# Equilibria

## The equilibrium constant, $K_c$

**1.** Match each of the reactions to the correct description;

(2 marks)

| Wood burning | Heating hydrated $CuSO_4.5H_2O$ | Making an ester; $CH_3COOH(aq) + CH_3OH(aq) \rightleftharpoons CH_3COOCH_3(aq) + H_2O(aq)$ |
|---|---|---|
| A reversible reaction at equilibrium | A reversible reaction | An irreversible reaction |

Explain your choice; ______________________________________________

______________________________________________

______________________________________________

______________________________________________

______________________________________________

(2 marks)

**2.** We can define a constant, $K_c$ for a reaction at equilibrium. Provided the temperature is constant, the value of $K_c$ is constant.
For each of the equilibria below, write an expression for the rate constant, $K_c$ and derive the units of the constant.

(a) Electrophilic addition of HCN to propanone;

$$CH_3COCH_3(aq) + HCN(aq) \rightleftharpoons CH_3C(OH)(CN)CH_3(aq)$$

$K_c$ = ______________________________ Units =

(2 marks)

(b) Esterification;

$$CH_3CH_2COOH(aq) + CH_3OH(aq) \rightleftharpoons CH_3CH_2COOCH_3(aq) + H_2O(aq)$$

$K_c$ = ______________________________ Units =

(2 marks)

(c) The Haber Process;

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

$K_c$ = ______________________________ Units =

(2 marks)

## Calculations with $K_c$

**1.** During the Contact process, $SO_2$ is converted into $SO_3$ in a reversible reaction;

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3\ \Delta H\ -197\ \text{kJ mol}^{-1}$$

The equilibrium was established at 1000 K and a small sample of the equilibrium mixture extracted. It was found to contain 1.0 mol dm$^{-3}$ of $SO_2$, 0.2 mol dm$^{-3}$ of $O_2$ and 1.4 mol dm$^{-3}$ of $SO_3$.

(a) Calculate $K_c$ at this temperature.

(3 marks)

(b) In the Contact process the temperature of choice is 700 K. What effect will this have on the value of $K_c$ compared to that calculated above?

(1 mark)

**2.** Catherine is studying the hydrolysis of ethyl butanoate;

$$CH_3CH_2CH_2COOCH_2CH_3 + H_2O \rightleftharpoons CH_3CH_2CH_2COOH + CH_3CH_2OH$$

She places exactly 1 mol of ethyl butanoate and 2 mol of water in a conical flask and allows the mixture to reach equilibrium. After this time the equilibrium mixture was analysed and found to contain 0.3 mol of butanoic acid. Calculate $K_c$ for the equilibrium at this temperature.

(3 marks)

**3.** In a different reaction, Catherine wants to make butyl ethanoate. She reacts butanol with ethanoic acid in 50 cm$^3$ of water in a round bottomed flask.

$$C_4H_9OH + CH_3COOH \rightleftharpoons CH_3COOC_4H_9 + H_2O$$

She wishes to make exactly 0.25 mol of butyl ethanoate. If she starts with 0.5 mol of ethanoic acid, how much butanol should she add? ($K_c$ for the equilibrium at 20 °C is 3.0. The density of water is 1 g cm$^{-3}$)

(3 marks)

## Le Châtelier and $K_c$

Le Châtelier has lost his glasses. He can't remember which floor of his lab he left them on! Consider the equilibrium below;

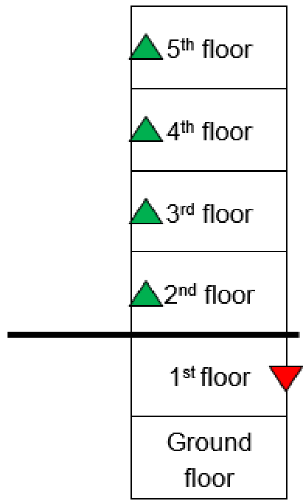
$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H = +40 \text{ kJ mol}^{-1}$$

Help Le Châtelier find his glasses by deciding what effect each of the changes in conditions **1-9** listed below will have on the value of $K_c$ for this equilibrium.
Le Châtelier is currently in his office on the second floor

- If the change in conditions increase $K_c$, move Le Châtelier one floor up
- If the change in conditions decrease $K_c$, move Le Châtelier one floor down
- If the change in conditions have no effect on $K_c$, Le Châtelier doesn't move

Unless stated otherwise assume that all conditions other than the one mentioned remain constant.

**1.** Adding a catalyst to the reaction mixture
**2.** Adding $CO_2$ to the reaction mixture
**3.** Increasing the pressure of the system
**4.** Increasing the reaction temperature
**5.** Adding CO to the reaction mixture
**6.** Decreasing the reaction temperature
**7.** Increasing the volume of the reaction container
**8.** Increasing the amount of $H_2$ gas in the reaction mixture
**9.** Increasing the surface area of the catalyst




(9 marks)

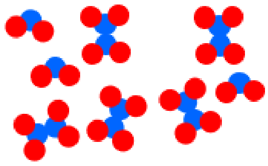
Le Châtelier will find his glasses on the ........................floor.

# The equilibrium constant, $K_p$

For gases it is easier to measure the pressure of a gas instead of its concentration. Therefore for equilibria involving only gases we quote the equilibrium constant in terms of pressure and give it the symbol $K_p$.

**1.** Complete the table below by calculating the equilibrium composition, the mole fractions, the total pressure or the partial pressures for the equilibria shown.

(4 marks)

| | | | |
|---|---|---|---|
| **Equilibrium** | $2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g)$ | $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$ | $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ |
| **Composition of equilibrium mixture** | 1 mol $H_2$<br>5 mol $O_2$<br>4 mol $H_2O$ |  | ............% $PCl_5$<br>............% $PCl_3$<br>............% $Cl_2$ |
| **Mole fractions** | $H_2$ = 0.1<br>$O_2$ = 0.5<br>$H_2O$ = 0.4 | $NO_2$ = ...............<br>$N_2O_4$ = ............... | $PCl_5$ = 0.1<br>$PCl_3$ = 0.55<br>$Cl_2$ = 0.35 |
| **Total pressure** | 20 kPa | 100 atm | ............................... |
| **Partial pressures** | $H_2$ = ...............<br>$O_2$ = ...............<br>$H_2O$ = ............... | $NO_2$ = 37.5 atm<br>$N_2O_4$ = 62.5 atm | $PCl_5$ = 4,600 Pa<br>$PCl_3$ = 25,300 Pa<br>$Cl_2$ = 16,100 Pa |
| **Expression for $K_p$** | $K_p$ = | $K_p$ = | $K_p$ = |
| **Value of $K_p$** | $K_p$ = ............................................... | $K_p$ = ......................................... | $K_p$ = ......................................... |

**2.** Write an expression for $K_p$, and calculate its value, assuming that each of the systems described above is at equilibrium.

(6 marks)

## The solubility product, $K_{sp}$

**1.** Define the following terms. Illustrate your definitions with examples from the box.

| |
|---|
| $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^-(aq)$ |
| $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ |
| $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ |

*Homogeneous equilibrium*

*Heterogeneous equilibrium*

(4 marks)

The solubility product is a special example of a heterogeneous equilibrium.
When writing an expression for the equilibrium constant for a heterogeneous equilibrium, terms for pure solids or pure liquids are left out of the expression.

**2.** A student tests for the presence of chloride ions in solution by adding a solution of lead nitrate. A white precipitate of lead chloride is formed.

The precipitate exists in equilibrium with its ions;

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^-(aq),\ K_{sp} = 1.6 \times 10^{-5}\ mol^3\ dm^{-9}\ at\ 298\ K$$

(a) Write an expression for $K_{sp}$ for this equilibrium.

(1 mark)

(b) Calculate the solubility of lead chloride at 298 K in mol $dm^{-3}$.

(2 marks)

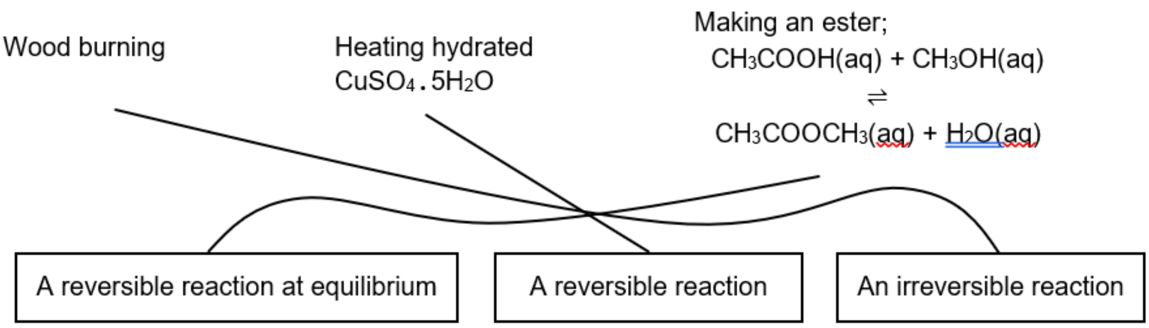
(c) Describe an experiment the student could do to obtain an experimental value for the solubility product, $K_{sp}$ of lead chloride.

(3 marks)

# Equilibria – Answers

## The equilibrium constant, $K_c$

1.




*(2 marks for all three correct, 1 mark for 1 correct)*

The products from burning wood cannot be turned back into wood so it is irreversible. The copper sulphate once dehydrated can be turned back into the hydrated form by the addition of water. Hence it is a reversible reaction *(1 mark for above two points).* The esterification reaction is in a <u>closed system</u> so neither products nor reactants can escape so it is a reaction at equilibrium *(1 mark).*

2.

(a) $K_c = \dfrac{[CH_3C(OH)(CN)CH_3(aq)]}{[CH_3COCH_3(aq)][HCN(aq)]}$  Units = $\dfrac{\cancel{mol\ dm^{-3}}}{\cancel{mol\ dm^{-3}} \times mol\ dm^{-3}}$ = <u>$mol^{-1}\ dm^3$</u> *(2 marks)*

(b) $K_c = \dfrac{[CH_3CH_2COOCH_3(aq)]\ [H_2O(aq)]}{[CH_3CH_2COOH(aq)]\ [CH_3OH(aq)]}$  Units = $\dfrac{\cancel{mol\ dm^{-3}} \times \cancel{mol\ dm^{-3}}}{\cancel{mol\ dm^{-3}} \times \cancel{mol\ dm^{-3}}}$ = <u>no units</u> *(2 marks)*

(c) $K_c = \dfrac{[NH_3(g)]^2}{[N_2(g)]\ [H_2(g)]^3}$  Units = $\dfrac{(mol\ dm^{-3})^2}{mol\ dm^{-3} \times (mol\ dm^{-3})^3}$ = <u>$mol^{-2}\ dm^6$</u> *(2 marks)*

## Calculations with $K_c$

**1.** (a) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2\ [O_2]}$ *(1 mark)* $= \dfrac{(1.4\ mol\ dm^{-3})^2}{(1\ mol\ dm^{-3})^2\ (0.2\ mol\ dm^{-3})}$ = <u>$9.8\ mol^{-1}\ dm^3$</u> *(1 mark for value, 1 mark for units)*

(b) The temperature has been decreased. Therefore the equilibrium will shift in favour of the exothermic reaction (to the right) in order to oppose the temperature decrease. Therefore <u>the value of $K_c$ will increase</u>.

*(1 mark)*

**2.**

| | ethyl butanoate | + water | ⇌ butanoic acid | + ethanol |
|---|---|---|---|---|
| **I**nitial | 1 mol | 2 mol | 0 mol | 0 mol |
| **C**hange | –0.3 mol | –0.3 mol | +0.3 mol | +0.3 mol |
| **E**quilibrium | 0.7 mol | 1.7 mol | 0.3 mol | 0.3 mol |

*(1 mark)*

$$K_c = \frac{[\text{acid}]\,[\text{alcohol}]}{[\text{ester}]\,[\text{water}]} = \frac{[0.3\text{ mol / V}]\,[0.3\text{ mol / V}]}{[0.7\text{ mol / V}]\,[1.7\text{ mol / V}]} = \underline{0.076\text{ no units}}$$

*(1 mark for value, 1 mark for units)*

**3.** No. of moles in 50 $cm^3$ of water;

Mass = 50 $cm^3$ × 1 g $cm^{-3}$ = 50 g

Moles = 50 g / 18 g $mol^{-1}$ = 2.78 mol *(1 mark)*

Substituting into the equilibrium;

| | butanol + | ethanoic acid | ⇌ ester | + water |
|---|---|---|---|---|
| **I**nitial | x mol | 0.5 mol | 0 mol | 2.78 mol |
| **C**hange | –0.25 mol | –0.25 mol | +0.25 mol | +0.25 mol |
| **E**quilibrium | (x – 0.25 ) mol | 0.25 mol | 0.25 mol | 3.03 mol |

$$K_c = \frac{[\text{ester}]\,[\text{water}]}{[\text{butanol}]\,[\text{ethanoic acid}]} = \frac{[0.25\text{ mol / V}]\,[3.03\text{ mol / V}]}{[(x - 0.25\text{ mol}) / V]\,[0.25\text{ mol / V}]}$$ *(1 mark)*

Knowing that $K_c$ = 3.0 under the reaction conditions;

$$3.0 = \frac{[0.25\text{ mol / V}]\,[3.03\text{ mol / V}]}{[(x - 0.25\text{ mol}) / V]\,[0.25\text{ mol / V}]} = \frac{0.7575}{0.25x - 0.0625}$$

3.0 (0.25x – 0.0625) = 0.7575

0.75x – 0.1875 = 0.7575

0.75x = 0.945

<u>x = 1.26 mol</u> *(1 mark)*

## Le Châtelier and $K_c$

| | Effect on $K_c$ | Location of Le Châtelier |
|---|---|---|
| **1.** Adding a catalyst to the reaction mixture | no change | 2nd floor |
| **2.** Adding $CO_2$ to the reaction mixture | no change | 2nd floor |
| **3.** Increasing the pressure of the system | no change | 2nd floor |
| **4.** Increasing the reaction temperature | increases | 3rd floor |
| **5.** Adding CO to the reaction mixture | no change | 3rd floor |
| **6.** Decreasing the reaction temperature | decreases | 2nd floor |
| **7.** Increasing the volume of the reaction container | no change | 2nd floor |
| **8.** Increasing the amount of $H_2$ gas in the reaction mixture | no change | 2nd floor |
| **9.** Increasing the surface area of the catalyst | no change | 2nd floor |

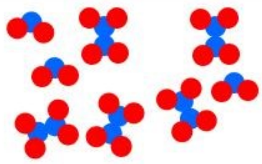
*(9 marks)*

Le Châtelier can find his glasses on the 2nd floor …… they were in his office all along!

*(1 mark)*

## The equilibrium constant, $K_p$

*4 marks – one for each box fully completed correctly*

| **Equilibrium** | $2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$ | $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$ | $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ |
|---|---|---|---|
| **Composition of equilibrium mixture** | 1 mol $H_2$<br>5 mol $O_2$<br>4 mol $H_2O$ |  | 10% $PCl_5$<br>55% $PCl_3$<br>35% $Cl_2$ |
| **Mole fractions** | $H_2$ = 0.1<br>$O_2$ = 0.5<br>$H_2O$ = 0.4 | $NO_2$ = ⅜ or 0.375<br>$N_2O_4$ = ⅝ or 0.625 | $PCl_5$ = 0.1<br>$PCl_3$ = 0.55<br>$Cl_2$ = 0.35 |
| **Total pressure** | 20 kPa | 100 atm | 46,000 Pa |
| **Partial pressures** | $H_2$ = 2 kPa<br>$O_2$ = 10 kPa<br>$H_2O$ = 8 kPa | $NO_2$ = 37.5 atm<br>$N_2O_4$ = 62.5 atm | $PCl_5$ = 4,600 Pa<br>$PCl_3$ = 25,300 Pa<br>$Cl_2$ = 16,100 Pa |
| **Expression for $K_p$** | $K_p = \dfrac{(P_{H_2O})^2}{(P_{H_2})^2\,(P_{O_2})}$ | $K_p = \dfrac{(P_{N_2O_4})}{(P_{NO_2})^2}$ | $K_p = \dfrac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})}$ |
| **Value of $K_p$** | $K_p = 8^2 / (2^2 \times 10)$<br>$K_p = 1.6\ kPa^{-1}$ | $K_p = 62.5 / 37.5^2$<br>$K_p = 0.0444\ atm^{-1}$ | $K_p = \dfrac{(25{,}300 \times 16{,}100)}{4{,}600}$<br>$K_p = 88{,}550$ Pa |

*(6 marks, 1 for each correct expression for $K_p$ and 1 for each correct value for $K_p$ with correct units)*

## The solubility product, $K_{sp}$

**1.** *Homogeneous equilibrium* = an equilibrium where all the substances are in the same phase.

e.g. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

*Heterogeneous equilibrium* = an equilibrium where all the substances are not all in the same phase.

e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ or $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\ I^{-}(aq)$

*(2 marks for each correct definition with matching correct example from the table)*

**2.** (a) $K_{sp} = [Pb^{2+}][Cl^{-}]^2$ *(1 mark)*

(b) At equilibrium call $[Pb^{2+}]$ '*s*' and $[Cl^{-}]$ '*2s*'

Substituting into the equation for $K_{sp}$;

$1.6 \times 10^{-5} = s \times (2s)^2$ *(1 mark)*

$1.6 \times 10^{-5} = 4\ s^3$

$4 \times 10^{-6} = s^3$ and hence $s = 0.0158$

Therefore the solubility of lead chloride at 298 K is $0.016\ mol\ dm^{-3}$. *(1 mark)*

(c) **Step 1**: Dissolve as much lead chloride as possible in water, allowing the solution time to equilibrate.

**Step 2**: Filter off the undissolved lead chloride and measure out a known volume of the filtrate.

**Step 3**: Evaporate this volume of filtrate to dryness and record the mass of lead chloride left.

**Step 4**: Use this mass of lead chloride to determine $[Pb^{2+}]$ and $[Cl^{-}]$ in the original volume of filtrate and from these values calculate $K_{sp}$.

*(3 marks for steps 1-3 clearly described)*