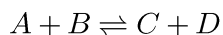


## Chemical equilibrium

### Dynamic equilibrium

Consider a reversible reaction:

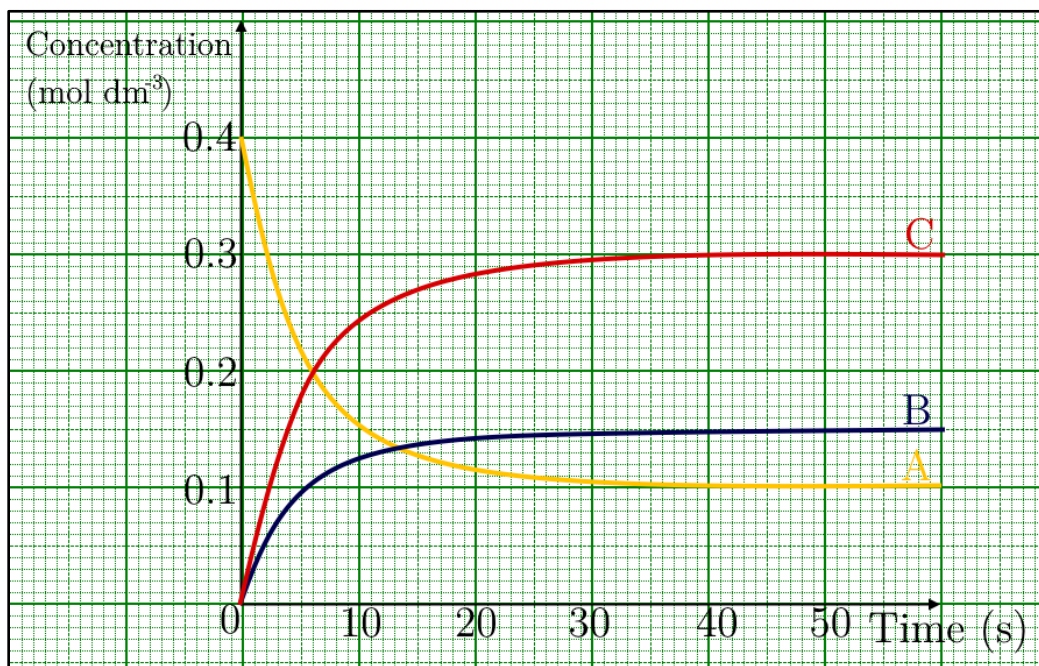


At some point, the reaction mixture will reach *dynamic equilibrium*.

Characteristics of *dynamic equilibrium*:

- Forward rate of reaction = Backward rate of reaction
- Both the forward rate of reaction and the backward rate of reaction are non-zero
- No change in the concentration of reactants and products
- The concentration of reactants and products are non-zero

Example 1:

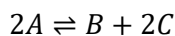


1. Refer to the graph above to answer the following questions

- a. When did the system reach dynamic equilibrium, explain your answer. (2 marks)

The system reaches equilibrium at 40s, the concentration of all reactants and products are **constant and non-zero** after 40s.

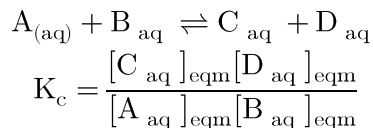
- b. Write down the equation for the reaction occurring in the system, explain your answer. (2 marks)



0.3 mol dm<sup>-3</sup> of A reacted to form 0.15 mol dm<sup>-3</sup> of B and 0.3 mol dm<sup>-3</sup> of C.

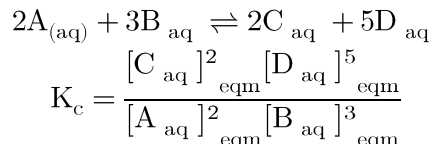
## Equilibrium constant ( $K_c$ )

In the following reaction:



$K_c$  can be used to describe the *completeness* of a reversible reaction. When  $K_c$  is large, the forward reaction is complete to a large extent, and vice versa.

In reactions such as,



Warmup: Calculate the  $K_c$  of the system in example 1. (include units!)

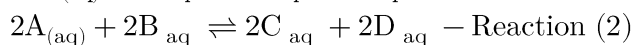
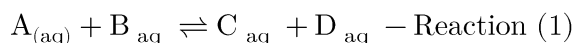
$$K_c = \frac{0.15 * 0.3^2}{0.3^2} = 0.15 \text{ mol dm}^{-3}$$

Example 2: write out expressions of  $K_c$  of the following reactions, include the unit for the  $K_c$

(Hint: Divide and multiply units of concentration to find the unit of  $K_c$ )

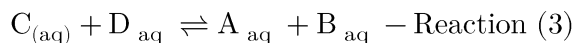
|   |  |
|---|--|
| $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$  | $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$   |
| $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $K_c = \frac{[HI_{(g)}]_{eqm}^2}{[H_{2(g)}]_{eqm}[I_{2(g)}]_{eqm}}$ <p>Unit: (no unit)</p> | $2C_2H_{4(g)} + O_{2(g)} \rightleftharpoons 2CH_3CHO_{(g)}$ $K_c = \frac{[CH_3CHO_{(g)}]_{eqm}^2}{[O_{2(g)}]_{eqm}[C_2H_{4(g)}]_{eqm}^2}$ <p>Unit: <math>\text{mol}^{-1} \text{ dm}^3</math></p> |

## $K_c$ properties



$$K_{c1} = \frac{[C_{aq}]_{eqm}[D_{aq}]_{eqm}}{[A_{aq}]_{eqm}[B_{aq}]_{eqm}}; \quad K_{c2} = \frac{[C_{aq}]_{eqm}^2 [D_{aq}]_{eqm}^2}{[A_{aq}]_{eqm}^2 [B_{aq}]_{eqm}^2} = K_{c1}^2$$

When the coefficients of a reaction is double,  $K_c$  is doubled. In fact, when the coefficients of a reaction equation is multiplied by  $n$  times, new  $K_c = (\text{old } K_c)^n$ . Here,  $n$  can be any positive real number.



It's obvious that reaction (3) is the backward reaction of reaction (1).

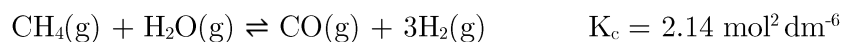
$$K_{c3} = \frac{[A_{aq}]_{eqm}[B_{aq}]_{eqm}}{[C_{aq}]_{eqm}[D_{aq}]_{eqm}} = \frac{1}{K_{c1}}$$

$K_c$  of the backward reaction is the reciprocal of  $K_c$  of the forward reaction and vice versa.

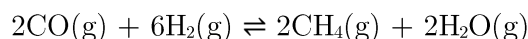
Bottom line is, if you are not sure about how to manipulate  $K_c$  values, just follow the reaction equation and derive a new expression of  $K_c$  and use indices laws to relate it to the old  $K_c$ .

Example 1:

Consider the following equilibrium system :



What is the value of  $K_c$  of the following reaction ?



A. 0.218

B. 0.935

C. 4.28

D. 4.58

Example 2: DSE 2020 1A Q26

Consider the information given below:

| Reaction  | $K_c$ at 298K                            |
|---|--|
| $\rightarrow \text{H}_2\text{A}_{aq} \rightleftharpoons \text{H}_{aq}^+ + \text{HA}_{aq}^-$     | $1.3 \times 10^{-3} \text{ mol dm}^{-3}$ |
| $\text{HA}_{aq}^- \rightleftharpoons \text{H}_{aq}^+ + \text{A}_{aq}^{2-}$                      | $3.1 \times 10^{-6} \text{ mol dm}^{-3}$ |
| $\rightarrow 2\text{HA}_{aq}^- \rightleftharpoons \text{H}_2\text{A}_{aq} + \text{A}_{aq}^{2-}$ | $x$                                      |

Find the value of  $x$ .

A.  $4.2 \times 10^2$

B.  $2.4 \times 10^{-3}$

C.  $4.0 \times 10^{-9}$

D.  $2.5 \times 10^8$

$$x = \frac{[\text{H}_2\text{A}][\text{A}^{2-}][\text{H}^+]}{(\text{HA}^-)(\text{HA}^-)[\text{H}^+]} = \frac{1}{K_{c1}} \cdot K_{c2} = 2.38 \cdot 10^{-3}$$

$K_c$  for heterogenous equilibrium

Key concept: The concentration for solid and **pure** liquid reactants (and products) are omitted **when they remain almost constant throughout the reaction.**

Write the expressions for  $K_c$  for the following reactions, including the units

|  |  |
|--|--|
| $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}_{aq}^+ + \text{Cl}_{aq}^-$ $K_c = [\text{Ag}_{(aq)}^+]_{eqm} [\text{Cl}_{(aq)}^-]_{eqm}$ | $\text{H}_2\text{O}_{(g)} + \text{C}_{(s)} \rightleftharpoons \text{H}_{2(g)} + \text{CO}_{(g)}$ $K_c = \frac{[\text{H}_{2(g)}][\text{CO}_{(g)}]}{[\text{H}_2\text{O}_{(g)}]}$ |
|--|--|

|   |  |
|---|--|
| $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$   | $\text{NH}_{3(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}$ $K_c = \frac{[\text{NH}_4^+_{(aq)}][\text{OH}^-_{(aq)}]}{[\text{NH}_{3(aq)}]}$ |
| <p>Special case:</p> $\text{CH}_3\text{COOH}_{(l)} + \text{CH}_3\text{CH}_2\text{OH}_{(l)} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3_{(l)} + \text{H}_2\text{O}_{(l)}$ $K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3_{(l)}][\text{H}_2\text{O}_{(l)}]}{[\text{CH}_3\text{COOH}_{(l)}][\text{CH}_3\text{CH}_2\text{OH}_{(l)}]}$ |  |

### Reaction Quotient ( $Q_c$ )

$$\text{A}_{(aq)} + \text{B}_{(aq)} \rightleftharpoons \text{C}_{(aq)} + \text{D}_{(aq)}$$

$$Q_c = \frac{[\text{C}_{(aq)}][\text{D}_{(aq)}]}{[\text{A}_{(aq)}][\text{B}_{(aq)}]}$$

Difference between  $Q_c$  and  $K_c$ :  $K_c$  will not change due to the concentration of the reactants at a certain point of time, it only depends on the equilibrium conditions.  $Q_c$  can be described as an “indicator” for the completeness of the reaction at an instant.  $Q_c$  can change with time as the concentration of reactants change.

### Relationship between $Q_c$ and $K_c$

| $Q_c < K_c$  | $Q_c = K_c$   | $Q_c > K_c$   |
|--|---|---|
| There are too much reactants, the rate of forward reaction is higher than the rate of backward reaction. | At dynamic equilibrium. The rate of forward reaction = rate of backward reaction. | There are too much products. The rate of backward reaction is higher than the rate of the forward reaction. |

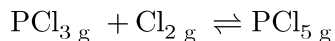
Generally saying, the concentration of reactants will change in a way such that  $Q_c$  will approach  $K_c$ .

## Calculations involving $K_c$ and $Q_c$

General steps:

1. Write down the expression for  $K_c$
2. Determine how the concentration of reactants will change and set an unknown if needed
3. Substitute and solve the resulting (quadratic) equation.

Example 4:  $\text{PCl}_3$  and  $\text{Cl}_2$



In an experiment, a mixture of phosphorus trichloride and chlorine was heated in a  $12.0\text{ dm}^3$  reaction vessel to  $500\text{ }^\circ\text{C}$  and allowed to reach equilibrium. Analysis showed that  $0.180$  mole of  $\text{PCl}_3$ ,  $0.120$  mole of  $\text{Cl}_2$  and  $0.600$  mole of  $\text{PCl}_5$  were present. Calculate the equilibrium constant at  $500\text{ }^\circ\text{C}$ .

$$K_c = \frac{\left(\frac{0.6}{12}\right)}{\left(\frac{0.12}{12} \cdot \frac{0.18}{12}\right)} = 333\text{ mol}^{-1}\text{dm}^3$$

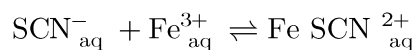
Example 5: Phosgene

Phosgene decomposes at a certain temperature as follows:



A  $1\text{ mol}$  container contains  $1.00\text{ mol}$  of phosgene originally. At equilibrium the concentration of  $\text{Cl}_2$  is  $0.028\text{ mol dm}^{-3}$ . Calculate the equilibrium constant.

Example 6:  $\text{Fe}(\text{SCN})^{2+}$



At a certain temperature, the  $K_c$  for the above reaction is  $137.5 \text{ mol}^{-1} \text{ dm}^3$ . In an experiment,  $500 \text{ cm}^3$  of  $0.200 \text{ M Fe}(\text{NO}_3)_3(\text{aq})$  was mixed with  $500 \text{ cm}^3$  of  $0.200 \text{ M KSCN}(\text{aq})$  at the given temperature. Calculate the equilibrium concentrations of all species.

$$K_c = \frac{[\text{Fe SCN}^{2+}_{\text{aq}}]_{\text{eqm}}}{[\text{SCN}^{-}_{\text{aq}}]_{\text{eqm}} [\text{Fe}^{3+}_{\text{aq}}]_{\text{eqm}}} = 137.5$$

|         | $[\text{SCN}^{-}_{\text{aq}}]$ | $[\text{Fe}^{3+}_{\text{aq}}]$ | $[\text{Fe SCN}^{2+}_{\text{aq}}]$ |
|---------|--------------------------------|--------------------------------|------------------------------------|
| Initial | 0.1                            | 0.1                            | 0                                  |
| Final   | $0.1-u$                        | $0.1-u$                        | $u$                                |

$$\frac{u}{(0.1-u)^2} = 137.5$$

$$u = 137.5(u^2 - 0.2u + 0.1^2)$$

$$u = 137.5u^2 - 27.5u + 1.375$$

$$137.5u^2 - 28.5u + 1.375 = 0$$

$$u = 0.131 \text{ (rej.) or } 0.0764$$

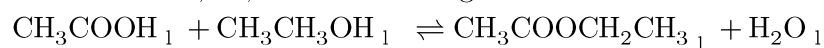
$$[\text{SCN}^{-}_{\text{aq}}]_{\text{eqm}} = 0.0236 \text{ mol dm}^{-3}$$

$$[\text{Fe}^{3+}_{\text{aq}}] = 0.0236 \text{ mol dm}^{-3}$$

$$[\text{Fe SCN}^{2+}_{\text{aq}}] = 0.0764 \text{ mol dm}^{-3}$$

Example 7: Esterification

At  $25^\circ\text{C}$ , the equilibrium constant,  $K_c$ , for the following reaction is 5.00.



A mixture of  $0.35 \text{ mol}$  of ethanoic acid and  $0.35 \text{ mol}$  of ethanol and a few drops of concentrated sulphuric acid was allowed to attain equilibrium at  $25^\circ\text{C}$

a. What is the function of concentrated sulphuric acid in the reaction.

b. Calculate the equilibrium concentration of ethyl ethanoate.

## Changes to equilibrium position

Equilibrium position may change due to:

- Addition of products or reactants
- Changing volume of the container (only applicable for gas)
- Changing temperature
- Adding inert gases to gas mixture (change in pressure)

General steps to determine how equilibrium moves:

- Look at what your change is
- See how the change affects  $Q_c$ 
  - $Q_c < K_c \rightarrow$  Equilibrium position shifts to product side
  - $Q_c > K_c \rightarrow$  Equilibrium position shifts to reactant side

## Adding products/reactants

- Add reactants  $\rightarrow$  equilibrium position shifts to product side
- Add products  $\rightarrow$  equilibrium position shifts to reactant side

## Changing volume/pressure<sup>1</sup>

Recap: ideal gas law

$$PV = nRT = \text{Constant}$$
$$\Rightarrow P \propto \frac{1}{V}$$

Pressure increase can be treated as volume decreasing, and vice versa.

When volume decreases, concentration increases since concentration = mol/volume, and vice versa.

Consider:

$$a_g + b_g \rightleftharpoons c_g, K_c = k$$
$$Q_c = \frac{[c_g]}{[a_g][b_g]} = \frac{n_c/V}{(n_a/V)(n_b/V)} = \frac{n_a n_b}{n_c} V$$

Suppose  $Q_c$  was originally equal to  $K_c$ . When volume decreases (pressure increase),  $Q_c$  decreases so  $Q_c < K_c$ , so the rate of forward reaction is higher than the backward reaction, the equilibrium position shifts towards the product side. When volume increases (pressure decreases),  $Q_c > K_c$ , so the rate of the backward reaction is higher than the rate of the forward reaction, the equilibrium position shifts to reactant side.

Rule of thumb:

- **Volume increase**/Pressure decrease, equilibrium position shifts to side with **more** no. of moles of gases
- **Volume decrease**/ Pressure increase, equilibrium position shifts to side with **less** no. of moles of gases.

---

<sup>1</sup> In actuality effects of pressure on equilibrium position has never been assessed. At least not to my knowledge.

## Changing temperature

When temperature changes,  $K_c$  itself changes. In fact,  $K_c$  is only changed by changing temperature. How  $K_c$  varies with temperature depends on whether the forward reaction is exothermic or endothermic.

- Exothermic forward reaction
  - $K_c$  increases when temperature decreases. i.e. equilibrium position shifts to product side when temperature decreases.
  - $K_c$  decreases when temperature increases. i.e. equilibrium position shifts to reactant side when temperature increases.
- Endothermic forward reaction
  - $K_c$  increases when temperature increases. i.e. equilibrium position shifts to product side when temperature increases.
  - $K_c$  decreases when temperature decreases. i.e. equilibrium position shifts to reactant side when temperature decreases.

## Catalyst

A catalyst increases the rate of the forward and backward reactions by the same extent, it will NOT have an effect on the equilibrium position, but it does increase the rate at which the equilibrium is reached.

## Le Chatelier's principle

If the equilibrium of a system is disturbed by a change in one or more of the determining factors (as temperature, pressure, or concentration) the system tends to adjust itself to a new equilibrium by counteracting as far as possible the effect of the change

—Le Chatelier's principle, Merriam-Webster Dictionary

Examples:

Increase in temperature (hotter) → Endothermic reaction proceeds quicker to absorb extra heat

Decrease in temperature (colder) → Exothermic reaction proceeds quicker to release heat

Increase in volume (decrease in pressure) → more mol of gas will be formed to increase pressure

Decrease in volume (increase in pressure) → Less moles of gas will be present to decrease pressure

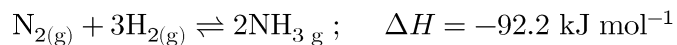
Sudden increase in one reactant → React that reactant away

Sudden decrease in one reactant → React other substances to form the reactant

Le Chatelier's principle can help you to more easily think about the effects on the equilibrium position after a disturbance to the system. However, when two or more variables in the system change simultaneously, then Le Chatelier's principle does not hold.



For instance:

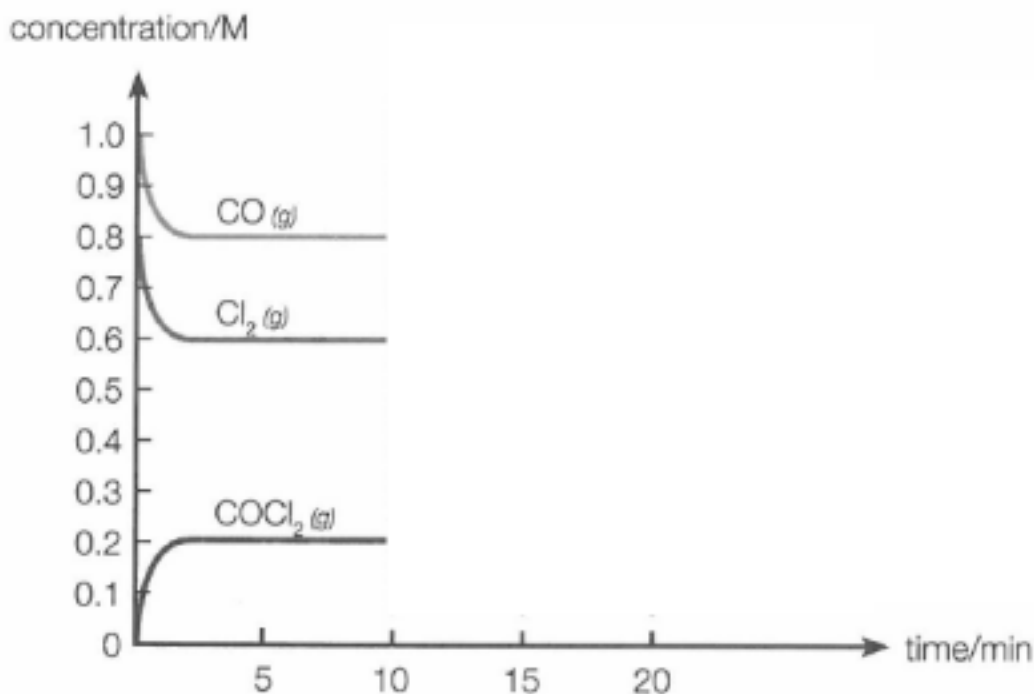
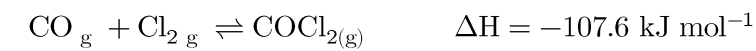


When the reaction chamber's temperature increases and volume decreases (pressure increases), it is not sufficient to use Le Chatelier's principle to determine what will happen to the equilibrium position.

Increasing temperature shifts the equilibrium position to the reactant side since the backward reaction is endothermic, it is favoured by the increase in temperature. Increasing pressure shifts the equilibrium position to the product side since there is less number of moles of gases on the product side. Le Chatelier's principle is insufficient to determine which shift is larger. I.e. net movement of the equilibrium position.

Example 8: Adding reactants

8. The reaction between carbon monoxide (CO) and chlorine (Cl<sub>2</sub>) is studied by preparing a mixture of the two gases.

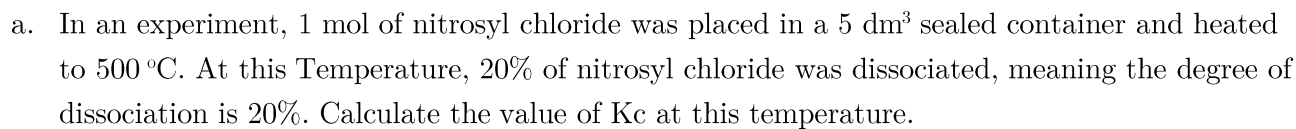


Complete the curves in the above graph if

(a) at 10th minute, there is a decrease in temperature and a new equilibrium position is established before 15th min.

(b) at 15th minute, there is an addition of Cl<sub>2</sub> to the reaction mixture and a new equilibrium position is achieved at 20th min.

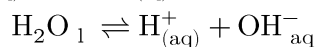
9. When nitrosyl chloride ( $\text{NOCl}$ ) is heated, it forms an equilibrium mixture with nitrogen monoxide and chlorine according to the following equation:



- b. State and explain the change in the degree of dissociation when temperature is increased.
- c. State and explain the change in the degree of dissociation when volume is decreased.

Example 10: Ionization of water molecules

Water molecules can ionize to give  $\text{H}^+_{(\text{aq})}$  and  $\text{OH}^-_{(\text{aq})}$



The equilibrium constant for the above reaction and the pH value of water at different temperatures are shown below:

| Temperature / °C | Equilibrium constant / $\text{mol}^2 \text{dm}^{-6}$ | pH value of water |
|------------------|--|-------------------|
| 0                | $1.14 \times 10^{-15}$                               | 7.47              |
| 10               | $2.93 \times 10^{-15}$                               | 7.27              |
| 25               | $1.00 \times 10^{-14}$                               | 7.00              |
| 30               | $1.47 \times 10^{-14}$                               | 6.92              |
| 50               | $5.48 \times 10^{-14}$                               | x                 |

- Give the expression of the equilibrium constant for the above reaction
- What is the value of  $x$  in the table?
- A student said 'Water becomes slightly alkaline at 10°C since it has a pH value of 7.27' Comment on his statement.
- State the effect on the electrical conductivity of water when temperature is increased, explain your answer.