

Reaction at equilibrium – part II

Dissociation reactions at equilibrium

- ◆ In dissociation reactions of the type $A \rightleftharpoons B+C$
it is possible to calculate the equilibrium constant in terms of % dissociation, expressed as the ratio α between the dissociated mol and the total no.mol
- ◆ In case at the beginning the molar concentration of A was (n/V)
$$[A] = n/V$$
- ◆ At equilibrium the molar concentration of B and C will be:
$$[B] = n\alpha/V; \quad [C] = n\alpha/V$$
- ◆ Hence the molar concentration of A at equilibrium will be:
$$[A] = (n-n\alpha)/V = [n(1-\alpha)]/V$$
- ◆ Thereby the equilibrium constant of the reaction can be expressed in terms of the initial concentration of A and of the dissociation coefficient α

$$K = \frac{[B][C]}{[A]} = \frac{\left(n\frac{\alpha}{V}\right)\left(n\frac{\alpha}{V}\right)}{n\frac{(1-\alpha)}{V}} = \frac{n\alpha^2}{V(1-\alpha)} = C \frac{\alpha^2}{(1-\alpha)}$$

Exercise 1

8 g of PCl_5 are introduced in a cylinder of 0.5L at 250°C . The value of the equilibrium constant of the reaction in the gas phase:



is 0.041 M. Calculate the concentration of the three species at equilibrium.

Let's calculate the molar concentration of PCl_5 at the beginning:

$$[\text{PCl}_5]_{\text{start}} = \text{g}/(\text{V} \cdot \text{FW}) = 8 / (0.5 \cdot 208) = 7.7 \cdot 10^{-2} \text{ M}$$

$$\rightarrow \text{no. Moles} = \text{g}/\text{FW} = 0.038 \text{ mol}$$

moles	PCl_5	PCl_3	Cl_2
At equilibrium	$0.038(1-\alpha)$	0.038α	0.038α

$$K_c = \frac{C \alpha^2}{(1-\alpha)} = \frac{0.077 \alpha^2}{1-\alpha} = 0.041 \text{ M}$$

$$0.077\alpha^2 + 0.041\alpha - 0.041 = 0$$

$$\alpha = \frac{-0.041 \pm \sqrt{(0.041)^2 + 4(0.077)(0.041)}}{2 \cdot 0.077}$$

$$\alpha = \frac{-0.041 \pm \sqrt{1.68 \cdot 10^{-3} + 12.6 \cdot 10^{-3}}}{0.154}$$

$$\alpha = \frac{-0.041 \pm \sqrt{0.014}}{0.154} = \frac{-0.041 \pm 0.118}{0.154}$$

$$\alpha_1 = 0.502 \quad \alpha_2 = -1.03$$

$$[\text{PCl}_5] = C(1-\alpha) = 0.077 \cdot 0.498 = 0.038\text{M}$$

$$[\text{PCl}_3] = [\text{Cl}_2] = C\alpha = 0.077 \cdot 0.502 = 0.039\text{M}$$

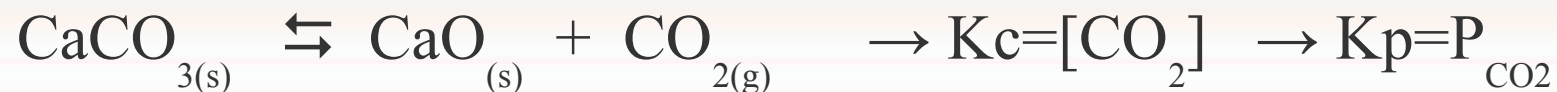
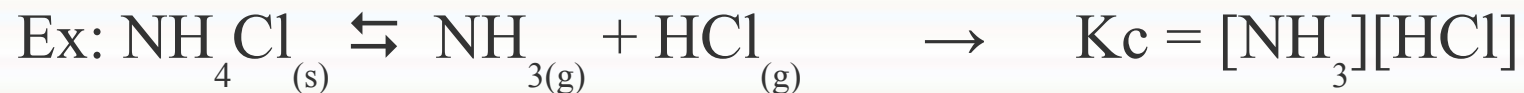
Heterogeneous equilibria

- ◆ A given equilibrium is heterogeneous when its components belong to different states of the matter
- ◆ In case the equilibrium is between compounds in the gas and solid phases, the equilibrium constant expressed in terms of partial pressure K_p only contains the quantities of the components in the gas phase
- ◆ This is because solid and liquid phases display a constant pressure at any given temperature, hence their value is included directly in K_p



Heterogeneous equilibria

- ◆ The same happens for K_c , since usually the solid is in large excess with respect to the components in the gas phase



Exercise 2

- ◆ 0.1 mol of CO and 0.05 mol of H₂O are filling in a box of 5L at 680°C. The constant of the gaseous equilibrium $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ is 1.9. Calculate the concentration of the 4 species at equilibrium.

	CO	H ₂ O	CO ₂	H ₂
Moles at the beginning	0.1	0.05	0	0
Consumed/produced	-x	-x	+x	+x
At equilibrium	0.1-x	0.05-x	x	x

$$K = \frac{\left(\frac{x}{5}\right)\left(\frac{x}{5}\right)}{\left[\frac{(0.1-x)}{5}\right]\left[\frac{(0.05-x)}{5}\right]} = 1.9$$

$$x^2 = 1.9(0.005 - 0.15x + x^2)$$

$$0.9x^2 - 0.285x + 0.0095 = 0$$

$$x = \frac{0.285 \pm \sqrt{0.0812 - 0.0342}}{1.8}$$

$$x_1 = 0.038$$

$$x_2 = 0.287$$

$$[\text{CO}] = (0.1 - 0.038)/5 = 1.24 \cdot 10^{-2} \text{M}$$

$$[\text{H}_2\text{O}] = (0.05 - 0.038)/5 = 2.4 \cdot 10^{-3} \text{M}$$

$$[\text{CO}_2] = [\text{H}_2] = 0.038/5 = 7.6 \cdot 10^{-3} \text{M}$$

Exercise 3

- ◆ In a box of 3L there are 9 mol of H_2 and 9 mol of O_2 . The homogeneous equilibrium in the gas phase $2H_2 + O_2 \rightleftharpoons 2H_2O$ is reached when 3 mol of H_2O are formed. Calculate K_c .

no. moles	H_2	O_2	H_2O
At start	9	9	0
Pace of the reaction	-2x	-x	+2x
At equilibrium			3

$$0 + 2x = 3 \quad \rightarrow \quad x = 1.5$$

$$[H_2] = (9 - 2x)/3 = 2M$$

$$[O_2] = (9 - x)/3 = 2.5M$$

$$[H_2O] = 3/3 = 1M$$

$$K_c = \frac{[H_2O]^2}{[H_2]^2 [O_2]} = \frac{1^2}{(2)^2 (2.5)} = \frac{1}{4 \cdot 2.5} = 0.1 M^{-1}$$

Exercise 4

- ◆ $K_c = 1.56 \cdot 10^{-2}$ for the reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ at 793K. The reaction is started by inserting 0.5 mol of I_2 and 1 mol of H_2 in a box of 10L. Calculate the number of moles of the three species at equilibrium.

no.moles	HI	H_2	I_2
start	0	1	0.5
during	+2x	-x	-x
end	2x	1-x	0.5-x

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(1-x)(0.5-x)}{2x^2} = 1.56 \cdot 10^{-2}$$

$$0.5 - 1.5x + x^2 = 4x^2 \cdot 1.56 \cdot 10^{-2}$$

$$0.938x^2 - 1.5x + 0.5 = 0$$

$$x = \frac{1.5 \pm \sqrt{2.25 - 1.876}}{1.876}$$

$$x_1 = 0.47$$

$$x_2 = 1.12$$

$$\text{Mol of HI} = 2 \cdot 0.47 = 0.94 \text{ mol}$$

$$\text{Mol of H}_2 = 1 - 0.47 = 0.53 \text{ mol}$$

$$\text{Mol of I}_2 = 0.5 - 0.47 = 0.03 \text{ mol}$$

Exercise 5

- Some N_2 is filling in a box of 4.12L at 500K and 1 atm. Later on 0.5 mol of CO and 0.5 mol of N_2O are inserted. At this temperature the following reaction is taking place: $CO + N_2O \rightleftharpoons CO_2 + N_2$, with $K_c = 1.5 \cdot 10^{-2}$. Calculate the composition of the gaseous mixture at equilibrium.

Initial quantity of N_2 : $n = PV / RT = (1 \cdot 4.12) / (0.082 \cdot 500) = 0.1 \text{ mol}$

	CO	N_2O	CO_2	N_2
start	0.5	0.5	0	0.1
Cons./prod.	-x	-x	+x	+x
equilibrium	0.5-x	0.5-x	x	0.1+x

$$K_c = \frac{[CO_2][N_2]}{[CO][N_2O]} = \frac{x(0.1+x)}{(0.5-x)(0.5-x)} = 1.5 \cdot 10^{-2}$$

$$x^2 + 0.1x = 0.015(0.25 - x + x^2)$$

$$0.985x^2 + 0.115x - 0.00375 = 0$$

$$x = \frac{-0.115 \pm \sqrt{0.013 + 0.015}}{1.97}$$

$$x_1 = 0.026$$

$$x_2 = -0.09$$

$$\text{CO} = \text{N}_2\text{O} = 0.5 - x = 0.474 \text{ mol}$$

$$\text{CO}_2 = x = 0.026 \text{ mol}$$

$$\text{N}_2 = 0.1 + x = 0.126 \text{ mol}$$

Exercise 6

- ◆ A box of 5L is filled in with 103g of a mixture made by equal volumes of SO_2Cl_2 and Cl_2 . At equilibrium the following values are measured: $T=300\text{K}$ and $P=5.33\text{atm}$. Calculate K_c for the following dissociation reaction:
- $$\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$$

Recalling Avogadro's law: equal volumes of different gases contain the same number of moles $\rightarrow n_{\text{SO}_2\text{Cl}_2} = n_{\text{Cl}_2}$

$$n = \frac{g}{\text{FW}} \rightarrow \frac{x}{135} = \frac{103 - x}{70.9}$$

$$70.9x = 13905 - 135x$$

$$205.9x = 13905$$

$$x = 67.5 \text{ g of } \text{SO}_2\text{Cl}_2 \rightarrow n_{\text{SO}_2\text{Cl}_2} = n_{\text{Cl}_2} = 0.5\text{mol}$$

no.mol	SO ₂ Cl ₂	SO ₂	Cl ₂
start	0.5	0	0.5
Cons/prod	-x	+x	+x
equilibrium	0.5-x	x	0.5+x

We can calculate the total no. of moles from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{5.33 \cdot 5}{0.082 \cdot 300} = 1.08 \text{ mol}$$

The total number of moles correspond to the sum over the last row:

$$(0.5-x) + x + (0.5+x) = 1.08$$

$$1+x = 1.08 \quad \rightarrow \quad x = 0.08 \text{ mol}$$

$$K_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]} = \frac{\left(\frac{0.08}{5}\right) \cdot \left(\frac{0.58}{5}\right)}{\left(\frac{0.42}{5}\right)} = 2.2 \cdot 10^{-2} M$$

Exercise 7

- ◆ Calculate the dissociation coefficient α of the reaction $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$, when 2 mol of HI are placed in a cylinder of 1L at 450°C . It is known that K_c for the equilibrium of association at the same T is 50.

$$K_d = 1/ K_a = 1/50 = 0.02$$

HI	H_2	I_2
$n(1-\alpha)$	$n\alpha$	$n\alpha$

$$K_d = \frac{\frac{n\alpha}{V} \cdot \frac{n\alpha}{V}}{\left[\frac{2n(1-\alpha)}{V}\right]^2} = \frac{n^2 \alpha^2}{4n^2(1-\alpha)^2} = \frac{\alpha^2}{4(1-\alpha)^2} = 0.02$$

$$\alpha^2 = 0.08(1-2\alpha+\alpha^2)$$

$$0.92 \alpha^2 + 0.16 \alpha - 0.08 = 0 \quad \rightarrow \alpha = 0.21$$

Exercise 8

- ◆ At 100°C the following association reaction occurs with $K_c=0.068$:
 $H_2(g) + S(s) \rightleftharpoons H_2S(g)$. Should 0.2 mol of H_2 and 1 mol of S be heated at 100°C in a sealed flask of 1L, which value of P_{H_2S} will be measured at equilibrium?

This is a heterogeneous equilibrium between solid and gas phases:

no.mol	H_2	H_2S
start	0.2	0
Consumed/produced	-x	+x
equilibrium	0.2-x	x

$$K = \frac{[H_2S]}{[H_2]} = \frac{x/1}{(0.2-x)/1} = \frac{x}{0.2-x} = 0.068$$

$$x = 0.0136 - 0.068x$$

$$x = \frac{0.0136}{1.068} = 1.27 \cdot 10^{-2} \text{ mol}$$

$$P_{H_2S} = \frac{nRT}{V} = \frac{0.0127 \cdot 0.082 \cdot 373}{1} = 0.388 \text{ atm}$$