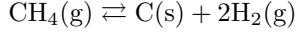


Solutions Exercise Classes 3 Physical Chemistry 1 2021/2022

Exercise 9

The equilibrium is given by



This is the inverse reaction of the formation of $\text{CH}_4(\text{g})$. The products are elements in their reference state at 298 K ($\text{C}(\text{s})$ and $\text{H}_2(\text{g})$), so $\Delta_f G^\ominus(\text{C},\text{s}) = \Delta_f G^\ominus(\text{H}_2,\text{g}) = 0$. The standard reaction Gibbs free energy $\Delta_r G^\ominus$ therefore is

$$\Delta_r G^\ominus = \sum_i \nu_i \Delta_f G_i^\ominus = 0 + 0 - \Delta_f G^\ominus(\text{CH}_4,\text{g}) = -\Delta_f G^\ominus(\text{CH}_4,\text{g}).$$

We can determine $\Delta_f G^\ominus(\text{CH}_4,\text{g})$ with the standard enthalpy and entropy of formation at that (given) temperature:

$$\Delta_f G^\ominus(\text{CH}_4,\text{g}) = \Delta_f H^\ominus(\text{CH}_4,\text{g}) - T \Delta_f S^\ominus(\text{CH}_4,\text{g}) = -74850 - 298 \cdot (-80.67) = -5.081 \cdot 10^4 \text{ J/mol.}$$

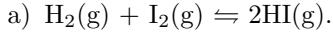
The equilibrium constant K then follows with

$$\ln K = -\frac{\Delta_r G^\ominus}{RT} = \frac{\Delta_f G^\ominus(\text{CH}_4,\text{g})}{RT} = \frac{-5.081 \cdot 10^4}{8.314 \cdot 298} = -20.51,$$

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



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)

$$K = \frac{\left(\frac{P(\text{HI})}{P^\ominus}\right)^2}{\left(\frac{P(\text{H}_2)}{P^\ominus}\right) \left(\frac{P(\text{I}_2)}{P^\ominus}\right)} = \frac{x^2(\text{HI}) \left(\frac{P}{P^\ominus}\right)^2}{x(\text{H}_2) \frac{P}{P^\ominus} x(\text{I}_2) \frac{P}{P^\ominus}} = \frac{x^2(\text{HI})}{x(\text{H}_2) x(\text{I}_2)} = \frac{\left(\frac{0.200 + 0.600\xi_{eq}}{0.900}\right)^2}{\frac{0.300 - 0.300\xi_{eq}}{0.900} \cdot \frac{0.400 - 0.300\xi_{eq}}{0.900}} = 50.5.$$

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

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

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 H₂, 0.158 mol I₂ 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 2CO₂(g) \rightleftharpoons 2CO(g) + O₂(g). The progression of the reaction ξ (the extent of reaction) is the degree of dissociation α and is defined per mol CO₂ for the reaction CO₂(g) \rightleftharpoons CO(g) + $\frac{1}{2}$ O₂(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 CO₂ with which we start, n , disappears in the mole fractions and in the

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

partial pressures. Eventually only the total pressure P is what counts and we chose this pressure to be constant (1 bar).

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 $\alpha \ll 1$)

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

c) The equilibrium constant for the reaction 2CO₂(g) \rightleftharpoons 2CO(g) + O₂(g) has the value K^2 . More general, for the reaction ν CO₂(g) \rightleftharpoons ν CO(g) + $\frac{\nu}{2}$ O₂(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 ν CO₂ 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 $\Delta_r H^\ominus = 290 \text{ kJ/mol}$, using column 2 and 3: 309 kJ/mol and for column 1 and 3: 300 kJ/mol ; on average $\Delta_r H^\ominus = 300 \text{ kJ/mol}$.

$\Delta_r S^\ominus$ then follows using $\Delta_r S^\ominus = \frac{\Delta_r H^\ominus - \Delta_r G^\ominus}{T}$ and taking the average value for $\Delta_r H^\ominus$.

$T(\text{K})$	1395	1443	1498
α	$1.44 \cdot 10^{-4}$	$2.50 \cdot 10^{-4}$	$4.71 \cdot 10^{-4}$
K	$1.22 \cdot 10^{-6}$	$2.80 \cdot 10^{-6}$	$7.23 \cdot 10^{-6}$
$\Delta_r G^\ominus (\text{kJ/mol})$	158	153	147
$\Delta_r S^\ominus (\text{J/mol K})$	102	102	102