Solutions Exercise Classes 3 Physical Chemistry 1 2021/2022

Exercise 9

The equilibrium is given by

$$\mathrm{CH_4(g)} \rightleftarrows \mathrm{C(s)} + \mathrm{2H_2(g)}$$

This is the inverse reaction of the formation of CH_4(g). The products are elements in their reference state at 298 K (C(s) and H_2(g)), so $\Delta_f G^\ominus$(C,s) = $\Delta_f G^\ominus$(H_2,g) = 0. The standard reaction Gibbs free energy $\Delta_r G^\ominus$ therefore is

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_i^\ominus = 0 + 0 - \Delta_f G^\ominus(\mathrm{CH_4,g}) = -\Delta_f G^\ominus(\mathrm{CH_4,g}).$$

We can determine $\Delta_f G^\ominus(\mathrm{CH_4,g})$ with the standard enthalpy and entropy of formation at that (given) temperature:

$$\Delta_f G^\ominus(\mathrm{CH_4,g}) = \Delta_f H^\ominus(\mathrm{CH_4,g}) - T\Delta_f S^\ominus(\mathrm{CH_4,g}) = -74850 - 298 \cdot (-80.67) = -5.081 \cdot 10^4 \text{ J/mol}.$$

The equilibrium constant K then follows with

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = \frac{\Delta_f G^\ominus(CH_4,g)}{RT} = \frac{-5.081 \cdot 10^4}{8.314 \cdot 298} = -20.51,$$

such that $K = 1.24 \cdot 10^{-9}$.
As expected the reaction at 298 K and $P = P^\ominus$ lies almost completely on the methane side of the equilibrium.

Exercise 10

a) $H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$.
H_2 might react fully (corresponding to an extent of reaction $\xi = 1$) and therefore we take H_2 as reference in the table. The total number of mol does not change as a consequence of the proceeding reaction.

	H_2	I_2	HI	Total
Initially (mol)	0.300	0.400	0.200	0.900
Change (mol)	-0.300ξ	-0.300ξ	$+0.600\xi$	0
Equilibrium (mol)	$0.300(1-\xi_{eq})$	$0.400 - 0.300\xi_{eq}$	$0.200 + 0.600\xi_{eq}$	0.900
Eq. mole fraction (x_i)	$\frac{0.300(1-\xi_{eq})}{0.900}$	$\frac{0.400-0.300\xi_{eq}}{0.900}$	$\frac{0.200+0.600\xi_{eq}}{0.900}$	1

b) The equilibrium constant is given by (using Dalton's law we can write $\frac{P_i}{P^\ominus} = \frac{P_i}{P}\frac{P}{P^\ominus}$ as $\frac{P_i}{P^\ominus} = \frac{n_i}{n}\frac{P}{P^\ominus} = x_i\frac{P}{P^\ominus}$, moreover the total pressure does not change due to the reaction stoichiometry)

$$K = \frac{\left(\frac{P(\mathrm{HI})}{P^\ominus}\right)^2}{\left(\frac{P(\mathrm{H_2})}{P^\ominus}\right)\left(\frac{P(\mathrm{I_2})}{P^\ominus}\right)} = \frac{x^2(\mathrm{HI})\left(\frac{P}{P^\ominus}\right)^2}{x(\mathrm{H_2})\frac{P}{P^\ominus}x(\mathrm{I_2})\frac{P}{P^\ominus}} = \frac{x^2(\mathrm{HI})}{x(\mathrm{H_2})x(\mathrm{I_2})} = \frac{\left(\frac{0.200+0.600\xi_{eq}}{0.900}\right)^2}{\frac{0.300-0.300\xi_{eq}}{0.900} \cdot \frac{0.400-0.300\xi_{eq}}{0.900}} = 50.5.$$

c) We can rewrite this equation into a quadratic equation in ξ_{eq} by rewriting the right-hand part to

$$\left(\frac{0.200 + 0.600\xi_{eq}}{0.900}\right)^2 = 50.5\left[\frac{0.300 - 0.300\xi_{eq}}{0.900} \cdot \frac{0.400 - 0.300\xi_{eq}}{0.900}\right],$$

which simplifies to

$$(0.200 + 0.600\xi_{eq})^2 = 50.5\left[(0.300 - 0.300\xi_{eq}) \cdot (0.400 - 0.300\xi_{eq})\right].$$

Collecting all terms in powers of ξ_{eq} leads to

$$4.185\xi_{eq}^2 - 10.845\xi_{eq} + 6.02 = 0.$$

The proper solution to this equation is $\xi_{eq} = 0.805$ since the other solution (1.786) is larger than the maximum value for ξ; $\xi_{max} = 1$.

d) Thus in equilibrium we have 0.058 mol H_2, 0.158 mol I_2 and 0.683 mol HI; besides a small numerical error in total 0.900 mol. Therefore the mole fractions are 0.065, 0.176 and 0.759, respectively; summing up to 1.

Exercise 11

a) The equilibrium reaction is $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$. The progression of the reaction ξ (the extent of reaction) is the degree of dissocation α and is defined per mol CO_2 for the reaction $CO_2(g) \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$. The total number of moles in the mixture is at every moment equal to $(1-\alpha)n + \alpha n + \frac{1}{2}\alpha n = (1+\frac{\alpha}{2})n$, leading to the following table.
N.B.: The number of mol CO_2 with which we start, n, disappears in the mole fractions and in the partial pressures. Eventually only the total pressure P is what counts and we chose this pressure to be constant (1 bar).

	$CO_2(g)$	$CO(g)$	$O_2(g)$
Amount	$(1-\alpha)n$	αn	$\frac{1}{2}\alpha n$
Mole fraction	$\frac{1-\alpha}{1+\frac{\alpha}{2}}$	$\frac{\alpha}{1+\frac{\alpha}{2}}$	$\frac{\frac{\alpha}{2}}{1+\frac{\alpha}{2}}$
Partial pressure	$\frac{(1-\alpha)P}{1+\frac{\alpha}{2}}$	$\frac{\alpha P}{1+\frac{\alpha}{2}}$	$\frac{\alpha P}{2(1+\frac{\alpha}{2})}$

b) The equilibrium constant of the reaction can be expressed in the partial pressures of the perfect gases ($P = 1$ bar and use that at the given temperatures $\alpha \ll 1$)

$$K = \left(\Pi_j \left(\frac{P_j}{P^\ominus}\right)^{\nu_j}\right)_{eq} = \frac{\left(\frac{P_{CO}}{P^\ominus}\right)\left(\frac{P_{O_2}}{P^\ominus}\right)^{\frac{1}{2}}}{\left(\frac{P_{CO_2}}{P^\ominus}\right)} = \frac{\left(\frac{\alpha}{1+\frac{\alpha}{2}}\right)\left(\frac{\frac{\alpha}{2}}{1+\frac{\alpha}{2}}\right)^{\frac{1}{2}}\left(\frac{P}{P^\ominus}\right)^{\frac{1}{2}}}{\left(\frac{1-\alpha}{1+\frac{\alpha}{2}}\right)} = \left(\frac{\alpha}{1-\alpha}\right)\left(\frac{\frac{\alpha}{2}}{1+\frac{\alpha}{2}}\right)^{\frac{1}{2}} \approx \frac{\alpha^{\frac{3}{2}}}{\sqrt{2}}.$$

c) The equilibrium constant for the reaction $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ has the value K^2. More general, for the reaction $\nu CO_2(g) \rightleftharpoons \nu CO(g) + \frac{\nu}{2}O_2(g)$ we find the value K^ν. In other words, the equilibrium constant K depends on the way we express the stoichiometry in the chemical reaction. This is in agreement with the expression for the reaction Gibbs free energy $\Delta_r G = \Delta_r G^\ominus + RT\ln Q$ which for the last reaction in terms of νCO_2 becomes equal to $\nu\Delta_r G = \nu\Delta_r G^\ominus + \nu RT\ln Q = \nu\Delta_r G^\ominus + RT\ln Q^\nu$.

d) In equilibrium $\Delta_r G = 0$ and $Q_{eq} = K$.
Substituting the values for α in the expression for K leads to the values in the table below. The standard reaction Gibbs free energy is obtained using $\Delta_r G^\ominus = -RT\ln K$ (see table). We find the temperature dependence of the equilibrium constant as follows ($\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$)

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = -\frac{\Delta_r H^\ominus}{RT} + \frac{\Delta_r S^\ominus}{R}$$

Assuming that $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$ are constant for the temperature range of the table we can rewrite this equation to

$$\ln K(T_2) = \ln K(T_1) - \frac{\Delta_r H^\ominus}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

We can use this equation for every combination of two from the given temperatures and K-values to determine $\Delta_r H^\ominus$. Combining column 1 and 2 we find $\Delta_r H^\ominus = 290$ kJ/mol, using column 2 and 3: 309 kJ/mol and for column 1 and 3: 300 kJ/mol; on average $\Delta_r H^\ominus = 300$ kJ/mol. $\Delta_r S^\ominus$ then follows using $\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T}$ and taking the average value for $\Delta_r H^\ominus$.

T(K)	1395	1443	1498
α	$1.44\cdot10^{-4}$	$2.50\cdot10^{-4}$	$4.71\cdot10^{-4}$
K	$1.22\cdot10^{-6}$	$2.80\cdot10^{-6}$	$7.23\cdot10^{-6}$
$\Delta_r G^\ominus$ (kJ/mol)	158	153	147
$\Delta_r S^\ominus$ (J/mol K)	102	102	102