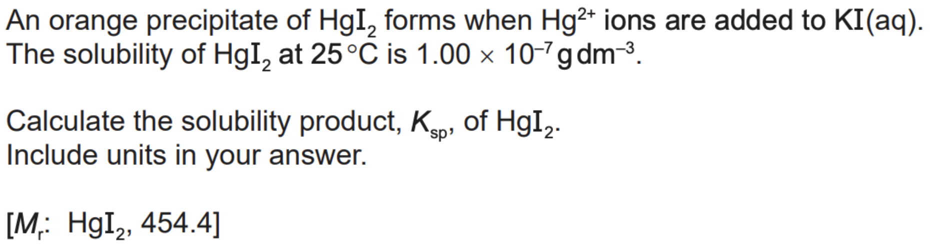
25. EQUILIBRIA

25.1 Acids and bases

Suggest the variation in pH of saturated solutions of the hydroxides of magnesium, calcium and strontium. Explain your answer.

- pH increases as concentration of OH^- ions increases.

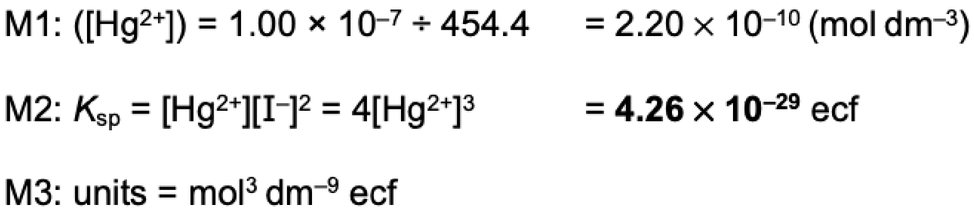


An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq).
The solubility of HgI_2 at 25 °C is 1.00×10^{-7} g dm^{-3}.

Calculate the solubility product, K_{sp}, of HgI_2.
Include units in your answer.

[M_r: HgI_2, 454.4]

Ans:



M1: $([Hg^{2+}]) = 1.00 \times 10^{-7} \div 454.4$ $= 2.20 \times 10^{-10}$ (mol dm^{-3})

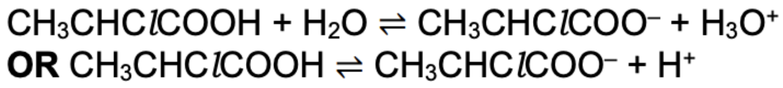
M2: $K_{sp} = [Hg^{2+}][I^-]^2 = 4[Hg^{2+}]^3$ $= \mathbf{4.26 \times 10^{-29}}$ ecf

M3: units = mol^3 dm^{-9} ecf

NOTE: solubility is given in g/dm3. REMEMBER to convert to mol/dm3!!!

An equilibrium is set up when CH3CHClCOOH is added to water. Write the equation for this equilibrium.

Ans:



$CH_3CHClCOOH + H_2O \rightleftharpoons CH_3CHClCOO^- + H_3O^+$

OR $CH_3CHClCOOH \rightleftharpoons CH_3CHClCOO^- + H^+$

Aqueous CH3CHClCOOH pH of 1.51. An equal concentration of aqueous propanoic acid has pH 2.55. Explain the difference in the pH of solutions of equal concentration of CH3CHClCOOH and propanoic acid.

- CH3CHClCOOH is a stronger acid than propanoic acid, owing to higher [H+].
- because electron-withdrawing effect of Cl (substituent) AND weakens O—H / carboxylate anion stabilised.

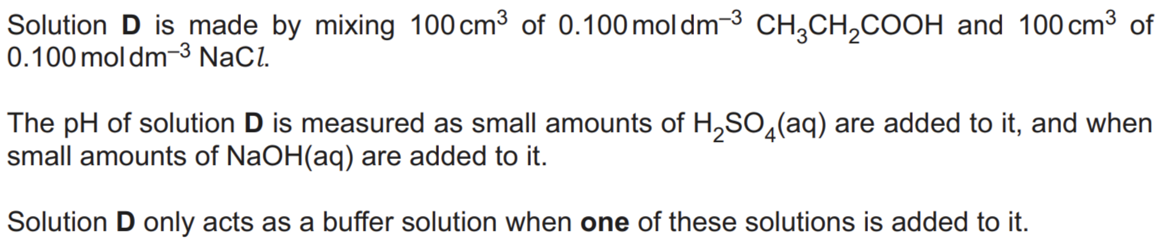
Define conjugate acid–base pair.

- two species that differ by one proton / H+

Give the formulas of the conjugate acid and the conjugate base of the hydrogen phosphate ion, HPO_4^{2-} .

- Conjugate acid: $H_2PO_4^-$
- Conjugate base: PO_4^{3-}

If you're finding the conjugate acid, treat HPO_4^{2-} as a base. It should accept a proton, forming $H_2PO_4^-$. If you're finding the conjugate base, treat HPO_4^{2-} as an acid. It should donate a proton, forming PO_4^{3-}.



Solution **D** is made by mixing 100 cm^3 of 0.100 mol dm^{-3} CH_3CH_2COOH and 100 cm^3 of 0.100 mol dm^{-3} NaC*l*.

The pH of solution **D** is measured as small amounts of H_2SO_4(aq) are added to it, and when small amounts of NaOH(aq) are added to it.

Solution **D** only acts as a buffer solution when **one** of these solutions is added to it.

When does solution D act as a buffer? Give the equation for the reaction.

- Acts as a buffer when NaOH is added.
- $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H2O$

When does solution D not act as a buffer? Explain why.

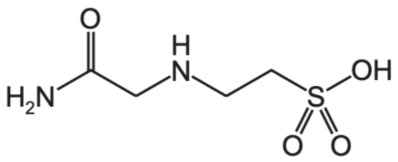
- Does not act as a buffer when H_2SO_4 is added
- This is because conjugate base of CH_3CH_2COOH is not present

Explanation

- You're mixing CH_3CH_2COOH (a weak acid) with NaCl (a neutral salt – Na^+ and Cl^- do nothing with pH).
- A buffer needs a weak acid + conjugate base //
  A weak base + conjugate acid.
- Thus solution D is not a buffer by itself, because it does not contain the conjugate base. NaCl is not a conjugate base.
- When you add NaOH, NaOH provides OH^-, which reacts with the weak acid CH_3CH_2COOH to form the conjugate base, $CH_3CH_2COO^-$.
  - $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H2O$
    Now you have:
    CH_3CH_2COOH (weak acid) and $CH_3CH_2COO^-$ (conjugate base)
    ✅ This is a buffer system
- When you add H_2SO_4, it provides H^+. There is no significant amount of conjugate base present to remove H^+. NaCl cannot react with H^+ to control pH
  - ❌ So the pH changes significantly.

The weak acid **ACES** is a compound that can be used to make a buffer solution for electrophoresis experiments.

ACES



The anion of the sodium salt of **ACES**, $C_4H_9N_2O_4SNa$, is a strong base.

A buffer solution is prepared by the following steps.

- 3.50 g of $C_4H_9N_2O_4SNa$ is dissolved in 100 cm^3 of distilled water.
- 50.0 cm^3 of 0.200 mol dm^{-3} dilute hydrochloric acid is added to the solution.
- The resulting mixture is transferred to a 250.0 cm^3 volumetric flask, and the solution made up to the mark.

$C_4H_9N_2O_4SNa$ reacts with HCl with a 1 : 1 stoichiometry.

The pK_a of **ACES** is 6.88 at 298 K.

Calculate the pH of the buffer solution formed at 298 K.

[M_r: $C_4H_9N_2O_4SNa$, 204.1]

Initial mol salt $= \frac{3.5}{204.1} = 0.017148$

mol HCl $= \frac{50}{1000} \times 0.2 = 0.01$

at eq: mol salt $= 0.017148 - 0.01$

$= 7.148 \times 10^{-3}$

(∵ they react in a 1:1 ratio)

ACES = weak acid   salt contains $ACES^-$
↓
conjugate base

weak acid + conj. base = buffer

When HCl (strong acid) added, it converts some $ACES^-$ to ACES

$$\overset{0.01}{HCl} + \overset{0.017148}{ACES^-} \longrightarrow \overset{0.01}{ACES} + Cl^-$$

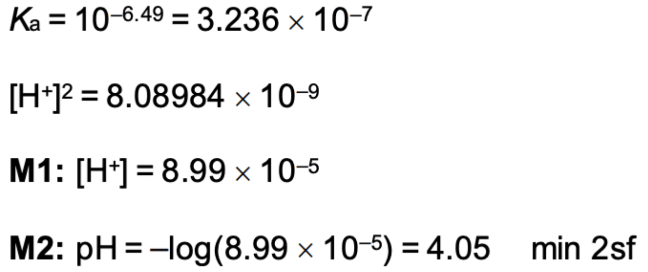
∴ mol ACES ~~at~~ formed = 0.01 mol
↳ at eq.

$$pH = pK_a + \log\frac{[salt]}{[acid]} \quad \cancel{= 6.88 + \log\left(\frac{0.017148}{0.01}\right)}$$

$$= 6.88 + \log\left(\frac{7.148 \times 10^{-3}}{250 \div 1000} \Big/ \frac{0.01}{250 \div 1000}\right)$$

$$= \boxed{6.73}$$

The hydrogenchromate ion, HCrO4⁻, is a weak acid. The pKa of HCrO4⁻ is 6.49. Calculate the pH of a 0.0250moldm−3 HCrO4⁻ solution.



$K_a = 10^{-6.49} = 3.236 \times 10^{-7}$

$[H^+]^2 = 8.08984 \times 10^{-9}$

M1: $[H^+] = 8.99 \times 10^{-5}$

M2: pH $= -\log(8.99 \times 10^{-5}) = 4.05$ min 2sf

25.2 Partition coefficients

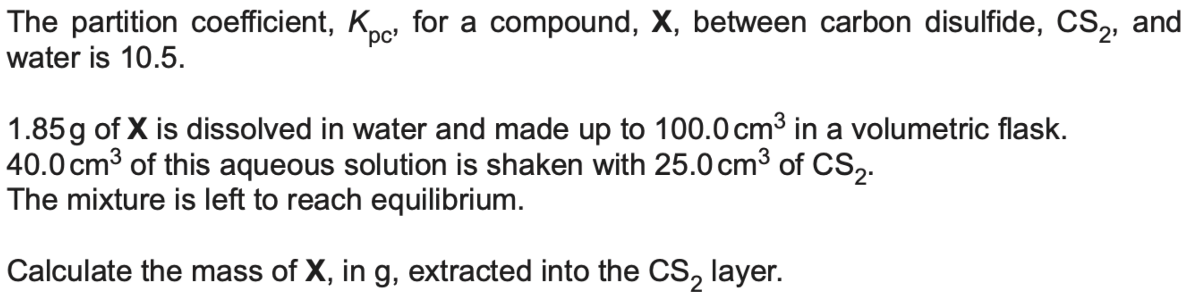
State what is meant by partition coefficient, K_{pc}

- ratio of the concentrations of solute in two solvents

The partition coefficient of I_2 between C_6H_{12} and water, Kpc, is 93.8.
Suggest how the value of Kpc of I_2 between hexan-2-one, CH3(CH2)3COCH3, and water compares to the above value given. Explain your answer.

- Kpc would be lower
- hexan-2-one is more polar (than cyclohexane)
  OR hexan-2-one is polar AND cyclohexane is non-polar
- I_2 is (therefore) less soluble in hexan-2-one

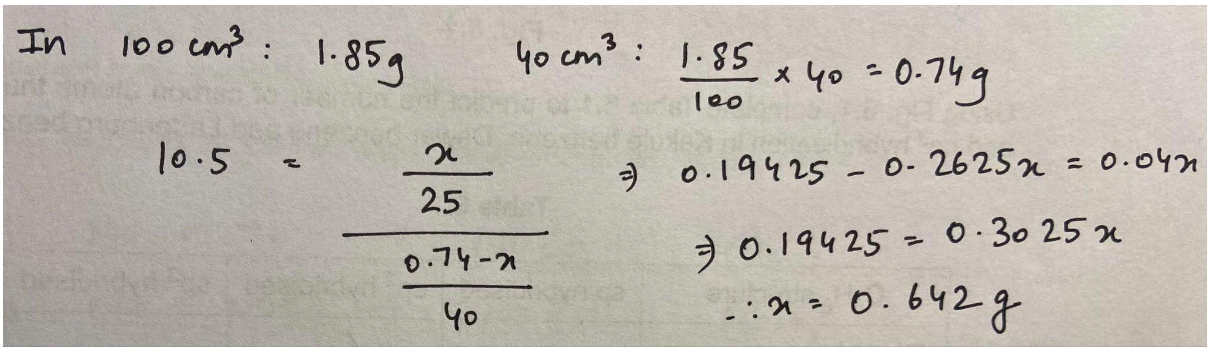
NOTE: hexan-2-one is a polar solvent due to its carbonyl (C=O) group, making it moderately polar, though less polar than water, and it readily dissolves in water and organic solvents.



The partition coefficient, K_{pc}, for a compound, **X**, between carbon disulfide, CS_2, and water is 10.5.

1.85 g of **X** is dissolved in water and made up to 100.0 cm^3 in a volumetric flask.
40.0 cm^3 of this aqueous solution is shaken with 25.0 cm^3 of CS_2.
The mixture is left to reach equilibrium.

Calculate the mass of **X**, in g, extracted into the CS_2 layer.



In $100\ cm^3$: $1.85g$ $40\ cm^3$: $\frac{1.85}{100} \times 40 = 0.74g$

$$10.5 = \frac{\frac{x}{25}}{\frac{0.74-x}{40}}$$

$\Rightarrow 0.19425 - 0.2625x = 0.04x$

$\Rightarrow 0.19425 = 0.3025x$

$\therefore x = 0.642g$

Silver(I) chromate, Ag2CrO4, is sparingly soluble in water. Write an ionic equation to show the equilibrium between solid Ag2CrO4 and its aqueous solution. Include state symbols.

$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$