Exercise Classes 3 Physical Chemistry 1 2021/2022

Exercise 9

Consider the decomposition of methane CH_4(g) into the elements H_2(g) and graphite C(s).
The standard enthalpy and entropy of formation at 298 K are given by $\Delta_f H^{\ominus}(CH_4,g)$ = -74.85 kJ/mol and $\Delta_f S^{\ominus}(CH_4,g)$ = -80.67 J/molK.
Calculate the equilibrium constant at 298 K. What does this result imply for the position of the equilibrium (to the left hand side or the right hand side of the reaction)?

Exercise 10

A closed vessel is filled with 0.300 mol H_2(g), 0.400 mol I_2(g) and 0.200 mol HI(g) at 721 K and at a total pressure of 1.00 bar. Consider the gases to behave as perfect gases.
The equilibrium constant of the reaction

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g).$$

at that pressure and temperature is given by $K = 50.5$.
We will determine the composition of the mixture at 721 K in terms of mole fractions. $x_i = \frac{n_i}{n_{tot}}$.

a) Since H_2 might fully react, we express the extent of reaction ξ in that component. Now finish the table below (the mole fraction $x_i = \frac{n_i}{n} = \frac{P_i}{P}$, with n the total number of moles).

	H_2	I_2	HI	Total
Initially (mol)	0.300	0.400	0.200	0.900
Change (mol)	-0.300ξ			
Equilibrium (mol)	$0.300(1-\xi_{eq})$			
Eq. mole fraction (x_i)				

b) Express the equilibrium constant $K = \left(\Pi_j \left(\frac{P_j}{P^{\ominus}}\right)^{\nu_j}\right)_{eq}$ in terms of ξ_{eq}.

c) Then calculate ξ_{eq} at $T = 721$ K.

d) Determine the mole fractions of the components in thermodynamic equilibrium at $T = 721$ K.

Exercise 11

We consider the temperature dependence of the equilibrium constant.
The degree of dissociation α of a molecule is defined between $\alpha = 0$ (not dissociated) and $\alpha = 1$ (completely dissociated), such that the amount of that molecule can be written as $(1-\alpha)n$.
The degree of dissociation α of CO_2(g) into CO(g) and O_2(g) at high temperature and a pressure of 1 bar measured at three temperatures is given in table 1. Assume that the gases can be considered perfect and that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are constant for the temperatures in the table.

T(K)	1395	1443	1498
α	$1.44 \cdot 10^{-4}$	$2.50 \cdot 10^{-4}$	$4.71 \cdot 10^{-4}$

Table 1: The degree of dissocation α of CO_2(g) at three temperatures and 1 bar

a) Make a table of the amounts n_i, the mole fractions x_i and the partial pressures P_i of the components in terms of the degree of dissociation α, the initial amount of mol CO_2 (n) and the pressure P.

b) Express the equilibrium constant in terms of α and approximate the result ($\alpha << 1$) such that only the most important term remains.

c) Verify to what extent the equilibrium constant of reactions depends on the choice of the stoichiometric coefficients, in other words compare $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$ and $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$.

d) Calculate $\Delta_r G^{\ominus}$, $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$
Hint: use that for a given (constant) temperature $\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$ and assume that $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ are only weakly dependent on the temperature for the temperatures considered here.