

The Equilibrium Law

States "If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant" ... **WOW!**

Calculating Equilibrium Constants

Types K_c equilibrium values are **concentrations** in mol dm^{-3}
 K_p equilibrium values are **partial pressures** - system at constant temperature

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form $a A + b B \rightleftharpoons c C + d D$

then (at constant temperature)

$$\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \text{a constant, } (K_c)$$

[] denotes the equilibrium concentration in mol dm^{-3}

K_c is known as the Equilibrium Constant

Value of K_c

- **AFFECTED** by a change of **temperature**
- **NOT AFFECTED** by a change in **concentrations**
a change of **pressure**
adding a **catalyst**

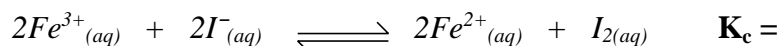
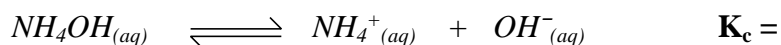
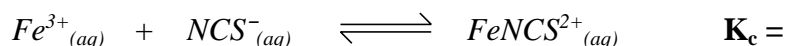
Q.1 What happens to the theoretical yield of a reaction if...

- K_c increases
- K_c decreases ?

Q.2 What happens to the value of K_c if...

- the **temperature is increased** in an **exothermic** reaction
- the **temperature is decreased** in an **exothermic** reaction
- the **temperature is increased** in an **endothermic** reaction
- the **temperature is decreased** in an **endothermic** reaction

Q.3 Write expressions for the equilibrium constant, K_c of the following reactions. Remember, equilibrium constants can have units.



Calculating value of K_c

- construct the balanced equation, including state symbols (aq), (g) etc.
- determine the number of moles of each species at equilibrium
- divide moles by volume (dm^3) to get the equilibrium concentrations in $mol\ dm^{-3}$ (If no volume is quoted, use a V; it will probably cancel out)
- from the equation constructed in the first step, write out an expression for K_c .
- substitute values from third step and calculate the value of K_c with any units

Example 1 Ethanoic acid (1 mol) reacts with ethanol (1 mol) at 298K. When equilibrium is reached, two thirds of the acid has reacted. Calculate the value of K_c .



initial moles	1	1	0	0
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equilibrium moles	$1 - \frac{2}{3}$	$1 - \frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
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If $\frac{2}{3}$ mol of the acid has reacted then take the value away from the initial number of moles of acid

If $\frac{2}{3}$ mol of the acid has reacted, then $\frac{2}{3}$ mol of ethanol will also have reacted. Take $\frac{2}{3}$ mol away from the original.

According to the equation, for every mol of acid that reacts you make 1 mol of ester and 1 mol of water. Therefore, if $\frac{2}{3}$ mol of acid has reacted, $\frac{2}{3}$ mol of ester and $\frac{2}{3}$ mol of water are produced.

equilibrium concs.	$\frac{1}{3} / V$	$\frac{1}{3} / V$	$\frac{2}{3} / V$	$\frac{2}{3} / V$
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$V =$ volume (dm^3) of the equilibrium mixture

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{2}{3} / V \cdot \frac{2}{3} / V}{\frac{1}{3} / V \cdot \frac{1}{3} / V} = 4$$

Example 2 Consider the reaction $P + 2Q \rightleftharpoons R + S$ (all are aqueous)

1 mol of P and 1 mol of Q are mixed. Once equilibrium has been achieved, 0.6 mol of P are present. How many moles of Q, R and S are present at equilibrium ?

	P	+	2Q	\rightleftharpoons	R	+	S
Initial moles	1		1		0		0
At equilibrium	0.6		0.2		0.4		0.4
	(0.4 reacted)		(2 x 0.4 reacted)		(get 1 R and 1 S for every P that reacts)		
	1 - 0.6 remain		1 - 0.8 remain				

- Explanation*
- if 0.6 moles of P remain of the original 1 mole, 0.4 moles have reacted
 - the equation states that 2 moles of Q react with every 1 mole of P
 - this means that 0.8 (2 x 0.4) moles of Q have reacted, leaving 0.2 moles
 - one mole of R and S are produced from every mole of P that reacts
 - this means 0.4 moles of R and 0.4 moles of S are present at equilibrium

Q.4 The questions refer to the equilibrium $A + B \rightleftharpoons C + D$ (all aqueous)

- (a) If the original number of moles of A and B are both 1 and 0.4 moles of A are present at equilibrium, how many moles of B, C and D are present?

What will be the value of K_c ?

- (b) At a higher temperature, the original moles of A and B were 2 and 3 respectively. If 1 mole of A is present at equilibrium, how many moles of B, C and D are present? What else does this tell you about the reaction?

Calculations involving Gases

Method

- carried out in a similar way to those involving concentrations
- one has the choice of using K_c or K_p for the equilibrium constant
- when using K_p only take into account gaseous species for the expression
- quotes the partial pressure of the gas in the equilibrium mixture
- pressure is usually quoted in Nm^{-2} or Pa - atmospheres are sometimes used
- the units of the constant K_p depend on the stoichiometry of the reaction

$$\begin{aligned} \text{total pressure} &= \text{sum of the partial pressures} \\ \text{partial pressure} &= \text{total pressure} \times \text{mole fraction} \\ \text{mole fraction} &= \frac{\text{number of moles of a substance}}{\text{number of moles of all substances present}} \end{aligned}$$

Example 1 A mixture of 16g of O_2 and 42g of N_2 , exerts a total pressure of 20000 Nm^{-2} . What is the partial pressure of each gas ?

$$\begin{aligned} \text{moles of } \text{O}_2 &= \text{mass} / \text{molar mass} = 16\text{g} / 32\text{g} = 0.5 \text{ mol} \\ \text{moles of } \text{N}_2 &= \text{mass} / \text{molar mass} = 42\text{g} / 28\text{g} = 1.5 \text{ mol} \quad \text{Total} = 2 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{mole fraction of } \text{O}_2 &= 0.5 / 2 = 0.25 \\ \text{mole fraction of } \text{N}_2 &= 1.5 / 2 = 0.75 \quad \text{sum of mole fractions} = 1 \end{aligned}$$

$$\begin{aligned} \text{partial pressure of } \text{O}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.25 \times 20000 \text{ Nm}^{-2} = 5000 \text{ Nm}^{-2} \end{aligned}$$

$$\begin{aligned} \text{partial pressure of } \text{N}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.75 \times 20000 \text{ Nm}^{-2} = 15000 \text{ Nm}^{-2} \end{aligned}$$

Example 2 Nitrogen (1 mol) and hydrogen (3 mol) react at constant temperature at a pressure of 1MPa. At equilibrium, half the nitrogen has reacted. Calculate K_p .

	$\text{N}_{2(\text{g})}$	+	$3\text{H}_{2(\text{g})}$	\rightleftharpoons	$2\text{NH}_{3(\text{g})}$
initial moles	1		3		0
at equilibrium	$1 - 0.5 = 0.5 \text{ mol}$		$3 - 1.5 = 1.5 \text{ mol}$		$2 \times 0.5 = 1 \text{ mol}$
mole fractions	$0.5 / 3$		$1.5 / 3$		$1 / 3$
partial pressures	$(0.5 / 3) \times 1\text{MPa}$		$1.5 / 3 \times 1\text{MPa}$		$1 / 3 \times 1\text{MPa}$

$$\text{applying the equilibrium law} \quad K_p = \frac{(\text{PNH}_3)^2}{(\text{PN}_2) \cdot (\text{PH}_2)^3} = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{1}{6} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}} \text{ MPa}^{-2}$$

Substituting in the expression gives $K_p = 5.33 \text{ MPa}^{-2}$