

Here are the 5-mark answers for Unit 1 questions of your chemistry syllabus:

1) DERIVATION OF The Born–Landé equation

ANS---- The Born–Landé equation is a means of calculating the [lattice energy](#) of a crystalline [ionic compound](#). In 1918^[1] [Max Born](#) and [Alfred Landé](#) proposed that the lattice energy could be derived from the [electrostatic potential](#) of the ionic lattice and a repulsive potential energy term.

Where:

- E = the lattice energy
- N_A = [Avogadro constant](#)
- M = [Madelung constant](#), relating to the geometry of the crystal
- z^+ = numeric charge number of cation
- z^- = numeric charge number of anion
- e = [elementary charge](#), $1.6022 \times 10^{-19} \text{ C}$
- ϵ_0 = [permittivity of free space](#)

$$4\pi\epsilon_0 = 1.112 \times 10^{-10} \text{ C}^2/(\text{J}\cdot\text{m})$$

- r_0 = distance between closest cation [+ve] and anion [-ve]
- n = Born exponent, typically a number between 5 and 12, determined experimentally by measuring the [compressibility](#) of the solid, or derived theoretically

Derivation

The ionic lattice is modeled as an assembly of hard elastic spheres which are compressed together by the mutual attraction of the electrostatic charges on the ions. They achieve the observed equilibrium distance apart due to a balancing short range repulsion.

Electrostatic potential

The electrostatic potential energy, E_{pair} , between a pair of ions of equal and opposite charge is:

where

z = magnitude of charge on one ion

e = elementary charge, 1.6022×10^{-19} [C](#)

ϵ_0 = [permittivity of free space](#)

$4\pi\epsilon_0 = 1.112 \times 10^{-10} \text{ C}^2/(\text{J}\cdot\text{m})$

r = distance separating the ion centers

For a simple lattice consisting ions with equal and opposite charge in a 1:1 ratio, interactions between one ion and all other lattice ions need to be summed to calculate E_M , sometimes called the [Madelung](#) or lattice energy:

where

M = [Madelung constant](#), which is related to the geometry of the crystal

r = closest distance between two ions of opposite charge

Repulsive term

[\[edit\]](#)

Born and Lande suggested that a repulsive interaction between the lattice ions would be proportional to $1/r^n$ so that the repulsive energy term, E_R , would be expressed:

where

B = constant scaling the strength of the repulsive interaction

r = closest distance between two ions of opposite charge

n = Born exponent, a number between 5 and 12 expressing the steepness of the repulsive barrier

2) Importance of Lattice Energy in Explaining Solubility of Ionic Compounds

- **Lattice energy (U):** Energy required to separate one mole of an ionic solid into gaseous ions.
- **Hydration energy:** Energy released when ions are solvated by water molecules.

Solubility depends on:

- If hydration energy > lattice energy, the ionic compound is soluble.
- If lattice energy > hydration energy, the compound is less soluble or insoluble.

Examples:

- NaCl dissolves easily: hydration energy \approx lattice energy
- BaSO₄ is insoluble: lattice energy > hydration energy

Thus, lattice energy is crucial in predicting ionic solubility in water.

3) Potential Energy vs Internuclear Distance Curve (Hydration)

- The curve shows the variation of potential energy with distance between two nuclei.
- At long distances: attractive forces dominate \rightarrow potential energy decreases.
- At short distances: repulsive forces dominate \rightarrow potential energy increases.
- The minimum point on the curve represents equilibrium bond length and bond energy.

For hydration:

- Ion–dipole interaction forms stable ion–water complexes.
 - Energy decreases as water molecules approach and hydrate the ion
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4) Hybridization, Geometry, Structure & Bond Angle of Compounds

Compound	Hybridization	Geometry	Shape	Bond Angle
PCl ₅	sp ³ d	Trigonal bipyramidal	Same	90°, 120°
ClF ₃	sp ³ d	Trigonal bipyramidal	T-shaped	~87°

Compound	Hybridization	Geometry	Shape	Bond Angle
IF ₅	sp ³ d ²	Octahedral	Square pyramidal	~90°
XeF ₄	sp ³ d ²	Octahedral	Square planar	90°
XeO ₃	sp ³	Tetrahedral	Pyramidal	~103°
XeOF ₄	sp ³ d ²	Octahedral	Square pyramidal	~90°

5) Mechanism of Cornforth Synthesis:

Cornforth synthesis is used to prepare **substituted oxazoles** from **α-amino ketones** and **formic acid** or its derivatives.

General Mechanism:

1. Formation of Schiff base (imine) between the amino group and carbonyl group.
2. Cyclization and dehydration lead to the oxazole ring.

Steps:

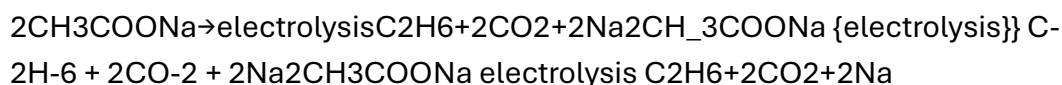
- α-Amino ketone + formic acid → Schiff base
- Intramolecular attack → oxazoline intermediate
- Dehydration → oxazole

Note: Include a ring formation and dehydration in mechanism if diagram is allowed.

6) Kolbe's Synthesis (Kolbe Electrolysis)

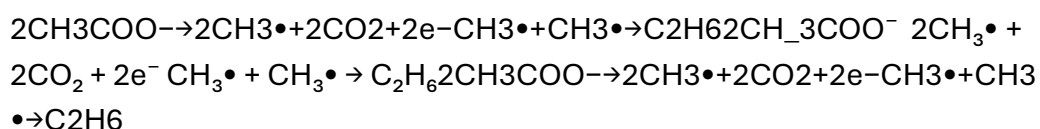
Kolbe's synthesis is used to prepare **alkanes** by the **electrolysis of sodium or potassium salts of carboxylic acids**.

Reaction:

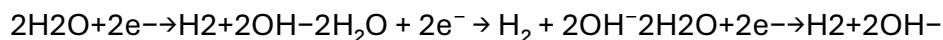


Mechanism:

- At anode:



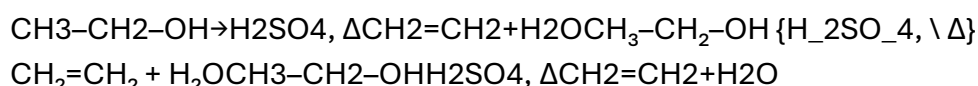
- At **cathode**:



3) Mechanism of Dehydration of Alcohols

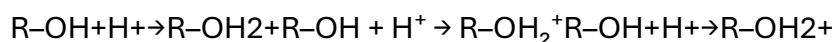
Alcohol → Alkene by loss of water (acidic medium, heat)

Example:

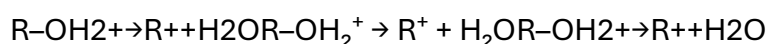


Mechanism (E1 mechanism for 2°/3° alcohols):

1. **Protonation:**



2. **Formation of Carbocation:**



3. **Elimination of Proton:**

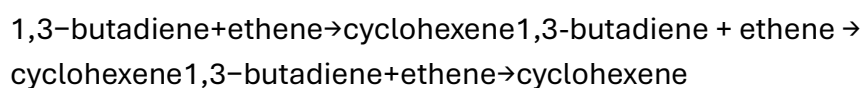


In **primary alcohols**, it may follow **E2** pathway due to unstable carbocations.

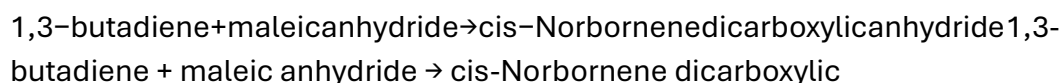
7) Mechanism of Diels–Alder Reaction with Example (2 and 2A)

Diels–Alder reaction is a [4+2] cycloaddition between a **conjugated diene** and a **dienophile** to form a **six-membered ring**.

Example 2:



Example 2A:



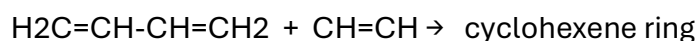
anhydride 1,3-butadiene + maleic anhydride \rightarrow cis-Norbornene dicarboxylic anhydride

Mechanism:

- Concerted one-step mechanism
- π electrons shift cyclically forming new sigma bonds
- Stereospecific and occurs via **suprafacial** interaction

Diagram:

ini



5) Addition of 1,3-Butadiene

1,3-Butadiene undergoes **electrophilic addition**, forming **1,2-addition** and **1,4-addition** products.

Example: Addition of HBr

Mechanism:

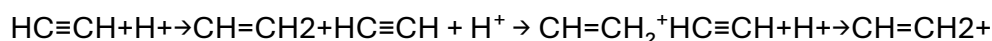
- Proton adds to form resonance-stabilized allylic carbocation
 - Br^- attacks either at position 2 or 4 \rightarrow two products formed
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8) Mechanism of Addition of HBr to Ethyne

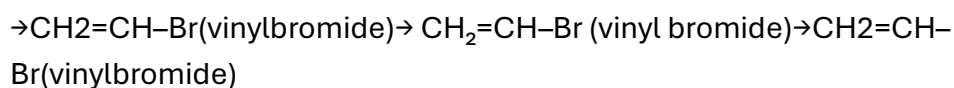
Ethyne ($\text{HC}\equiv\text{CH}$) reacts with **HBr** in presence of peroxide (or without):

Without Peroxide – Markovnikov's Rule:

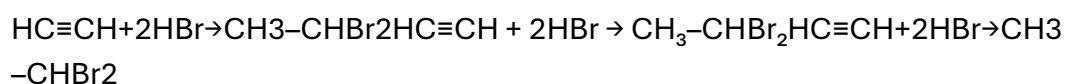
1. Formation of vinyl carbocation:



2. Br^- attacks the carbocation:



With **2 mol HBr**:



With Peroxide – Anti-Markovnikov (Free Radical Mechanism):

- Br adds first (as radical), then H
- Product: $\text{CH}_2=\text{CHBr}$ (opposite regiochemistry)

9) Derivation of Second Order Rate Constant When A = B

Step 1 . Write the differential rate law.

- **For a second-order reaction where**



10) Experimental Determination of Rate Constant – Saponification



Equal volumes of ester and NaOH are mixed.

At different times, aliquots are withdrawn and quenched with ice-cold acid.

Then, **titrate** unreacted NaOH with standard HCl

Let:

- V_0 : Initial volume of NaOH
- V_t : Volume of NaOH left at time t

For second-order reaction:

$$K = 1/t (v - v_t / v_0 v_t)$$

This method is called **titrimetric method** and is useful for **kinetic studies**.

11) Methods of Determining Order of Reaction

1. Method of Integration:

Use rate law equations for different orders and compare with experimental data.

- ### 2. Half-Life Method:
- The half-life ($t_{1/2}$) of a reaction is the time it takes for the concentration of a reactant to decrease to half of its initial value.

The half-life formula varies depending on the reaction order.

Half-Life Formulas for Different Orders:

Zero-order: $t_{1/2} = [R]_0 / 2k$, where $[R]_0$ is the initial concentration and k is the rate constant.

First-order: $t_{1/2} = 0.693 / k$.

Second-order: $t_{1/2} = 1 / (k[R]_0)$

3) Initial Rate Method:

Measure initial rates at different concentrations and plot $\log(\text{rate})$ vs $\log(\text{concentration})$.

4) Graphical Method: Steps Involved:

1. Collect concentration data:

Measure the concentration of the reactant(s) at different times during the reaction.

2. Plot the data:

3. **Zero-order:** Plot concentration of reactant (on the y-axis) versus time (on the x-axis).
4. **First-order:** Plot the natural logarithm of the concentration of the reactant ($\ln[\text{reactant}]$) versus time.
5. **Second-order:** Plot the inverse of the concentration of the reactant ($1/[\text{reactant}]$) versus time.
6. **3. Analyze the plot:**
7. The plot that yields a straight line indicates the order of the reaction with respect to that reactant.
8. Examples:
9. **Zero-order:**
10. If a graph of concentration vs. time is linear, the reaction is zero-order with respect to that reactant.
11. **Ostwald's Isolation Method:**
Keep one reactant in large excess so it remains nearly constant, simplifying the rate law.

12) Lindemann's Theory of Unimolecular and Bimolecular Reactions

. **Lindemann Theory** explains **unimolecular reactions** that appear first-order but involve molecular collisions.

Steps:

1. **Activation Step** (bimolecular): $A + M \rightarrow A^* + M$
(M is any molecule providing energy)
2. **Decomposition** (unimolecular): $A^* \rightarrow \text{Products}$

Key Concepts:

- At **high pressure**: $A^* \xrightarrow{k_1} A^*$ formed quickly \rightarrow rate \sim unimolecular
- At **low pressure**: activation step is slow \rightarrow rate \sim bimolecular

$$\text{Rate} = k_1(A) / (1 + k_2(M)/k_3)$$

Explains transition between **first-order and second-order kinetics** depending on pressure.

13) Composition Curves for Phenol-Water and Nicotine-Water Systems

These are **partially miscible liquid pairs** that show temperature-composition curves.

(A) Phenol-Water System:

- Exhibits **Upper Critical Solution Temperature (UCST)** at $\sim 66^{\circ}\text{C}$.
- Below this temperature, **two layers** form.
- Above UCST, they become **completely miscible**.
- The curve is **concave upwards**.
- At UCST: both phases have the **same composition**.

(B) Nicotine-Water System:

- Shows **Lower Critical Solution Temperature (LCST)** at $\sim 60^{\circ}\text{C}$.
- Above LCST, they are **immiscible**.
- Below LCST, they form a **single phase**.
- The curve is **concave downwards**.

Key Points to Draw in Composition Curves:

- Temperature on Y-axis, composition on X-axis
- Show one-phase and two-phase regions
- Mark UCST or LCST clearly

