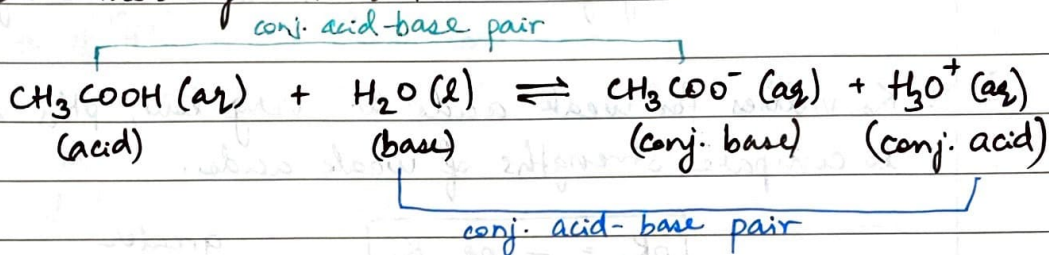


EQUILIBRIA

- Brønsted-Lowry acid = species that can donate a proton.
- Brønsted-Lowry base = species that can accept a proton.
- Conjugate acid-base pairs = 2 species that are diff. from each other by a H^+ ion.



pH

↳ indicates acidity/basicity of an acid/alkali.

→ pH scale: 0.0 - 14.0

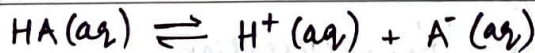
$$\text{pH} = -\log_{10} [\text{H}^+]$$

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

$[\text{H}^+] = \text{conc. of } H^+ \text{ ions (mol dm}^{-3}\text{)}$

K_a & $\text{p}K_a$

→ K_a = acid dissociation constant; equilibrium constant for dissociation of weak acid at 298K.



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Assumptions made when writing eq. expression for weak acids:

- H^+ ion conc. due to ionisation of water is negligible.
- dissociation of weak acid is so small that conc. of HA can be approximated by its initial value.

K_a value \Rightarrow extent of dissociation

High value

- eq. position lies to right
- acid almost completely ionised
- acid is strongly acidic

Low value

- eq. position lies to left
- acid is only ^{slightly} ~~weakly~~ ionised
- acid is weakly acidic

$\therefore K_a$ values for weak acids are very low, pK_a values are used to compare strengths of weak acids.

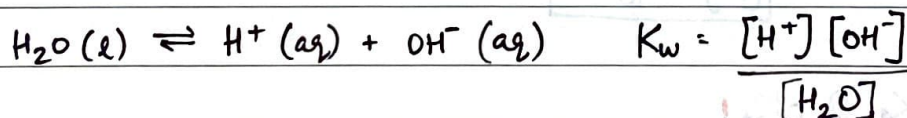
$$pK_a = -\log_{10} K_a$$

* ~~less~~ ^{greater} $pK_a \Rightarrow$ ~~more~~ ^{less} acidic
 greater $K_a \Rightarrow$ more acidic

K_w

$\rightarrow K_w$ = ionic product of water; eq. constant for the dissociation of water at 298K.

$$\rightarrow K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$



extent of ionisation is v. low \therefore only small amounts of H^+ and OH^- ions are formed.

\therefore conc. of H_2O can be considered constant and removed from equation K_w expression.

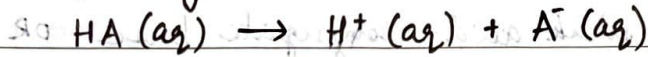
$$K_w = [\text{H}^+][\text{OH}^-]$$

As $[\text{H}^+] = [\text{OH}^-]$ in pure water,

$$K_w = [\text{H}^+]^2$$

[H⁺] and pH calculations1) Strong acids

- completely ionised in solution



- ~~conc~~ $[\text{H}^+] = [\text{HA}]$

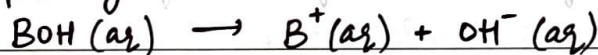
- ~~most~~ $[\text{H}^+]$ formed from ionisation of water is very small compared to $[\text{H}^+]$ due to ionisation of strong acid.

\therefore this is neglected.

- total $[\text{H}^+] = \text{total } [\text{HA}]$

2) Strong alkalis

- completely ionised in solution



- $[\text{OH}^-] = [\text{BOH}]$ (they also have small amounts of H^+ due to ionisation of water)

\rightarrow conc. of OH^- in solution can be used to calc. pH using K_w .

$$K_w = [\text{H}^+][\text{OH}^-] \quad [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{[\text{OH}^-]}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]}$$

3) Weak acids

pH can be calc. when following are known:

\rightarrow conc. of acid

$\rightarrow K_a$ value of acid

Buffers

Solution that resists change in pH when small amounts of acids/alkalis are added.

→ can consist of weak acid - conjugate base OR weak base - conjugate acid

Ethanoic acid & Sodium ethanoate

$\text{CH}_3\text{COOH (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$
(weak acid) partially ionises to form low conc. of CH_3COO^- .

$\text{CH}_3\text{COONa (aq)} \rightarrow \text{Na}^+ \text{(aq)} + \text{CH}_3\text{COO}^- \text{(aq)}$
(salt) fully ionises to form high conc. of CH_3COO^- .

There are reserve supplies of acid CH_3COOH and conj. base CH_3COO^- .
↳ Buffer solution contains relatively high conc. of CH_3COOH (due to ionisation of ethanoic acid) and CH_3COO^- (due to ionisation of sodium ethanoate)

ethanoic acid is in equilibrium w/ H^+ & CH_3COO^- .

When H^+ ions added

- eq. position shifts to LHS as H^+ reacts w/ CH_3COO^- to form more CH_3COOH until eq. re-established.
 - large reserve supply of CH_3COO^- ∴ its conc. doesn't change much when reacted w/ added H^+ .
 - large reserve supply of CH_3COOH ∴ its conc. doesn't change much as more forms from $\text{H}^+ + \text{CH}_3\text{COO}^-$.
- ∴ pH remains reasonably constant.

When OH^- ions added

- $\text{OH}^- (\text{aq}) + \text{H}^+ (\text{aq}) \rightarrow \text{H}_2\text{O} (\text{l})$
- H^+ conc. decreases.
- eq. position shifts to RHS: more CH_3COOH ionise to form more H^+ and CH_3COO^- until eq. re-established.
- large reserve supply of CH_3COOH \therefore its conc. doesn't change when it dissociates.
- large reserve supply of CH_3COO^- \therefore its conc. doesn't change when more forms.
- \therefore pH remains reasonably constant.

Buffer solutions to control pH in blood

- HCO_3^- ions = buffer; maintains pH btwn 7.35 - 7.45
- $\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq})$
 \hookrightarrow produced during aerobic respiration.
- Increase in H^+ : eq. shifts to LHS ^{until eq. restored,} which reduces H^+ and keeps pH constant.
- Decrease in H^+ : eq. shifts to RHS ^{until eq. restored,} which increases H^+ and keeps pH constant.

If conc. of H^+ not regulated, blood pH would drop, causing acidosis: too much acid in blood/body fluids; could lead to coma.

Buffer Solution pH Calculations

- pH of buffer solution can be calculated using:
- K_a of weak acid
 - eq. conc. of weak acid and conjugate base (salt)

$$K_a = \frac{[\text{salt}][\text{H}^+]}{[\text{acid}]} \quad [\text{H}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}$$

$$-\log [\text{H}^+] = -\log K_a \times -\log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

K_{sp}

↳ Solubility product: number of grams / moles of compound needed to saturate 100g of water, at a given temperature.

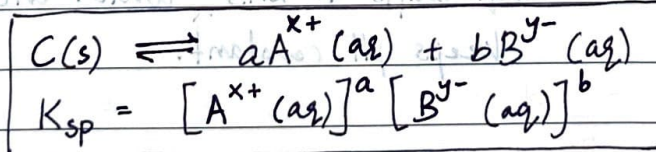
eg. NaCl, soluble: saturated solution contains 36g NaCl per 100g H₂O.

PbCl₂, insoluble: Saturated solution contains 0.99g PbCl₂ per 100g H₂O.

solubility product = • product of the concentrations of each ion in a saturated solution of a relatively ⁱⁿsoluble salt.

• at 298K

• raised to the power of their relative concentrations.

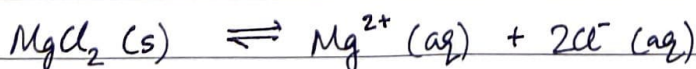


→ K_{sp} only used for sparingly soluble salts.

* lower K_{sp} ⇒ lower solubility

Ions in saturated solution

- when undissolved ionic compound is in contact w/ saturated solution of its ions, equilibrium is established.
- ions move from saturated solution → undissolved salt AND undissolved salt → saturated solution at the same rate.

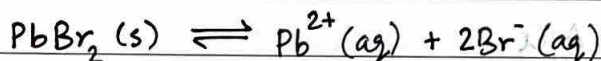


$$K_{sp} = [Mg^{2+}(aq)][Cl^{-}(aq)]^2$$

Solubility Product Calculations

- calculating K_{sp} of compound from solubility
- calculating solubility of compound from K_{sp}

Eg. 1: K_{sp} of saturated solution of $PbBr_2$ w/ solubility $1.39 \times 10^{-3} \text{ mol dm}^{-3}$



$$K_{sp} = [Pb^{2+}(aq)][Br^{-}(aq)]^2$$

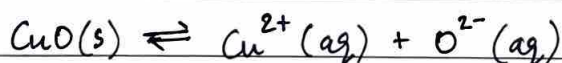
$$[PbBr_2(s)] = 1.39 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Pb^{2+}(aq)] = [PbBr_2(s)] = 1.39 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Br^{-}(aq)] = 2[PbBr_2(s)] = 2.78 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_{sp} = (1.39 \times 10^{-3})(2.78 \times 10^{-3})^2 = 1.07 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$$

Eg. 2: solubility of saturated solution of CuO w/ $K_{sp} 5.9 \times 10^{-36} \text{ mol}^2 \text{ dm}^{-6}$



$$K_{sp} = [Cu^{2+}(aq)][O^{2-}(aq)]$$

$$[Cu^{2+}(aq)] = [O^{2-}(aq)] \Rightarrow K_{sp} = [Cu^{2+}(aq)]^2$$

$$5.9 \times 10^{-36} = [Cu^{2+}(aq)]^2 \Rightarrow [Cu^{2+}(aq)] = \sqrt{5.9 \times 10^{-36}} = 2.4 \times 10^{-18} \text{ mol dm}^{-3}$$

$$[CuO(s)] = [Cu^{2+}(aq)] \therefore \text{solubility of } CuO = 2.4 \times 10^{-18} \text{ mol dm}^{-3}$$

NOTE: K_{sp} is NOT used for:

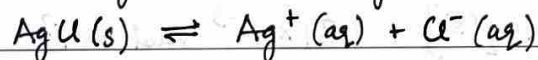
- group 1 element salts
- all nitrate and ammonium salts
- many sulfate salts
- many halide salts (except Pb & Ag halides)

Common Ion Effect

- Saturated solution: contains max. amount of dissolved salt.
- if a second compound which has an ion in common w/ dissolved salt is added to saturated solution, solubility of salt reduces and ppt forms — common ion effect.
- K_{sp} is used to predict whether or not ppt will form.
if product of ion conc. $> K_{sp}$, ppt forms.

Common ion effect in AgCl

- when KCl solution added to saturated AgCl solution, AgCl ppt forms.
- in saturated AgCl solution, AgCl is in eq. w/ its ions:



- when KCl added:

→ Both KCl & AgCl have common ion effect

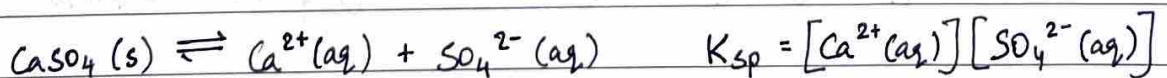
→ $[\text{Cl}^-] \uparrow \therefore$ eq. position shifts to LHS

→ $[\text{Cl}^-] \uparrow \Rightarrow [\text{Ag}^+(aq)][\text{Cl}^-(aq)] > K_{sp}$ for AgCl

\therefore AgCl precipitated

Eg. Predict whether ppt of CaSO_4 forms if saturated solution of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ CaSO_4 is mixed w/ equal volume of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ Na_2SO_4 .

$$K_{sp} \text{ CaSO}_4 = 2.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$



- equal volumes of each solution

- \therefore total solution diluted by factor of 2.

- new conc. of Ca^{2+} halved

$$[\text{Ca}^{2+}] = \frac{1 \times 10^{-3}}{2} = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$$

- SO_4^{2-} conc. same as it is common ion and its conc. is same in both solutions.

$$- [\text{Ca}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = (5 \times 10^{-4})(1 \times 10^{-3}) = 5.0 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

$$5.0 \times 10^{-7} < 2.0 \times 10^{-5} \quad \therefore \text{no ppt forms.}$$

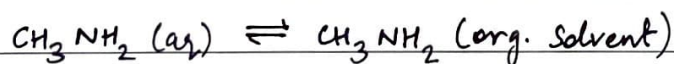
Partition Coefficient K_{pc}

Ratio of the concentrations of a solute in 2 diff. immiscible solvents in contact w/ each other when equilibrium has been established, at a particular temperature.

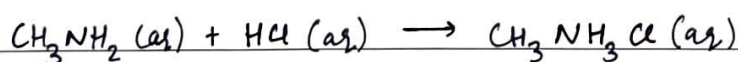
Eg. 100 cm^3 of $0.150 \text{ mol dm}^{-3}$ solution of aq. CH_3NH_2 was shaken w/ 75.0 cm^3 of organic solvent at 25°C and left in separating funnel for eq. to be established.

only 50.0 cm^3 of aq. layer was run off and titrated against $0.225 \text{ mol dm}^{-3}$ dil. HCl with endpoint of 14.1 cm^3 HCl.

K_{pc} of CH_3NH_2 btwn org. solvent & H_2O ?



$$K_{pc} = \frac{[\text{CH}_3\text{NH}_2(\text{org. solvent})]}{[\text{CH}_3\text{NH}_2(\text{aq})]}$$



$$\text{mol HCl} = \text{mol CH}_3\text{NH}_2 = \frac{14.1 \times 0.225}{1000} = 0.0031725 \text{ mol}$$

0.0031725 mol was present in 50 cm^3 of aq. layer

\therefore in 100 cm^3 , $6.345 \times 10^{-3} \text{ mol}$

~~or~~

$$\text{mol CH}_3\text{NH}_2(\text{org. layer}) = \text{mol CH}_3\text{NH}_2(\text{total}) - \text{mol CH}_3\text{NH}_2(\text{aq.})$$

$$= 0.1 \times 0.15 - 6.345 \times 10^{-3} = 8.655 \times 10^{-3}$$

$$[\text{CH}_3\text{NH}_2(\text{aq})] = \frac{6.345 \times 10^{-3}}{0.1} = 0.06345 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{NH}_2(\text{org})] = \frac{8.655 \times 10^{-3}}{0.075} = 0.1154 \text{ mol dm}^{-3}$$

$$K_{pc} = \frac{0.1154}{0.06345} = 1.82$$

$K_{pc} > 1 \therefore \text{CH}_3\text{NH}_2$ more soluble in org. solvent than water.

Factors affecting K_{pc}

→ solubilities of the solute in the 2 solvents.

- degree of solubility of solute is determined by strength of IM bonds btwn solute & solvent.
- strength of IM bonds depend on polarity of solute & solvent molecules.

$K_{pc} < 1 \Rightarrow$ solute more soluble in water than org. solvent.

$K_{pc} > 1 \Rightarrow$ solute ~~is~~ more soluble in org. solvent than water.