CSE-A

MATERIAL CHEMISTRY:

1) Derive Nernst Equation for $aA + bB \longrightarrow cC + dD$. (reversible reaction). And write its applications:

Ans: Given equation / reaction:

Reversible reaction: $aA + bB \rightleftharpoons cC + dD$

Let E° be the standard electrode potential of the above reaction:

E° = Standard electrode potential

E = Electrode potential.

→ Nernst Equation gives the relation between E and E°:

$$\Delta G = -\text{Work}$$

$$\text{Work} = \text{Electrical energy} = n \cdot F \cdot E$$

where ΔG = Gibb's free energy

n = charge transfer e's.

$F = 96500$

E = Potential of the electrodes

∴ $\boxed{\Delta G = -nFE}$ and at standard conditions: $\boxed{\Delta G^\circ = -nFE^\circ}$

⇒ Vanthoff's Isotherm Equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

$$\boxed{E = E^\circ - \frac{RT}{nF} \ln Q}$$

For equilibrium equation / reaction $\Rightarrow K = Q$

where $\boxed{K = \frac{[C]^c [D]^d}{[A]^a [B]^b}}$ Equilibrium Constant.

$$\boxed{E = E^\circ - \frac{2.303\,RT}{nF} \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)}$$

where $R = 8.314$; $T(K) = 300K$ $F = 96500F$.

$$\Rightarrow \boxed{E = E^\circ - \frac{2.303RT}{nF} \log K} \quad \because K = \frac{[P]}{[R]}$$

$$\boxed{E = E^\circ - \frac{0.059}{n} \log \frac{\cancel{K}[P]}{[R]}} \longrightarrow \text{Electrolytes}$$

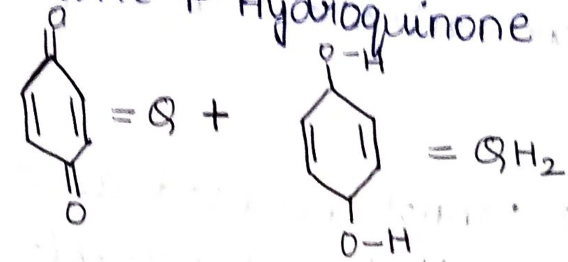
→ Applications:

1) We can determine E when we have the value E° and vice versa at any given conditions of temperatures
2) We can calculate Gibb's free energy from the value of E.
3) We can determine the equilibrium constant from the Nernst equation.
4) We can check the feasibility of the cell.
5) Find the concentration of the electrolytes (or) the ratio.

2) Describe the construction of Quinhydrone electrode. Derive its Nernst equation. Write its electrode reaction, notation and Write its limitations:

S: Quinhydrone Electrode: is a REDOX ELECTRODE:

* Quinhydrone powder = Quinone + Hydroquinone.



* Electrode Reaction:

$$Q + 2H^+ + 2e^- \underset{O}{\overset{R}{\rightleftharpoons}} QH_2.$$

* In Redox Electrode; electrode potential is developed due to the inter conversion of the same compound by oxidation and reduction.

- Platinum electrode is acting as a conductor.

* ANODE: $Pt, \underset{(s)}{Q}, \underset{(s)}{QH_2} \,|\, \underset{(l)}{H^+}$

* CATHODE: $\underset{(l)}{H^+} \,|\, \underset{(s)}{Q}, \underset{(s)}{QH_2}, Pt$

* Nernst Equation: $E^\circ_{QE} = 0.699V$.

$$E_{QE} = E^\circ_{QE} - \log \frac{[QH_2]}{[Q][H^+]^2} \times \frac{0.059}{2}.$$

$\because$ QH_2 and Q are in solid state $[QH_2] = 1$; $[Q] = 1$

$$\therefore E_{QE} = 0.699 - \frac{0.059}{2} \log \frac{1}{[H^+]^2}$$

$$E_{QE} = 0.699 + \frac{0.059}{\cancel{2}} \times \cancel{2} \log [H^+]$$

$$= 0.699 - 0.059 \left(-\log [H^+]\right)$$

$\boxed{E_{QE} = 0.699 - 0.059\,p^H}$ $\because -\log[H^+] = p^H$

∴ Quinhydrone electrode acts as p^H indicator.

→ Limitations:

1) This electrode cannot be used as reference electrode since it is not reliable.

2) The electrolyte used should be free of oxidising agents and reducing agents; because these will disturb the equilibrium.

3) Discuss the factors effecting the conductance and explain any 2 conductometric titrations with well labelled graphs:

Ans Factors effecting the conductance:

1) Nature of electrolyte → S.E, WE
2) Solvent
3) Temperature

→ Remains constant once the experiment starts

4) Concentration / no. of ions
5) Mobility of ions.

* Titration between strong acid and strong base:

Here, HCl and NaOH are strong acid and strong base respectively which are also strong electrolytes which undergo dissociation to form respective ions which are necessary to cause a change in the conductance.

* $HCl \longrightarrow H^+ + Cl^-$

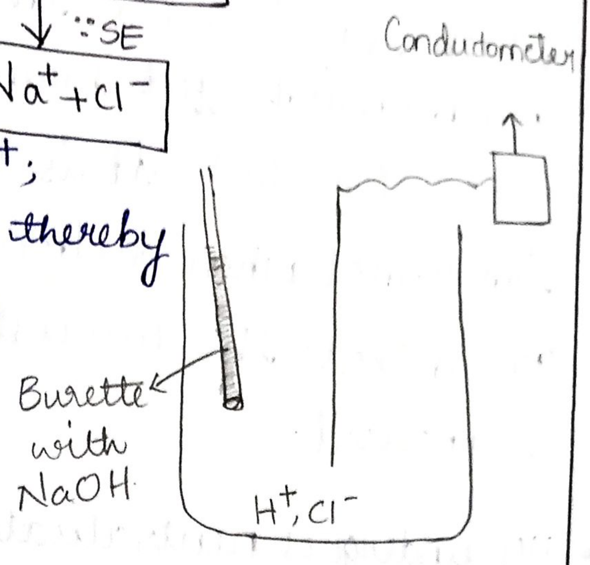
$NaOH \longrightarrow Na^+ + OH^-$

$$\boxed{Na^+ + Cl^- + H^+ + OH^- \longrightarrow NaCl + H_2O}$$

$\downarrow$ ∵SE

$\boxed{Na^+ + Cl^-}$

* ∵ No. of H^+ ions decreases. and Na^+ is heavier than H^+;
∴ Mobility of ions decreases; thereby conductance is decreased by the time titration is completed; it becomes minimum.



→ But no. of ions in the beaker remains same.

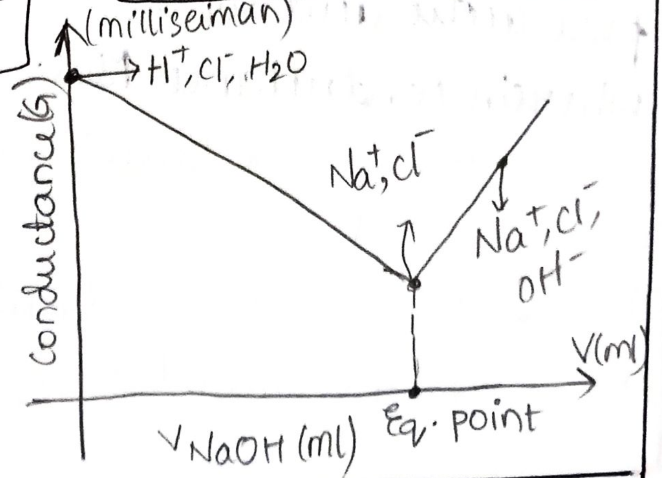
→ Till the point at which HCl is completely neutralised no. of ions decreases and thereby from that point no. of ions increases, & hence increasing the conductance.

* $V_{NaOH} = E.P.$

$$\boxed{N_{HCl} = \frac{(NV)_{NaOH}}{V_{HCl}}}$$

$$\boxed{* \ Wt_{HCl} = N_{HCl} \times Eq.wt \text{ of } HCl.}$$

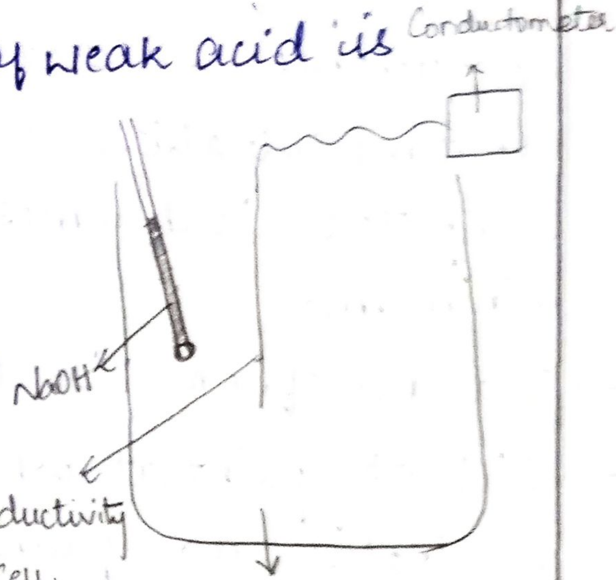
* The equivalence point where the reaction just completed gives the volume of NaOH..



* Titration of mixture of acids:

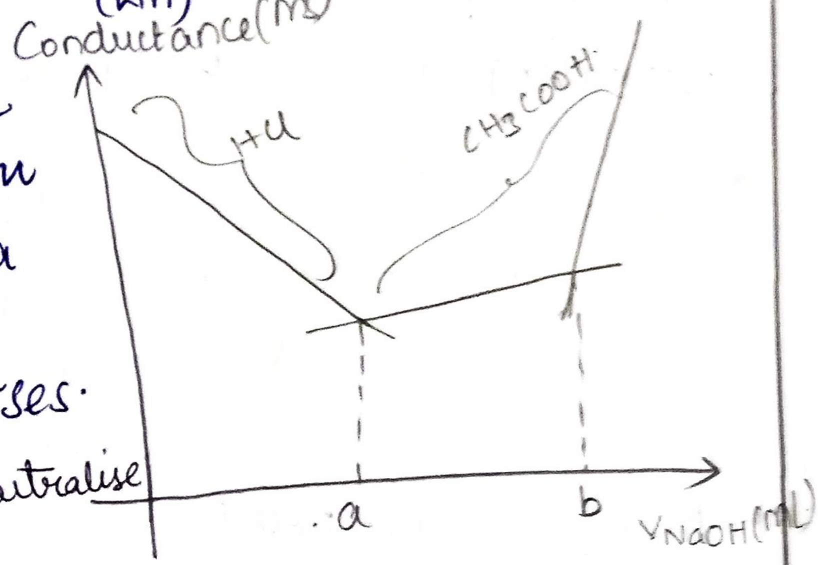
→ Titration of mixture of acids consists of 2 acids i.e. a strong acid (HCl) and weak acid (CH_3COOH) which have an ion in common which undergoes common ion effect during the titration.

* **Common Ion effect:** It is defined as the common ion formed when a strong acid and a weak acid are mixed; the dissociation of weak acid is suppressed.



→ HCl undergoes neutralisation initially whereas CH_3COOH do not undergo neutralisation due to common ion effect i.e. Neutralisation of CH_3COOH (WA) is suppressed.

→ Once HCl is neutralised completely; the solution in the beaker acts as a pure acetic acid sol^n; wherein conductance ↑ses.



a = V_{NaOH} required to neutralise HCl.

b = V_{NaOH} required to neutralise $HCl + CH_3COOH$.

b − a = V_{NaOH} required to neutralise CH_3COOH

$$N_{HCl} = \frac{(NV)_{NaOH}}{V_{HCl}}$$

* Wt. of HCl $= N_{HCl} \times 36.5$ g/L

$$N_{CH_3COOH} = \frac{(NV)_{NaOH}}{V_{CH_3COOH}}$$

* Wt of CH_3COOH $= N_{CH_3COOH} \times 60$ g/L

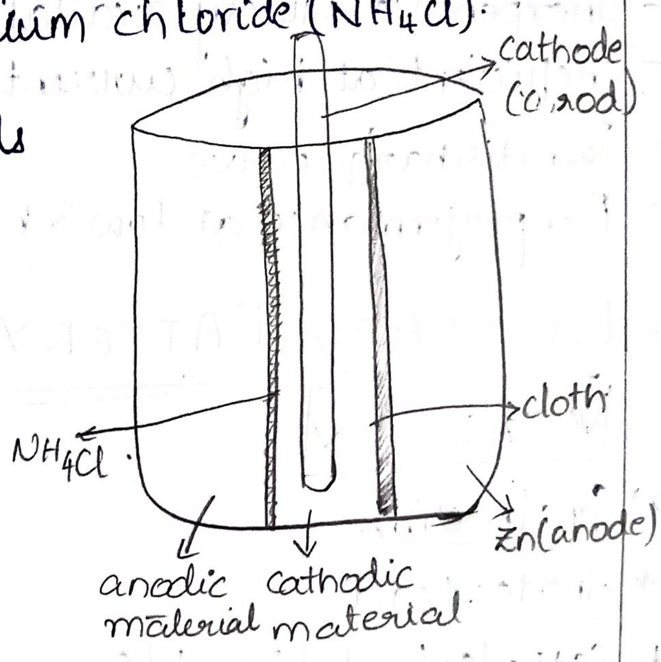
4) Discuss the construction, chemistry, and applications of any one primary, secondary and fuel cell, mention their advantages over others:

* PRIMARY BATTERY: Zinc-Carbon Battery:

→ Construction:

* Cathode: Graphite Rod.
* Anode: Zinc Rod.
* Cathodic Material: Mn_2O_3 + graphite.
* Anodic Material: (Zn + ZnO + graphite) powder.
* Electrolyte: Aqueous Ammonium chloride (NH_4Cl).

→ The anode & cathode materials are made into paste so as to avoid reactions.



* Cell Notation:

$$Zn | Zn^{+2} // NH_4^+ / MnO_2, C$$

* Cell Reactions:

→ Anode: $Zn \rightarrow Zn^{+2} + 2e^-$.

$NH_4Cl + H_2O \longrightarrow NH_4^+ + Cl^-$

$\boxed{NH_4^+ \longrightarrow NH_3}$

→ Cathode:

$\boxed{\text{VOLTAGE} = 1.5V}$

$Mn^{+4} + e^- \longrightarrow Mn^{+3}$

$Zn^{+2} + 2NH_3 + 2Cl^- \longrightarrow [Zn(NH_3)_2Cl_2]$

* Total reaction:

$Zn + MnO_2 + NH_4Cl \longrightarrow [Zn(NH_3)_2Cl_2] + 2H_2O$

* Applications:

1) Remote controls for television, clocks, smoke detectors and flashlights.
2) Hand cranked telephone magneto phones; powering microphone & speaker.

* Features:

- Inexpensive, widely available
- Inefficient at high current drain
- Poor discharge curve
- Poor performance at low & high temperatures.

* SECONDARY BATTERY: Lead Acid Battery:

$\boxed{\text{VOLTAGE} = 2V}$

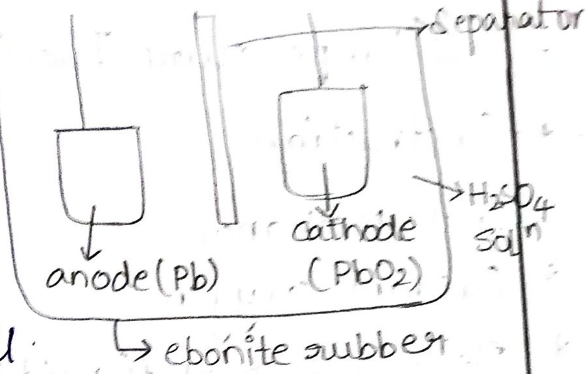
→ Construction:

* Anode: Lead.
* Cathode: Lead di-oxide.
* Electrolyte: Sulphuric acid (specific gravity = 1.2)

Separator: Polymer (polypropylene) sheet.

* Cell Notation:

$Pb, PbSO_4 || H_2SO_4 / PbSO_4, PbO_2 / Pb$



* Cell Reactions:

During discharge: Galvanic Cell

- Spontaneous redox reaction.

$$(H_2SO_4 \longrightarrow 2H^+ + SO_4^{-2}) \times 2$$

Anode: $Pb^\circ \longrightarrow Pb^{+2} + 2e^-$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$
deposited on lead plate.

Cathode: $PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{+2} + 2H_2O$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$

Total Reaction:

$$Pb + 2H_2SO_4 + PbO_2 \longrightarrow 2PbSO_4 + 2H_2O.$$

* During charging reactions are exactly opp. to the above.

* Applications:

1) Used in back-up power supplies for alarms; for electric scooters, wheelchairs.
2) Also used in marine applications; micro hybrid vehicles.

* Features:

- Low self discharge
- cannot be stored when discharged.
- 40% in one year.

* FLOW BATTERY: $CH_3OH - O_2$ FUEL CELL:

- Low Temperature Fuel Cell and Alkaline Fuel Cell.

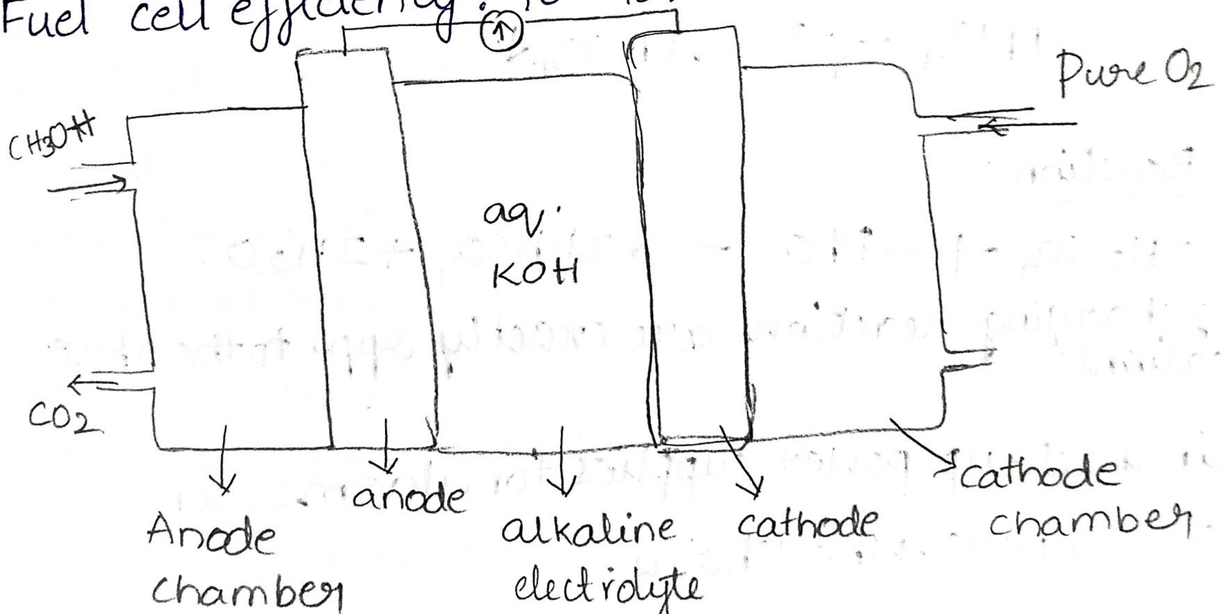
→* Construction:

* Fuel: Methanol
* Oxidant: oxygen
* Electrolyte: KOH (liquid).
* Anode: Porous Ni impregnated with Pt/Pd catalyst

Cathode: Porous Ni coated with Silver catalyst.

* Catalysts: Pt/Pd & Ag
* Operating temperature: 40-90°C.

Fuel cell efficiency: 40-45%



* Cell Reactions:

→ Anode: $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$

→ Cathode: $\frac{3}{2}O_2 + 6e^- + 3H_2O \longrightarrow 6OH^-$

Total reaction:

$$\frac{3}{2}O_2 + CH_3OH \longrightarrow CO_2 + 2H_2O + EE.$$

* Applications:

1) Power for man-portable tactical equipment; battery chargers.
2) Autonomous power for test; training instrumentation.

* Features:

- Products formed i.e. CO_2 is not dangerous compared to the products formed during burning coal i.e. CO, SO_2, SO_3, NO_x.

* NUMERICALS:

1) Calculate the standard EMF of a cell containing Sn^{+2}/Sn and Br_2/Br^- electrodes.

$E^0 (Sn^{+2}/Sn) = 0.14V.$ $\quad E^0(Br_2|Br^-) = 1.08V$

A: $Sn^{+2} + 2e^- \longrightarrow Sn$ $\quad E^\circ = 0.14V \longrightarrow$ Anode

$Br^- \longleftrightarrow Br_2 + e^-$ $\quad E^\circ = +1.08V \longrightarrow$ Cathode

SRP

∴ Cell Notation: $Br^-/Br_2 // Sn^{+2}/Sn$.

$$\therefore E_{cell} = E_C - E_A$$
$$= 1.08 - 0.14$$
$$= 0.94V$$

2) Calculate E°_{cell} when the following half cell reactions are combined:

(i) $Fe^{+3} + e^- \rightarrow Fe^{+2}$
$E^\circ = 0.77V$
↳ Anode

(ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$
$E^\circ = 1.49V$
↳ Cathode

Net reaction:

~~$5Fe^{+3} + 5e^-$~~

$$5Fe^{+2} \longrightarrow 5Fe^{+3} + 5e^-$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

$$\boxed{5Fe^{+2} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O}$$

$$E^\circ_{cell} = E_C - E_A$$
$$= 1.49 - 0.77$$
$$= 0.72V$$

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3) Calculate the equivalent conductivity of 1M H_2SO_4 solution whose conductivity is $26 \times 10^{-2}\ ohm^{-1} cm^{-1}$

$$\lambda_M = \frac{K \times 1000}{M}$$

$$K = 26 \times 10^{-2}$$

$$N = M \times n_f = \cancel{1}\ \cancel{2} = 2 \times 1$$

$$\lambda_{eq} = \frac{K \times 1000}{N}$$

$$= \frac{26 \times 10^{-2} \times 10^{3}}{2}$$

$$\lambda_{eq} = 13 \times 10 = 1.3 \times 10^{2}\ ohm^{-1} eq^{-1}.$$

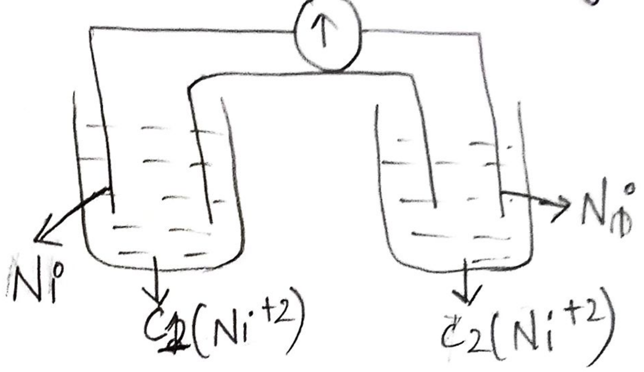
1) Construct a concentration cell with Nickel electrodes. The electrode potential of Ni° is $-0.24V$ and the concentrations of solutions are 0.5 and 0.05 respectively.

$C_1 = 0.05 \rightarrow$ Anode

oxidation

$C_2 = 0.5 \rightarrow$ Cathode

Reduction.



$E^{\circ}_{cell} = 0$ $\because$ for any concentration cell.

$$E = -\frac{0.0591}{n} \log \frac{C_1}{C_2}$$

A: $Ni \rightarrow Ni^{+2} + 2e^-$

C: $Ni^{+2} + 2e^- \rightarrow Ni$

$$= -\frac{0.0591}{2} \log \frac{0.05}{0.5}$$

$$= -\frac{0.0591}{2} \log \frac{\cancel{5} \times 10^{-2}}{\cancel{5} \times 10^{-1}}$$

$$= -\frac{0.0591}{2} \times -1 = 0.029V.$$

$$\boxed{E = 0.029V}$$