

CHEMICAL EQUILIBRIA

Reactions:

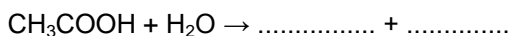
- going to completion – reaction continues until one of the reactants is completely used up, e.g.

.....

reactants → products

- reversible** – reaction going both directions

reactants ↔ products



↔ reversible reaction → forward reaction ← backward reaction

Chemical equilibrium = the state of a reaction system of a reversible reaction where the forward and the backward reaction occur at the same rate.

- What can you tell about the concentrations of reactants and products in an equilibrium mixture?

This kind of equilibrium is called **dynamic equilibrium**. It means that however the concentrations of reactants and products it does not mean that there are no reactions proceeding. They occur but the forward and the backward reaction occur at

The equilibrium constant, K_c

$a A + b B \leftrightarrow c C + d D$... reversible reaction

rate of the forward reaction: $v_1 = k_1 \times [\text{A}]^a \times [\text{B}]^b$

rate of the backward reaction: $v_2 = k_2 \times [\text{C}]^c \times [\text{D}]^d$

At equilibrium: $v_1 = v_2$

$$k_1 \times [\text{A}]^a \times [\text{B}]^b = k_2 \times [\text{C}]^c \times [\text{D}]^d \quad \frac{k_1}{k_2} = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b} \quad K_c = \frac{[\text{C}]^c \times [\text{D}]^d}{[\text{A}]^a \times [\text{B}]^b} = \text{Guldberg – Waage expression}$$

K_c , equilibrium constant, depends on the temperature and pressure

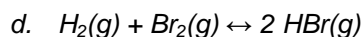
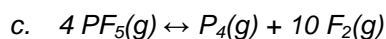
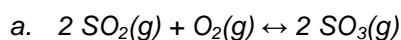
Reactions involving solids:

Concentration of molecules within any solid is constant, it does not affect the equilibrium, chemists do not include the concentrations of any solid reactants or products in the equilibrium constant expression.

Reactions involving aqueous solutions:

Concentration of water is very high in dilute solutions, it is not changed during a reaction, chemists do not include the concentrations of water in the equilibrium constant expression.

- Derive an expression for the equilibrium constant, K_c for the reaction:



- e. $\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- f. $(\text{NH}_4)_2\text{CO}_3(\text{s}) \leftrightarrow \text{CO}_2(\text{g}) + 2 \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$
3. The same equilibrium system may be represented by two different equations:
- $$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{NO}(\text{g})$$
- $$2 \text{NO}(\text{g}) \leftrightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g})$$
- a. Write expressions for two equilibrium constants, K_c and K_c' .
- b. What is the mathematical relation between K_c and K_c' ?
4. The equilibrium between SO_3 , SO_2 and O_2 may be represented equally well by two different equations:
- $$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g}) \quad K_c$$
- $$\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \leftrightarrow \text{SO}_3(\text{g}) \quad K_c'$$
- a. Write expressions for two equilibrium constants, K_c and K_c' .
- b. At 852 K $K_c = 1.28 \times 10^4 \text{ mol}\cdot\text{dm}^{-3}$ and at 1000 K $K_c = 2.8 \times 10^2 \text{ mol}\cdot\text{dm}^{-3}$. What are the values of K_c' at these temperatures?
- c. What are the values of the equilibrium constants of the reaction $2 \text{SO}_3(\text{g}) \leftrightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ at both above mentioned temperatures?
5. What can you say about the relative concentrations of reactants and products when:
- a. K_c is very large
- b. K_c is very small
6. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{NO}(\text{g})$ equilibrium at 1500 K:
- $$[\text{N}_2(\text{g})] = 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$$
- $$[\text{O}_2(\text{g})] = 10^{-1} \text{ mol}\cdot\text{dm}^{-3}$$
- $$[\text{NO}(\text{g})] = 10^{-4} \text{ mol}\cdot\text{dm}^{-3},$$
- calculate the value of the equilibrium constant at this temperature.
- (10⁻⁵)
7. Calculate K_c for the equilibrium $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2 \text{HI}(\text{g})$ at 350°C if the equilibrium mixture contains $[\text{H}_2(\text{g})] = 0.2 \text{ mol}\cdot\text{dm}^{-3}$, $[\text{I}_2(\text{g})] = 0.02 \text{ mol}\cdot\text{dm}^{-3}$ and $[\text{HI}(\text{g})] = 0.59 \text{ mol}\cdot\text{dm}^{-3}$.
- (87)
8. A sealed container ($V = 2 \text{ dm}^3$) contains at 1400 K an equilibrium mixture of 0.002 mol of $\text{S}_2(\text{g})$, 0.06 mol of $\text{H}_2(\text{g})$ and 0.04 mol of $\text{H}_2\text{S}(\text{g})$. Calculate the equilibrium constant for the reaction $2 \text{H}_2\text{S}(\text{g}) \leftrightarrow 2 \text{H}_2(\text{g}) + \text{S}_2(\text{g})$ at this temperature.
- (2.25 mol·dm⁻³)
9. The equilibrium constant for the reaction $\text{PCl}_5(\text{g}) \leftrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ at the temperature of 250°C is $0.19 \text{ mol}\cdot\text{dm}^{-3}$. An equilibrium mixture contains $[\text{PCl}_5(\text{g})] = 0.48 \text{ mol}\cdot\text{dm}^{-3}$ and $[\text{PCl}_3(\text{g})] = 0.22 \text{ mol}\cdot\text{dm}^{-3}$. Calculate the equilibrium concentration of chlorine.
- (0.41 mol·dm⁻³)

10. A vessel of the volume of 0.5 dm^3 contains at 35°C an equilibrium mixture of 0.010 mol of $\text{CO}(\text{g})$, 0.012 mol of $\text{Br}_2(\text{g})$ and $\text{COBr}_2(\text{g})$. Calculate the mass of $\text{COBr}_2(\text{g})$ in the equilibrium mixture knowing that $\text{CO}(\text{g}) + \text{Br}_2(\text{g}) \leftrightarrow \text{COBr}_2(\text{g})$ has $K_c = 79 \text{ mol}^{-1} \cdot \text{dm}^3$ at such a temperature.

(3.56 g)

Factors affecting equilibria

11. What is the effect of:

- change in concentrations
- change in pressure
- change in temperature
- introducing a catalyst

on the following equilibrium: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$?

Solution:

- a. p , t stays the same, we add or remove reactants or products.

$$p, t \text{ stays the same, then } K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3} \dots\dots\dots$$

N_2 is added \Rightarrow the concentration of N_2 $\dots\dots\dots \Rightarrow [\text{NH}_3]$ $\dots\dots\dots$

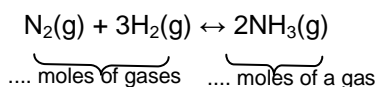
Equilibrium is shifted to the $\dots\dots\dots$

NH_3 is added \Rightarrow the concentration of ammonia $\dots\dots\dots$ and so the concentrations of nitrogen and hydrogen must $\dots\dots\dots$

Equilibrium is shifted to the $\dots\dots\dots$

- b. Pressure is changed \Rightarrow equilibrium constant $\dots\dots\dots$

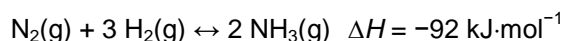
Pressure has an effect on equilibrium systems involving gases only.



Higher pressure – system tends to reach the *smallest/highest* possible volume and so the equilibrium is shifted towards *smaller/higher* number of moles of gases.

Equilibrium is shifted to the $\dots\dots\dots$

- c. temperature is changed \Rightarrow equilibrium constant $\dots\dots\dots$



Increased temperature has the effect on the rate of both backward and forward reaction.

However, it has a bigger effect on the reaction, which *needs/liberate* heat = *exothermic/* *endothermic* reaction. In this case the forward reaction is *exothermic/endothermic* and the backward reaction is *exothermic/endothermic*. The *exothermic/endothermic* reaction will

be proceeding faster, so the equilibrium is shifted in the direction of the *forward/backward* reaction.

d. introducing a catalyst

A catalyst increases the rate of both the forward and the backward reaction \Rightarrow
catalyst has no effect on the composition of an equilibrium mixture.

Le Chatelier's principle: "A system at equilibrium will react to oppose any change imposed on it."

12. State whether the forward or backward reaction is likely to take place when:

- Hydrogen is removed
- Ammonia is removed

from the equilibrium mixture described in the question 11.

13. What effect does an increase in temperature have on the position of equilibrium on:

- $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$ $\Delta H = 131 \text{ kJ}\cdot\text{mol}^{-1}$
- $2 \text{H}_2\text{S}(\text{g}) + \text{SO}_2(\text{g}) \leftrightarrow 3 \text{S}(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$ $\Delta H = -233.7 \text{ kJ}\cdot\text{mol}^{-1}$
- $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \leftrightarrow 2 \text{CO}(\text{g})$ $\Delta H = 174 \text{ kJ}\cdot\text{mol}^{-1}$
- $\text{AgClO}_2(\text{s}) \leftrightarrow \text{Ag}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) + \text{O}_2(\text{g})$ $\Delta H = 0.0 \text{ kJ}\cdot\text{mol}^{-1}$

14. What is the effect of decreasing the pressure on:

- $\text{CaCO}_3(\text{s}) \leftrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{N}_2\text{O}_4(\text{g}) \leftrightarrow 2 \text{NO}_2(\text{g})$
- $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g})$
- $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$

15. What is the effect of increasing the pressure on:

- $3 \text{Fe}(\text{s}) + 4 \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{Fe}_3\text{O}_4(\text{s}) + 4 \text{H}_2(\text{g})$
- $2 \text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- $\text{S}(\text{s}) + \text{O}_2(\text{g}) \leftrightarrow \text{SO}_2(\text{g})$
- $2 \text{CO}_2(\text{g}) \leftrightarrow 2 \text{CO}(\text{g}) + \text{O}_2(\text{g})$

16. In each of the following cases state the effect of a catalyst (if one is used) on the equilibrium system and the conditions of temperature and pressure which give the highest yield of products in the equilibrium mixture.

- Contact process $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3$ $\Delta H = -97 \text{ kJ}\cdot\text{mol}^{-1}$
- Haber process $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$ $\Delta H = -92 \text{ kJ}\cdot\text{mol}^{-1}$
- Bosch process $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \leftrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$ $\Delta H = 131 \text{ kJ}\cdot\text{mol}^{-1}$