

EQUILIBRIA 2 – K_c and K_p

The Equilibrium Law

Le Chatelier's principle gives us an idea of the direction of change, but, where concentrations are involved, we can calculate precisely what happens using the equilibrium law.

The Equilibrium Law states - At equilibrium the concentrations of the species in the reaction system are constant.

For the general reaction $m\text{A} + n\text{B} \rightleftharpoons p\text{C} + q\text{D}$

Therefore
$$\frac{[\text{C}]^p_{\text{eq}}[\text{D}]^q_{\text{eq}}}{[\text{A}]^m_{\text{eq}}[\text{B}]^n_{\text{eq}}} = \text{a constant } K_c$$

K_c is the **Equilibrium constant**.

$$K_c = \frac{[\text{Right hand side}]_{\text{eq}}}{[\text{Left hand side}]_{\text{eq}}}$$

[] refers to the concentration of the species.

e.g. For the equilibrium $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

when the system has come to equilibrium, the ratio given by K_c will be constant:

$$K_c = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b} \quad \text{where } [\text{C}] \text{ means concentration at equilibrium, normally in mol dm}^{-3}$$

(The main mistakes students make over this are to forget that the *right hand side of the equation goes on top*, and to forget that *concentrations are multiplied together*, not added).

Equilibria involving gases

For gases, it is often more convenient to express the equilibrium constant in terms of partial pressures:

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \quad \text{where } P_C \text{ is the partial pressure of C at equilibrium}$$

K_p is called the pressure equilibrium constant.

Note that the both types of equilibrium constant will have units, unless (c + d) = (a + b). They therefore normally have different numerical values, for the same position of equilibrium.

Partial pressure and concentration.

Concentration refers to number of moles of a substance dissolved in one dm^3 of solution. For example aqueous sodium hydroxide solution having a concentration of 2 mol dm^{-3} . This is represented as $[\text{NaOH}(\text{aq})] = 2 \text{ mol dm}^{-3}$. Note [] indicates a concentration.

The same idea can be applied to a gas, if one knows the number of moles of gas and the volume of the container:

$$\text{concentration of gas} = \frac{\text{amount in moles}}{\text{volume of vessel}}$$

Units can be mol dm^{-3} or mol m^{-3} depending on how the volume of the vessel is specified.

Mole fractions

The **mole fraction** of a gas in a mixture is the fraction of the total number of moles of gas present:

$$\text{mole fraction of A} = \frac{\text{no. of moles of A}}{\text{total no. of moles}}$$

The sum of all the mole fractions must always be 1.0.

In a gas the *proportion by volume* is always the same as the *proportion by moles*, or mole fraction.

Example: a 4.00 dm^3 vessel contains 0.20 mol H_2 , 0.40 mol N_2 and 0.30 mol Ar . Calculate (i) the concentration of hydrogen; (ii) the mole fraction of hydrogen.

Answer: (i) concentration of hydrogen = $0.20 \div 4.00 = 0.050 \text{ mol dm}^{-3}$
(ii) total number of moles of gas = $0.20 + 0.40 + 0.30 = 0.90$
mole fraction of H_2 = $0.20 \div 0.90 = 0.22$

In a vessel containing a mixture of gases, the **partial pressure** of one gas is the pressure it would exert if it occupied the vessel alone.

The total pressure in a mixture of gases is the sum of all the partial pressures. It follows that:

$$\text{partial pressure of A} = \text{mole fraction of A} \times \text{total pressure}$$

For example, if one gas makes up 15% by volume of the mixture (or 15% of the molecules) its partial pressure will be $0.15 \times P$, where P is the total pressure.

If nitrogen and hydrogen are mixed in a 1:3 molar ratio, and together they have a partial pressure of 800 MPa , then:

$$\begin{aligned} \text{partial pressure of nitrogen} &= \frac{1}{4} \times 800 = 200 \text{ MPa} \\ \text{partial pressure of hydrogen} &= \frac{3}{4} \times 800 = 600 \text{ MPa}. \end{aligned}$$

Values of K_c and K_p

If K_c is large the equilibrium mixture contains mostly products and the reaction has nearly gone to completion. (A large value is any value >100).

If K_c is small the equilibrium mixture contains mostly reactants and the reaction has not proceeded very far. (A small value is any value <0.01).

The value of K_c is not altered by the addition of more reactants or products to an equilibrium mixture, it is a constant.

If more reactants are added the system will move in the forward direction to keep K_c constant.

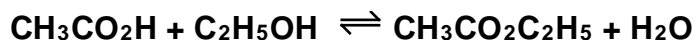
If more products are added the system will move in the reverse direction to keep K_c constant.

When K_c for a reaction is known, the relative portions of reactants and products at equilibrium can be calculated for any mixture of reactants used initially.

Calculating K_c and K_p

We normally find values for K_c and K_p from experimental data.

Example 1: Calculate K_c for the esterification of ethanoic acid by ethanol given that for a 1dm^3 of this homogeneous liquid equilibrium the amounts present are as shown below.

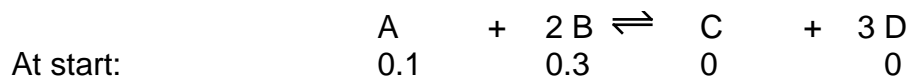


Equilibrium amount/mol 0.0255 0.0245 0.0584 0.0457

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}] [\text{C}_2\text{H}_5\text{OH}]}$$

$$K_c = \frac{0.0584 \times 0.0437}{0.0255 \times 0.0245} = 4.1 \text{ (no units for esterification reaction)}$$

Example 2; In the reaction given below, 0.1 mol of A is mixed with 0.3 mol of B, dissolved in 0.5 dm³ of water, and allowed to come to equilibrium, when the amount of D is found to be 0.06 mol. Find the equilibrium constant, K_c.



At equilibrium, we know: 0.06

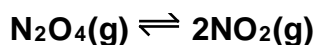
therefore: 0.1-0.02 0.3-0.04 0.02

(since 1 A → 3 D, 0.02 A → 0.06 D; 0.04 B → 0.06 D, and 0.02C is formed).

$$\begin{aligned} K_c &= \frac{[\text{C}] \times [\text{D}]^3}{[\text{A}] \times [\text{B}]^2} = \frac{(0.02/0.5) \times (0.06/0.5)^3}{(0.08/0.5) \times (0.26/0.5)^2} \\ &= \frac{0.04 \times 0.001728}{0.16 \times 0.2704} = 1.60 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

Note that the number of moles is divided by the total volume (0.5) to obtain the concentration.

Example 3: If at 55°C the partial pressure of nitrogen dioxide in an equilibrium mixture is 0.67atm and the partial pressure of dinitrogen tetraoxide in the mixture is 0.33atm what is the value of K_p for the reaction at this temperature?



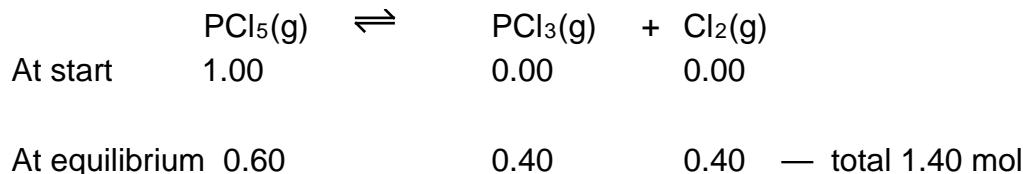
$$K_p = \frac{p_{\text{NO}_2(\text{g})}^2}{p_{\text{N}_2\text{O}_4(\text{g})}}$$

$$K_p = \frac{0.67\text{atm}^2}{0.33\text{atm}}$$

$$K_p = 1.36\text{atm}$$

Example 4: In the dissociation of phosphorus pentachloride, at 180°C and 2.00 atm pressure, the phosphorus pentachloride is found to be 40% dissociated. Find K_p .

Consider 1 mole of reactant.



mole fractions

$\frac{0.6}{1.40}$	$\frac{0.4}{1.40}$	$\frac{0.4}{1.40}$
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partial pressures

$\frac{0.6}{1.40} \times 2$	$\frac{0.4}{1.40} \times 2$	$\frac{0.4}{1.40} \times 2$
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0.857atm	0.571atm	0.571atm
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$$K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{0.571 \times 0.571}{0.857} = \underline{\underline{0.380 \text{ atm}}}$$

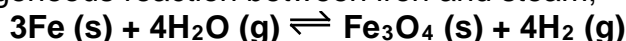
Values for solid and liquid phase in K_c and K_p .

Some equilibrium reactions involve only substances in the same phase e.g. all aqueous solutions or all gases. These are **homogeneous** reactions.

Some equilibrium reactions involve substances in different phases e.g. a pure liquid and a gas or a solid and a gas. These are **heterogeneous** reactions.

Expressions for K_c and K_p do not include values for solid and pure liquid phases in heterogeneous reactions.

For example, the heterogeneous reaction between iron and steam;

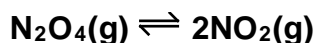


$$K_p = \frac{p^4\text{H}_2}{p^4\text{H}_2\text{O}}$$

Solids do not appear in the expression because their vapour pressures remain constant (at a constant temperature) as long as there is some of each solid present (same applies for liquids). These constant vapour pressures are incorporated into the value of K_p .

Finding equilibrium partial pressures given K_p values.

Example: What is the partial pressure of nitrogen dioxide in an equilibrium mixture if the partial pressure of dinitrogen tetraoxide in the mixture is 0.33atm and K_p at 55°C is 1.36atm for the reaction.



$$K_p = p^2\text{NO}_2(\text{g}) / p\text{N}_2\text{O}_4(\text{g})$$

$$p^2\text{NO}_2(\text{g}) = K_p * p\text{N}_2\text{O}_4(\text{g}) = 1.36\text{atm} * 0.33\text{atm} = 0.45\text{atm}$$

$$p\text{NO}_2(\text{g}) = 0.67\text{atm}.$$

The effect of temperature on K_c and K_p.

The equilibrium constant is only affected by temperature.

it does not change if concentrations or pressures are varied, nor in the presence of catalysts.

Catalysts do not alter the equilibrium constant (K_p or K_c) or the position of equilibrium. They only affect the time needed for the system to reach equilibrium.

K_c, K_p and the position of equilibrium are affected by temperature in endothermic and exothermic equilibria.

The effects are the same as predicted by Le Chateliers principle.

Exothermic reactions:

Temperature rise: - position of equilibrium moves to left, K_p and K_c become smaller.

Temperature fall: - position of equilibrium moves to right, K_p and K_c become bigger

Endothermic reactions:

Temperature rise: - position of equilibrium moves to right, K_p and K_c become bigger.

Temperature fall: - position of equilibrium moves to left, K_p and K_c become smaller.