II

QUESTION 1

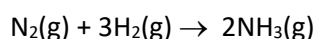
Values of some thermodynamic parameters for Br₂, Cl₂ and BrCl at 298 K are given below.

| Material | $\Delta_f H^\ominus / \text{kJ mol}^{-1}$ | $S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ |
|---------------------|---|---|
| Br ₂ (l) | 0 | 152.3 |
| Cl ₂ (g) | 0 | 223.0 |
| BrCl(g) | 14.69 | 239.9 |

- Why are the enthalpies of formation of chlorine and bromine equal to zero?
- Calculate $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ for the reaction at 298 K.
- Comment on the value you have obtained for $\Delta_r S^\ominus$.
- Calculate $\Delta_r G^\ominus$ and K_p for the reaction at 298 K.
- Explain how a change in (i) pressure and (ii) temperature might affect the relative amounts of reactants and products at equilibrium.
- Discuss the effect that a catalyst for this reaction would have on the rates of the forward and reverse reactions and on the position of equilibrium.

QUESTION 2

In the Haber process, ammonia is produced by passing a mixture of nitrogen and hydrogen over a catalyst:



The standard enthalpies of formation, standard entropies, and heat capacities are given in the table below for each of the three species at 298 K:

| Species | $\Delta_f H^\ominus / \text{kJ mol}^{-1}$ | $S_m^\ominus / \text{J K}^{-1} \text{mol}^{-1}$ | $C_{p,m} / \text{J K}^{-1} \text{mol}^{-1}$ |
|---------------------|---|---|---|
| N ₂ (g) | 0 | 192 | 29.1 |
| H ₂ (g) | 0 | 131 | 28.8 |
| NH ₃ (g) | -46.2 | 193 | 35.7 |

- Calculate $\Delta_r H^\ominus$, $\Delta_r S^\ominus$, $\Delta_r G^\ominus$, and K for the reaction at 298 K.
- An industrial reactor operates at 600 K. Calculate K at this temperature, assuming heat capacities to be independent of temperature.
- The gas flowing into the reactor has the composition ratio 3 mol H₂: 1 mol N₂. If the mole fraction of ammonia in the exhaust gas from the reactor is 0.35, what is the total pressure in the reactor? (Assume that equilibrium is established in the reactor at 600 K).

QUESTION 3

- a) For the equilibrium $\text{CH}_4 \rightleftharpoons 2\text{H}_2(\text{g}) + \text{C}(\text{s, graphite})$, find an expression relating the equilibrium constant, K_p , to the degree of dissociation of methane, α , and the total pressure, p . Hence predict how compression would affect the mole fraction of CH_4 in an equilibrium mixture of CH_4 , H_2 , and graphite.
- b) The following table gives the degree of dissociation of methane at equilibrium and a total pressure, $p = 1.00 \text{ kPa}$ for the above reaction at a series of temperatures:

| | | | | | |
|---------------|------|------|------|------|------|
| T / K | 298 | 320 | 340 | 360 | 380 |
| $10^4 \alpha$ | 1.79 | 5.07 | 11.6 | 24.2 | 46.7 |

Assuming $\Delta_r H^\circ$ for the reaction is independent of temperature over the above range, use a graphical means to evaluate $\Delta_r H^\circ$, and hence calculate $\Delta_r S^\circ$ and $\Delta_r G^\circ$ for the reaction at 298 K.

QUESTION 4

- a) Starting from the equations

$$\Delta_r G^\circ = -RT \ln K \quad \text{and} \quad \frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) = -\frac{\Delta_r H^\circ}{T^2}$$

derive an equation which shows how the equilibrium constant for a reaction, K , varies with temperature, stating any assumptions you make.

- b) The vapour of pentane-2,4-dione consists of a mixture of two tautomers in equilibrium:



The vapour contains 92% *enol* at 298K and 84% *enol* at 373 K. Calculate the enthalpy of reaction and the entropy of reaction, assuming them to be independent of temperature.

- c) For the equilibrium $\text{CoO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Co}(\text{s}) + \text{CO}_2(\text{g})$ in the temperature range 900K to 1000K

$$\ln K = 12.745 - 6341 / (T/\text{K})$$

Calculate $\Delta_r H^\circ$, $\Delta_r G^\circ$ and $\Delta_r S^\circ$ for this reaction at 1000 K.

QUESTION 5

- a) Show that $dG = Vdp - SdT$, define the term chemical potential, and show that for a perfect gas,

$$\mu = \mu^\circ + RT \ln(p/p^\circ)$$

- b) Show that for two phases α and β to be in equilibrium, their chemical potentials must be equal.

- c) Show, by considering the variation of G with pressure and temperature, how the existence of solid, liquid and vapour phases of a substance, and of transitions between these phases, can be rationalised. Include the possibility of sublimation.