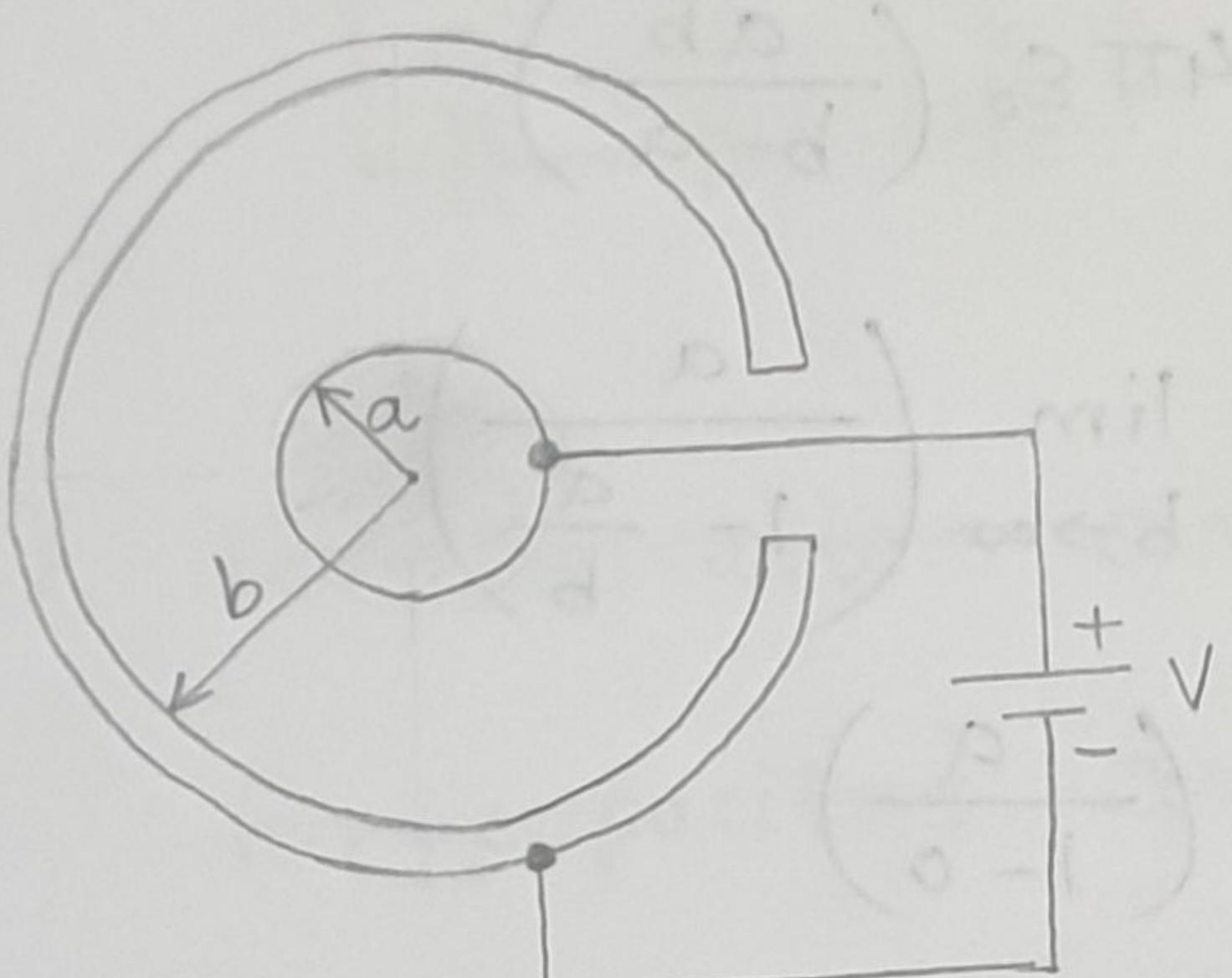
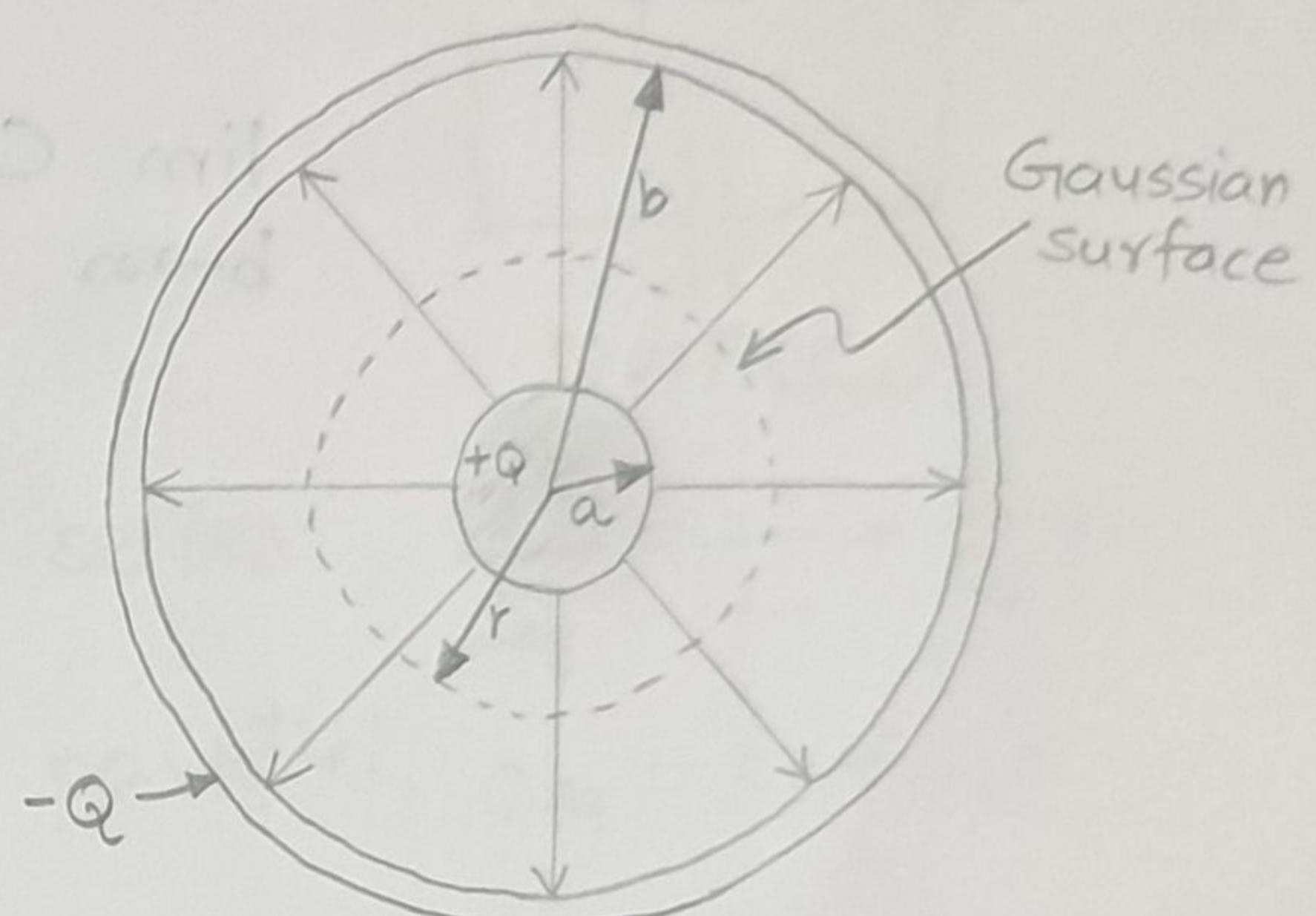


- Q.1 (a) Show that the capacitance depends only on the physical dimensions, a and b for a spherical capacitor of two concentric spherical shells (inner shell with $+Q$ and $-Q$ charge distribution) of radii 'a' and 'b'. Use Gauss's law and show the Gaussian surface for the spherical capacitor.
- (b) What is the capacitance if one of the conductor is placed at infinity ($b \rightarrow \text{infinity}$). Calculate the corresponding energy density of this spherical capacitor.

Ans:- (a)



Spherical Capacitor with two concentric spherical cells of radii a and b



Gaussian surface for calculating the electric field

Here, electric field is non-vanishing only in region $a < r < b$.

Using Gauss's law, $\oint \vec{E} \cdot d\vec{A} = E_r A = \frac{Q}{\epsilon_0}$

$$\Rightarrow E_r (4\pi r^2) = \frac{Q}{\epsilon_0}$$

$$\Rightarrow E_r = \frac{1}{4\pi \epsilon_0} \frac{Q}{r^2} \quad \dots \textcircled{1}$$

Therefore, the potential difference between the two conducting shells is :

$$\begin{aligned} \Delta V = V_b - V_a &= - \int_a^b E_r dr = - \frac{Q}{4\pi \epsilon_0} \int_a^b \frac{1}{r^2} dr \quad \dots \text{Using } \textcircled{1} \\ &= - \frac{Q}{4\pi \epsilon_0} \left[-\frac{1}{r} \right]_a^b \\ &= - \frac{Q}{4\pi \epsilon_0} \left[-\frac{1}{b} - \left(-\frac{1}{a} \right) \right] \\ &= - \frac{Q}{4\pi \epsilon_0} \left[\frac{1}{a} - \frac{1}{b} \right] \end{aligned}$$

$$\therefore \Delta V = -\frac{Q}{4\pi\epsilon_0} \left[\frac{b-a}{ab} \right] \quad \dots (2)$$

Capacitance is given by, $C = \frac{Q}{|\Delta V|}$

$$\Rightarrow C = 4\pi\epsilon_0 \left(\frac{ab}{b-a} \right)$$

Since ϵ_0 is constant,

$$C = f(a, b)$$

If outer shell conductor placed at infinity ($b \rightarrow \infty$), then capacitance becomes,

$$\begin{aligned} \lim_{b \rightarrow \infty} C &= \lim_{b \rightarrow \infty} 4\pi\epsilon_0 \left(\frac{ab}{b-a} \right) \\ &= 4\pi\epsilon_0 \lim_{b \rightarrow \infty} \left(\frac{a}{1 - \frac{a}{b}} \right) \\ &= 4\pi\epsilon_0 \left(\frac{a}{1-0} \right) \end{aligned}$$

$$C = 4\pi\epsilon_0 a$$

(b) Energy stored in Capacitor (Spherical)

$$U = \frac{1}{2} \frac{Q^2}{C} = \frac{1}{2} CV^2 = \frac{1}{2} \left[4\pi\epsilon_0 \left(\frac{ab}{b-a} \right) \right] \left[-\frac{Q}{4\pi\epsilon_0} \left(\frac{b-a}{ab} \right) \right]^2$$

$$\Rightarrow U = \frac{1}{2} \frac{Q^2}{4\pi\epsilon_0} \frac{b-a}{ab}$$

$$\Rightarrow U = \frac{Q^2}{8\pi\epsilon_0} \left(\frac{b-a}{ab} \right)$$

Energy Density of Spherical Capacitor

$$u = \frac{1}{2} \epsilon_0 E_r^2$$

$$\Rightarrow u = \frac{1}{2} \epsilon_0 \left[\frac{1}{4\pi\epsilon_0} \frac{Q}{r^2} \right]^2$$

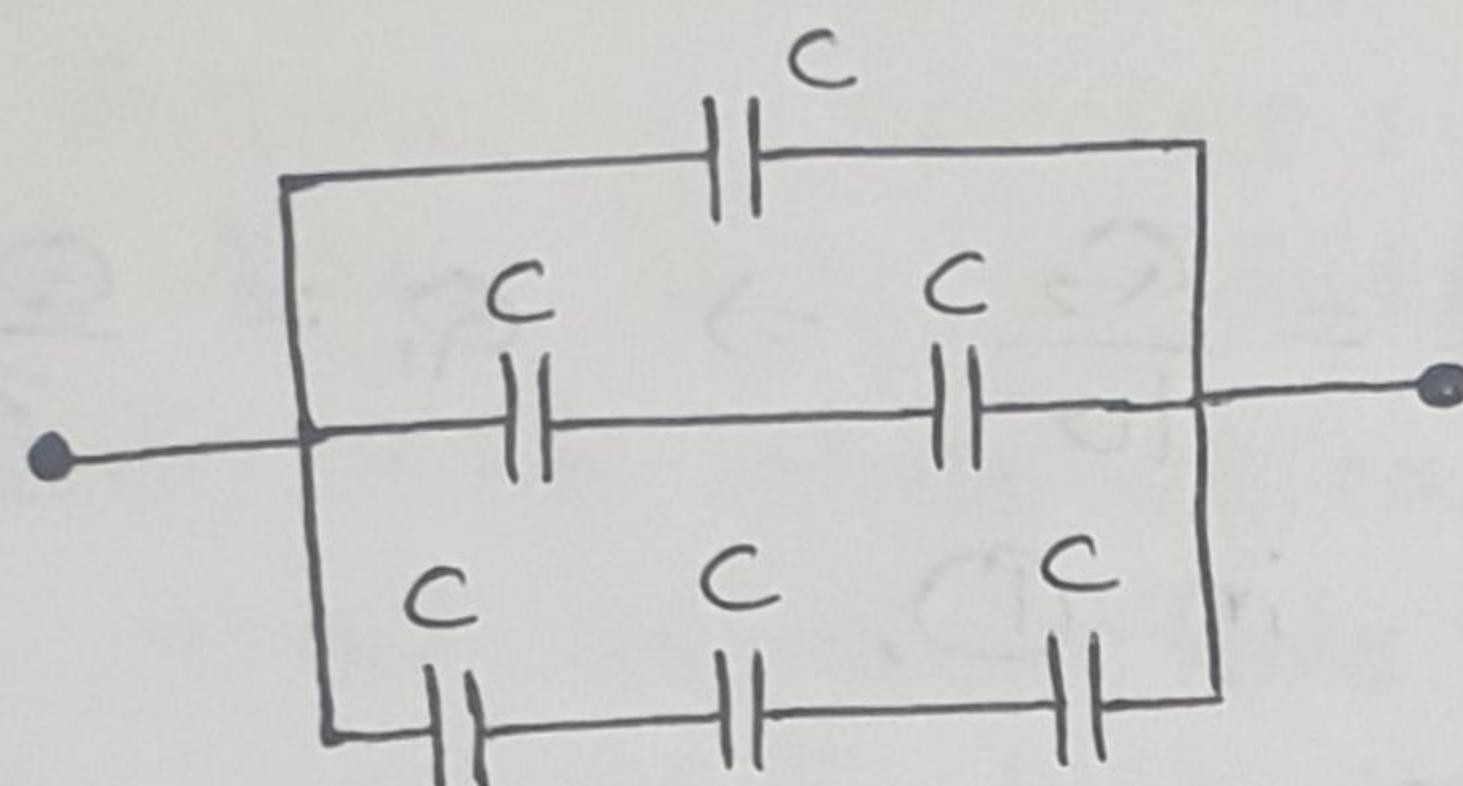
$$\Rightarrow u = \frac{Q^2}{32\pi^2 \epsilon_0 r^4}$$

Note :- $U = \int u dV = \int_a^b u (4\pi r^2) dr = \frac{Q^2}{32\pi^2 \epsilon_0} (4\pi) \int_a^b \frac{1}{r^2} dr$

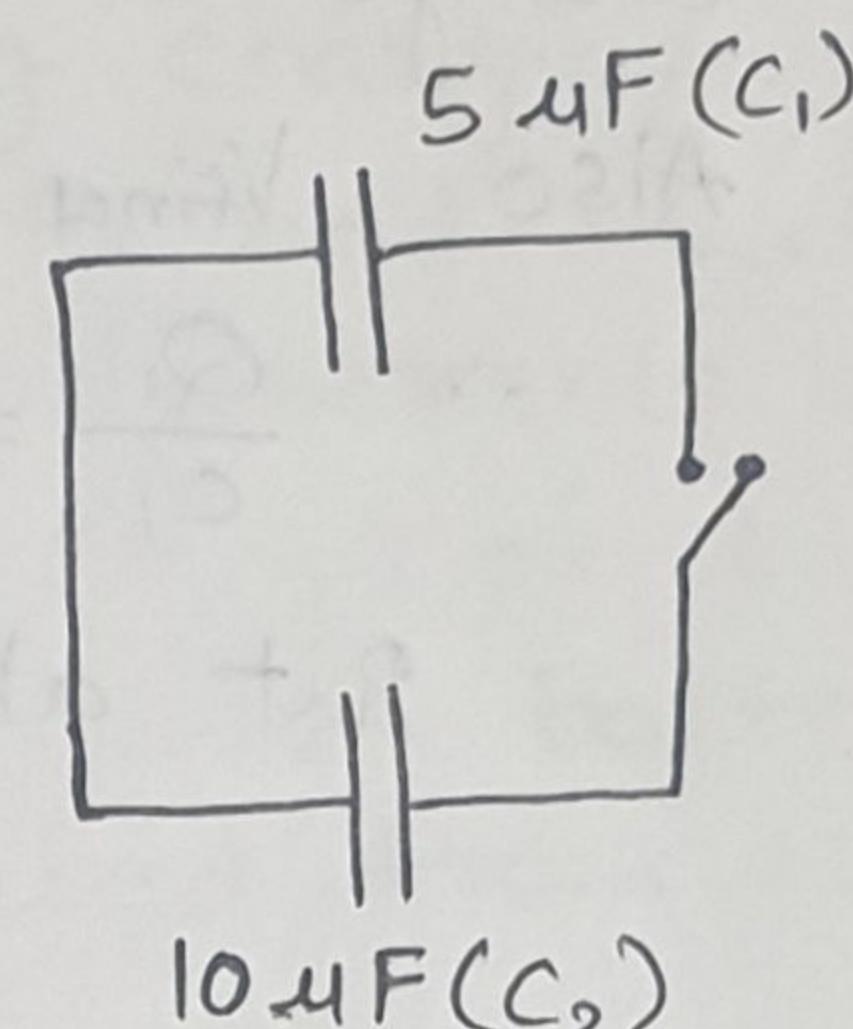
$$\begin{aligned} &= \frac{Q^2}{8\pi \epsilon_0} \left[-\frac{1}{r} \right]_a^b \\ &= \frac{Q^2}{8\pi \epsilon_0} \left(\frac{1}{a} - \frac{1}{b} \right) \\ &= \frac{Q^2}{8\pi \epsilon_0} \left(\frac{b-a}{ab} \right) \end{aligned}$$

Q.2 As per the given configuration (a) below : Find the equivalent capacitance assuming all the capacitors have equal capacitance, c. for the capacitor configuration given in (b), the $5\text{ }\mu\text{F}$ capacitor is initially charged to 100 V , and the $10\text{ }\mu\text{F}$ capacitor is initially uncharged. The switch is closed so that the system attains equilibrium. Calculate the amount of energy dissipated in the process.

(a)



(b)



Ans:- (a) For capacitors connected in series, $\frac{1}{C_{eq}} = \frac{1}{C_1} + \frac{1}{C_2} + \dots$

For capacitors connected in parallel, $C_{eq} = C_1 + C_2 + \dots$

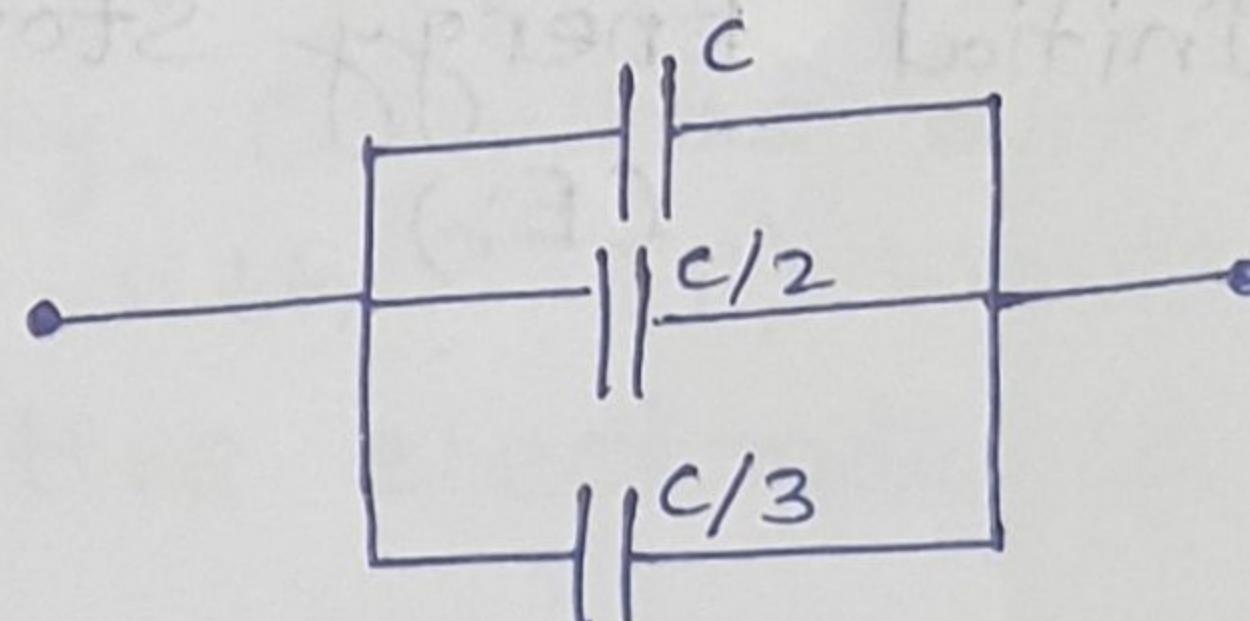
Equivalent Configuration 1 :-

Using series formulae,

$$\text{Row 1 : } C_{eq} = C$$

$$\text{Row 2 : } C_{eq} = \frac{C \times C}{C+C} = \frac{C}{2}$$

$$\text{Row 3 : } C_{eq} = \frac{C \times C \times C}{C \times C + C \times C + C \times C} = \frac{C}{3}$$

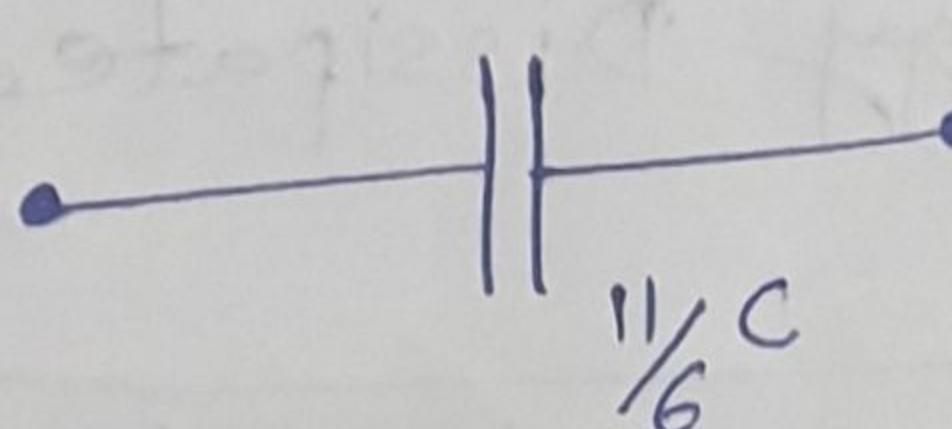


Equivalent Configuration 2 :-

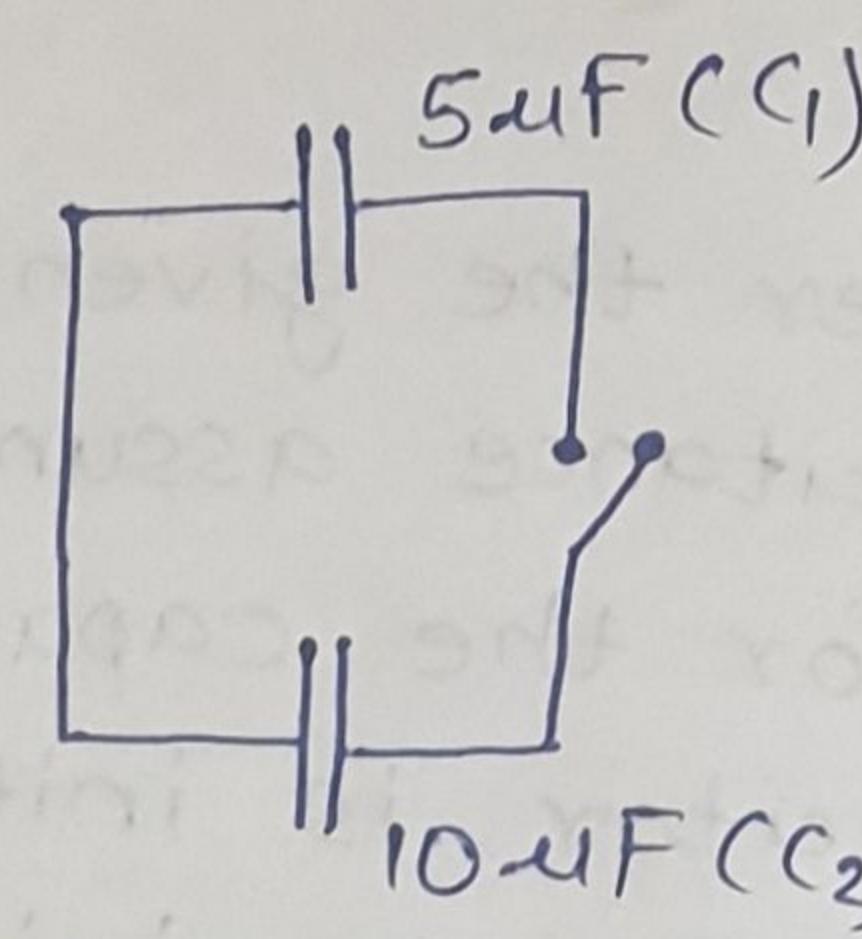
Using parallel formula, $C_{eq} = C + \frac{C}{2} + \frac{C}{3}$

$$= \frac{6C + 3C + 2C}{6}$$

$$C_{eq} = \frac{11}{6}C$$



(b) $C_1(5\mu F)$ is initially charged to 100 V.
 $C_2(10\mu F)$ is initially uncharged.



- Initial charge on $C_1 = (5\mu F)(100 V) = 500 \mu C$
- After switch is closed, let charges be Q_1 and Q_2 .
 Charge is conserved. So, $Q_1 + Q_2 = 500 \mu C$ — (1)
- Also V_{final} is same.

$$\therefore \frac{Q_1}{C_1} = \frac{Q_2}{C_2} \Rightarrow \frac{Q_1}{5} = \frac{Q_2}{10} \Rightarrow Q_1 = \frac{Q_2}{2} \quad — (2)$$

Put above expression in (1),

$$\Rightarrow \frac{Q_2}{2} + Q_2 = 500$$

$$\Rightarrow \frac{3Q_2}{2} = 500$$

$$\Rightarrow Q_2 = \frac{1000}{3}$$

$$\Rightarrow Q_2 = 333.33 \mu C$$

$$\text{Using (2), } Q_1 = \frac{Q_2}{2} = \frac{333.33}{2} = 166.67 \mu C$$

$$\therefore V_{final} = \frac{Q_1}{C_1} = \frac{166.67}{5} = 33.33 V$$

$$\begin{aligned} \text{Initial Energy stored} &= \frac{1}{2} C_1 V_{initial}^2 = \frac{1}{2} (5\mu F) (100 V)^2 \\ &= \frac{1}{2} \times 5 \times 10^{-6} \times 100^2 \\ &= 0.025 J \\ &= 25 mJ \end{aligned}$$

$$\begin{aligned} \text{Final Energy stored} &= \frac{1}{2} (C_1 + C_2) V_{final}^2 = \frac{1}{2} (5\mu F + 10\mu F) (33.33 V)^2 \\ &= \frac{1}{2} \times 15 \times 10^{-6} \times \left(\frac{100}{3}\right)^2 \\ &= 8.333 \times 10^{-3} J \\ &= 8.333 mJ \end{aligned}$$

$$\begin{aligned} \therefore \text{Energy Dissipated} &= E_i - E_f \\ &= 25 - 8.333 \end{aligned}$$

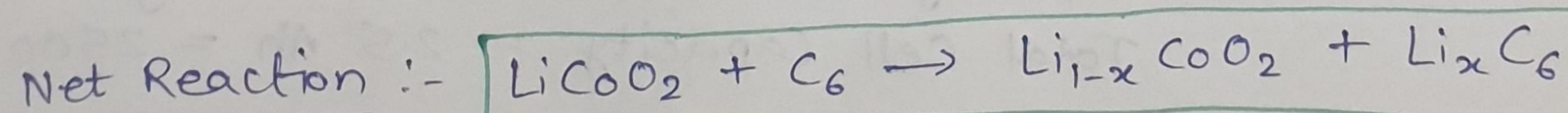
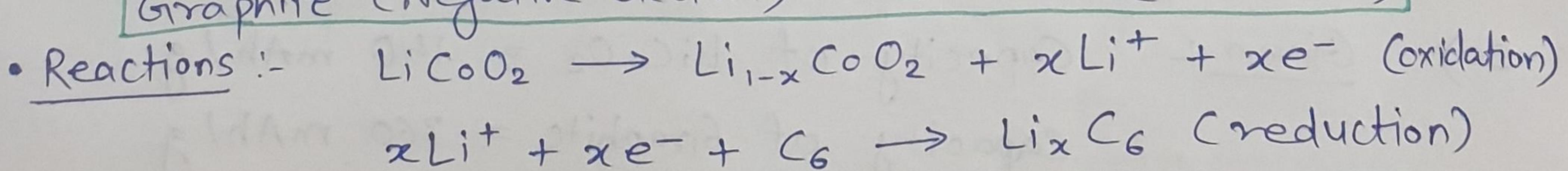
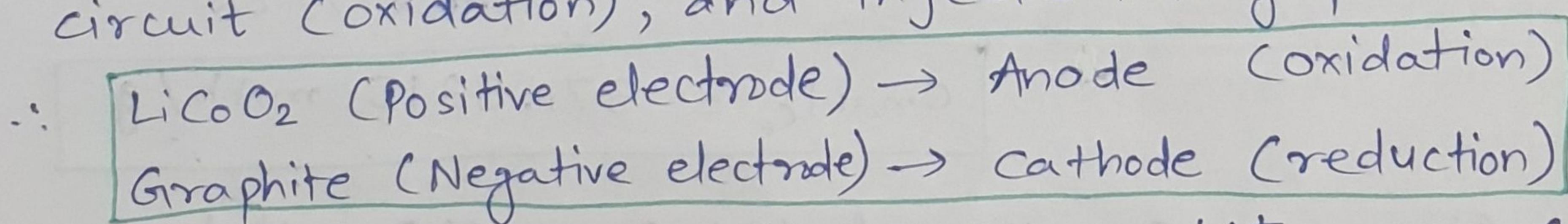
$$\boxed{\text{Energy Dissipated} = 16.667 mJ}$$

Q.3 Consider a typical lithium-ion battery with LiCoO_2 as the positive electrode material and graphite as the negative electrode material, which can be found in cellphones & laptops.
 $[F = 96485 \text{ C/mol}; M(\text{Li}) = 6.94 \text{ g/mol}; M(\text{Co}) = 58.93 \text{ g/mol}; M(\text{O}) = 16.00 \text{ g/mol}; M(\text{C}) = 12.01 \text{ g/mol}]$

- (a) Which one is the cathode and which one is the anode during charging according to the IUPAC definition? Write down the overall reaction during charging using the following species: C_6 , Li_xC_6 , LiCoO_2 and $\text{Li}_{1-x}\text{CoO}_2$. Write down the oxidation states of all elements involved.
- (b) Calculate the theoretical capacity (mAh/g) of LiCoO_2 and C used as electrode materials in a Li-ion battery. [Assume one equivalent lithium is extracted from the cathode and inserted in the anode.]
- (c) Consider a 2.5 Ah LiCoO_2 /graphite cell. Calculate the mass (in grams) of LiCoO_2 and graphite needed to build a 2.5 Ah cell. In this case, a practical specific energy capacity of 140 mAh/g for LiCoO_2 and 360 mAh/g for graphite is used. What is the specific capacity of such a cell at the end, considering only the mass of active materials in the electrode?
- (d) Imagine you want to design a new material for the lithium-ion battery. In order to improve the specific energy of the cell efficiently, (i) what are the two parameters that you can play with? (ii) Would you work on the materials for positive electrode or negative electrode? Why?

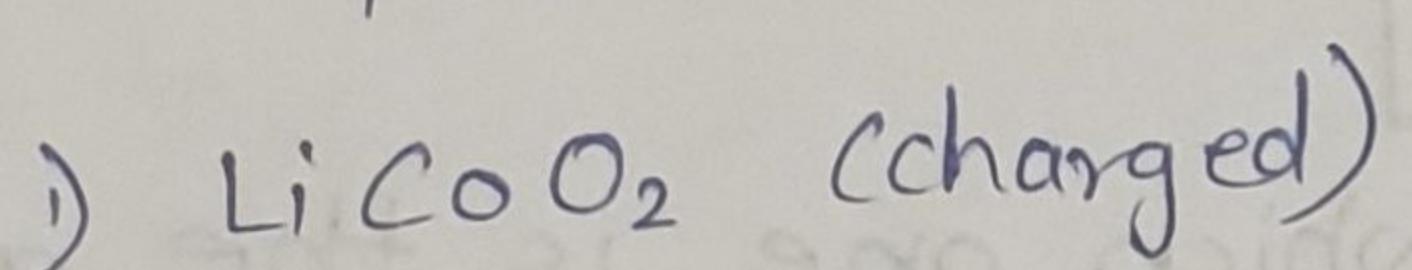
Ans:- (a) As per IUPAC definition, Anode : Where oxidation occurs
 Cathode : Where reduction occurs.

- During charging, Li^+ ions are extracted from LiCoO_2 (positive electrode) and move towards graphite (negative electrode).
- Electrons are pulled from LiCoO_2 to external circuit (oxidation), and injected into graphite (reduction).



- Oxidation state or oxidation number - It is hypothetical charge of an atom if all of its bonds to other atoms are fully ionic.

Species



+1

Co

C

O

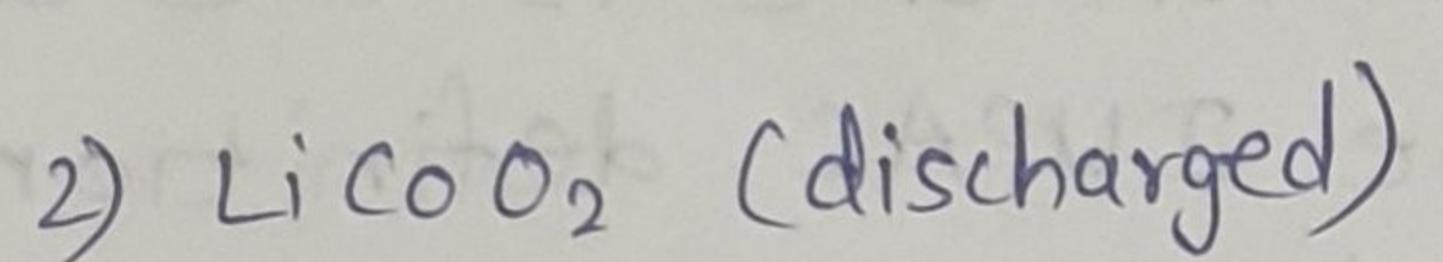
O

O

O

O

O



-1

O

+4

O

O

O

O

O

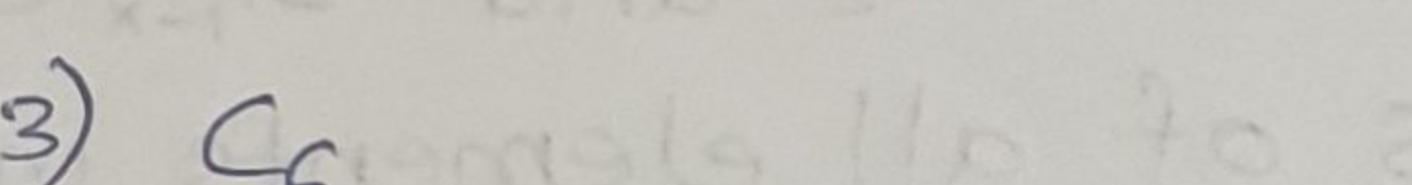
O

O

O

O

O



0

0

0

0

0

0

0

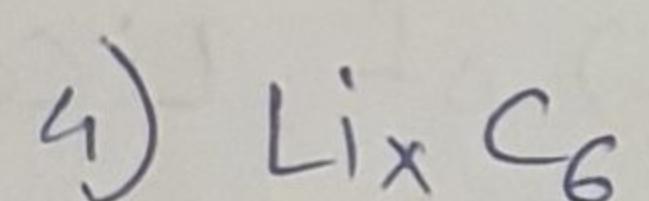
0

0

0

0

0



+1

0

0

0

0

0

0

0

0

0

0

0

(b) Theoretical specific capacity (mAh/g)

$$C_{m,th} = \frac{1000 \cdot n \cdot F}{3600 \cdot M} \quad \dots \quad n = \text{Number of Electrons}$$

$F = \text{Faraday's Constant (C/mol)}$

$M = \text{Molar mass (g/mol)}$

For LiCoO_2 , $n = 1$ (For Li)

$F = 96485 \text{ C/mol}$

$M = M_{\text{Li}} + M_{\text{Co}} + 2M_{\text{O}}$

$$= 6.94 + 58.93 + 2 \times 16$$

$$= 97.87 \text{ g/mol}$$

$$\therefore C_{m,th}|_{\text{LiCoO}_2} = \frac{1000 \times 1 \times 96485}{3600 \times 97.87}$$

$$C_{m,th}|_{\text{LiCoO}_2} = 273.8468 \text{ mAh/g}$$

For graphite (C_6), $n = 1$

$F = 96485 \text{ C/mol}$

$M = 6M_{\text{C}}$

$$= 6 \times 12.01$$

$$= 72.06 \text{ g/mol}$$

$$\therefore C_{m,th}|_{\text{C}_6} = \frac{1000 \times 1 \times 96485}{3600 \times 72.06}$$

$$C_{m,th}|_{\text{C}_6} = 371.9315 \text{ mAh/g}$$

(c) Given :- Capacity of $\text{LiCoO}_2 = 140 \text{ mAh/g}$

Capacity of Graphite = 360 mAh/g

Total Cell Capacity = $2.5 \text{ Ah} = 2500 \text{ mAh}$

$$\text{Soln: - Mass of LiCoO}_2 = \frac{\text{Total cell capacity}}{\text{Capacity of LiCoO}_2}$$

$$= \frac{2500 \text{ mAh}}{140 \text{ mAh/g}}$$

$$= 17.857 \text{ g}$$

$$\text{Mass of Graphite} = \frac{\text{Total cell capacity}}{\text{Capacity of Graphite}}$$

$$= \frac{2500 \text{ mAh}}{360 \text{ mAh/g}}$$

$$= 6.944 \text{ g}$$

$$\text{Total active mass} = m_{\text{LiCoO}_2} + m_{\text{Graphite}}$$

$$= 17.857 + 6.944$$

$$= 24.801 \text{ g}$$

$$\text{Specific Capacity of whole cell} = \frac{\text{Total Cell Capacity}}{\text{Total active mass}}$$

$$= \frac{2500 \text{ mAh}}{24.81 \text{ g}}$$

Method 2:

$$\frac{1}{C_{m,\text{th/whole}}} = \frac{1}{140} + \frac{1}{360}$$

$$\Rightarrow C_{m,\text{th/whole}} = 100.8 \text{ mAh/g}$$

$$C_{m,\text{th/whole cell}} = 100.8 \text{ mAh/g}$$

(d) Designing a New Material

(i) Two parameters to improve specific energy

Ans:- 1) Specific capacity ($C_{m\text{Ah/g}}$) \rightarrow depends on how many Lit a material can store.

2) Voltage of electrode reaction (V) \rightarrow Higher potential difference means more energy

(Logic:- Energy = capacity \times voltage)

(ii) Which electrode should you work on? Why?

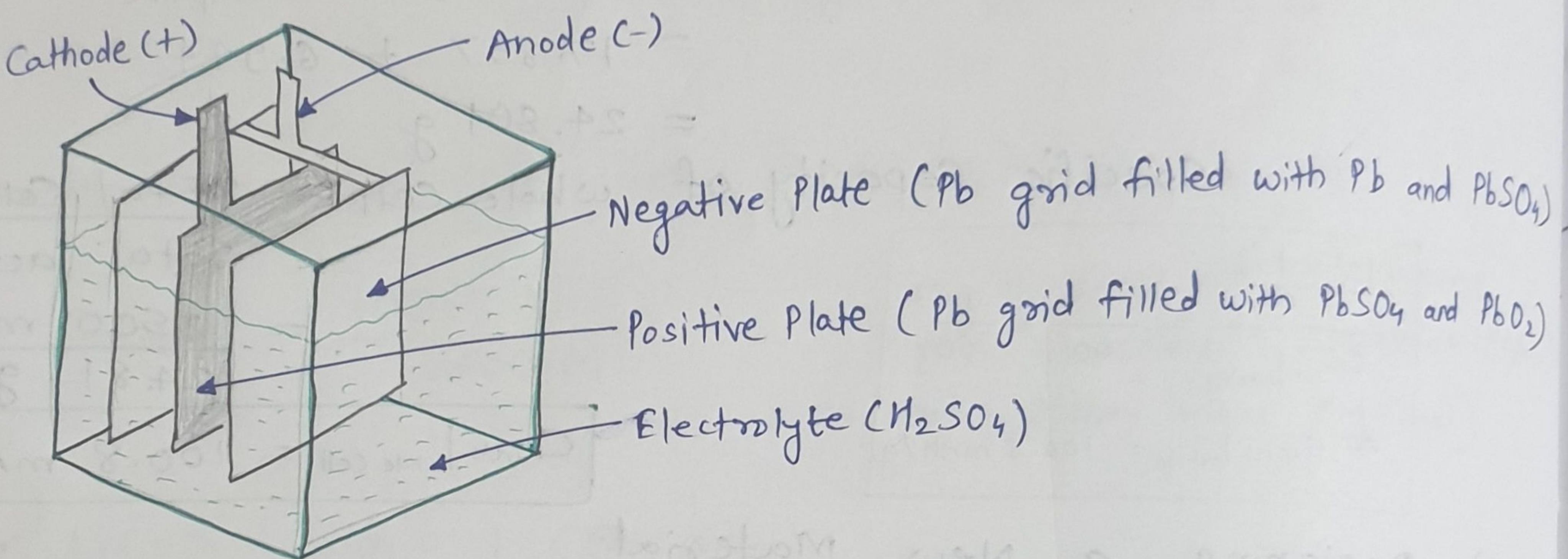
Ans:- Work on positive electrode (cathode)

Reason:-

- 1) Graphite is already near optimal for negative electrode (high capacity, low potential)
- 2) Cathode materials (like LiCoO_2) are heavier and more limiting in terms of energy density & capacity.
- 3) Boosting the voltage or lithium storage capacity in cathode materials will raise overall cell voltage and specific energy.

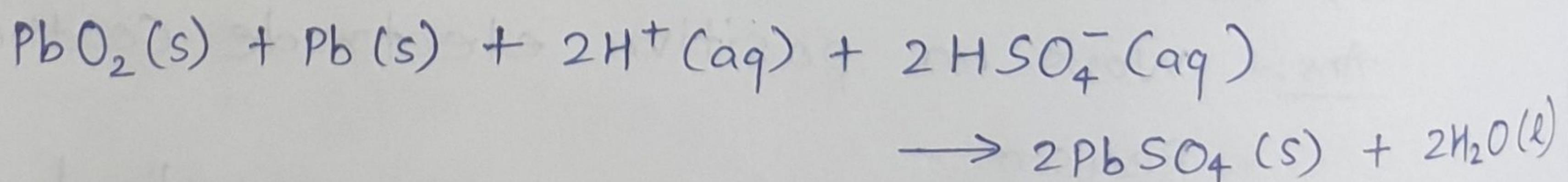
Q.4 Write the negative plate, positive plate, and total reactions happening during (a) the discharge of the battery (b) during the charge of the battery in a lead-acid battery.
 (c) what are the advantages and types of valve-regulated lead acid batteries (VRLA)? When 10 Ah of charge flows through the cell in a lead acid battery, calculate in grams
 (d) the amount of Pb oxidized at the negative electrode
 (e) the amount of PbO_2 reduced at the positive electrode, and
 (f) the amount of H_2SO_4 that react at both the electrodes?

Ans:-

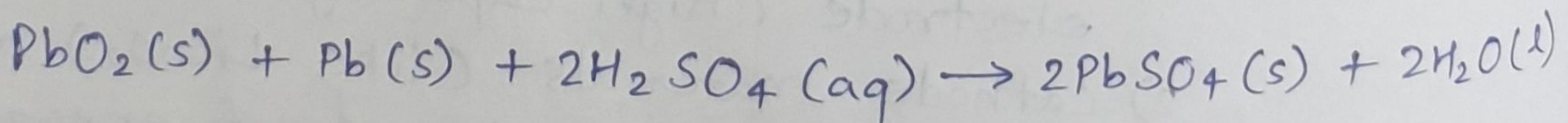


(a) Cell Discharge Reaction

- At negative plate (Anode): Lead (Pb) is oxidised
- $$\text{Pb}(\text{s}) + \text{HSO}_4^-(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) + 2\text{e}^-$$
- At positive plate (Cathode): Lead Dioxide (PbO_2) is reduced.
- $$\text{PbO}_2(\text{s}) + 3\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$$
- Overall Cell Reaction during discharge :



[OR]

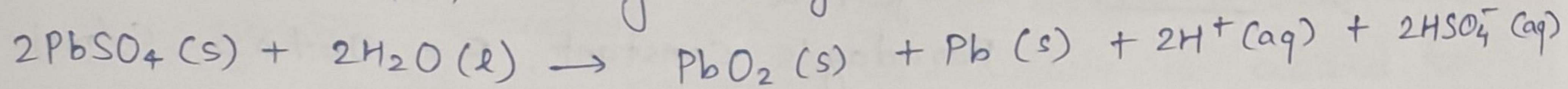


(b) Cell Charging Reaction

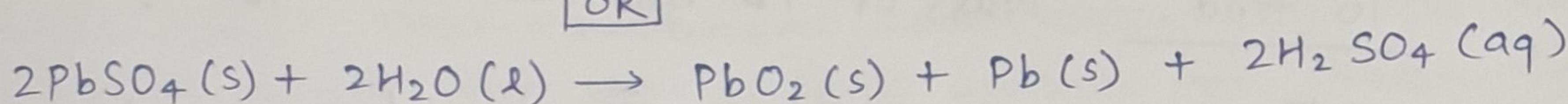
(During charging, the discharge reactions are reversed.)

- At negative plate (Cathode): Lead sulphate reduced to lead
- $$\text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{HSO}_4^-(\text{aq})$$
- At positive plate (Anode): Lead sulphate oxidized to lead dioxide
- $$\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \cancel{\text{Pb}(\text{s})} + \text{PbO}_2(\text{s}) + 3\text{H}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) + \cancel{\text{2e}^-}$$

• Overall cell reaction during charge :-



[OR]



(c) Valve-Regulated Lead Acid (VRLA) Batteries :

- It has limited amount of electrolyte either absorbed in glass separator or as a gel.
- It retains any generated gases within the battery if the pressure remains within a safe level and if the pressure exceeds the limits, then the safety valve will function and let the gases go and regulate the pressure back to normal.

• Types of VRLA battery

1) Absorbent Glass Mat (AGM)

- Electrolyte is soaked in thin fiberglass mat betⁿ plates.
- AGM works in various range of temperatures.
- AGM is vibration-resistant
- It is good for mobile applications

2) Gel battery

- Silica dust added to electrolyte can form a thick putty such as gel.
- Difference betⁿ AGM battery & Gel battery is charge rate is lower in AGM as compared to Gel.
- However, gel battery is widely used to hot temperature condition such as solar system to reach its full performance.

• Advantages of VRLA battery

1) Maintenance free - Adding distilled water for chemical reaction is not required

2) Fast Recharge - Sealed AGM or gel cell recharges faster than VLA batteries (due to additives to plates to reduce water loss)

3) Mounted in any orientation - Unlike VLA which are always straight as there is threat of acid leaking, VRLA can be mounted in any direction.

4) Low self-discharge rate - For wide temperature range, self-discharging is marginal in AGM batteries.

5) Portable - VRLA cater need of portable electronics.

6) Long Service Life - VLA matches life span of VRLA only when it maintained well.

(d) Given :- Charge, $Q = 10 \text{ Ah} = 10 \times 3600 = 36000 \text{ C}$
 Faraday's constant, $F = 96485 \text{ C/mol}$

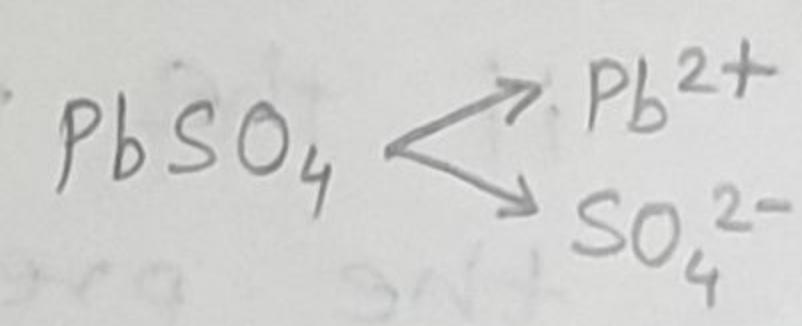
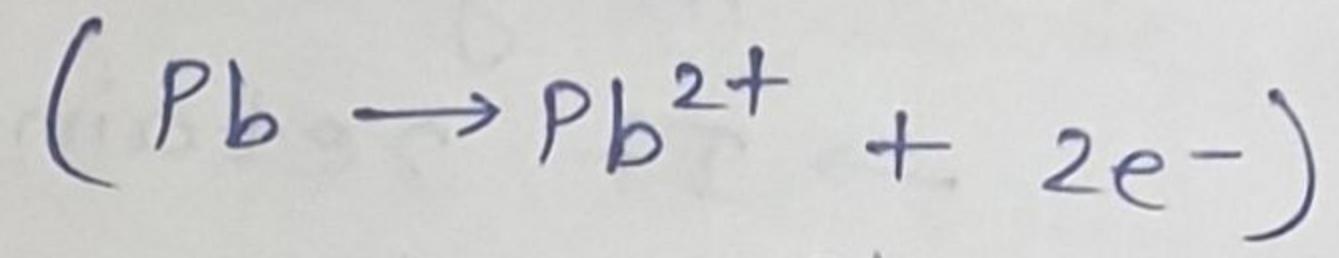
To find :- Mass of Pb oxidised, $m_{\text{Pb}} = ?$

$$\text{Soln} :- m = RF \cdot M \cdot \frac{Q}{nF}$$

$$= 1 \times 207.2 \times \frac{36000}{2 \times 96485}$$

$$m_{\text{Pb}} = 38.6547 \text{ grams}$$

... $RF = \text{Faradaic Efficiency} = 1$
 $M = \text{Molar mass of Pb} = 207.2 \text{ g/mol}$
 $n = \text{No. of electrons exchanged per mole} = 2$



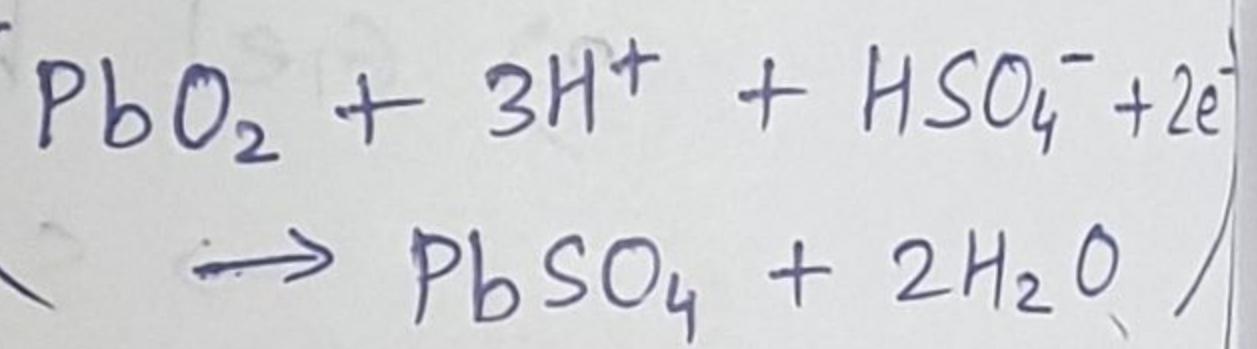
(e) To find :- Mass of PbO_2 reduced, $m_{\text{PbO}_2} = ?$

$$\text{Soln} :- m = RF \cdot M \cdot \frac{Q}{nF}$$

$$= 1 \times 207.2 + 2 \times 16$$

$$= 239.2 \text{ g/mol}$$

$$n = 2$$



$$= 1 \times 239.2 \times \frac{36000}{2 \times 96485}$$

$$m_{\text{PbO}_2} = 44.6245 \text{ grams}$$

(f) To find :- H_2SO_4 mass reacted at both electrodes, $m_{\text{H}_2\text{SO}_4} = ?$

$$\text{Soln} :- m = RF \cdot M \cdot \frac{Q}{nF}$$

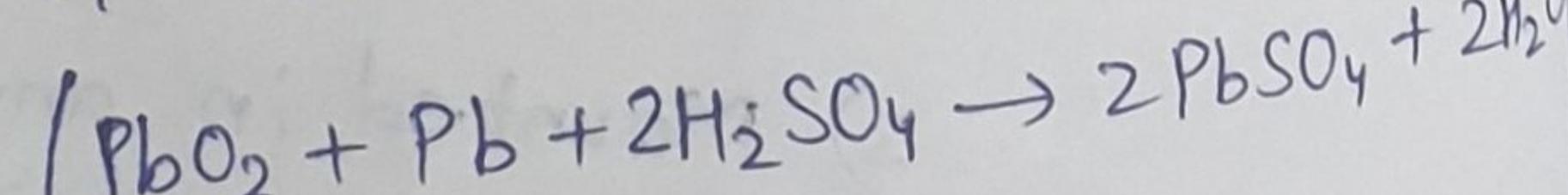
$$RF = 1$$

$$M = 2M_H + M_S + 4M_O$$

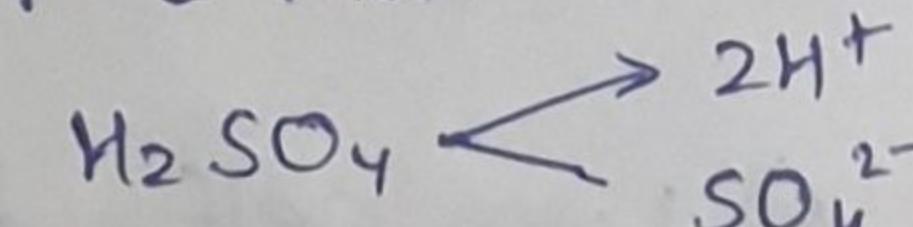
$$= 2 \times 1.008 + 32.06 + 4 \times 16$$

$$= 98.08 \text{ g/mol}$$

$$n = 2$$



For 1 mole of H_2SO_4 ,



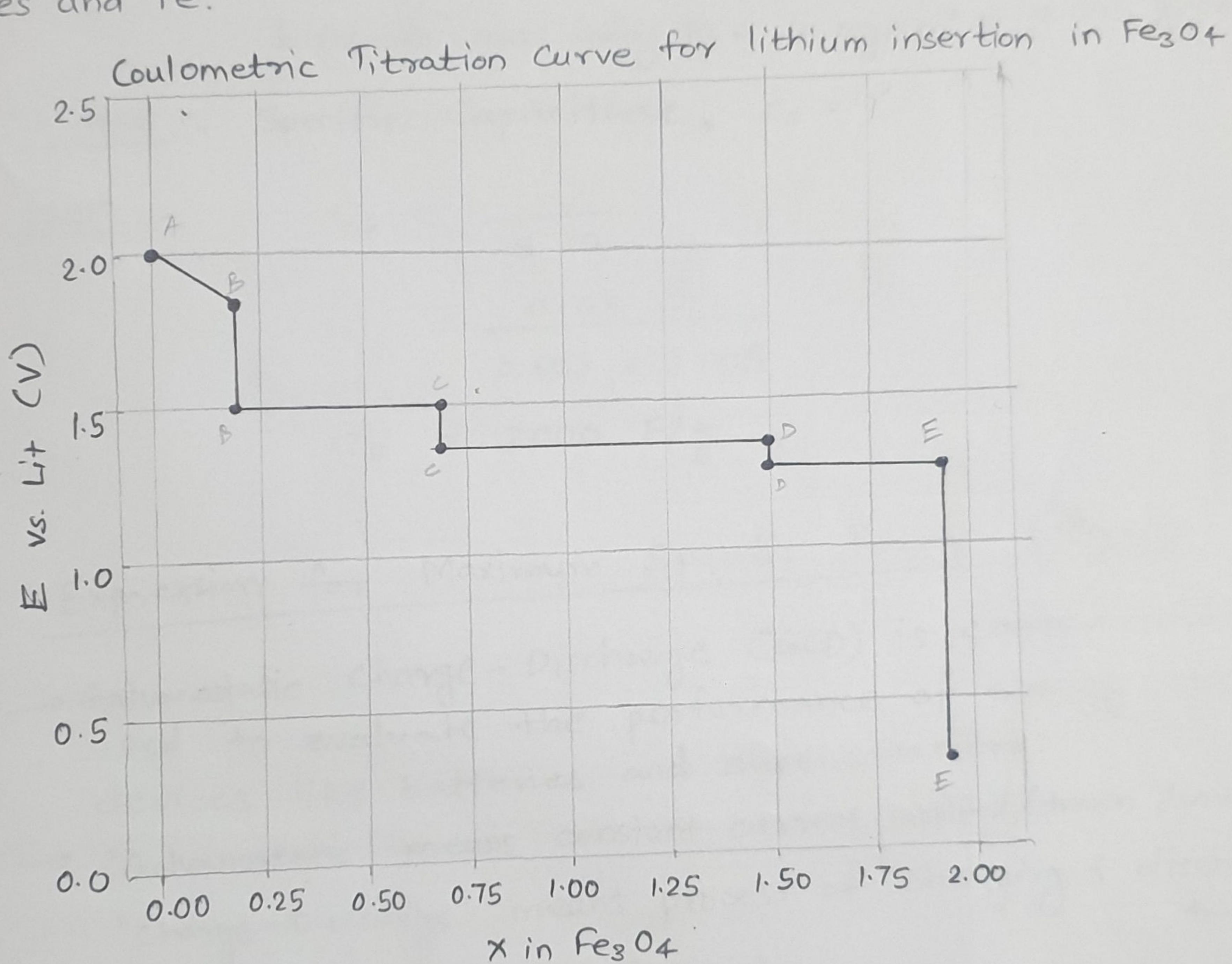
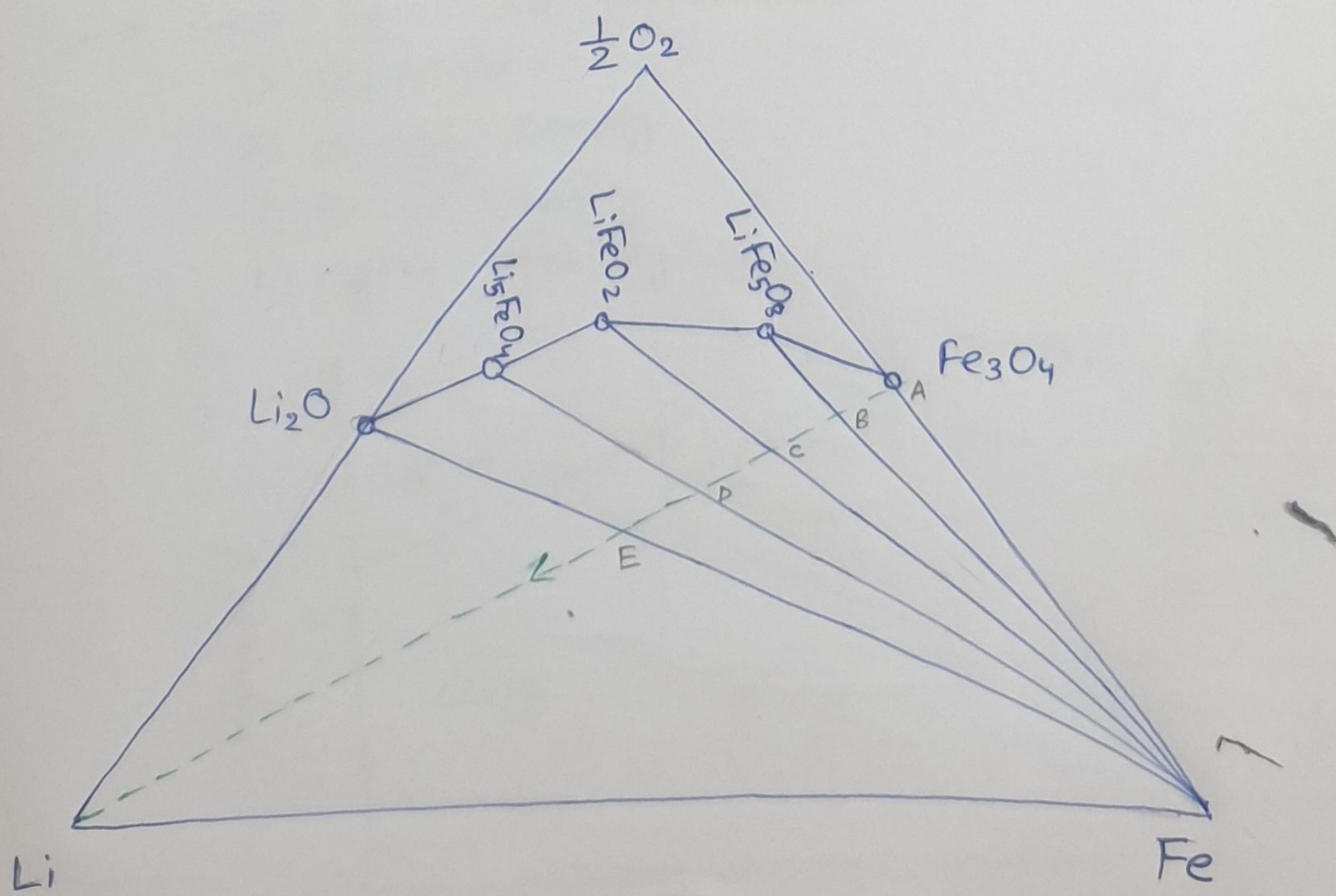
Two electrons exchanged

$$= 1 \times 98.08 \times \frac{36000}{2 \times 96485}$$

$$m_{\text{H}_2\text{SO}_4} = 18.2975 \text{ grams}$$

Q.5

The Coulometric titration curve given below shows the variation of equilibrium potential as lithium is added to Fe_3O_4 under near-equilibrium conditions. Plot the ternary phase diagram for the Li-Fe-O system for lithium insertion in Fe_3O_4 , which can be obtained from the coulometric titration graph below. Consider the stable binary phases - Li_2O and Fe_3O_4 and the stable ternary phases LiFe_5O_8 , LiFeO_2 , and Li_5FeO_4 . Stable tie lines exist between all the ternary phases and Fe.

Ans:-

Q.6 Cyclic voltammetry measurements were done on a supercapacitor with a current density, $i = 20 \text{ mA/cm}^2$, at a scan rate $s = 2 \text{ mV/s}$, with an electrode mass loading of 5 mg/cm^2 .

(a) Calculate the specific capacitance.

(b) Obtain the expression for maximum specific power, P_{\max} , for a supercapacitor device.

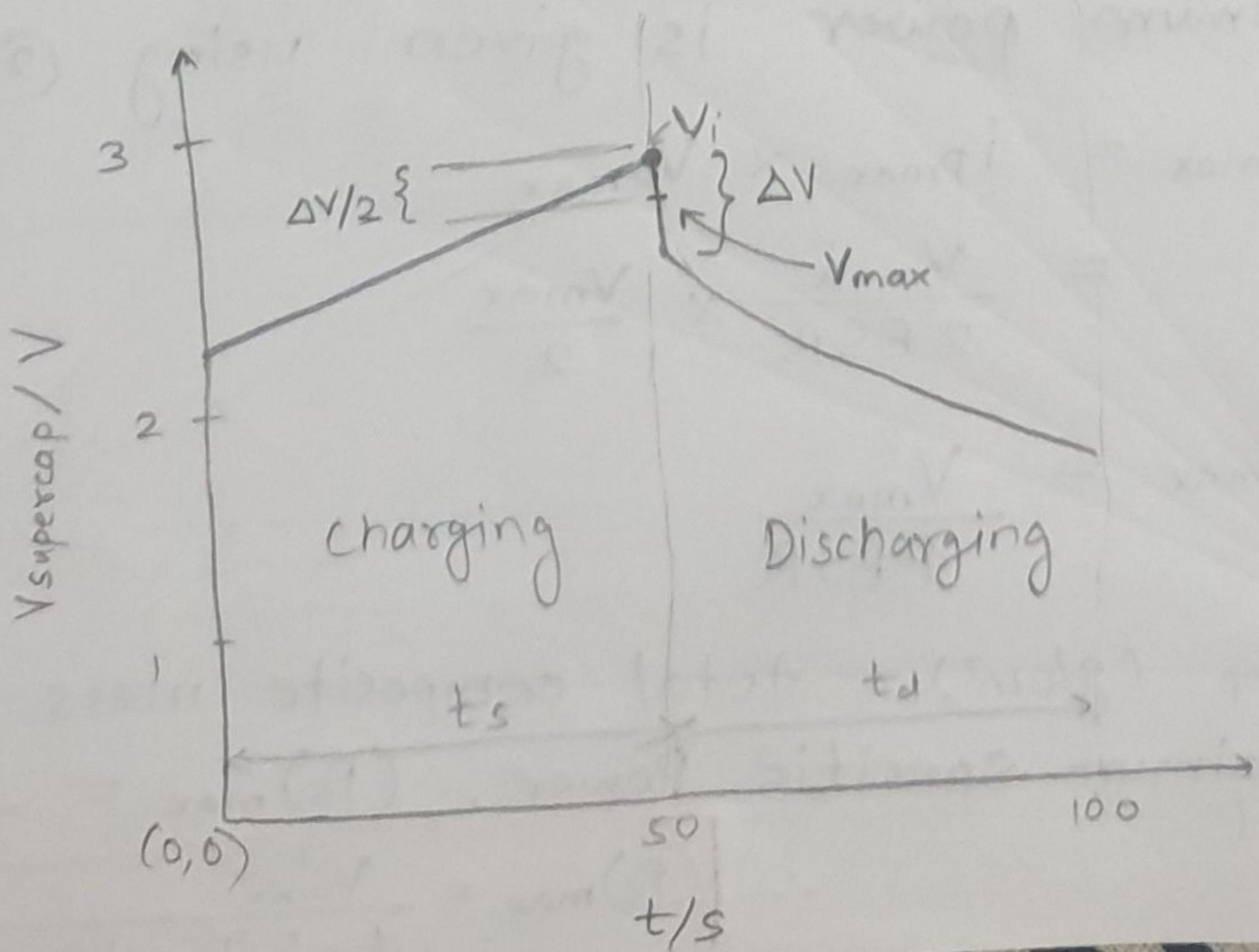
Ans :- (a) Given :- Current Density, $i = 20 \text{ mA/cm}^2 = 0.02 \text{ A/cm}^2$
 Scan Rate, $s = 2 \text{ mV/s} = 0.002 \text{ V/s}$
 Electrode mass loading, $m = 5 \text{ mg/cm}^2 = 0.005 \text{ g/cm}^2$

To find :- Specific Capacitance, $C_s = ?$

$$\begin{aligned}\text{Soln :- } C_s &= \frac{i}{s \cdot m} \\ &= \frac{0.02}{0.002 \times 0.005} \\ C_s &= 2000 \text{ F/g}\end{aligned}$$

(b) Expression for Maximum Specific Power (P_{\max}) :

- Galvanostatic charge-discharge (GCD) is common method used to evaluate the performance of energy storage devices like batteries and supercapacitors.
- "Galvanostatic" means constant current applied/drawn during test.
- "charge-discharge" means process of charging & discharging the device.
- GCD helps to determine
 - 1) capacitance
 - 2) Energy Density
 - 3) Power Density
 - 4) cycle stability



$$\begin{aligned}t_c &= \text{Time of Charge} \\ t_d &= \text{Time of Discharge} \\ V_{\max} &= \text{Maximum Cell Voltage} \\ \text{ESR} &= \text{Equivalent Series Resistance } (-\Omega \text{cm}^2) \\ &= \frac{\Delta V}{2i}\end{aligned}$$

$$i = \text{Current Density } (\text{A/cm}^2)$$

When current flows through a real device, then there's some resistance inside (the ESR). This resistance causes voltage drop in device. Here, ESR affects voltage of supercapacitor during discharge.

$$\therefore V = V_{max} - i \times ESR \quad \text{where } ESR = \frac{\Delta V}{2i} \quad \dots (1)$$

Power expression is given as,

$$P = i \times V \quad \dots (2)$$

$$\Rightarrow P = i \times (V_{max} - i \times ESR) \quad \dots \text{using (1)}$$

$$\Rightarrow P = i \times V_{max} - i^2 \times ESR$$

For maximum power,

$$\Rightarrow \frac{dP}{di} = \frac{d}{di} (i \times V_{max} - i^2 \times ESR) = 0$$

$$\Rightarrow V_{max} - 2i \times ESR = 0$$

$$\Rightarrow i = \frac{V_{max}}{2 ESR}$$

Since this current expression is only valid for P_{max} .

$$\therefore i \equiv i_{P_{max}}$$

$$i_{P_{max}} = \frac{V_{max}}{2 ESR} \quad \dots (2)$$

Similarly, voltage for P_{max} is obtain from (1),

$$V_{P_{max}} = V_{max} - i_{P_{max}} \times ESR$$

$$= V_{max} - \frac{V_{max}}{2 ESR} \times ESR$$

$$= V_{max} - \frac{V_{max}}{2}$$

$$\therefore V_{P_{max}} = \frac{V_{max}}{2} \quad \dots (4)$$

So, maximum power is given using (2), (3) & (4),

$$P_{max} = i_{P_{max}} \times V_{P_{max}}$$

$$= \frac{V_{max}}{2 ESR} \times \frac{V_{max}}{2}$$

$$P_{max} = \frac{V_{max}^2}{4 ESR}$$

Let w_{comp} (g/cm^2) = total composite mass, (sometimes in kg)

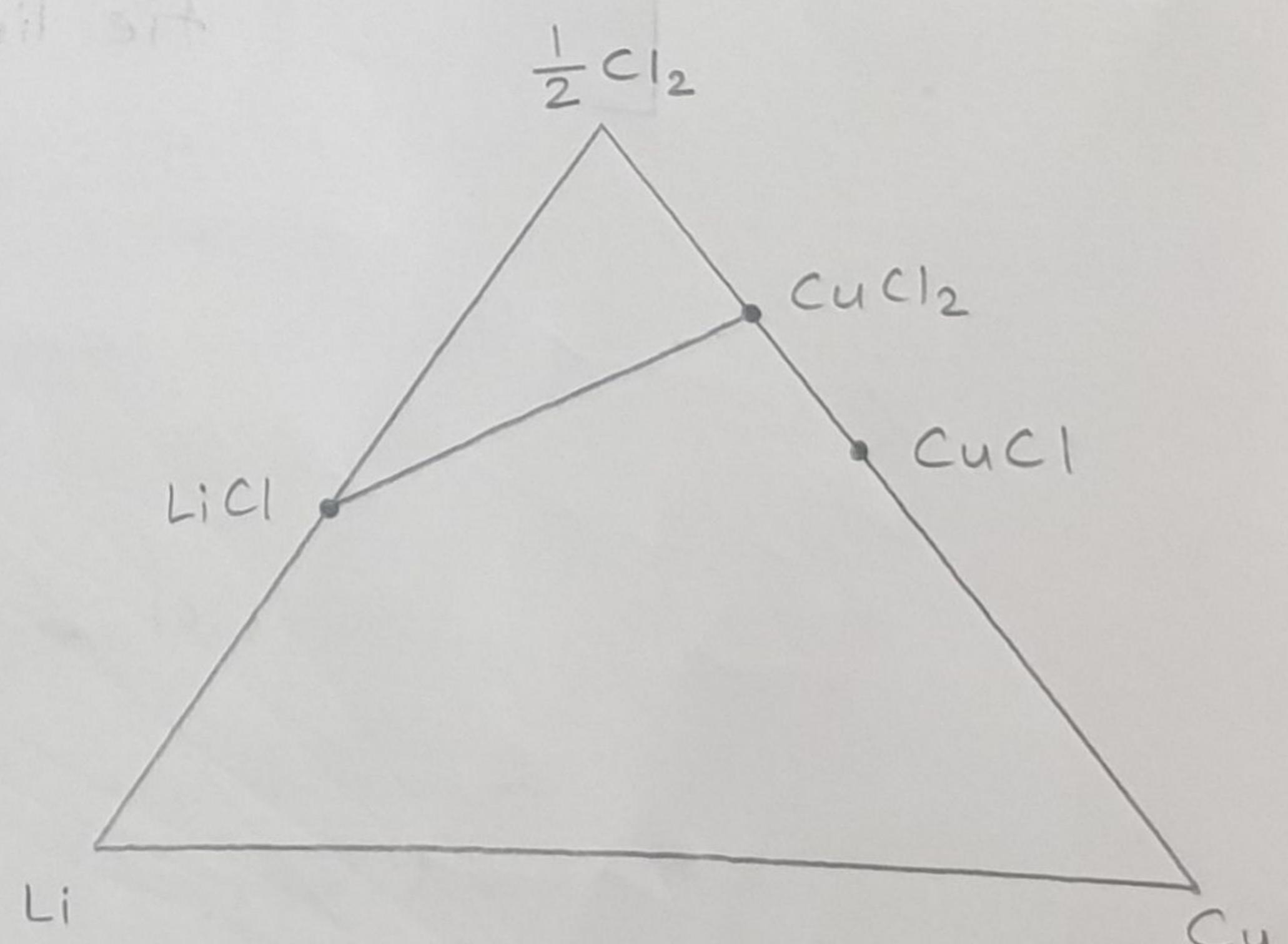
so, Maximum Specific Power, $(Ps)_{max} = \frac{P_{max}}{w_{comp}}$ in W/kg

$$\therefore (Ps)_{max} = \frac{V_{max}^2}{4 \times ESR \times w_{comp}}$$

Q.7 The thermodynamic information of the Li-Cu-Cl system shows three stable binary phases within the system at 298K. The isothermal phase stability ternary diagram and Gibbs Free energies of the formation of phases in the Li-Cu-Cl system at 298K are given below.

- Draw the stable tie lines in the system among the four possibilities: Li and CuCl₂, Li and CuCl, LiCl and CuCl, LiCl and Cu. Justify your answers through virtual equations and by calculating the standard Gibbs free energy of reactions.
- Using the resulting isothermal phase stability diagram and the thermodynamic data, calculate the voltages in the system for (i) the reaction of Li with the positive electrode CuCl. (ii) the reaction of Li with the positive electrode CuCl₂.
- Plot the variation of the equilibrium voltage of (i) Li/CuCl cell and (ii) Li/CuCl₂ cell as a function of extent of the reaction. (iii) Explain the voltage behaviour based on the ternary phase stability diagram generated earlier.
- Calculate the maximum theoretical specific energies (in Wh/kg) of (i) Li/CuCl and (ii) Li/CuCl₂ cells.
[F = 96500 C/mol; atomic weight of Li, Cu and Cl are 7 g/mol, 63.55 g/mol, and 35.45 g/mol respectively.]

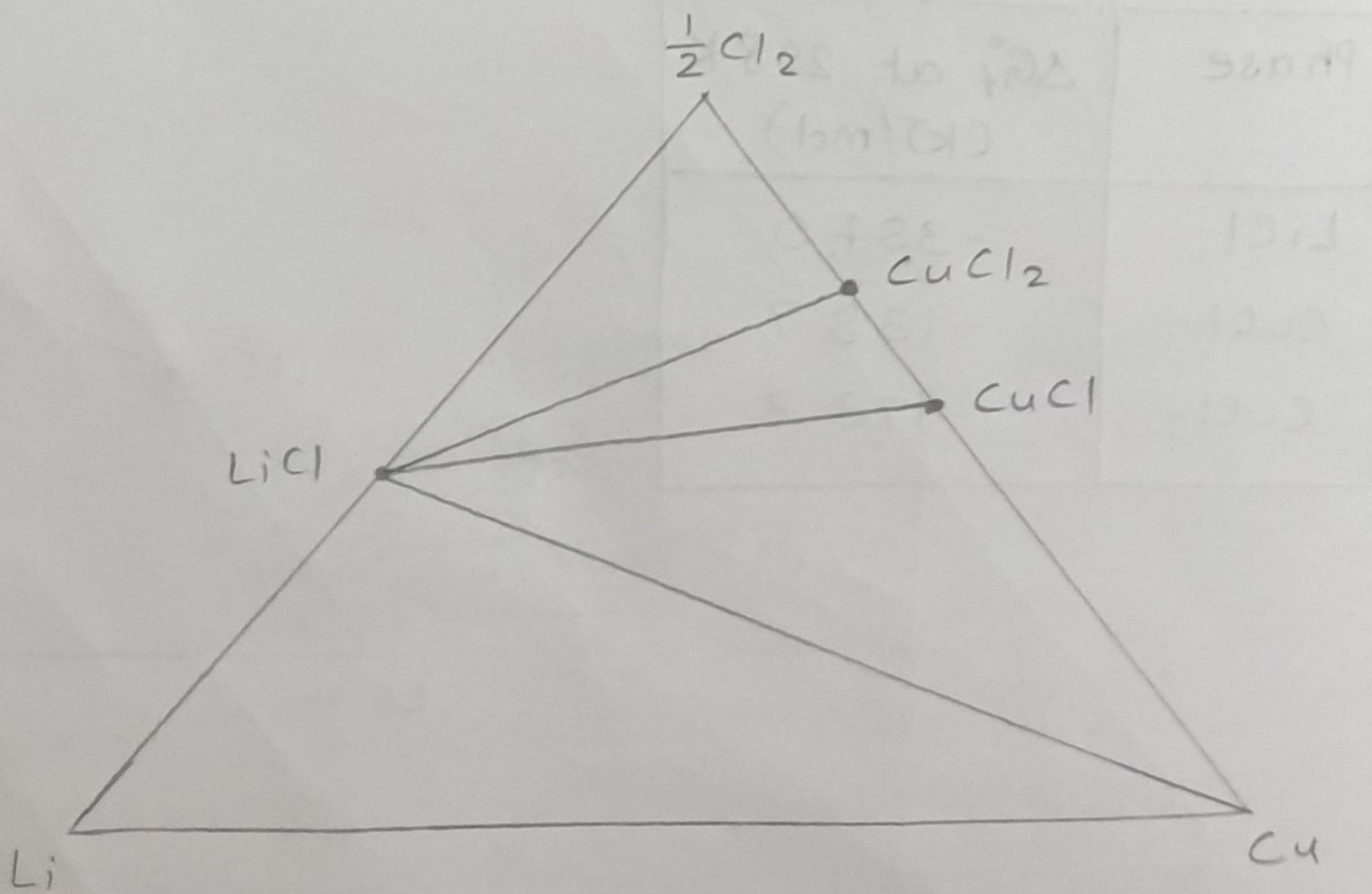
Phase	ΔG_f° at 298 K (kJ/mol)
LiCl	-384.0
CuCl	-138.7
CuCl ₂	-173.8



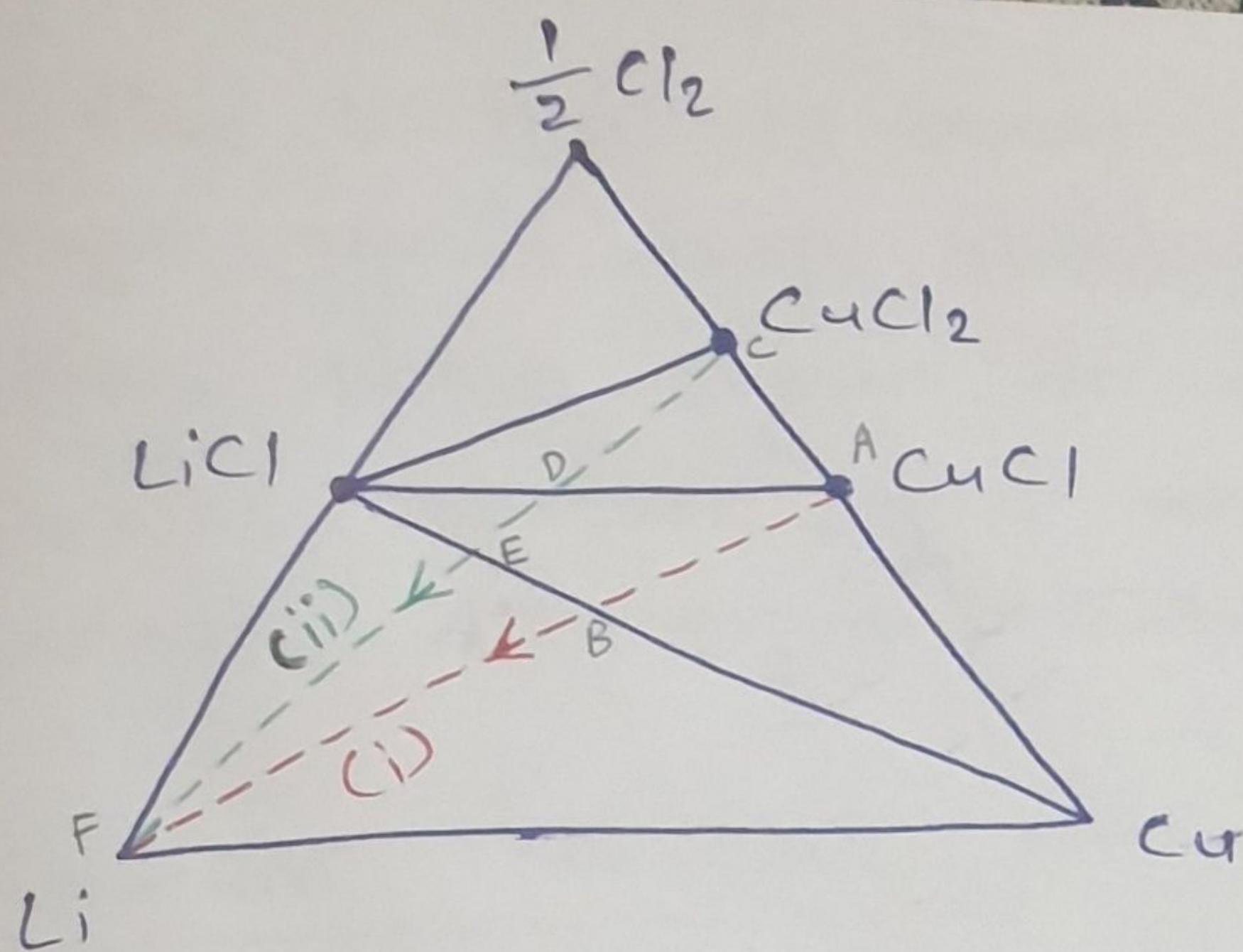
Ans :- (a)

Sr.	Virtual Reaction	ΔG° of Reaction (kJ/mol)	Tie Line (Stable/Unstable)
1(a)	$\text{Li} + \text{CuCl}_2 \rightarrow \text{LiCl} + \text{CuCl}$	$= \Delta G^\circ(\text{LiCl}) + \Delta G^\circ(\text{CuCl}) - \Delta G^\circ(\text{CuCl}_2)$ $= -384 - 138.7 - (-173.8)$ $= -348.9 \text{ kJ/mol}$	Stable
1(b)	$2\text{Li} + \text{CuCl}_2 \rightarrow 2\text{LiCl} + \text{Cu}$ $\text{Li} + \frac{1}{2}\text{CuCl}_2 \rightarrow \text{LiCl} + \frac{1}{2}\text{Cu}$	$= \Delta G^\circ(\text{LiCl}) - \frac{1}{2}\Delta G^\circ(\text{CuCl}_2)$ $= -384 - \frac{1}{2}(-173.8)$ $= -297.1 \text{ kJ/mol}$	Stable
2	$\text{Li} + \text{CuCl} \rightarrow \text{LiCl} + \text{Cu}$	$= \Delta G^\circ(\text{LiCl}) - \Delta G^\circ(\text{CuCl})$ $= -384 - (-138.7)$ $= -245.3 \text{ kJ/mol}$	Stable
3	$\text{LiCl} + \text{CuCl} \rightarrow \text{CuCl}_2 + \text{Li}$	$= \Delta G^\circ(\text{CuCl}_2) - \Delta G^\circ(\text{LiCl}) - \Delta G^\circ(\text{CuCl})$ $= -173.8 - (-384) - (-138.7)$ $= 348.9 \text{ kJ/mol}$	Unstable
4	$\text{LiCl} + \text{Cu} \rightarrow \text{CuCl} + \text{Li}$	$= \Delta G^\circ(\text{CuCl}) - \Delta G^\circ(\text{LiCl})$ $= -138.7 - (-384)$ $= 245.3 \text{ kJ/mol}$	Unstable

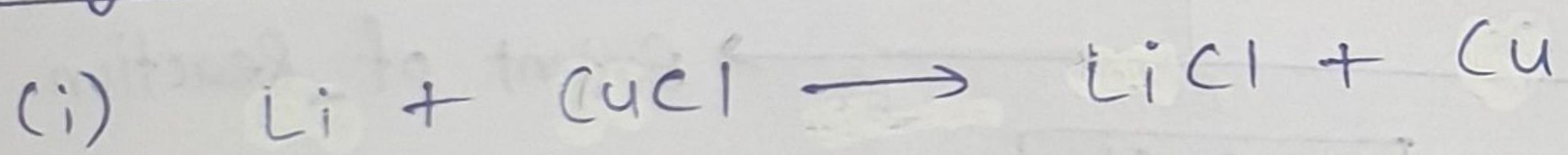
- Note:-
- $\Delta G^\circ_{\text{Reaction}} = \Delta G^\circ_{\text{Products}} - \Delta G^\circ_{\text{Reactants}}$
 - $\Delta G^\circ_{\text{Pure Metal}} \approx 0$ eg. $\Delta G^\circ(\text{Li}) = \Delta G^\circ(\text{Cu}) = 0$
 - $\Delta G^\circ_{\text{Reaction}} = +\text{ve} \rightarrow \text{Unstable (Non-Spontaneous Reaction)}$
 $\Delta G^\circ_{\text{Reaction}} = -\text{ve} \rightarrow \text{Stable (Spontaneous Reaction)}$
 - Refer Products of virtual reaction to draw tie line.



(b)



Voltages for Reactions :-



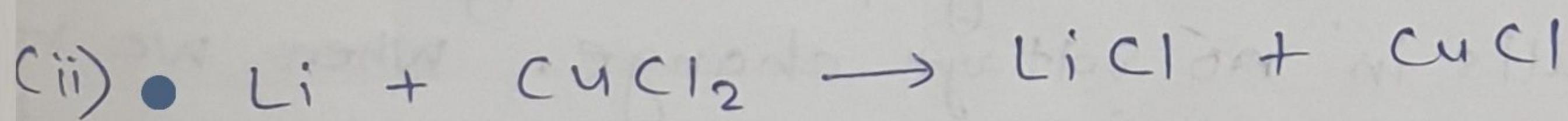
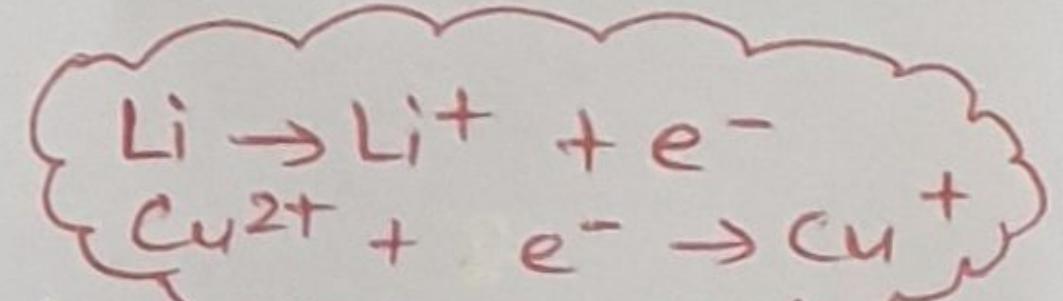
$$\begin{aligned}\Delta G^\circ_{\text{Reaction}} &= \Delta G^\circ_{\text{LiCl}} - \Delta G^\circ_{\text{CuCl}} \\ &= -384 - (-138.7) \\ &= -245.3 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\text{Voltage, } E &= -\frac{\Delta G^\circ_{\text{Reaction}}}{n \times F} \\ &= -\frac{(-245.3)}{1 \times 96500} \\ &= 2.542 \times 10^{-3} \text{ KV} \\ \boxed{E = 2.542 \text{ V}}\end{aligned}$$

- Lithium is oxidised
 $\text{Li} \rightarrow \text{Li}^+ + e^-$
- Copper is reduced
 $\text{Cu}^+ + e^- \rightarrow \text{Cu}$
- ∴ One electron transferred per Li atom
∴ $n=1$

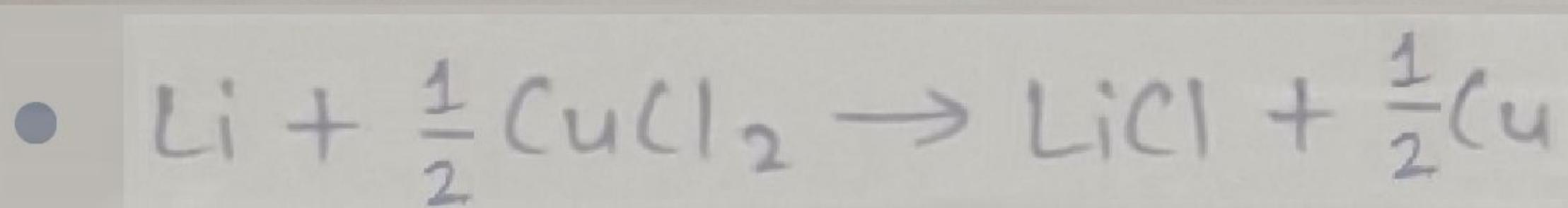
$$\frac{\text{kJ/mol}}{\text{C/mol}} = \frac{\text{kJ}}{\text{C}} = V$$

- $P = VI$
(Watt) = (Volt) (Ampere)
- $E = VQ$
(Joule) = (Volt) (Coulomb)



$$\begin{aligned}\Delta G^\circ_{\text{Reaction}} &= \Delta G^\circ_{\text{LiCl}} + \Delta G^\circ_{\text{CuCl}} - \Delta G^\circ_{\text{CuCl}_2} \\ &= -384 - 138.7 - (-173.8) \\ &= -348.9 \text{ kJ/mol}\end{aligned}$$

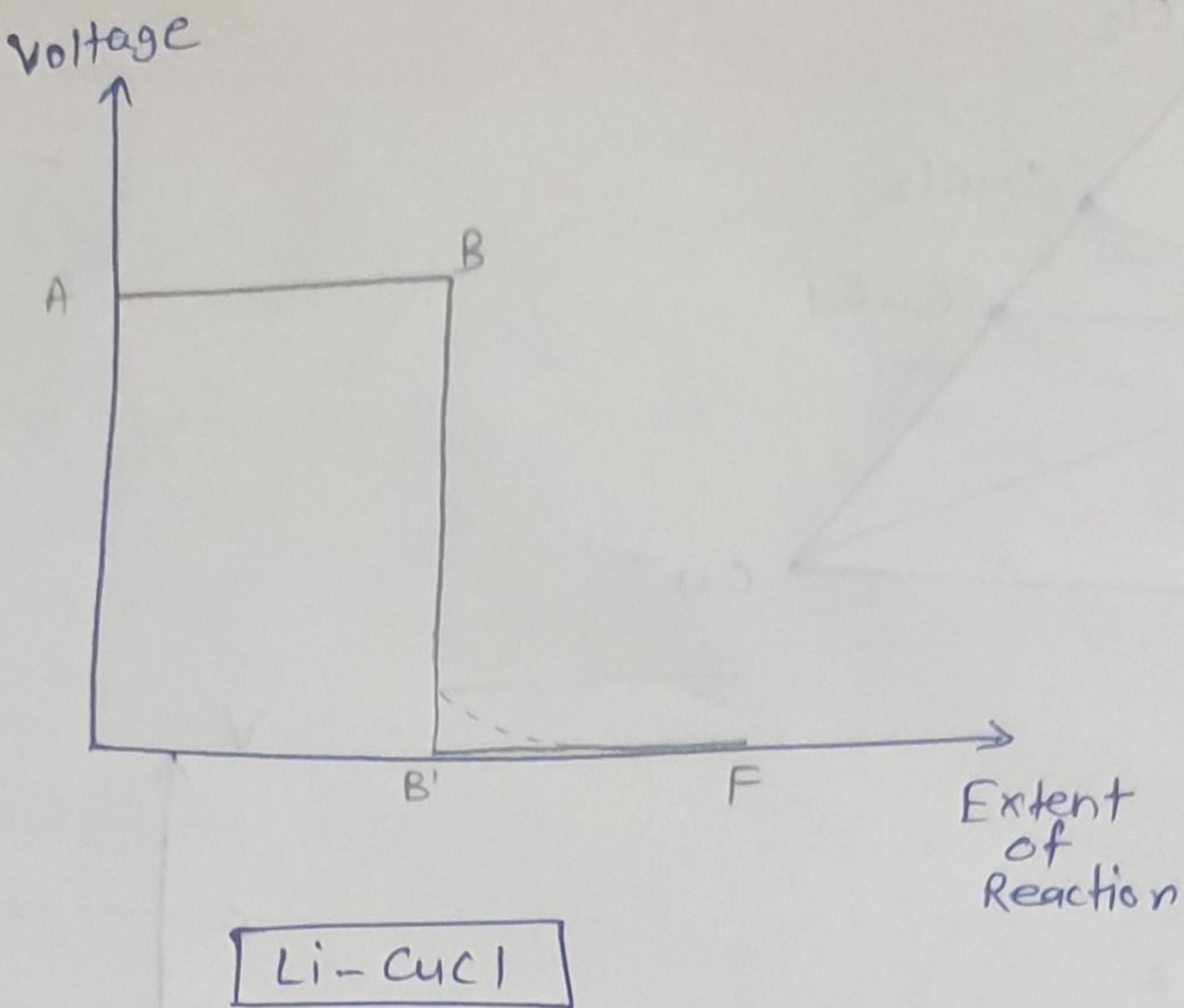
$$\begin{aligned}\text{Voltage, } E &= -\frac{\Delta G^\circ_{\text{Reaction}}}{n \times F} = -\frac{-348.9}{1 \times 96500} \\ &= 3.6155 \times 10^{-3} \text{ KV} \\ \therefore \boxed{E = 3.6155 \text{ V}}\end{aligned}$$



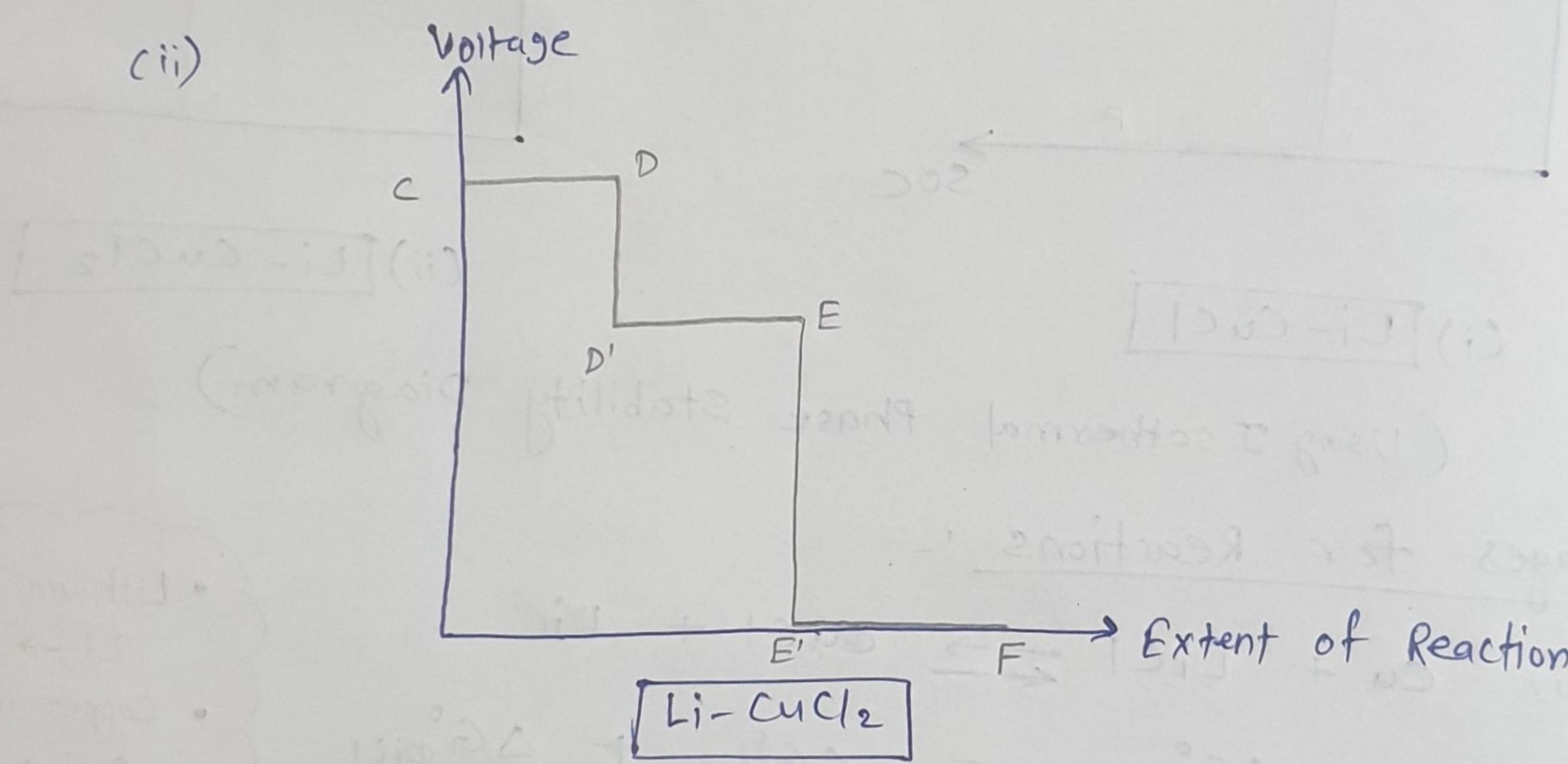
$$\begin{aligned}\Delta G^\circ_{\text{Reaction}} &= \Delta G^\circ_{\text{LiCl}} - \frac{1}{2}\Delta G^\circ_{\text{CuCl}_2} \\ &= -384 - \frac{1}{2}(-173.8) \\ &= -297.1 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\text{Voltage, } E &= -\frac{\Delta G^\circ_{\text{Reaction}}}{n \times F} = -\frac{-297.1}{1 \times 96500} \\ &= 3.0787 \times 10^{-3} \text{ KV} \\ \therefore \boxed{E = 3.0787 \text{ V}}\end{aligned}$$

(c) (i)



(ii)



- For Li-CuCl, as we keep adding Li into CuCl, we initially get tertiary phase. This phase exist between triangle with vertices CuCl, LiCl and Cu. This phase is represented by dotted line 'AB'. ~~At point B~~ Voltage remains constant at this state. When we reach point B, there is sudden drop in voltage due to change from one tertiary phase to another tertiary phase. Again addition of Li, results in no voltage change. When we reach Li (at pure metal stage), voltage correspond to zero.

- For Li-CuCl₂, as Li is added to CuCl₂, from point C to D there is first tertiary phase region where voltage remains constant. At point D, voltage drops suddenly due to change from one tertiary phase to another. Then from D to E, there is second tertiary phase region where voltage remains const.

but this voltage is lower than previous voltage. At point E, voltage again drops suddenly due to change from second tertiary phase region to third. From point E to F, voltage remains constant, and when we reach pure metal Li, voltage corresponds to zero.

(d) Maximum Theoretical Specific Energy $(E_s)_{\max}$ (Wh/kg)

(i) For Li/CuCl,

$$\cancel{(P_s)_{\max}} = \frac{\Delta G^\circ}{nF}$$

$$(E_s)_{\max} = \frac{\text{Charge} \times \text{Voltage}}{\text{Total Molar Mass}}$$

$$(E_s)_{\max} = \frac{nFE}{M} = \frac{-\Delta G^\circ_{\text{Reaction}}}{M}$$

$$= \frac{1 \times 96500 \times 2.542}{0.106}$$

$$\dots M = M_{\text{Li}} + M_{\text{Cu}} + M_{\text{Cl}} \\ = 7 + 63.55 + 35.45 \\ = 106 \text{ g/mol} \\ = 0.106 \text{ kg/mol}$$

$$= \frac{245.3 \times 10^3}{0.106} \frac{\text{J/mol}}{\text{kg/mol}}$$

$$= 2314150.943 \text{ J/kg}$$

$$\dots 1 \text{ Wh} = 3600 \text{ J} \\ \therefore 1 \text{ J} = \frac{1}{3600} \text{ Wh}$$

$$= \frac{2314150.943}{3600} \text{ Wh/kg}$$

$$(E_s)_{\max} = 642.82 \text{ Wh/kg}$$

(ii) ● For Li/CuCl₂,

$$(E_s)_{\max} = \frac{nFE}{M}$$

$$= \frac{1 \times 96500 \times 3.6155}{0.14145}$$

$$\dots M = M_{\text{Li}} + M_{\text{Cu}} + 2M_{\text{Cl}} \\ = 7 + 63.55 + 2 \times 35.45 \\ = 141.45 \text{ g/mol} \\ = 0.14145 \text{ kg/mol}$$

$$= 2466595.97 \text{ J/kg}$$

$$= \frac{2466595.97}{3600} \text{ Wh/kg}$$

$$(E_s)_{\max} = 685.1655 \text{ Wh/kg}$$

(ii) • For Li/CuCl₂,

$$\begin{aligned} (E_s)_{\max} &= \frac{nFE}{M} \\ &= \frac{1 \times 96500 \times 3.0787}{0.074225} \quad \dots M = M_{Li} + 0.5(M_{Cu} + 2M_{Cl}) \\ &= 4002621.085 \text{ J/kg} \\ &= \frac{4002621.085}{3600} \text{ Wh/kg} \\ (E_s)_{\max} &= 1111.8392 \text{ Wh/kg} \end{aligned}$$

$$\begin{aligned} M &= M_{Li} + 0.5(M_{Cu} + 2M_{Cl}) \\ &= 7 + 0.5(63.55 + 2 \times 35.45) \\ &= 74.225 \text{ g/mol} \\ &= 0.074225 \text{ kg/mol} \end{aligned}$$