

NEET/JEE 2019

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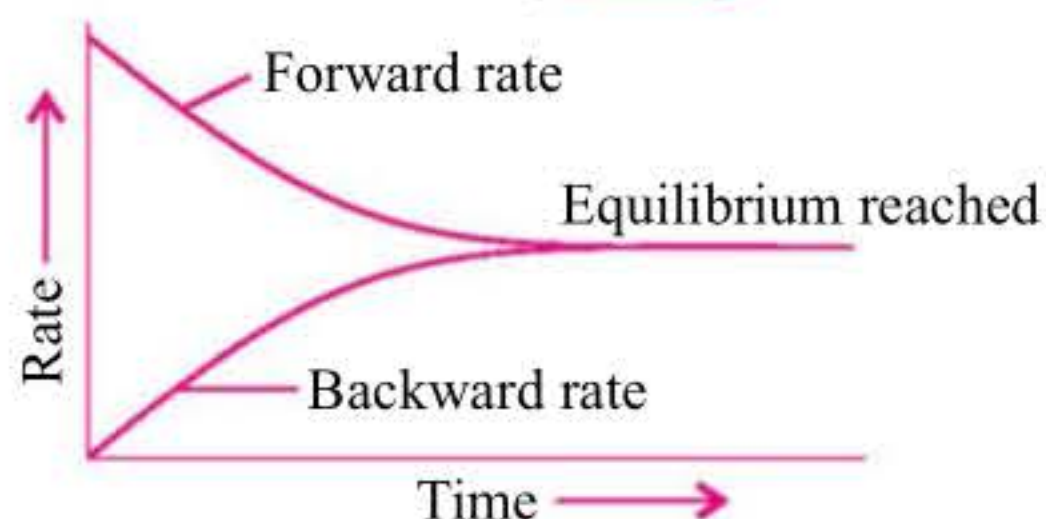
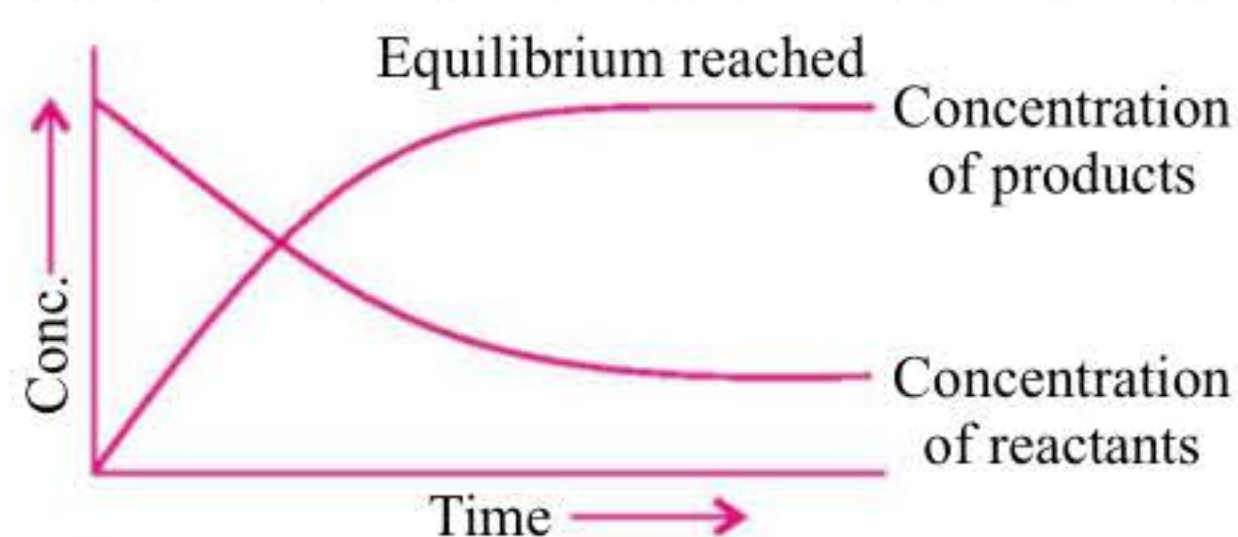
UNIT - 4 : Equilibrium | Redox Reactions

EQUILIBRIUM

- At equilibrium, two opposing processes (forward and reverse) take place at equal rates hence it is called dynamic equilibrium.
- Equilibrium can be established for both physical processes and chemical reactions.

REVERSIBLE REACTIONS

- A reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.



- Ultimately a stage comes in reversible reaction where concentration of both reactant and product becomes equal which is said to be equilibrium.

LAW OF CHEMICAL EQUILIBRIUM

- Law of chemical equilibrium is a result obtained by applying the law of mass action to a reversible reaction in equilibrium.
- For example, consider a general reversible reaction,
 $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}; \text{ where, } K_c \text{ is equilibrium constant.}$$

K_c is specific for a reaction and this equation is known as law of chemical equilibrium.

- Relations between equilibrium constants for a general reaction and its multiples :

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K'_c = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K''_c = (K_c)^n$

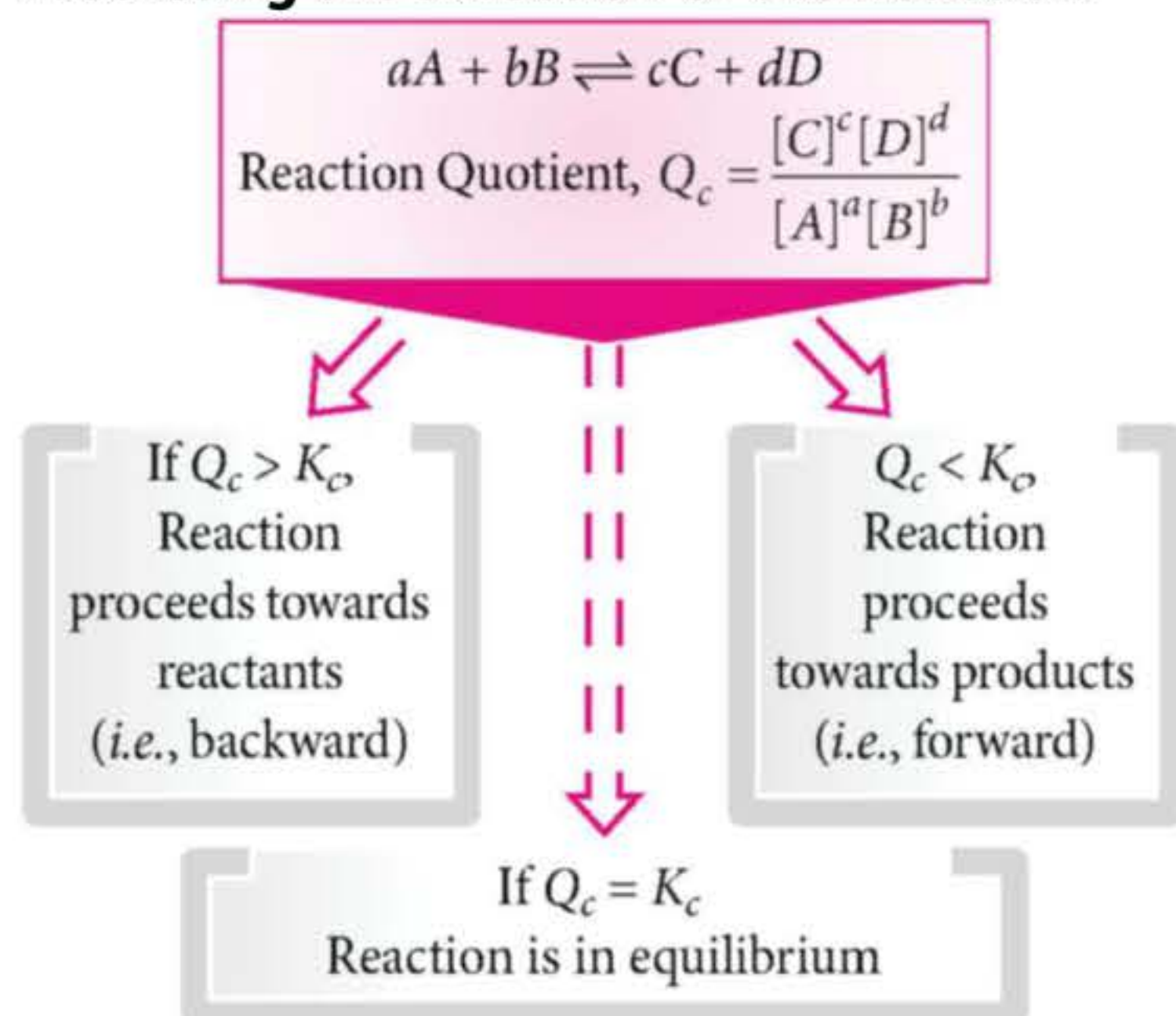
- For a gas phase reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \quad \text{and} \quad K_p = K_c (RT)^{\Delta n};$$

where, $\Delta n = (n_{\text{gaseous products}} - n_{\text{gaseous reactants}})$

- If $\Delta n_g = 0$, $K_p = K_c$
- If $\Delta n_g = +ve$ (i.e., $n_p > n_r$), $K_p > K_c$
- If $\Delta n_g = -ve$ (i.e., $n_p < n_r$), $K_p < K_c$

Predicting the Direction of the Reaction



Effect of Temperature on Equilibrium Constant

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}; \log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

- If $\Delta H = 0$, i.e., no heat is evolved or absorbed in the reaction, $\log (K_2/K_1) = 0$, i.e., $K_2/K_1 = 1$ or $K_2 = K_1$ i.e., equilibrium constant does not change with temperature.
- If $\Delta H = +ve$, i.e., heat is absorbed in the reaction, then $\log (K_2/K_1) = +ve$, or $\log K_2 > \log K_1$ or $K_2 > K_1$ i.e., equilibrium constant increases with increase in temperature.
- If $\Delta H = -ve$, i.e., heat is evolved in the reaction, $\log (K_2/K_1) = -ve$, i.e., $\log K_2 < \log K_1$ or $K_2 < K_1$ i.e., equilibrium constant decreases with increase in temperature.

LE CHATELIER'S PRINCIPLE

- If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed.
- **Effect on chemical equilibria :**

	Change imposed at equilibrium	Equilibrium shift
1.	Increase in the concentration of one or more reactants	in forward direction

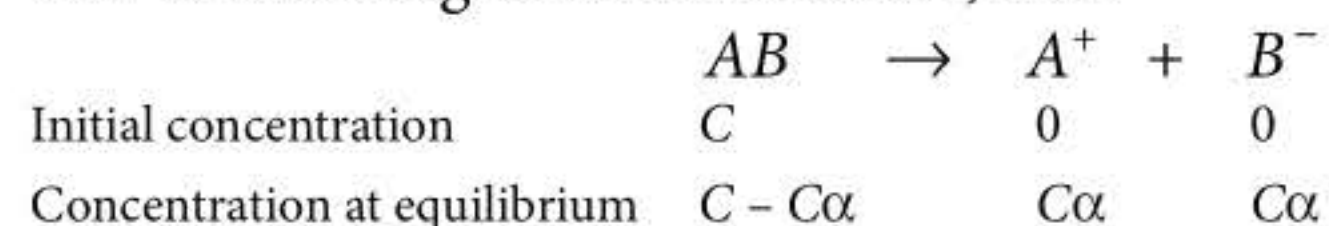
2.	Increase in the concentration of one or more products	in backward direction
3.	Increase in temperature	towards endothermic reaction
4.	Decrease in temperature	towards exothermic reaction
5.	Increase in pressure	favours lesser number of gaseous moles
6.	Decrease in pressure	favours larger number of gaseous moles
7.	Addition of catalyst	has no effect
8.	Addition of inert gas (a) at constant volume (b) at constant pressure	has no effect favours larger number of gaseous moles

IONIC EQUILIBRIUM

- Those substances which conduct electricity in their aqueous solutions are called electrolytes. Faraday further classified electrolytes into two types :
 - Strong electrolytes on dissolution in water are ionized almost completely. They are excellent conductors of electricity, e.g., HCl, HNO₃.
 - Weak electrolytes are partially ionized in their aqueous solution. They are poor conductors of electricity, e.g., CH₃COOH, H₃PO₄, NH₄OH.

Ostwald's Dilution Law

- It is applicable for weak electrolytes only.
- Consider the dissociation of a weak electrolyte 'C' moles of which has been dissolved in one litre and 'α' is its degree of dissociation, then



$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

In the case of weak electrolytes, $1 \gg \alpha$, so $1 - \alpha \approx 1$

$$\text{So, } K = \frac{C\alpha \times C\alpha}{C} = C\alpha^2; \alpha^2 = \frac{K}{C} \text{ or } \alpha = \sqrt{\frac{K}{C}}$$

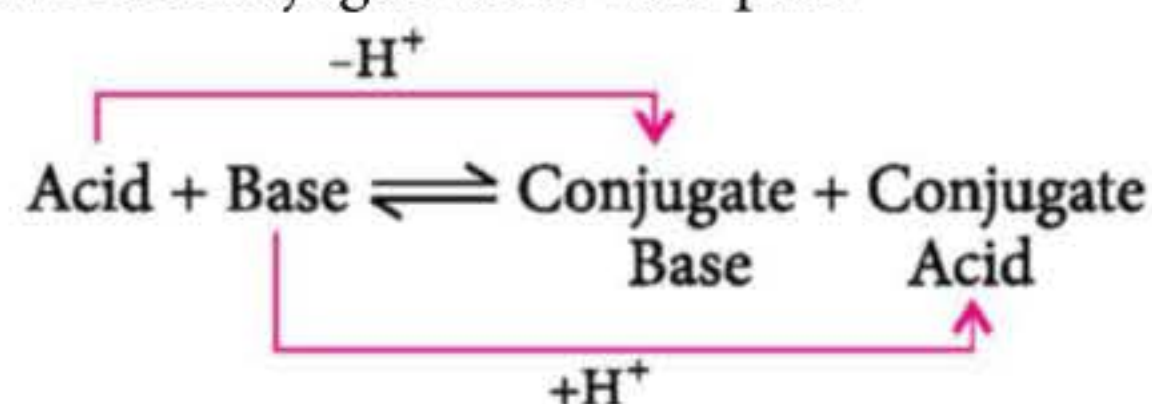
But C is concentration in moles/litre i.e., n/V

If n is constant (for dilution), $\alpha \propto \sqrt{V}$

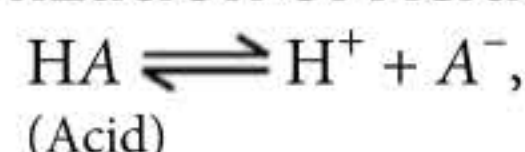
i.e., degree of ionization of weak electrolyte increases with dilution. The above expression is known as Ostwald's dilution law.

Conjugate Acid-Base Pair

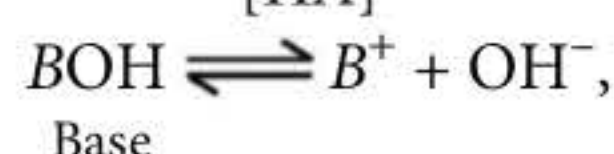
- A pair of acid and base, which differs by a proton is known as conjugate acid-base pair.



Ionization of Acids and Bases



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



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \quad \text{and} \quad \alpha = \sqrt{\frac{K_b}{C}}$$

Greater the degree of ionization (α) or greater the dissociation constant (K_a or K_b), stronger is the acid

or base.

- The ionic product of water :**

$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ at 298 K, where K_w is the ionic product of water.

The ionic product of water is constant only at constant temperature. With increase of temperature, the degree of ionization of water increases. Thus the concentration of H^+ and OH^- increases and hence the ionic product also increases.

- The pH scale :** The pH of a solution is a measure of the acidity of a solution.
 $\text{pH} = -\log[\text{H}^+]$
 If $\text{pH} < 7$, acidic solution; if $\text{pH} = 7$, neutral solution; if $\text{pH} > 7$, basic solution.
 $\text{p}K_w = \text{pH} + \text{pOH} = 14$
- Relation between K_a and K_b :**
 For a weak acid, $\text{p}K_a = -\log K_a$;
 For a weak base, $\text{p}K_b = -\log K_b$
 $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$ at 298 K

Salt Hydrolysis

- Salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is neutral.

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline $\text{pH} > 7$	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic $\text{pH} < 7$	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and cationic both	Neutral, $\text{pH} = 7$ (If $K_a = K_b$)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

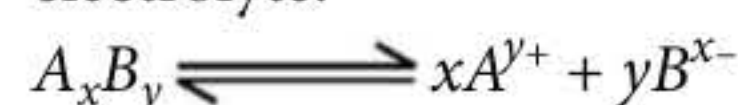
Calculation of pH

	Types of solution	Formula
1.	Dilute aqueous solution of a strong acid or a strong base	$\text{pH} = -\log \{[\text{H}^+]_{\text{acid}} + [\text{H}^+]_{\text{H}_2\text{O}}\}$ $\text{pOH} = -\log \{[\text{OH}^-]_{\text{base}} + [\text{OH}^-]_{\text{H}_2\text{O}}\}$
2.	Highly concentrated solution of a strong acid or a strong base (concentration > 1 M)	pH of acidic solution is taken as 0. pH of basic solution is taken as 14.
3.	Solution of a weak acid or a weak base	$\text{pH} = -\log (C\alpha) = -\log(\sqrt{K_a C})$ $\text{pOH} = -\log (C\alpha) = -\log(\sqrt{K_b C})$
4.	Mixture of two or more strong monoprotic acids or strong bases	$\text{pH} = -\log\left(\frac{\sum \text{NV}}{\sum \text{V}}\right)$, $\text{pOH} = -\log\left(\frac{\sum \text{NV}}{\sum \text{V}}\right)$

5.	Mixture of an acid and a base	$\text{pH} = -\log \left(\frac{(N_1 V_1)_{\text{acid}} - (N_2 V_2)_{\text{base}}}{V_1 + V_2} \right)$ (if acid is in excess) $\text{pOH} = -\log \left(\frac{(N_2 V_2)_{\text{base}} - (N_1 V_1)_{\text{acid}}}{V_1 + V_2} \right)$ (if base is in excess)
6.	Amphiprotic system	$\text{pH} = \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2}$

Solubility product

- It is defined as the product of molar concentration of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.



$$\text{Applying law of mass action, } K_{eq} = \frac{[A^{y+}]^x [B^{x-}]^y}{[A_x B_y]}$$

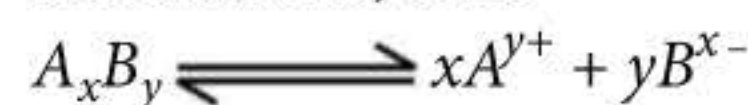
As conc. of $[A_x B_y]$ undissociated is almost constant.

$$K_{eq} [A_x B_y] = [A^{y+}]^x [B^{x-}]^y$$

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Relation between solubility and solubility product

- If solubility of a sparingly soluble salt, $A_x B_y$ is S moles/litre, then



S moles xS moles yS moles

Thus, $[A^{y+}] = xS$ and $[B^{x-}] = yS$

$$\therefore K_{sp} = [A^{y+}]^x [B^{x-}]^y = (xS)^x (yS)^y \text{ or } x^x \cdot y^y \cdot S^{(x+y)}$$

Buffer Solutions

- The property of resisting change in pH of a solution when an acid or an alkali is added to it is known as buffer action and such solutions are called buffer solutions.
- Such solution usually consist a mixture of weak acid and salt of its conjugate base (acidic buffer) or weak base and salt of its conjugate acid (basic buffer) and a salt of a weak acid and a weak base, e.g., ammonium acetate ($\text{CH}_3\text{COONH}_4$) has a buffer action.

- Henderson-Hasselbalch equation**

$$\text{For acidic buffer : } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{For basic buffer : } \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{or, } \text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Salt}]}$$

- On dilution, the ratio of concentrations of salt and acid or salt and base will still remain same thus pH will remain unchanged.

REDOX REACTIONS

CONCEPT OF OXIDATION AND REDUCTION

Oxidation

- Addition of oxygen or some other electronegative atom.
- Removal of hydrogen or some other electropositive atom.
- Loss of one or more electrons by an atom or an ion or a molecule.

Reduction

- Removal of oxygen or some electronegative atom.
- Addition of hydrogen or some other electropositive atom.

- Gain of one or more electrons by an atom or an ion or a molecule.
- Oxidising agent** : The species, which gets reduced, i.e., undergoes reduction and oxidises other species.
- Reducing agent** : The species, which gets oxidised, i.e., undergoes oxidation and reduces other species.

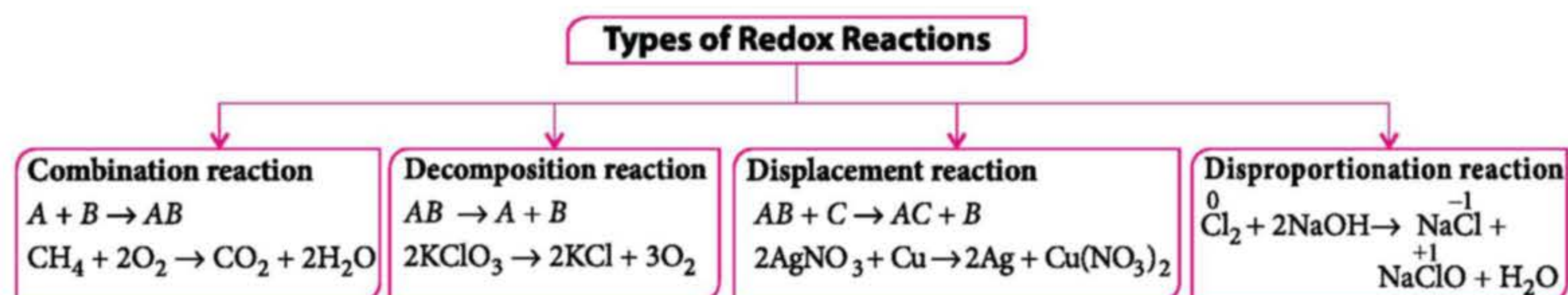
MONTHLY TUNE UP CLASS XII

ANSWER KEY

- | | | | | |
|-------------|-------------|-----------|---------|-----------|
| 1. (a) | 2. (d) | 3. (c) | 4. (a) | 5. (d) |
| 6. (b) | 7. (b) | 8. (b) | 9. (b) | 10. (b) |
| 11. (d) | 12. (a) | 13. (c) | 14. (c) | 15. (b) |
| 16. (d) | 17. (c) | 18. (a) | 19. (a) | 20. (b,d) |
| 21. (a,b) | 22. (b,c,d) | 23. (a,d) | 24. (3) | 25. (6) |
| 26. (1.546) | 27. (a) | 28. (c) | 29. (a) | 30. (d) |

OXIDATION NUMBER RULES

Applies to	Rule
Elements	The oxidation number of an atom in an element is zero.
Monoatomic ion	The oxidation number of an atom in a monoatomic ion equals the charge on the ion.
Oxygen	The oxidation number of oxygen is -2 in most of its compounds (an exception is O in H_2O_2 and other peroxides, where oxidation number is -1) and in oxygen fluoride (OF_2), it is $+2$.
Hydrogen	The oxidation number of hydrogen is $+1$ in most of its compounds. (The oxidation number of hydrogen is -1 in metallic hydrides such as CaH_2 , NaH_2 .)
Halogens	The oxidation number of fluorine is -1 , in all of its compounds. Each of other halogens (Cl, Br, I) has an oxidation number of -1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation number of the atoms in a polyatomic ion equals the charge on the ion.
Alkali metals	The oxidation number of alkali metals (Na, K, Li, etc) in compounds is $+1$.
Alkaline earth metals	The oxidation number of alkaline earth metals (Mg, Ca, Ba, Sr, etc.) in compounds is $+2$.
Sulphides	In all sulphides the oxidation number of sulphur is -2 .
Transition elements and <i>p</i> -block elements	Variable oxidation number is most commonly shown by transition elements as well as <i>p</i> -block elements. <i>e.g.</i> , Fe ($+2$ and $+3$), Cu ($+1$ and $+2$), Mn ($+7$, $+6$, $+5$, $+4$, $+3$, $+2$), As ($+3$ and $+5$), Sb ($+3$ and $+5$), Sn ($+2$ and $+4$) etc.



BALANCING OF REDOX REACTIONS

Oxidation Number Method

- Identify atoms which undergo change in oxidation number in the reaction.
- Calculate the increase or decrease in the oxidation number per atom and multiply it by number of atoms undergoing that change, if increase or decrease is not equal then multiply by suitable number to make them equal.
- Add H^+ (if medium is acidic) or OH^- (if medium is basic) on the appropriate side so that the total ionic charges of reactants and products are equal.
- Make the number of hydrogen atoms in the expression on the two sides equal by adding H_2O to the reactants or products and finally check the number of oxygen atoms.

Half Reaction Method

- Separate the equation into half-reactions.
- Balance the atoms other than O and H in each half-reaction individually.
- For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms and for basic medium, H atoms are balanced by adding H_2O molecule to the side deficient in H atoms and equal number of OH^- ions are added to opposite side and then duplicacy is removed if any.
- Add electrons to one side of the half-reaction to balance the charges and make the number of electrons equal in two half-reactions by multiplying one or both half-reactions by appropriate number.
- Add two half-reactions to achieve the overall reaction and cancel the electrons on both sides.

REDOX REACTIONS AND ELECTRODE PROCESSES

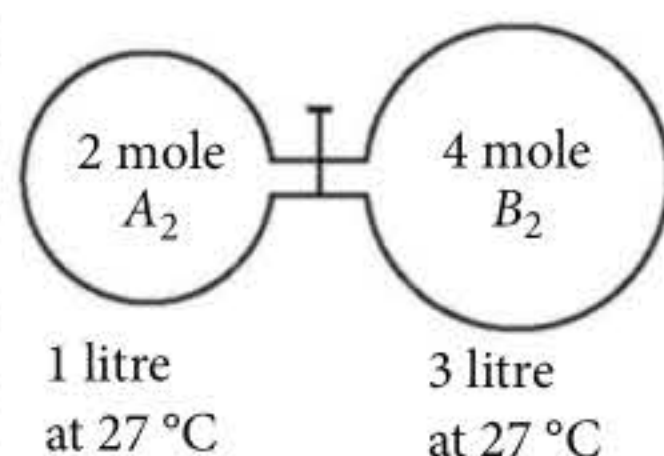
- **Redox couple** : It is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half-reaction *i.e.*, a metal dipped in the solution of its own ions.
- **Electrode potential** : The potential difference set up between the metal and its own ions in the solution is called the electrode potential. In general, it is the tendency of an electrode to gain or lose electrons.
- **Standard electrode potential (E°)** : If the concentration of each species taking part in the electrode reaction is unity and further the reaction

is carried out at 298 K, then the potential of each electrode is called standard electrode potential.

- Standard electrode potential of hydrogen is taken as 0.00 volts by convention.
- Electrochemical series is a series in which a list of oxidising agents are arranged in decreasing order of their strength. It is also called activity or electromotive series.
- A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
- A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

SPEED PRACTICE

1. The gas A_2 in the left flask allowed to react with gas B_2 present in right flask as $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$; $K_c = 4$ at 27 °C. What is the concentration of AB when equilibrium is established ?

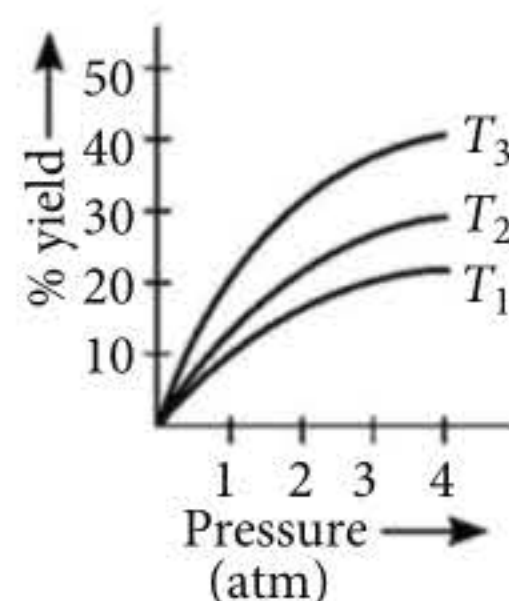


- (a) 1.33 M (b) 2.66 M
(c) 0.66 M (d) 0.33 M
2. According to Bronsted–Lowry concept of acids and bases, mark the option in which conjugate pair is not correctly matched.

Species	Conjugate acid	Conjugate base
(a) HCO_3^-	CO_3^{2-}	H_2CO_3
(b) HPO_4^{2-}	$H_2PO_4^-$	PO_4^{3-}
(c) NH_3	NH_2^-	NH_4^+
(d) HS^-	S^{2-}	H_2S

3. The preparation of $SO_{3(g)}$ by reaction, $SO_{2(g)} + 1/2 O_{2(g)} \rightleftharpoons SO_{3(g)}$, is an exothermic reaction.

If the preparation follows the following temperature–pressure relationship for its % yield, then for temperatures T_1 , T_2 and T_3 , the correct option is



- (a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
(c) $T_1 = T_2 = T_3$
(d) Nothing could be predicted about temperature from given information
4. Identify the compounds which are reduced and oxidised in the following reaction :
- $$3N_2H_4 + 2BrO_3^- \rightarrow 3N_2 + 2Br^- + 6H_2O$$
- (a) N_2H_4 is oxidised and BrO_3^- is reduced.
(b) BrO_3^- is oxidised and N_2H_4 is reduced.
(c) BrO_3^- is both reduced and oxidised.
(d) This is not a redox reaction.
5. From the given data, identify the most stable oxide of nitrogen.
- (a) $2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$; $K = 6.7 \times 10^{16} \text{ mol L}^{-1}$
(b) $2N_2O_{5(g)} \rightleftharpoons 2N_{2(g)} + 5O_{2(g)}$;
 $K = 1.2 \times 10^{24} \text{ mol}^5 \text{ L}^{-5}$
(c) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$; $K = 2.2 \times 10^{30}$
(d) $2N_2O_{(g)} \rightleftharpoons 2N_{2(g)} + O_{2(g)}$; $K = 3.5 \times 10^{33} \text{ mol L}^{-1}$
6. Consider the following reaction,
- $$\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array} + \text{OH}^- \rightarrow \begin{array}{c} \text{COO}^- \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- Select the incorrect statement.
- (a) It is not a disproportionation reaction.
(b) It is intramolecular redox reaction.
(c) OH^- is a reducing as well as oxidising agent.