

## Exercise Classes 3 Physical Chemistry 1 2021/2022

### Exercise 9

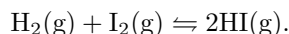
Consider the decomposition of methane  $\text{CH}_4(\text{g})$  into the elements  $\text{H}_2(\text{g})$  and graphite  $\text{C}(\text{s})$ . The standard enthalpy and entropy of formation at 298 K are given by  $\Delta_f H^\ominus(\text{CH}_4, \text{g}) = -74.85 \text{ kJ/mol}$  and  $\Delta_f S^\ominus(\text{CH}_4, \text{g}) = -80.67 \text{ J/molK}$ .

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  $\text{H}_2(\text{g})$ , 0.400 mol  $\text{I}_2(\text{g})$  and 0.200 mol  $\text{HI}(\text{g})$  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



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.  $x_i = \frac{n_i}{n_{\text{tot}}}$ .

- a) Since  $\text{H}_2$  might fully react, we express the extent of reaction  $\xi$  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).

	$\text{H}_2$	$\text{I}_2$	$\text{HI}$	Total
Initially (mol)	0.300	0.400	0.200	0.900
Change (mol)	$-0.300\xi$			
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  $\xi_{eq}$ .

- c) Then calculate  $\xi_{eq}$  at  $T = 721 \text{ K}$ .

- d) Determine the mole fractions of the components in thermodynamic equilibrium at  $T = 721 \text{ K}$ .

### Exercise 11

We consider the temperature dependence of the equilibrium constant.

The degree of dissociation  $\alpha$  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  $\alpha$  of  $\text{CO}_2(\text{g})$  into  $\text{CO}(\text{g})$  and  $\text{O}_2(\text{g})$  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.

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

Table 1: The degree of dissociation  $\alpha$  of  $\text{CO}_2(\text{g})$  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  $\alpha$ , the initial amount of mol  $\text{CO}_2$  ( $n$ ) and the pressure  $P$ .
- b) Express the equilibrium constant in terms of  $\alpha$  and approximate the result ( $\alpha \ll 1$ ) 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  $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  and  $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$ .
- 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.