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Dynamic equilibrium

A **reversible reaction** is one which can be made to go in either direction depending on the conditions. When you have a reversible reaction in a closed system, a dynamic equilibrium is established.

In a **dynamic equilibrium** the rate of the forward reaction and backward reaction is the same; there is no further change in the concentrations of reactants and products.

The proportion of products to reactants in an equilibrium mixture is known as the position of equilibrium.

Le Chatelier's principle

If a system at equilibrium is subjected to a change then the position of equilibrium will shift to minimise that change.

If you change the conditions in a way which changes the relative rates of the forward and backward reactions, you change the position of equilibrium, i.e. the proportion of products to reactants in the equilibrium mixture.

The position of equilibrium is influenced by three factors:

concentration, pressure and temperature.

A catalyst decreases the time it takes to reach equilibrium but does not alter the position of equilibrium.

Effect of concentration change

If the concentration of a reactant is increased, the position of equilibrium moves to the right and more products are formed.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

yellow orange

Adding hydrochloric acid to the solution results in the position of equilibrium moving to the right. More H+ ions have been added so the equilibrium shifts to decrease the concentration of the H+ ions and the solution turns more orange.

If you add sodium hydroxide, the concentration of the H+ ions decreases, so the position of equilibrium shifts to the left and the solution turns more yellow.

Effect of pressure change

Increasing the pressure moves the position of equilibrium to whichever side of the equation has fewer gas molecules.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

brown colourless

If the pressure is increased, the position of equilibrium moves to the right. The pressure will decrease if the equilibrium system contains fewer gas molecules, so the equilibrium shifts to minimise the increase and the colour becomes lighter.

Effect of temperature change

An increase in temperature moves the position of equilibrium in the endothermic direction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\ \text{kJ mol}^{-1}$$

Since the enthalpy change is negative, the forward reaction is exothermic. If the temperature is increased, the position of equilibrium moves to the left. The system opposes the change by absorbing the extra heat, favouring the backward (endothermic) direction and decreasing the yield of ammonia.

Equilibrium constant, K_c

Kc is the equilibrium constant in terms of concentration.

In general for an equilibrium: $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Remember to use square brackets around your formulae for K_c calculations. They are shorthand for concentration in mol dm–³.

Solids are never included in the expression for K_c.

The value of K_c is not affected by pressure or concentration.

It is only affected by temperature.

The unit of K_c can vary. If it has no unit you must say so.

Examples

$$CH_3CO_2H(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3CO_2C_2H_5(aq) + H_2O(l)$$

$$K_c = \frac{[CH_3CO_2C_2H_5][H_2O]}{[CH_3CO_2H][C_2H_5OH]}$$ no units

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$ units → dm³ mol–¹

1.7 – Equilibria and acid-base reactions

Acids

An **acid** is a proton (H^+) donor; a **base** is a proton (H^+) acceptor.

A **strong acid** is fully dissociated (or ionised) in aqueous solution.

E.g. $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$

The aqueous hydrogen ion concentration is equal in magnitude to the concentration of the acid.

A **weak acid** is only partially dissociated in aqueous solution.

E.g. $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

The aqueous hydrogen ion concentration is much smaller in magnitude than the concentration of the acid.

A **concentrated acid** consists of a large quantity of acid and a small quantity of water.

A **dilute acid** contains a large quantity of water.

pH

The acidity of a solution is a measure of the concentration of aqueous hydrogen ions, $H^+(aq)$. However, $H^+(aq)$ concentration varies over a wide range and can be extremely small, e.g. from 1×10^{-14} to 1 mol dm^{-3}. To overcome this wide range and to use more manageable numbers, the pH scale is used.

$$pH = -\log[H^+]$$

The negative sign in the equation results in pH decreasing as the aqueous hydrogen ion concentration increases.

Examples

What is the pH of a sample of rainwater with a $H^+(aq)$ concentration of 3.9×10^{-6} mol dm^{-3}?

$$pH = -\log[H^+] = -\log(3.9 \times 10^{-6})$$

$$pH = 5.4$$

A sample of acid rain has a pH of 2.2. What is the aqueous hydrogen ion concentration of this sample?

$$[H^+] = 10^{-pH} = 10^{-2.2}$$

$$[H^+] = 6.3 \times 10^{-3} \text{ mol dm}^{-3}$$

Acid-base titrations

Titrations are often used to calculate the exact concentrations of acid or base solutions. To do this, one of the solutions must be a **standard solution** or it must have been standardised.

Standard solution

A standard solution is one whose concentration is accurately known. It is prepared from a solid as follows:

Calculate the mass of the solid required and accurately weigh this amount into a weighing bottle.

Transfer the solid into a beaker and wash out the weighing bottle so that **all** of the weighed solid is transferred.

Add water and stir until all the solid dissolves.

Pour all the solution carefully into a volumetric (graduated) flask, washing all the solution out of the beaker and off the stirring rod.

Add water until just below the graduation mark.

Add water drop by drop until the graduation mark is reached.

Invert the flask several times to mix the solution thoroughly.

Performing a titration

All titrations follow the same overall method.

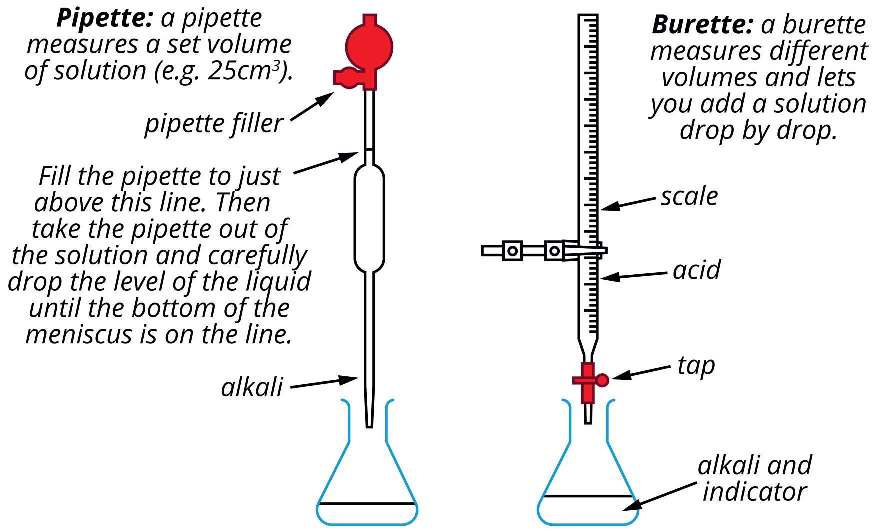
Pour one solution, say, an acid, into a **burette**, using a funnel, making sure that the jet is filled. Remove the funnel and read the initial burette volume.

Use a **pipette** to add a measured volume of the other solution, say, a base, into a **conical flask**.

Add a few drops of indicator to the solution in the flask.

Run the acid from the burette into the solution in the conical flask, swirling the flask.

Stop when the indicator just changes colour (the endpoint of the titration).



Read the final burette volume and calculate the volume of acid added (known as the titre).

Repeat the titration, making sure that the acid is added dropwise near the endpoint, until you have at least two readings that are within 0.20 cm^3 of each other.

Calculate a mean titre.