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SENIOR FIVE TERM 3

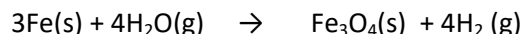
TOPIC 2/2: Equilibria I

Competency: The learner analyses principles of chemical equilibrium and applies them to explain and solve problems related to industrial processes, ionic equilibria, buffer systems, and solubility equilibria in various chemical and real-world contexts.

Chemical equilibrium

It is a branch of physical chemistry that deals with reversible reactions or reactions that proceed in either direction.

For example, when steam passed over heated iron, hydrogen and iron (II) diiron (III) oxide is formed. If, however, hydrogen is passed over heated iron (II) diiron (III) oxide, steam and iron are produced. Such reactions are said to be reversible and the equation for this reversible reaction is expressed as follows:



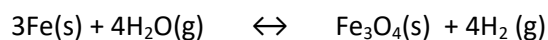
The direction of the reaction depends on the conditions: if hydrogen gas is removed as fast as it has formed, the reaction proceeds from left to right. Alternatively, if steam is removed as fast as it is formed the reaction will proceed from right to left.

By having steam and iron in a closed vessel, a state is reached at which all the four substance exist in equilibrium but the equilibrium in a balanced reaction is a dynamic one, that is, the substances are still reacting together except that the velocities of the forward and backward reaction are equal.

Equilibrium constant, K_c

The state of equilibrium of a reversible reaction at a given temperature is defined by equilibrium constant K_c as follows

For a reaction

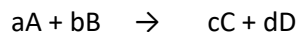


$$K_c = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$$

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Where [] means concentration of the item in moles per litre or moles per dm³

For a general equation



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

Units of K_c

The units of K_c are derived by principles of dimension

for instance

$$K_c = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4} = \frac{[mol\,dm^{-3}][mol\,dm^{-3}]^4}{[mol\,dm^{-3}]^3[mol\,dm^{-3}]^4}$$

\therefore units = mol⁻²dm⁶

Trail 1

Write expressions for K_c for the following reaction and state their units

- (i) $N_2 + 3H_2 \leftrightarrow 2NH_3$
- (ii) $2NH_3 \leftrightarrow N_2 + 3H_2$
- (iii) $N_2 + O_2 \leftrightarrow 2NO$
- (iv) $C_2H_5OH + HCl \leftrightarrow C_2H_5Cl + H_2O$

Solution to trial 1

- (i) $\frac{[NH_3]^2}{[H_2]^3[N_2]}$ units = $\frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}]^3[mol\,dm^{-3}]} = mol^{-2}dm^6$
- (ii) $\frac{[H_2]^3[N_2]}{[NH_3]^2}$ units = $\frac{[mol\,dm^{-3}]^3[mol\,dm^{-3}]}{[mol\,dm^{-3}]^2} = mol^2dm^{-6}$
- (iii) $\frac{[NO]^2}{[N_2][O_2]}$ units = $\frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}][mol\,dm^{-3}]} = \text{unitless}$
- (iv) $\frac{[C_2H_5Cl][H_2O]}{[C_2H_5OH][HCl]}$ units = $\frac{[mol\,dm^{-3}][mol\,dm^{-3}]}{[mol\,dm^{-3}][mol\,dm^{-3}]} = \text{unitless}$

Implication of K_c

When K_c is high it implies that there are more products at equilibrium than the reactants

Application of equilibrium constant K_c

To calculate the amounts of the reactants and product at equilibrium

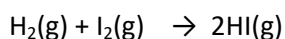
Summary of characteristics of equilibrium

- Occurs at constant temperature
- Occurs in closed system
- It is dynamic equilibrium

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Example 1

Hydrogen reacts with iodine according to the following equation



A mixture of 0.8 moles of hydrogen and 0.6 moles of iodine was allowed to react in a sealed tube at 450°C at equilibrium 0.2 moles of iodine had reacted.

- (i) Write the expression for the equilibrium constant, K_c for the reaction

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

- (ii) Calculate the value of K_c (2marks)

First we calculate the moles at equilibrium
mole of I_2 at equilibrium = 0.6 - 0.2 = 0.4 moles

Moles of H_2 at equilibrium

Mole of H_2 that reacted = moles I_2 that reacted
= 0.2 moles

Thus, mole of H_2 at equilibrium = 0.8 - 0.2
= 0.6 moles

Moles of HI at equilibrium

1 mole of I_2 that reacted produces 2 moles of HI

∴ 0.2 moles of I_2 produced 0.4 mole of HI

Secondly, we substitute in K_c expression

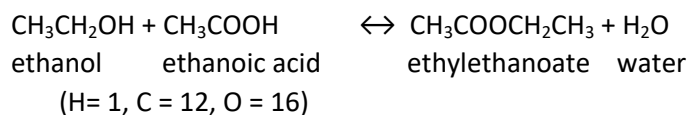
$$K_c = \frac{[0.4]^2}{[0.6][0.4]} = 0.67$$

Example 2

- (i) When 8.28g of ethanol were heated with 60g of ethanoic acid, 49.74g of the acid remained at equilibrium. Calculate K_c

- (ii) What mass of ethylethanoate should be present in equilibrium mixture formed from 13.8g of ethanol and 12g of ethanoic acid

Ethanol and ethanoic acid react as follow:



Solution

- (i) Relative molecular mass of ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ = 46
Initial moles of ethanol = $\frac{8.28}{46}$ = 0.18 moles

- Relative molecular mass of ethanoic acid, CH_3COOH = 60
Initial moles of ethanoic acid = $\frac{60}{60}$ = 1 moles

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$$\text{Final moles of ethanoic acid} = \frac{49.74}{60} = 0.829 \text{ moles}$$

From the reaction equation

Moles of ethanoic acid that reacted	=	Moles of ethanol that reacted	=	Moles of ethylethanoate that formed
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$$\text{Mole of ethanoic reacted} = 1 - 0.829 = 0.171 \text{ moles}$$

$$\text{Moles of water formed} = \text{moles of ethanoic acid reacted} = 0.171 \text{ moles}$$

$$\begin{aligned} \text{moles of ethanol that remained} &= 0.18 - 0.171 \\ &= 0.009 \text{ moles} \end{aligned}$$

$$K_c = \frac{[\text{ethylethanoate}][\text{water}]}{[\text{ethanoic acid}][\text{ethanol}]}$$

$$= \frac{0.171 \times 0.171}{0.829 \times 0.009} = 3.92$$

$$(ii) \quad 13.8 \text{ g of ethanol} = \frac{13.8}{46} = 0.3 \text{ moles}$$

$$12 \text{ g of ethanoic acid} = \frac{12}{60} = 0.2 \text{ moles}$$

Let the mass of ethylethanoate that formed be x moles; employing K_c for part (i)

$$3.92 = \frac{x^2}{(0.2-x)(0.3-x)}$$

$$\text{or } 2.92x^2 - 1.96x + 0.235 = 0$$

Using the general quadratic equation

$$x = 0.514 \text{ or } 0.158$$

The first value is inadmissible, since the number of moles of alcohol or acid which reacted cannot exceed the initial amount

$$\text{Hence } x = 0.158 \text{ moles}$$

Amount of ethylethanoate formed

$$= 0.158 \text{ moles}$$

$$\text{or } = 0.158 \times 88 = 13.9 \text{ g}$$

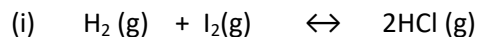
Trial 2

When 6.22 moles of hydrogen were heated with 5.71 moles of iodine in a sealed tube at 356°C it was found that 9.60 moles of hydrogen iodide were present at equilibrium. Calculate

- the equilibrium constant
- the moles of hydrogen iodide in equilibrium mixture formed by heating 6.41 moles of hydrogen and 10.40 moles of iodine at 356°C

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Solution to trial 2



Initially	6.22	5.71	-
At equilibrium	1.42	0.91	9.60

Working

$$\text{Mole of H}_2 \text{ reacted} = \frac{\text{moles of HI}}{2} = \frac{9.6}{2} = 4.8$$

$$\text{Moles of H}_2 \text{ remained} = 6.22 - 4.8 = 1.42 \text{ moles}$$

$$\text{moles of I}_2 \text{ reacted} = \text{moles of H}_2 \text{ reacted} = 4.8 \text{ moles}$$

$$\text{moles of I}_2 \text{ remained} = 5.71 - 4.8 = 0.91 \text{ moles}$$

$$K_c = \frac{9.6^2}{1.42 \times 0.91} = 71.32$$

(ii) Let the moles of HI formed be $2x$

	$\text{H}_2(\text{g})$	$+ \text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initially	6.41	10.40		-
At equilibrium	$(6.41-x)$	$(10.40-x)$		$2x$

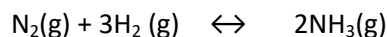
$$K_c = 71.32 = \frac{[2x]^2}{[6.41-x][10.40-x]}$$

$$x = 5.96$$

$$\text{Moles of HI} = 5.96 \times 2 = 11.92 \text{ moles}$$

Trial 3

Nitrogen reacts with hydrogen according to the following equation



- (a) Write expression for equilibrium constant, K_c
(b) Stoichiometric amounts of nitrogen and hydrogen were reacted in a 2litre vessel. At equilibrium, 0.8moles of ammonia was formed

Calculate

- (i) the amount of hydrogen at equilibrium
(ii) the value of equilibrium constant, K_c .

Solution to trial 3

(i) $\frac{[NH_3]^2}{[H_2]^3[N_2]}$

(ii)	Equation	$N_2(g)$	+	$3H_2(g)$	\leftrightarrow	$2NH_3$
	Initially	1		3		-
	Moles at equilibrium	0.6		1.8		0.8
	Concentration at equilibrium	$\frac{0.6}{2} = 0.3$		$\frac{1.8}{2} = 0.9$		$\frac{0.8}{2} = 0.4$

Working

Mole H_2 that reacted

2moles of NH_3 are formed by 3 mole of H_2 .

0.8 moles of NH_3 are formed by $\frac{3 \times 0.8}{2} = 1.2$

Moles of H_2 at equilibrium = $3 - 1.2 = 1.8$ moles

Mole N_2 that reacted

1moles of NH_3 are formed by 3 mole of N_2 .

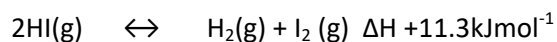
0.8 moles of NH_3 are formed by $\frac{1 \times 0.8}{2} = 0.4$

Moles of N_2 at equilibrium = $1 - 0.4 = 0.6$ moles

$$K_c = \frac{[0.4]^2}{[0.9]^3[0.3]} = 0.73$$

Trial 4

Hydrogen iodide decomposes when heated according to equation



- (a) Write an expression for equilibrium constant, K_c for the reaction (1mark)
- (b) 1.54g of HI was heated in a 600 cm^3 bulb at 530°C . When equilibrium was attained, the bulb was rapidly cooled to room temperature and broken down under potassium iodide solution. The iodine formed from decomposition required 67.0 cm^3 of 0.1M sodium thiosulphate solution.

Calculate

- (i) the number of moles of HI in 1.54g (1mark)
- (ii) number of moles of iodine formed when hydrogen iodide decomposed (3marks)
- (iii) The value of K_c
- (c) State what would be the effect on K_c if
- (i) the temperature was raised from 530°C to 800°C
- (ii) the volume of the bulb was increased to 1200 cm^3 .

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Solution to trial 4

$$(a) K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$(b) (i) HI = 1 + 127 = 128$$

$$\text{Moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.54}{128} = 0.012 \text{ moles}$$

$$(ii) \text{ Mole of sodium thiosulphate} = \frac{67 \times 0.1}{1000} = 0.0067 \text{ moles}$$

$$\text{Moles of iodine} = \frac{\text{moles of thiosulphate}}{2} = \frac{0.0067}{2} = 0.00335 \text{ moles}$$

$$\text{Mole of hydrogen formed} = \text{moles of iodine} = 0.00335 \text{ moles}$$

$$\text{Moles of HI decomposed} = \text{moles of iodine formed} \times 2 = 0.00335 \times 2 = 0.0067$$

$$\text{Moles of HI at equilibrium} = 0.012 - 0.0067 = 0.0053$$

$$(iii) K_c = \frac{0.00335 \times 0.00335}{[0.0053]^2} = 0.4$$

Since there is no change in number of moles of gas from left to the right, the volume of the container does not affect the value of K_c

$$(c) (i) K_c \text{ increases}$$

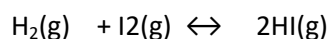
$$(ii) K_c \text{ remains unchanged}$$

Trial 5

1mole of H_2 and 1mole of I_2 were introduced into 2litre vessel at temperature at which the equilibrium constant is 55.3. How many moles of H_2 , I_2 and HI are there after equilibrium has been established.

Solution to trial 5

Let the moles of HI = 2x



$$\text{Initially} \quad 1 \quad 1 \quad -$$

$$\text{At equilibrium} \quad 1-x \quad 1-x \quad 2x$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[2x]^2}{[1-x][1-x]} = 55.3$$

$$x = 0.79$$

$$\text{Moles of } H_2 = \text{mole } I_2 = 1 - 0.79 = 0.21 \text{ moles}$$

$$\text{Moles of HI} = 2x = 2 \times 0.79 = 1.58 \text{ moles}$$

Trial 6

A reaction occurs according to the following Stoichiometric equation $A + 2B \leftrightarrow 2C$; 3moles of A and 5moles of B were brought together in a volume of 3litres and after equilibrium has been established, 1mole of A remained. Calculate the equilibrium constant K_c for the reaction. [48]

Trial 7

A reaction occurs according to the following Stoichiometric equation $2A + B \rightleftharpoons 3C$ and has equilibrium constant of $\frac{1}{10}$. How many moles of B must be brought into contact with 5moles of A to produce at equilibrium 5moles of C.? [457]

Trial 8

5moles of ethanol, 6 moles of ethanoic acid, 6moles of ethylethanoate and 4moles of water were mixed together in a stoppered bottle at 15°C . After equilibrium had been attained the bottle was found to contain only 4 moles of ethanoic acid.

- (i) Write an equation for the reaction between ethanol and ethanoic acid to form ethylethanoate and water.
(ii) Suggest a mechanism for the reaction
- Write an expression for the equilibrium constant, K_c for this reaction
- How many moles of ethanol, ethanoic acid, ethylethanoate and water are present in the equilibrium mixture?
- What is the value for K_c for this reaction
- Suppose 1mole of ethanol, 1mole of ethanoic acid, 3 moles of ethylethanoate and 3mole of water are mixed together in a stoppered flask at 15°C . How many moles of
 - ethanol,
 - ethanoic acid
 - ethylethanoate
 - water are present

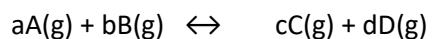
Solution to trial 8

- (i) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3$
- $K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{OH}][\text{CH}_3\text{COOH}]}$
- Ethanol = 3, ethanoic acid = 4, ethylethanoate = 8, water = 6
- $K_c = 4$
- Ethanol = 1.33, ethanoic acid = 1.33, ethylethanoate = 2.67, water = 2.67

Equilibrium Constant in terms of, K_p

When at least one of the substances in equilibrium is gases, the state of equilibrium may be defined by equilibrium constant K_p as follows

For a reaction;



$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

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where P_A, P_B, P_C, P_D are the respective partial pressures of components A, B, C and D

and $P_{total} = P_A + P_B + P_C + P_D$

$$P_A = X_A P_{total}$$

where X_A is mole fraction of A or the number of moles of component A over the total moles of components in the mixture and P_{total} is the total pressure of the system.

Implications of K_p

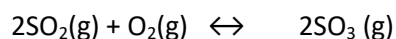
The bigger the value of K_p the higher the amount of product in the reaction mixtures

Application of K_p

Like K_c , K_p is used to predict the proportion of the products and reactants at the equilibrium point in the mixture

Example 3

At 700°C and total pressure of one atmosphere the partial pressure at equilibrium for sulphur dioxide and oxygen are 0.27 and 0.41 atmospheres respectively. Sulphur dioxide is oxidized to sulphur trioxide according to the following equation



Calculate the equilibrium constant, K_p , for the reaction (4marks)

Solution

$$\begin{aligned} \text{Partial pressure of SO}_3 &= (1 - (0.27 + 0.41)) \\ &= 0.32\text{atm.} \end{aligned}$$

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{[0.32]^2}{[0.27]^2 \times [0.41]} = 3.46\text{atm}^{-1}$$

Trial 9

1mole of hydrogen iodide at 25°C was introduced into a container of 20 liters

- Calculate the pressure of the gas, assuming ideal behavior (1mole of a gas occupies 22.4dm^3 under standard conditions).
- The sample of hydrogen iodide considered above was raised to a temperature of 300°C and partially decomposed into hydrogen and iodine gases; at equilibrium 0.1mole of iodine was found to be present
 - Write an equation for decomposition
 - Calculate the pressure of the equilibrium mixture at 300°C , assuming no volume change.
 - Calculate the equilibrium constant at 300°C
- $\Delta H_f^\circ \text{HI} = 26.5\text{kJmol}^{-1}$. Explain giving reasons how you would expect the equilibrium constant to change with temperature.

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Solution to trial 9

- (a) From $\frac{PV}{T} = \text{constant}$
 $\frac{P \times 20}{(273+25)} = \frac{1 \times 22.4}{273} \Rightarrow P = 1.2 \text{ atmospheres}$
- (b) (i) $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
 (ii) From $\frac{PV}{T} = \text{constant}$
 $\frac{P \times 20}{(273+300)} = \frac{1 \times 22.4}{273} \Rightarrow P = 2.35 \text{ atmospheres}$
- (ii) $2\text{HI}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
 Initially 1 - -
 At equilibrium 0.8 0.1 0.1
 Total mole at equilibrium = $0.8 + 0.1 + 0.1 = 1$

$$P_{\text{HI}} = X_A P = 0.8 \times 2.35 = 1.88 \text{ atmospheres}$$

$$P_{\text{H}_2} = 0.1 \times 2.35 = 0.235 \text{ atmospheres}$$

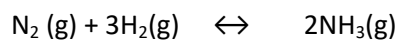
$$P_{\text{I}_2} = 0.1 \times 2.35 = 0.235 \text{ atmospheres}$$

$$K_p = \frac{P_{\text{H}_2} \cdot P_{\text{I}_2}}{P_{\text{HI}}^2} = \frac{0.235 \times 0.235}{1.88^2} = 0.016$$

- (c) K_p increases with increase in temperature because the reaction is endothermic.

Trial 10

Nitrogen reacts with hydrogen according to the following equation



- (a) Write the equation for the equilibrium constant for the reaction in terms of partial pressure and indicate units (2marks)
- (b) Stoichiometric amounts of nitrogen and hydrogen were reacted at 50 atmospheres and at equilibrium, 0.8 moles of ammonia were formed.
 calculate
 (i) the amount of hydrogen at equilibrium (2½ marks)
 (ii) The value of equilibrium constant for the reaction (4 ½ marks)

Solution to trial 10

(a) $K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \cdot P_{\text{H}_2}^3}$ units: $\frac{\text{atm}^2}{\text{atm} \cdot \text{atm}^3} = \text{atm}^{-2}$

- (b) (i)
- | | | | | | |
|----------------------|------------------------|---|-------------------------|-------------------|----------------|
| Equation | $\text{N}_2(\text{g})$ | + | $3\text{H}_2(\text{g})$ | \leftrightarrow | 2NH_3 |
| Initially | 1 | | 3 | | - |
| Moles at equilibrium | 0.6 | | 1.8 | | 0.8 |

Working

Mole H₂ that reacted

2moles of NH₃ are formed by 3 mole of H₂.

0.8 moles of NH₃ are formed by $\frac{3 \times 0.8}{2} = 1.2$

Moles of H₂ at equilibrium = 3 – 1.2 = 1.8 moles

Mole N₂ that reacted

1moles of NH₃ are formed by 3 mole of N₂.

0.8 moles of NH₃ are formed by $\frac{1 \times 0.8}{2} = 0.4$

Moles of N₂ at equilibrium = 1 – 0.4 = 0.6 moles

(ii) Total moles of a gas at equilibrium = 0.6 + 1.8 + 0.8 = 3.2

From $P_A = X_A P$

$$P_{NH_3} = \frac{0.8 \times 50}{3.2} = 12.5 \text{ atm}$$

$$P_{H_2} = \frac{1.8 \times 50}{3.2} = 28.125 \text{ atm}$$

$$P_{N_2} = \frac{0.6 \times 50}{3.2} = 9.375 \text{ atm}$$

$$K_p = \frac{12.5^2}{28.125^3 \cdot 9.375} = 7 \times 10^{-5} \text{ atm}$$

Trial 11

Consider the following reaction



At a certain temperature, analysis of an equilibrium mixture of the gases yielded the following results

$$P_{H_2} = 2.5 \times 10^{-1} \text{ atm.}$$

$$P_{I_2} = 1.6 \times 10^{-1} \text{ atm.}$$

$$P_{HI} = 4.0 \times 10^{-1} \text{ atm.}$$

- Calculate the equilibrium constant for the reaction and state its units.
- In second experiment at the same temperature, iodine and hydrogen were mixed together with each gas at a partial pressure of 3×10^{-1} atm. what are the partial pressures of hydrogen, iodine and HI at equilibrium?
- In the third experiment at the same temperature, pure hydrogen iodide was injected into the flask at a pressure of 6×10^{-1} atm. What are the partial pressures of hydrogen, iodine and hydrogen iodide at equilibrium?
- What effect, if any, will decreasing the temperature have on the value of K_p ? Explain your answer.

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Solution to trial 11

$$(a) K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \frac{0.4^2}{0.25 \times 0.16} = 4$$

$$(b) P_t = 0.6$$

Partial pressure (P_{H_2}) of H_2 = partial pressure (P_{I_2}) of I_2 at equilibrium

$$\Rightarrow P_{HI} = 0.6 - 2P_{H_2}$$

$$\Rightarrow K_p = \frac{(0.6 - P_{H_2})^2}{P_{H_2}^2} = 4$$

$$P_{H_2} = P_{I_2} = 0.15 \text{ atm}$$

$$P_{HI} = 0.30 \text{ atm}$$

$$(c) P_t = 0.3 + 0.3 = 0.6$$

Partial pressure (P_{H_2}) of H_2 = partial pressure (P_{I_2}) of I_2 at equilibrium

$$\Rightarrow P_{HI} = 0.6 - 2P_{H_2}$$

$$\Rightarrow K_p = \frac{(0.6 - P_{H_2})^2}{P_{H_2}^2} = 4$$

$$P_{H_2} = P_{I_2} = 0.15 \text{ atm}$$

$$P_{HI} = 0.30 \text{ atm}$$

(d) Decreasing temperature increases K_p because the reaction is exothermic

Trial 12

0.196g nitrogen and 0.146g hydrogen were heated together until equilibrium is established at a given temperature. The pressure found at equilibrium was found to be 90% its value at the beginning. Calculate the percentage composition by volume of the resulting mixture ($H = 1, N = 14$)

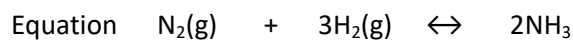
Solution to trial 12

$$\text{Moles of } N_2 = \frac{0.196}{28} = 0.007$$

$$\text{Mole of } H_2 = \frac{0.146}{2} = 0.073$$

Total initial moles of a gas = $0.007 + 0.073 = 0.08$ moles

Let the mole so NH_3 formed at equilibrium = $2x$



$$\text{Initially} \quad 0.007 \quad 0.073 \quad -$$

$$\text{Moles at equilibrium} \quad 0.007 - x \quad 0.073 - 3x \quad 2x$$

$$\text{Total moles at equilibrium} = 0.007 - x + 0.073 - 3x + 2x = 0.08 - 2x$$

Since pressure is proportional to the number of moles of a gas

$$\frac{0.8-2x}{0.08} = \frac{90}{100}$$

$$X = 0.004$$

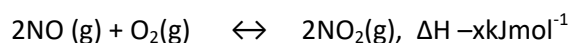
$$\%N_2 = \frac{(0.007-0.004) \times 100}{0.08-2 \times 0.004} = 4.2\%$$

$$\%H_2 = 84.7\%$$

$$\%NH_3 = 11.1\%$$

Trial 13

(a)(i) Nitrogen (II) oxide combines with O_2 at $80^\circ C$ and 200atmosphere to form Nitrogen (IV) oxide according to equation



- (i) Write an expression for the equilibrium constant K_p for the reaction
 (ii) Calculate K_p , if the mixture contained 67% nitrogen (IV) oxide (3 ½ marks)
- (b) State how the value of K_p will be affected if
 (i) Temperature is increased
 (ii) Catalyst is added

(c) The kinetic data for the reaction in (a) is shown in the table below

Initial rate/ $Nm^{-2}s^{-1}$	6.8	27.2	61.2	108
P_{NO}^2/N^2M^4	0.04	0.16	0.36	0.64

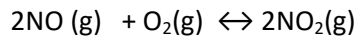
P_{NO} =the partial pressure of NO

- (i) Plot a graph of initial rate against P_{NO}^2 (03mark)
 (ii) Using a graph, determine the order of reaction with respect to nitrogen II oxide
 (iii) Give a reason for your answer
 (d) When the partial of O_2 was doubled to a new constant value, the gradient of the graph in C(i) doubles
 (i) Determine the order of reaction with respect to O_2 . Explain your answer.
 (ii) Write the rate equation for the reaction in (d)
 (iii) Calculate the rate constant when the initial rate is $170Nm^{-2}s^{-1}$, $P_{NO} = 0.1NM^{-2}$,
 $P_{O_2} = 1.36Nm^{-2} PO_2$
- (e) State the effect of the following on the rate of the reaction
 (i) Having partial of nitrogen II oxide while that of oxygen is kept constant
 (ii) Doubling partial pressure of both nitrogen II oxide and O_2 .

Solution to trial 13

$$(a)(i) K_p = \frac{P_{NO_2}^2}{P_{NO}^2 \cdot P_{O_2}} atm^{-1}$$

- (ii) let the moles of NO_2 at equilibrium be $2x$



Initially 2 1 -

At equilibrium (2-2x) (1-x) 2x

Then, $\frac{2x}{3-x} = 0.67 \Rightarrow x = 0.75$

Total moles at equilibrium = 3 - 0.75 = 2.25 moles

$$P_{\text{NO}_2} = \frac{1.5}{2.25} \times 200 = 133.3 \text{ atmospheres}$$

$$P_{\text{O}_2} = \frac{0.25}{2.25} \times 200 = 22.2 \text{ atmospheres}$$

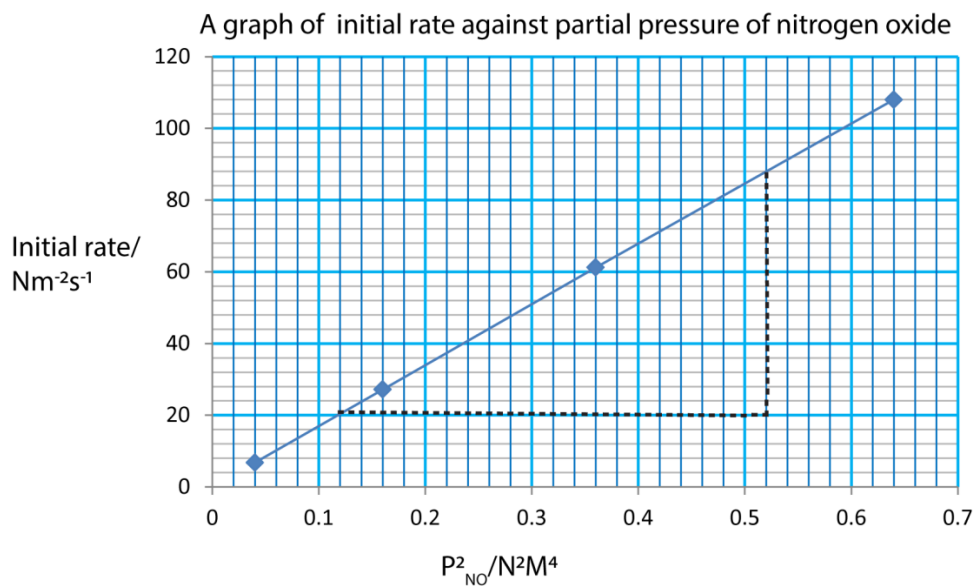
$$P_{\text{NO}} = \frac{0.5}{2.25} \times 200 = 44.4 \text{ atmospheres}$$

$$K_p = \frac{133.3^2}{44.4^2 \times 22.2} = 0.406 \text{ atm}^{-1}$$

(b) (i) K_p decreases

(ii) K_p remain unchanged

(c)(i)



(ii) 1st order

(iii) Rate is proportional to concentration

(d)(i) 1st order the rate is proportional to concentration

(ii) Rate = $K[\text{NO}][\text{O}_2]$

(iii) $K = \frac{170}{0.1 \times 1.36} = 1250 \text{ N}^{-1}\text{M}^2\text{s}^{-1}$

- (e) (i) the rate halves
 (iii) Rate is multiplied by 4

Relationship between K_c and K_p

We have already seen that equilibrium constants are normally expressed in term of concentration using the symbol K_c and that, for reaction involving gases; it is usually convenient to express the amount of gases in terms of partial pressure rather than its molar concentration using the Ideal equation

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

where p is the pressure in atmosphere, n is the number of moles, V, is the volume in cubic decimeter and T is the temperature in Kelvin. In this case R, the gas constant, has units are $\text{atmdm}^{-3}\text{K}^{-1}\text{mol}^{-1}$

$$P = [\text{gas}]RT$$

Where [gas] is the concentration of the gas in mol dm^{-3}

Thus, at constant temperature, the pressure of a particular gas is proportional to concentration

i.e. $P \propto [\text{gas}]$

This means that for equilibrium



we can either write

$$K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} \text{ or } K_p = \frac{P_{\text{HI}}^2}{P_{\text{I}_2} \times P_{\text{H}_2}}$$

Now since $P_{\text{HI}} = [\text{HI}(\text{g})]RT$

$$P_{\text{H}_2} = [\text{H}_2(\text{g})]RT$$

and $P_{\text{I}_2} = [\text{I}_2(\text{g})]RT$

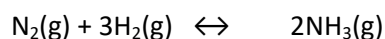
It follows that;

$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{I}_2} \times P_{\text{H}_2}} = \frac{[\text{HI}(\text{g})]^2 (RT)^2}{[\text{H}_2(\text{g})]RT \cdot [\text{I}_2(\text{g})]RT}$$

$$= \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = K_c$$

In this particular example $K_p = K_c$ and neither K_p nor K_c has units, but this is not always the case;

Consider another reaction



$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = \frac{[\text{NH}_3(\text{g})]^2 (RT)^2}{[\text{N}_2(\text{g})]RT \times [\text{H}_2(\text{g})]^3 [RT]^3}$$

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$$= \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \times [RT]^{-2}$$

$$= K_c(RT)^{-2}$$

It implies that the numerical value of K_p is the same as that of K_c only where there are the same number of moles on each side of the Stoichiometric equation.

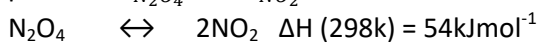
Although the SI unit of pressure is Nm^{-2} , it is standard practice to use atmospheres as pressure unit in expressing K_p values.

In general, $K_p = K_c(RT)^{\Delta n}$

where Δn = number moles on the right of the equation minus number of moles on the left.

Example 4

(a) Write an equation to show the relationship between the equilibrium constant, K_p and partial pressure $P_{N_2O_4}$ and P_{NO_2} of the reactants in the following gaseous equilibrium



solution

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

(b) State the effect, if any, on above equilibrium of

(i) increasing the pressure

Equilibrium shift from right to left leading to reduction in number of moles to fit in small volume.

(ii) raising the temperature . Give reason for your answer.

Equilibrium shifts from left to right to reduce on the increase in temperature since the forward reaction is endothermic.

(c) It was found that one dm^3 of the gaseous mixture weighed 2.777g at $50^\circ C$ and pressure of $1.01 \times 10^5 Nm^{-2}$ (1 atmosphere)

Calculate

(i) The fraction of N_2O_4 that dissociated

solution

$$\text{Moles of } N_2O_4 \text{ initially} = \frac{2.777}{(14 \times 2 + 16 \times 4)}$$

$$= 0.0302 \text{ moles}$$

Moles at equilibrium

From ideal gas equation, $PV = nRT$

$$n = \frac{1.01 \times 10^5 \times 10^{-3}}{8.31 \times (273+50)}$$

$$n = 0.03763 \text{ moles}$$

If α is the fraction ionizes

Then

[1 mole of a gas occupies $22.4dm^3$ at s.t.p]



Initial moles, 0.0302 0

mole at equilibrium 0.0302(1- α) 0.0302(2 α)

total moles at equilibrium

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$$= 0.0302(1-\alpha) + 0.0302(2\alpha) = 0.03763 \text{mole}$$

$$\Rightarrow \alpha = 0.25$$

Mole

(ii) The percentage of NO_2 molecules in the mixture

solution:

$$= \frac{2 \times 0.25 \times 0.0302}{0.03763} \times 100 = 40\%$$

(iii) The value of K_p

$$P_{\text{NO}_2} = \frac{40 \times 1.01 \times 10^5}{100} = 40400 \text{Nm}^{-2}$$

$$P_{\text{N}_2\text{O}_4} = 1.01 \times 10^5 - 40400 = 60600 \text{Nm}^{-2}$$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{40400^2}{60600} = 2.69 \times 10^4 \text{Nm}^{-2}$$

Factors affecting equilibriums

these are

1. Temperature
2. Pressure
3. Catalyst
4. Concentration

The effect of the above factors on equilibrium position for the equilibrium mixture can be explained qualitatively by Le Chatelier's Principles that states that; 'if a system in equilibrium is subjected to a change, processes occur which tend to counteract the change imposed'.

Alternatively, 'if the concentration of one of the reacting substance is altered, the equilibrium will shift in such a way as to oppose the change in concentration'

Effect of temperature

The effect of temperature on equilibrium depends on whether the reaction is endothermic or exothermic.

- (i) For exothermic reactions (ΔH^0 negative) equilibrium position shifts to the left as temperature rise leading to a reduction in equilibrium constants
- (ii) for endothermic reactions (ΔH^0 positive) equilibrium position shift the right as temperature increases leading to increase in the value of equilibrium constants.

Alternatively, the direction of change is given by Vant Hoff's Law of mobile equilibrium: "if a system is in equilibrium raising the temperature will favor that reaction which is accompanied by absorption of heat, and lowering temperature will favor that reaction which is accompanied by evolution of heat.

NB. It must be emphasized that it is only temperature that can alter the equilibrium positions and values of equilibrium constants among the factors states above whereas other factors alter only the equilibrium positions.

Effect of a catalyst

Catalysts have no effect on the equilibrium constants K_c or K_p because they increase the rate of both forward and backward reaction in an equilibrium equally. However, they increase the rate at which equilibrium is attained.

Effect of concentration on equilibrium mixture

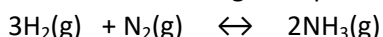
Variations in concentration of the reactant at constant temperature has no effect on the value of equilibrium constants K_c and K_p . However, if the concentration of one of the reacting substance in a reversible equilibrium is altered, the equilibrium will shift in such away as to oppose the change in concentration.

Effect of pressure changes on equilibrium

1. Pressure has appreciable effects when at least one of the reactant or product in a reversible reaction is a gas because unlike liquids and solids, gases are compressible.
2. The effect of pressure on equilibrium where reactants and/or products are in gaseous form depends on whether there is change in the number of molecules of the gases as the reaction proceeds from left to right.
 - (i) In general, for gaseous reaction in which there is a change in the number of molecules, increase in pressure favors a reaction which produces fewer molecules or number of moles of the products.
 - (ii) Pressure has no effect on those gaseous reactions in which there is no change in number of molecules as the reaction shifts from left to the right. e.g.
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$$
3. Generally high pressure increases the rate at which equilibrium is attained in gaseous mixture because it increases the rate of collision of the reacting molecules.
4. Pressure has no effect on numerical values of K_c and K_p at constant temperature although the equilibrium concentration of reactants and product can vary over a wide range.

Example 5

Hydrogen reacts with nitrogen to produce ammonia according the following equation



- (a) Write an expression for the equilibrium constant, K_c (1mark)

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}$$

- (b) State, giving reasons, what would happen to the value of the equilibrium constant when

- (i) Pressure is increased at constant temperature (3marks)

There will be no effect on the equilibrium constant because only temperature varies the value of the constant.

- (ii) argon is added to the reaction mixture at constant pressure (2marks)

There will be n effect on the equilibrium constant as long as temperature is constant.

- (ii) Argon is added to the reaction mixture at constant volume (3marks)

This will increase pressure but there will be no change on the value of equilibrium constant of mixture because this value is not altered by pressure.

Trial 14

(a) Manganese sulphate reacts with acids according to the following equation



State, giving a reason, what would happen to the equilibrium if

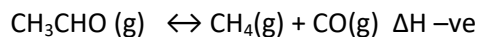
- (i) Water is added to the equilibrium mixture (2marks)
- (ii) Hydrogen chloride is bubbled into the equilibrium mixture (2marks)
- (iii) pH of equilibrium mixture is increased.

Solution to trial 14

- (i) Equilibrium shifts to the left to reduce the concentration of water added.
- (ii) Equilibrium shifts to the right to reduce the concentration of hydrogen ions.
- (iii) Equilibrium shifts to the left to produce hydrogen ions and lower the pH.

Trial 15

Ethanol decomposes according to the equation



(a) Write an expression for the equilibrium constant, K_p for the reaction

(b) Explain how K_p would be affected if

- (i) the temperature is increased
- (ii) Pressure is increased

Solution to trial 15

$$(a) K_p = \frac{P_{\text{CH}_4} \times P_{\text{CO}}}{P_{\text{CH}_3\text{CHO}}}$$

- (b) (i) K_p decrease because increasing temperature shifts equilibrium from right to the left since the reaction is endothermic.
- (ii) K_p remains unchanged since pressure has no effect on the value of K_p .

Trial 16

Phosphorous (V) chloride when heated decompose according to the following equation



A sample of pure phosphorus (V) chloride was heated in a closed vessel to 250°C. When equilibrium was attained the vessel was found to contain 40.7% chlorine

(a) Calculate

- (i) the molar concentration of phosphorus (V) chloride at equilibrium (4 ½ marks)
- (ii) the equilibrium constant K_c for the reaction at 250°C (2 ½ marks)

Solution to trial 16

Let the mole of PCl_5 decomposed be x



Initially 1 - -

At equilibrium $1 - x$ x x

Total moles = $1 - x + x + x = 1 + x$

$$\% \text{Cl}_2 = \frac{x}{1+x} = \frac{40.7}{100} \Rightarrow x = 0.69$$

Mole of PCl_5 at equilibrium = $1 - 0.69 = 0.31$

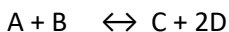
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{0.69 \times 0.69}{0.31} = 1.54 \text{ mol dm}^{-3}$$

Trial 17

(a) Discuss the effect of each of the following on the position of a reversible reaction, the rate of at which the equilibrium is attained and the value of the equilibrium constant.

- temperature (5marks)
- pressure (7marks)
- atalyst (2marks)

(b) Write an expression for the equilibrium constant K_c or K_p as appropriate to the following reactions at equilibrium and indicate units in each case

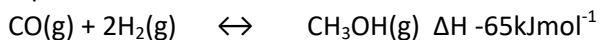


where under the conditions of experiment

- A, B, C, and D are all gases.
- A, B, C and D are all liquids
- A, B, C are solids and D is a gas

Trial 18

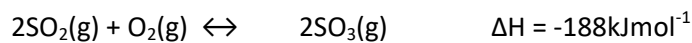
(a) In the manufacture of methanol, carbon monoxide and hydrogen react according to the following equation



- State the optimum temperature and pressure for the reaction. Explain your answer (3marks)
 - Calculate the standard enthalpy of formation of methanol (standard enthalpy of formation of Carbon monoxide = -108 kJ) (2marks)
- (b) (i) Write an expression for the equilibrium constant, K_p (1mark)
- At a certain equilibrium point, 15% of carbon monoxide had reacted. Calculate the pressure ($K_p = 4 \times 10^{-10} \text{ kP}^{-2}$)

Trial 19

During the manufacture of sulphuric acid by contact process, sulphur dioxide is oxidized to sulphur (VI) oxide according to the following equation.



State the effect on the yield of sulphur (VI) oxide if

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- (i) Temperature was increased
- (ii) Pressure was decreased
- (iii) Concentration of sulphur dioxide was increased

Equilibrium in solution, K_a , K_b , K_w , K_h , K_{in}

Ionization of a weak acid

A weak acid is one that is partially ionized in water. For instance a weak acid HA will ionize in water as follow



$$K_c = \frac{[H^+][A^-]}{[HA][H_2O]}$$

The concentration of H_2O is almost constant such that it can be incorporated in K_c to give another constant K_a

$$\text{thus, } K_a = K_c[H_2O] = \frac{[H^+][A^-]}{[HA]}$$

The greater the extent of dissociation, the greater are $[H^+]$ and $[A^-]$ in solution; the greater the K_a , and the stronger is the acid.

Alternatively, the strength of the acid is expressed in terms of pH. The 'p' in pH comes from the German word 'potenz' meaning power and 'H' from $[H^+]$. The pH of solution is the negative logarithm to base ten of the molar concentration of hydrogen ions.

$$\text{i.e., } pH = -\log_{10} [H^+]$$

Example 6

The pH of 0.1M ethanoic (acetic) acid, CH_3COOH , is 3.40 at $25^\circ C$. What is the dissociation constant of ethanoic acid at this temperature?

Solution

Equation



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

Since the concentration of H^+ ions from water is much smaller than the concentration of those from acid; $[H^+] \approx [CH_3COO^-] = \text{antilog}-3.4$

$$= 4.0 \times 10^{-4} \text{ mol dm}^{-3}$$

and $[CH_3COOH] = 0.01 - [H^+] \approx 0.01$

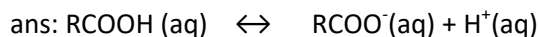
$$\text{Thus, } K_a = \frac{[4 \times 10^{-4}][4 \times 10^{-4}]}{[0.01]} \\ = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$$

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Example 7

RCO₂H is a weak acid

(a) Write the equation for the ionization of the weak acid RCOOH in water (1mark)



(b) Write the expression for the ionization constant K_a, for the acid.

$$K_a = \frac{[\text{H}^{\oplus}][\text{RCOO}^{\ominus}]}{[\text{RCOOH}]}$$

(c) Calculate the hydrogen ion concentration of 0.25M solution for the acid (K_a = 1.8 x 10⁻⁵) (4marks)

Solution

Let [H⁺] = x

Also, [H⁺] = [RCOO⁻] = x

[RCOOH] = [0.25 - x] ≈ 0.25 moldm⁻³, since the concentration of H⁺ is very small.

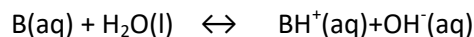
$$\Rightarrow 1.8 \times 10^{-5} = \frac{x^2}{0.25}$$

$$\Rightarrow x = 2.12 \times 10^{-3} \text{ moldm}^{-3}.$$

∴ Concentration of H⁺ = 2.12 x 10⁻³ moldm⁻³

Ionization of weak base

A base is a substance that abstracts a proton from water or dissociates in water to produce hydroxyl ion. Like weak acid, weak base are only partially dissociated in water.



$$K_c = \frac{[\text{BH}^{\oplus}][\text{OH}^{\ominus}]}{[\text{B}][\text{H}_2\text{O}]}$$

The concentration of H₂O is almost constant such that it can be incorporated in K_c to give another constant K_b

$$\text{thus, } K_b = K_c [\text{H}_2\text{O}] = \frac{[\text{BH}^{\oplus}][\text{OH}^{\ominus}]}{[\text{B}]}$$

Like K_a, K_b, is a function of temperature, and the higher the K_b, the stronger the base.

Example 8

(a) At 25°C ammonia has a base ionization constant K_b = 1.8 x 10⁻⁵ moldm⁻³.

$$K_b = \frac{[\text{NH}_4^{\oplus}][\text{OH}^{\ominus}]}{[\text{NH}_3]}$$

(b) Calculate the concentration of [OH⁻] in 0.1M ammonia solution at 25°C. state any assumption

Log [OH⁻] be x

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Assumption: OH^- ions from ionization of water are negligible compared to those from ionization of ammonia

$$[\text{OH}^-] = [\text{NH}_4^+] = x$$

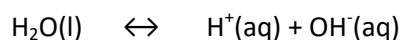
$$[\text{NH}_3] = (0.1 - x) \cong 0.1 \text{ since } x \text{ is very small}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.1} = 1.8 \times 10^{-5}$$

$$\Rightarrow x = 1.34 \times 10^{-3} \text{ mol dm}^{-3}$$

Dissociation of water

Water ionizes as follows



$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The concentration of H_2O is constant and is incorporated in the value of K_c to give a new constant K_w .

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

K_w is ionic product for water, at 25°C pure water has $K_w = 1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$.

Application of K_w

It is used to determine the pH of bases

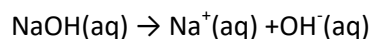
$$\text{Where } [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} \text{ or } \frac{1 \times 10^{-14}}{[\text{OH}^-]}$$

Example 9

Calculate the pH of 0.1M NaOH solution

Solution

Sodium hydroxide dissociate in water as follows



$$[\text{OH}^-] = [\text{NaOH}] = 0.1 \text{ moles}$$

$$[\text{H}^+] = \frac{10^{-14}}{0.1} = 10^{-13}$$

$$\text{pH} = -\log[\text{H}^+] = \log[10^{-13}] = 13$$

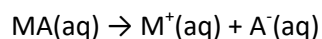
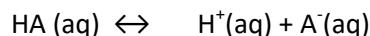
Buffers

These are solutions that resist changes in pH on addition of small amounts of either the acid or base.

Buffers are usually made of either a mixture of a weak acid and its salt with strong base (e.g. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^-\text{Na}^+$) or a mixture of a weak base and its salt with a strong acid (e.g. $\text{NH}_3 + \text{NH}_4\text{Cl}$)

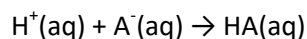
Mechanism of buffers

Consider a hypothetical weak acid, HA, in a solution with its salt MA. In this solution, HA, will be very slightly dissociated whilst MA is fully dissociated into ions;

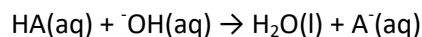


Hence the mixture contains a relatively high concentration of un-ionized HA (acid) and relatively high concentration of A^- (base)

If an acid is added to this system, the H^+ ions in the acid will combine with A^- ions to form HA thus removing nearly all the added H^+ ions and keeping the pH relatively unchanged.



When an alkali is added to a system, the added OH^- ions combine with the acid to produce water



By having the reserves of HA and A^- in buffer changes resulting from the addition of acid or alkali are minimized.

Calculating the pH of buffer solution

In a buffer composed of a weak acid HA and its salt MA



The expression for dissociation constant of HA is written as

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

In the buffer mixture $[\text{HA}] \cong [\text{acid}]$ since the acid will be very slightly dissociated in presence of its salt and $[\text{A}^-] \approx [\text{salt}]$ since the salt is fully dissociated

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

Introducing logarithms

$$\log_{10}[\text{H}^+] = \log_{10}K_a + \log_{10} \frac{[\text{acid}]}{[\text{salt}]}$$

Multiplying by - 1 on both sides

$$-\log_{10}[\text{H}^+] = -\log_{10}K_a - \log_{10} \frac{[\text{acid}]}{[\text{salt}]}$$

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$$\text{or } \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{salt}]}{[\text{acid}]}$$

Similarly, a buffer composed of a weak base (e.g. NH_3) and its salt with a strong acid (e.g. NH_4Cl)

$$\text{p}^{\text{OH}} = \text{p}K_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{Also. } \text{p}^{\text{OH}} + \text{p}^{\text{H}} = \text{p}K_w = 14$$

Example 10

Calculate the pH of the buffer made by adding 3.28g of sodium ethanoate to 1dm^3 of 0.01Methanoic acid.

$$K_a(\text{CH}_3\text{COOH}) = 1.75 \times 10^{-5} \text{mol dm}^{-3}$$

Solution

$$[\text{Acid}] = [\text{CH}_3\text{COOH}] = 0.01\text{M}$$

$$[\text{Salt}] = [\text{CH}_3\text{COONa}] = \frac{3.28}{82} = 0.04\text{M}$$

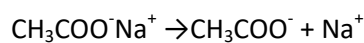
$$\begin{aligned} [\text{H}^+] &= K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COONa}]} = 1.7 \times 10^{-5} \times \frac{0.04}{0.01} \\ &= 6.8 \times 10^{-5} \text{mol dm}^{-3} \end{aligned}$$

$$\text{pH} = -\log_{10}[\text{H}^+] = 4.17$$

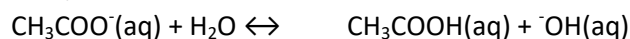
Hydrolysis of salts

It is the reaction of a salt with water to produce either acid or alkaline solution. The type of hydrolysis depends on the nature of salt.

- (i) A salt formed by reacting a weak acid and a strong base hydrolyzes to give an alkaline solution. for example, sodium ethanoate is highly dissociated while water is very slightly ionized. The reaction occurs in solution as follows:



then,



$$K_c = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]}$$

but $[\text{H}_2\text{O}]$ is almost constant

$$\text{Thus, } K_c(\text{H}_2\text{O}) = K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

K_h is called hydrolysis constant of a salt, the higher the K_h the more hydrolyzed the salt.

Expression of K_h in terms of K_w and K_a

Multiplying $[\text{H}^+]$ through the numerator and denominator give;

$$K_h = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} \times [\text{H}^+][\text{OH}^-] = \frac{K_w}{K_a}$$

- (ii) A salt of a weak base and a strong acid hydrolyzes in water to give acid solution e.g. NH_4Cl dissociate in water as follows

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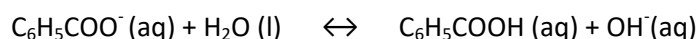


$$K_h = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \text{ or } \frac{K_w}{K_b}$$

Example 11

Sodium benzoate undergoes hydrolysis when dissolved in water

(a) Write an equation for hydrolysis of sodium benzoate



(b) Write an expression for the hydrolysis constant K_h .

$$K_h = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]}$$

(c) The hydrolysis constant of sodium benzoate is $1.6 \times 10^{-5} \text{ mol}^{-1}$.

(i) Calculate the concentration of the hydroxide ions in a 0.10M sodium benzoate at 25°C ($K_w = 1 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$) (4marks)

Solution

Let the concentration of OH^- ions be x

$$1.6 \times 10^{-5} = \frac{x^2}{0.1}$$

$$\Rightarrow x = 1.265 \times 10^{-3} \text{ mol dm}^{-3}$$

(ii) $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{1.265 \times 10^{-3}} = 7.9 \times 10^{-12} \text{ mol dm}^{-3}$

$$\Rightarrow \text{pH} = 11.1$$

(iii) State any assumption made in c(i) above

Hydrogen ions or hydroxyl ions from ionization of water are negligible

Solubility of sparingly soluble ionic solid in water

When a sparingly soluble salt such as silver chloride or barium sulphate, is added to water, a little dissolves and produces ions in solution. Equilibrium is established between the ions and the solid salt when the rate at which ions leave the crystal frame work of the solid is equal to the rate at which they are deposited again. Since the solubility is very small, the ions present in the liquid are few in number and are so far apart that they are free from mutual interference. We can therefore say that in the very dilute saturated solution the solution is completely dissociated.

With a solution of a sparingly soluble electrolyte A_xB_y in contact with the solid the dissociation can be expressed as follows



$$K_c = \frac{[\text{A}^{y+}]^x [\text{B}^{x-}]^y}{[\text{A}_x\text{B}_y][\text{aq}]}$$

Since the salt is only slightly dissociated in water, the $[\text{A}_x\text{B}_y]$ and $[\text{aq}]$ are constant

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$$\text{thus, } K_c[A_xB_y][aq] = K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

The constant K_{sp}/K_s is the solubility product of the electrolyte, A_xB_y . The solubility product of a sparingly soluble electrolyte is the product of the concentration of ions in a saturated solution raised to corresponding Stoichiometric ration in the salt. The higher the K_{sp} is the higher the solubility of the salt.

Example 12

The solubility of silver chloride at 18°C is $1.46 \times 10^{-3} \text{ gdm}^{-3}$. What is the solubility product

(Ag = 108, Cl = 35.5)

Solution

Note that in the calculation of solubility products the concentrations are expressed in **moledm⁻³ or mol l⁻¹**

Mass of 1mole of AgCl = 108 + 35.5 = 143.5g

$$\text{Solubility of AgCl} = \frac{1.46 \times 10^{-3}}{143.5} = 1.0 \times 10^{-5} \text{ moldm}^{-3}$$

Since one 'molecule' of silver chloride furnishes on dissociation one Ag^+ ion and one Cl^- ion, and since the dissolved silver chloride is completely dissociated in ions

$$\begin{aligned} K_{sp} &= [\text{Ag}^+][\text{Cl}^-] = (1 \times 10^{-5})(1 \times 10^{-5}) \\ &= 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

Example 13

The solubility of calcium hydroxide in water at 20°C is 2.78 gdm^{-3} . What is the solubility product? (Ca = 40, O = 16, H = 1)

Solution

$$\text{Molarity of Ca(OH)}_2 = \frac{2.78}{[40+2(16+1)]} = 0.0376 \text{ moldm}^{-3}$$

$$[\text{Ca}^{2+}] = 0.0376 \text{ moldm}^{-3}$$

$$[\text{OH}^-] = 2 \times 0.0376 = 0.0752 \text{ moldm}^{-3}$$

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{OH}^-]^2 = 0.0376 \times (0.0752)^2 \\ &= 2.13 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

Limitation to the solubility product concept

1. Salts like potassium nitrate of relatively high solubility, do not possess solubility products because the law of mass action does not hold in their case. The solubility product concept is only valid for saturated solution in which the total concentration of ions is no more than about 0.01M
2. The solubility product constant, like all other equilibrium constants change with temperature; consequently, the temperature at which solubility product is measured should always be specified unless it relates to the standard temperature of 298K or 25°C.

Application of solubility product concept

(a) The common ion effect

This is the reduction in the solubility of a sparingly soluble salt in a solution in which it has a common ion.

Although the solubility product of a particular salt is constant at a constant temperature, the concentrations of the individual ions may vary over a very wide range. When a saturated solution is obtained by dissolving the pure salt in water the concentration of the ions produced are in the ratio determined by the stoichiometry of the compound. E.g. concentration of Ag^+ and CrO_4^{2-} ions in pure saturated silver chromate solution must be in ratio 2:1. However, when a saturated solution is obtained by mixing two solutions containing a common ion (such as Ag_2CrO_4 and AgNO_3) there may be a big difference in the concentration of ions of any sparingly soluble electrolyte. In this case, the solubility product is used to determine the concentration of the ions in solution.

Example 14

Calculate the solubility of BaSO_4 in

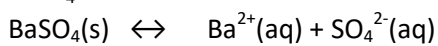
(i) Water?

(ii) in 0.1M sodium sulphate solution?

$$(K_{sp} = 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6})$$

Solution

(i) BaSO_4 dissociate as follows



Let the solubility be x

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = x$$

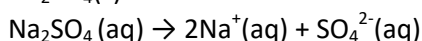
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x^2 = 1 \times 10^{-10}$$

$$\Rightarrow x = 1 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore \text{Solubility of } \text{BaSO}_4 \text{ in water} = 1 \times 10^{-5} \text{ mol dm}^{-3}$$

(ii) Let the solubility of BaSO_4 in 0.1M Na_2SO_4 be y

$\text{Na}_2\text{SO}_4(\text{s})$ dissociates as follows



$$[\text{Ba}^{2+}] = y$$

$$[\text{SO}_4^{2-}] = (0.1 + y)$$

$$K_1 = y(0.1 + y) = 1 \times 10^{-10}$$

y is very small that $(0.1 + y) \cong 0.1$

$$\text{thus } 0.1y = 1 \times 10^{-10}$$

$$y = 1 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\therefore \text{Solubility of } \text{BaSO}_4 \text{ in } 0.1\text{M } \text{Na}_2\text{SO}_4 \\ = 1 \times 10^{-9} \text{ mol dm}^{-3}$$

This example illustrate that BaSO_4 is more soluble in water than in Na_2SO_4 solution that contains a common ion (i.e. SO_4^{2-})

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(b) Prediction of Precipitation

The solubility product is used to predict the maximum concentration of ions in solution at a given temperature and hence whether or not precipitation will occur.

Suppose we mix 0.001M CaCl_2 solution (which contains 0.001M Ca^{2+} ions) with equal volume of 0.001M Na_2SO_4 (i.e. 0.001M SO_4^{2-} ions) solution at 25°C. Will a precipitate of CaSO_4 formed? ($K_{sp} \text{CaSO}_4 = 2 \times 10^{-5} \text{mol}^2 \text{dm}^{-6}$)

Immediately after mixing equal volumes of the two ions and before any precipitation

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 5 \times 10^{-4} \text{M}$$

(i.e. the concentration of each ion is halved since each solution is diluted by mixing with the other).

Hence the ionic product for CaSO_4 immediately after mixing

$$\begin{aligned} [\text{Ca}^{2+}][\text{SO}_4^{2-}] &= 5 \times 10^{-4} \times 5 \times 10^{-4} \\ &= 2.5 \times 10^{-7} \text{mol}^2 \text{dm}^{-6} \end{aligned}$$

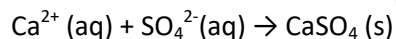
This ionic product is less than the value of K_{sp} for CaSO_4 and so no precipitation occurs.

Let ionic now suppose that we mix equal volumes of 0.01M solution of each. Immediately after mixing

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 5 \times 10^{-3} \text{M} \text{ and ionic product}$$

$$\begin{aligned} [\text{Ca}^{2+}][\text{SO}_4^{2-}] &= 5 \times 10^{-3} \times 5 \times 10^{-3} \\ &= 2.5 \times 10^{-5} \text{mol}^2 \text{dm}^{-6} \end{aligned}$$

In this case, the ionic product is greater than the solubility product and therefore precipitation of CaSO_4 occurs. The concentration of aqueous Ca^{2+} and SO_4^{2-} ions are lowered by the reaction.



Coral reef, stalagmite and stalactites are result of slow precipitation of CaCO_3 from water when concentration of Ca^{2+} and CO_3^{2-} exceed the K_{sp} of CaCO_3 .

(c) Selective precipitation

This is used to separate salts with different solubility, e.g. Ca^{2+} , Mg^{2+} and Ba^{2+} can be separated by adding $\text{K}_2\text{Cr}_2\text{O}_4(\text{aq})$, which precipitate out BaCrO_4 (which is the least soluble) and removed by filtration. The remaining solution that contain Mg^{2+} and Ca^{2+} is then separated by adding Na_2SO_4 that precipitate out CaSO_4 (CaSO_4 is less soluble than MgSO_4) leaving Mg^{2+} in solution

Note that the order in which reagents are added is important. If we had added Na_2SO_4 solution before adding $\text{K}_2\text{Cr}_2\text{O}_4$ solution a mixture of BaSO_4 and CaSO_4 would have been precipitated.

On the other hand, if Na_2CO_3 solution had been added to the mixture of the three cations; MgCO_3 , CaCO_3 and BaCO_3 would all have been precipitated. Thus, both the precipitating reagent and the order of addition must be selected with great care.

(d) Use of potassium chromate (VI) in silver nitrate titration

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When silver nitrate solution is titrated with sodium chloride solution containing a little potassium chromate (VI) only silver chloride is precipitated as long as there are any chloride ion in solution.

Only when all chloride ions have reacted does a red precipitate of silver chromate (VI) appear. This is explained by the solubility products of the two silver salts; i.e. $(\text{Ag}^+)(\text{Cl}^-) = 1 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ while $(\text{Ag}^+)_2(\text{CrO}_4^{2-}) = 2.5 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$. Suppose the concentration of Cl^- and CrO_4^{2-} ions in the liquid are both 0.1M. Then

$[\text{Ag}^+]$ needed to precipitate silver chloride

$$= \frac{1 \times 10^{-10}}{0.1} = 1 \times 10^{-9} \text{ mol dm}^{-3}$$

$[\text{Ag}^+]$ needed to precipitate silver chromate

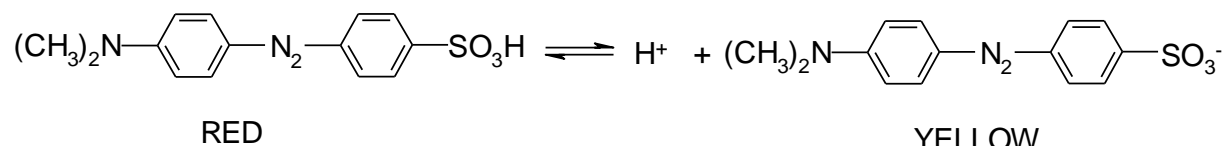
$$= \sqrt{\frac{2.5 \times 10^{-12}}{0.1}} = 5 \times 10^{-6} \text{ mol dm}^{-3}$$

Thus even if the concentration of the Cl^- ions and CrO_4^{2-} ions in the liquid are equal, it is easier by adding Ag^+ ions to reach the solubility product of the chloride than that of the chromate (VI) in spite of the lower solubility product of the latter. In practice $[\text{Cl}^-]$ is much larger than $[\text{CrO}_4^{2-}]$. Hence silver chloride is precipitated even more readily.

Indicators

Acid-base indicators are substances which change color according to the hydrogen ions concentration of the liquid in which they are placed. They are either weak acids or weak bases, and are therefore slightly dissociated when dissolved in water. The color of the indicator depends on the color of the undissociated molecules and the color of the ions produced. Taking methyl orange as an example, dissociation occurs as follows:

More precisely



When a drop of methyl orange is added to water, the resultant color is orange. If now an acid is added, the hydrogen ions of the acid drive back the ionization of methyl orange, very few Me^- ions remain, and the indicator becomes pink. Alternatively, addition of a base provides a large concentration of hydroxyl ions which combine with the H^+ of the indicator to form water. More of the indicator ionizes and a large concentration of Me^- ions are produced, giving a yellow color. Similarly, litmus has red HA and blue A^- ions.

Neutrality/ End point of indicator

The aim of any titration is to determine the volume of two solutions that just react with each other. Thus, the end point which is the point at which the titration is stopped, must coincide with equivalence point for the two reacting solutions.

In order to achieve this, the indicator should change color sharply at equivalent point on addition of a single drop of either acid or alkali. At the exact end point of the titration, the color of the indicator will be midway between the acid color HIn and the color of In⁻. If the dissociation constant of the indicator is represented by K_I, then $K_I = \frac{[H^+][In^-]}{[HIn]}$, or $[H^+] = K_I \frac{[HIn]}{[In^-]}$

When the color of HIn and In⁻ are equal,

$$[HIn] = [In^-] \text{ so } [H^+] = K_I$$

$$\text{or pH} = -\log K_I = pK_I$$

Range of an indicator

Every indicator has a definite range of pH over which it changes color given by

$$\text{pH range} = pK_I \pm 1$$

The colors and pH ranges of some common indicators are given in the table below:

Indicator	pH range	acid	alkali
Thymol blue	1.2-2.8	red	yellow
Methyl orange	2.9-4.6	pink	yellow
Congo red	3.0-5.0	blue	
Methyl red	4.2-6.3	pink	yellow
Litmus	5.0-8.0	red	blue
Phenolphthalein	7.4-9.0	colorless	red

PH change during titration

During a titration, there is a change in pH as alkali is added to acid or vice versa. At the equivalent point, the pH must change sharply by several units for it to be identifiable using an indicator.

The change in pH during the course of a titration depends largely upon the strength of the acid and alkali used.

The figure shows the effect on pH value of adding to 50cm³ molar HCl (strong acid) increasing quantities of molar solution of NaOH and secondary, a solution of NH₃ (a weak base)

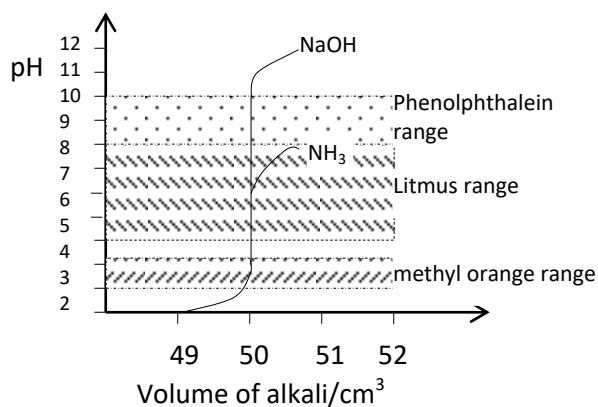


Figure 1

Note that, with NaOH addition of a very small volume of the base near the end point provides a very large change in the hydrogen ions concentration almost completely covering the pH ranges of methyl orange, litmus and phenolphthalein; In practice any of these indicator may be used during a titration of a strong acid with a strong base.

With ammonia solution adding a small amount of base near end point produces a small change in hydrogen ion concentration, and the end point is less sharp, no matter what indicator is used; although methyl orange provides the best choice.

The effect on pH value of adding to cm³ of molar ethanoic acid (weak acid) increasing quantities of first molar NaOH solution (strong base and secondly, molar ammonia (weak base) is illustrated in figure below

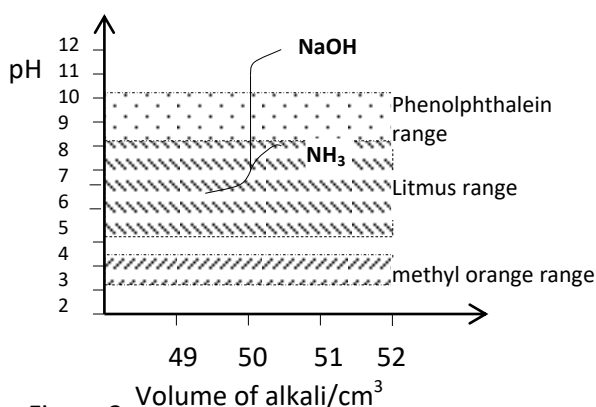


Figure 2

In the first case a less sharp end point that with a strong acid and strong base is again obtained with phenolphthalein as the best indicator for this titration. When the acid and the base are both weak, the end point is so indefinite that in practice a weak acid and weak base are never titrated against each other.

Choice of indicator

The true end point of neutralization in any titration occurs when the amount of acid and base added together are chemically equivalent to each other. The solution may not have a pH (i.e. neutral) equal to that of water at this point. With strong acids and strong base the final pH is about 7. In other cases hydrolysis of salt takes place, producing a pH greater or less than 7. Thus according to figure 1, the pH is about 5 for 0.5M NH₄Cl solution and from figure 2 about 9 for a 0.5M solution of sodium ethanoate (CH₃COONa).

For a strong acid and a strong base the theoretically correct indicator is litmus, but in practice both methyl orange and phenolphthalein can be used. Similarly, methyl orange (or more accurately methyl red) is the correct indicator for titrating aqueous ammonia and hydrochloric acid, and phenolphthalein for sodium hydroxide and ethanoic acid. The general rules for indicators can be summarized as follows:

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Strong acid and strong base – any indicator

Strong acid and weak base – methyl orange

Weak acid and strong base – phenolphthalein

Weak acid and weak base are not titrated.

Thank you
Dr. Bbosa Science