

OR IN A DIFFERENTIAL FORM

$$\frac{dq}{dt} = \frac{n_e F}{b} \frac{dn_B}{dt}$$

BUT FOR DIFFERENT SPECIES

$$\text{RATE OF REACTION} = \frac{1}{b} \frac{dn_B}{dt} = -\frac{1}{a} \frac{dn_A}{dt}$$

$$\therefore \frac{dq}{dt} = \frac{n_e F}{b} \frac{dn_B/dt}{dt} = -\frac{n_e F}{a} \frac{dn_A/dt}{dt}$$

BY DEFINITION

$$I = \frac{dq}{dt}$$

$$I = \frac{+n_e F}{b} \frac{dn_B}{dt} = -\frac{n_e F}{a} \frac{dn_A/dt}{dt} \quad (2)$$

2nd FORM of
Faraday's LAW

+ sign
 B^{2+} and e^-
are on the
SAME
SIDE

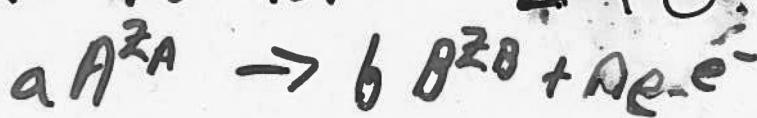
- sign
 A^{2+} and e^-
are on
opposite
sides

IF

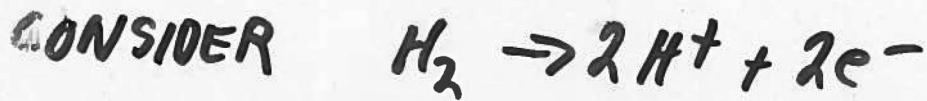
REACTION PROCEEDS LEFT \rightarrow RIGHT

$$\frac{dn_A/dt}{dt} < 0 \text{ and } \frac{dn_B/dt}{dt} > 0 \quad I > 0$$

REACTION IS ANODIC
RIGHT TO LEFT $I < 0$, CATHODIC



EXAMPLE



$$a_{H_2} = 1 \quad b_{H^+} = 2 \quad n_e = 2$$

$a_j \Rightarrow$ species on opposite side of e^-

$b_j \Rightarrow$ species on same side as e^-

APPLY FARADAY'S LAW

$$I = -\frac{n_e}{1} F \frac{dn_{H_2}}{dt} = -\frac{2}{1} F \frac{dn_{H_2}}{dt}$$

2 electrons generated for each H_2 consumed

H_2 and e^- on opposite sides

OR

$$I = +\frac{n_e}{b_{H^+}} F \frac{dn_{H^+}}{dt} = \frac{2}{2} F \frac{dn_{H^+}}{dt} = F \frac{dn_{H^+}}{dt}$$

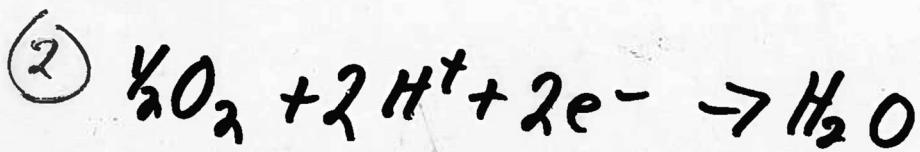
$$I = -2 F \frac{dn_{H_2}}{dt} = F \frac{dn_{H^+}}{dt}$$

$$\frac{dn_{H_2}}{dt} = -\frac{1}{2} \frac{dn_{H^+}}{dt}$$

$$\text{or } \frac{1}{a_{H_2}} \frac{dn_{H_2}}{dt} = -\frac{1}{b_{H^+}} \frac{dn_{H^+}}{dt}$$

IF THE REACTION PROCEEDS AS WRITTEN

$I > 0$ ANODIC REACTION $\frac{dn_{H_2}}{dt} < 0, \frac{dn_{H^+}}{dt} > 0$



$$b_{\text{O}_2} = \frac{1}{2} \quad b_{\text{H}^+} = 2 \quad a_{\text{H}_2\text{O}} = 1 \quad n_c = 2$$

$$I = \frac{-n_e}{a_{\text{H}_2\text{O}}} F \frac{dn_{\text{H}_2\text{O}}}{dt} = -\frac{2}{1} F \frac{dn_{\text{H}_2\text{O}}}{dt}$$

$$I = \frac{n_e}{b_{\text{O}_2}} F \frac{dn_{\text{O}_2}}{dt} = \frac{2}{\frac{1}{2}} F \frac{dn_{\text{O}_2}}{dt} = 4F \frac{dn_{\text{O}_2}}{dt}$$

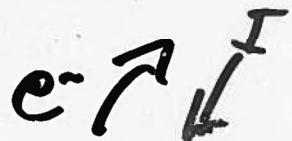
$$I = \frac{n_e}{b_{\text{H}^+}} F \frac{dn_{\text{H}^+}}{dt} = \frac{2}{2} F \frac{dn_{\text{H}^+}}{dt} = F \frac{dn_{\text{H}^+}}{dt}$$

IF PROCEESS AS WRITTEN

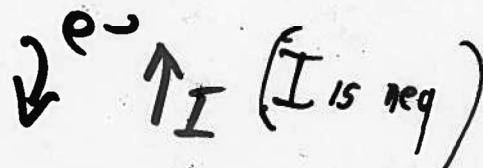
$$dn_{\text{O}_2} < 0$$

$$dn_{\text{H}^+} < 0$$

$\therefore I < 0$ cathodic reaction



ANODE

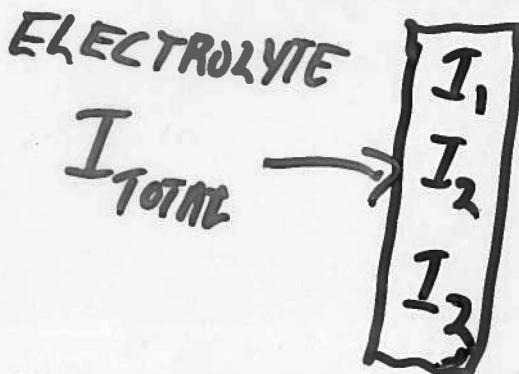


CATHODE

CURRENT EFFICIENCY

In many cases there is more than one electrode reaction on a single electrode

o^o simultaneous / parallel or competitive process



I_{TOT} = total current through the electrode

$$I_{TOT} = I_1 + I_2 + I_3 \text{ or } \sum I_j$$

$$\delta i_{tot} = i_1 + i_2 + i_3 = \sum i_j$$

where
 I_j = partial current due to reaction j

FARADAY'S LAW APPLIES TO EACH ELECTRODE REACTION

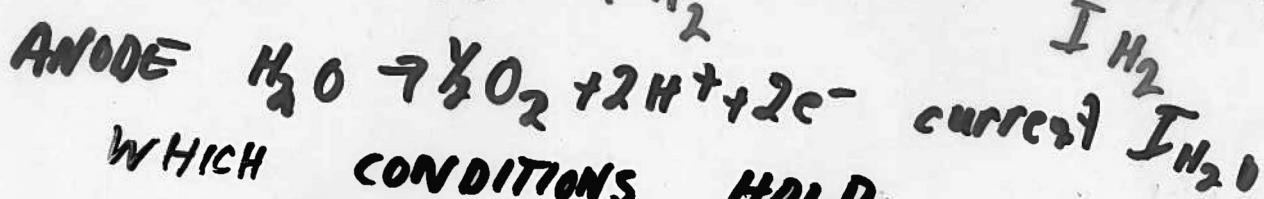
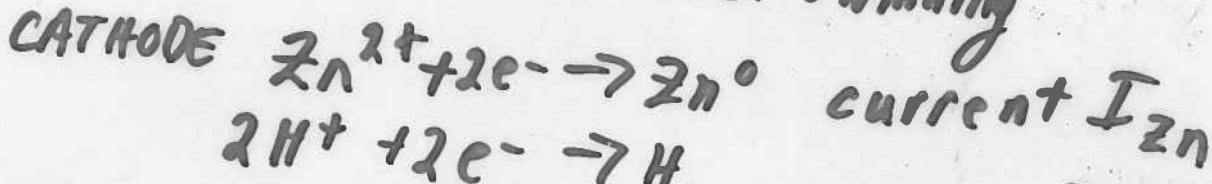
WE DEFINE CURRENT EFFICIENCY

ξ_j for reaction j as

$$\xi_j = \frac{I_j}{I_{TOT}} \times 100\% = \frac{I_j}{\sum I_j} \times 100\% \quad \text{OR} \quad \left(\frac{i_j}{\sum i_j} \times 100\% \right)$$

THE CURRENT EFFICIENCY REFERS TO AN ELECTRODE AND NOT TO THE ELECTROCHEMICAL CELL.

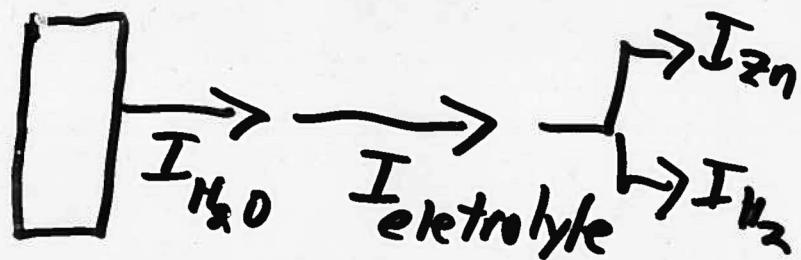
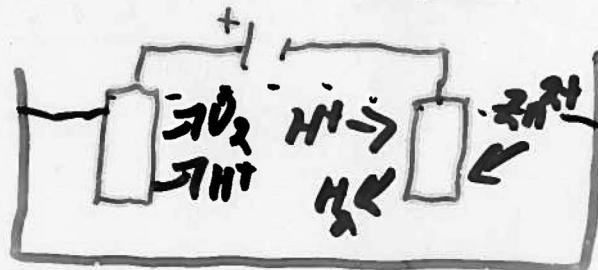
EXAMPLE \rightarrow Zn Electrowinning



$$I_{\text{CATHODE}} = I_{Zn} + I_{H_2}$$

$$I_{\text{ANODE}} = I_{H_2O}$$

$$|I_{\text{CATHODE}}| = I_{\text{ANODE}}$$



ANODE \rightarrow ELECTROLYTE \rightarrow CATHODE IN SERIES

$$I_{\text{ANODE}} = I_{H_2O} = I_{\text{ELECTROLYTE}} = |I_{Zn}| + |I_{H_2}| = |I_{\text{CATHODE}}|$$

CURRENT EFFICIENCY OF Zn REDUCTION
AT THE CATHODE

$$\epsilon_{Zn} = \frac{I_{Zn}}{I_{Zn} + I_{H_2}} \times 100\%$$

CURRENT EFFICIENCY OF H₂ EVOLUTION
AT CATHODE

$$\epsilon_{H_2} = \frac{I_{H_2}}{I_{Zn} + I_{H_2}} \times 100\% = 100 - \epsilon_{Zn}$$

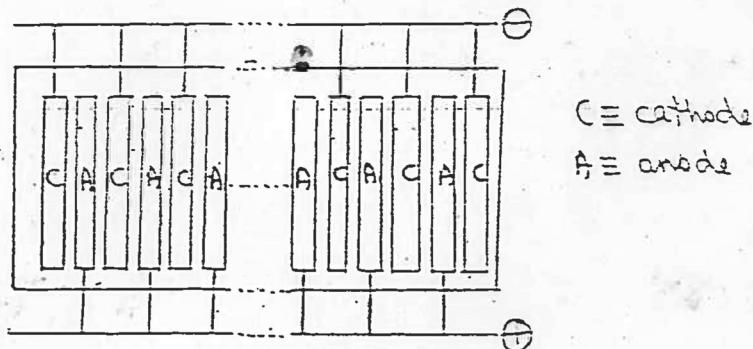
ANODE

$$\epsilon_{H_{2O}} = 100\%$$

CURRENT EFFICIENCIES AT CATHODE
AND ANODE ARE NOT
NECESSARILY EQUAL

Example

A lead electrorefining cell is operating at an overall current density of 230 A m^{-2} . Each tank contains 40 anodes and 41 cathodes in a monopolar connection, as shown below:



The electrodes are arranged in an alternating sequence of cathode and anode sheets in each tank. The last electrodes at both ends of the sequence in each tank are cathodes. Lead is plated onto both sides of each cathode, except for the cathodes at the end of each sequence that are plated on only one side each.

The portion of each electrode immersed in the electrolyte measures 0.9 m by 1.2 m. If the current efficiency for lead deposition is 93 %, calculate the number of tanks (each is identical to the one shown above) that must be added if the aim is to increase the daily lead production by 30,000 kg.

The oxidation state of dissolved lead is +2.

(1)

Pb EXAMPLE

PRODUCTION RATE IS GIVEN BY FARADAY'S LAW

$$\text{CURRENT FOR Pb}^{\circ} \text{ PRODUCTION} = I_{\text{Pb}} = -\frac{n_e}{a_{\text{Pb}}} F \frac{dn_{\text{Pb}}}{dt}$$

WHERE n_{Pb} = # of moles of Pb° PLATED

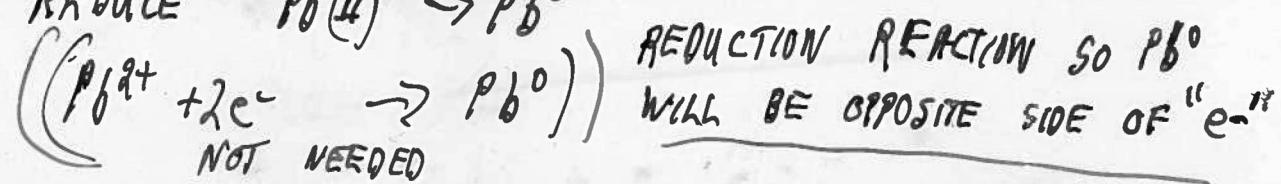
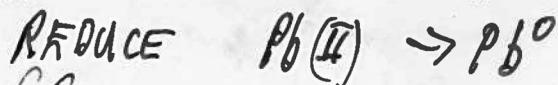
a_{Pb} = STOICHIOMETRIC COEFFICIENT
OF Pb°

WHY THE NEGATIVE SIGN?

EXACT REACTION IS NOT KNOWN

BUT

THE AIM OF THE REACTION IS TO

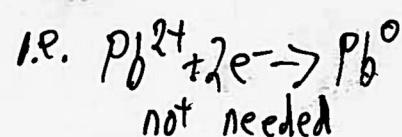


WHAT VALUE TO USE FOR $\frac{n_e}{a_{\text{Pb}}}$?

n_e/a_{Pb} → MEANS THE # OF ELECTRONS TRANSFERRED
FOR EACH Pb° FORMED

THUS Pb(II) is reduced from +2 OXIDATION STATE
to "0" OXIDATION STATE

$$\stackrel{0}{\text{Pb}}_0 \stackrel{0}{\text{Pb}}_2 \frac{n_e}{a_{\text{Pb}}} = 2$$



$$I_{\text{Pb}} = -2F \frac{dn_{\text{Pb}}}{dt}$$

$$\text{PRODUCTION RATE OF Pb}^{\circ} = \frac{dn_{\text{Pb}}}{dt} = -\frac{I_{\text{Pb}}}{2F} = \frac{|I_{\text{Pb}}|}{2F}$$

1a

Faraday Constant

$$F = 96,485.3383 \text{ coulombs/mol}$$

$$F = N_A e$$

$$= 6.02 \times 10^{23} \text{ /mol} \times 1.602 \times 10^{-19} \text{ coulombs/electron}$$

$$F = 96,485 \text{ C/mole}$$

$$(N_A F)$$

$$\frac{\text{mole}}{\text{mole}} \times \frac{\text{C}}{\text{mole}} = \text{C/mole}$$

GIVEN 41 CATHODES BUT ONLY 39
INTERIOR ONES (2)

THUS THE TWO END PLATES HAVE ONLY
ONE SIDE EACH

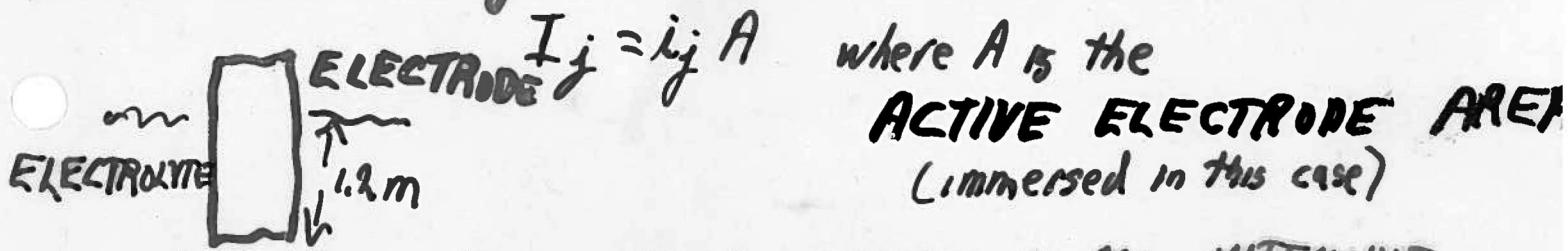
$$\therefore \text{TOTAL # of faces on which Pb}^{\circ} \text{ is plated} \\ = 2(39) + 2 \\ = 80 \text{ faces}$$

IN EACH TANK $I_{\text{TANK}} = 80 I_j$

WHERE I_j = CURRENT BETWEEN Adjacent CATHODE
AND ANODE PLATES

I_{TANK} = TOTAL CURRENT THROUGH EACH
TANK

WHAT IS I_j ?



$\leftarrow 0.9m \rightarrow$ Now current density is an intensive variable.

so current density over the entire cell is
THE SAME current density over each electrode.

i.e. $i_j = i_{\text{CELL}}$

$$I_j = (230 \text{ A/m}^2)(0.9 \text{ m})(1.2 \text{ m}) \\ = 248.4 \text{ A}$$

$$I_{\text{TANK}} = 80 (248.4 \text{ A}) \\ = 19,872 \text{ A}$$

GIVEN CURRENT
EFFICIENCY FOR
 Pb° FORMATION
 $\epsilon_{Pb} = 93\%$

BUT NOT ALL CURRENT IS USED FOR Pb PLATING. (93%)

$$|I_{Pb}| = \frac{\epsilon_{Pb}}{100} I_{\text{TANK}} = 0.93 (19,872 \text{ A}) = 18,480.96 \text{ A}$$

(3)

$$\therefore \text{Pb production rate per tank} = \frac{1 F_{\text{Pb}}}{2F}$$

$$= \frac{18,480 \cdot 961}{2(96,485 \text{ C/mol})}$$

$$= 0.0958 \frac{\text{A} \cdot \text{mol}}{\text{C}}$$

$$1 \text{ coulomb/sec} = 1 \text{ A}$$

$$= 0.0958 \frac{\text{A} \cdot \text{mol}}{\text{A} \cdot \text{sec}}$$

$$= 1 \text{ Amp}$$

$$= \frac{0.0958 \text{ mol}}{\text{sec}} / \frac{207.19 \text{ g}}{\text{mol Pb}} / \frac{10^{-3} \text{ kg}}{\text{g}} / \frac{3600 \text{ sec}}{\text{hr}} / \frac{24 \text{ hr}}{\text{day}}$$

$$(AW \text{ of Pb}) \qquad \qquad \qquad = 1714.4 \text{ kg/day}$$

\therefore # of tanks needed to increase production rate by 30,000 kg/day

$$= \frac{30000}{1714.4 \text{ kg/day}} \text{ TANK}$$

= 17.5 TANKS

SAY 18 TANKS NEEDED

Composition of Solutions

Mole Fraction

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_n} = \frac{n_i}{\sum_{j=1}^n n_j}$$

$$x_1 + x_2 + \dots + x_n = \sum_{j=1}^n x_j = 1$$

Molality

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Molarity

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Important: molarity varies with temperature

Percentage

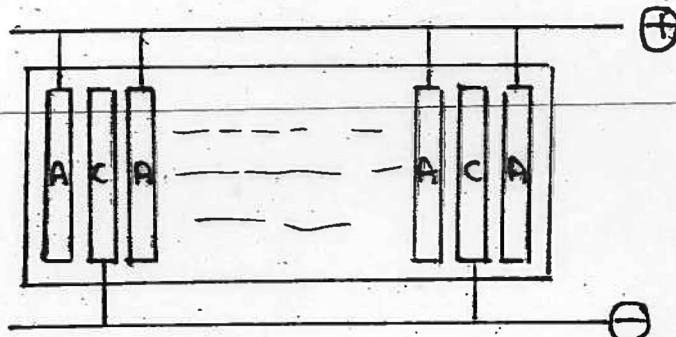
25% (v/v) 25 ml of solute in 100 ml of solution

25% (w/v) 25 g of solute in 100 ml of solution

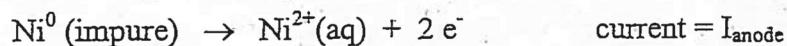
25% (w/w) 25 g of solute in 100 g of solution

Nickel Plating Example

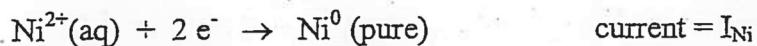
Nickel electrorefining is being carried out continually under steady-state conditions in a tank containing 61 anodes and 60 cathodes that is electrically wired according to a monopolar connection, as shown below.



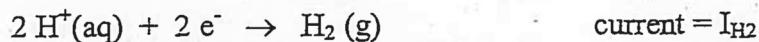
The operation of this process can be modelled as a CSTR. In this process, impure nickel anodes are dissolved according to the reaction



and pure nickel is plated at the cathodes via the reaction



A secondary reaction



also occurs at the cathode. No secondary reaction occurs at the anode.

Both the cathodes and anodes are rectangular in shape, but they have different dimensions. Each cathode is 0.8 m wide and is immersed to a depth of 1.1 m in the electrolyte. Each anode is 0.9 m wide and is immersed to a depth of 1.2 m. Each cathode is plated on both sides. Each anode dissolves on both sides except the end ones that dissolve on only 1 side each.

During operation of the cell, the tank is continually fed by a stream containing dissolved NiSO_4 (strong electrolyte). The volumetric flowrate of the electrolyte through the tank is $2 \times 10^{-4} \text{ m}^3/\text{s}$ under steady-state conditions. Laboratory experiments have shown that a current efficiency of 95 % for Ni deposition at the cathode can be achieved if the electrolyte composition within the tank is maintained at 70 g/L Ni^{2+} and pH 4.0 throughout the process.

Determine the NiSO_4 concentration and pH in the feed stream to ensure that 700 kg/day of Ni can be deposited in the tank for the conditions obtained in the laboratory experiments.

Assume the electrolyte behaves ideally.

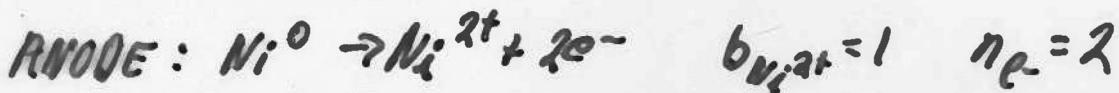
①

NICKEL PLATING EXAMPLE

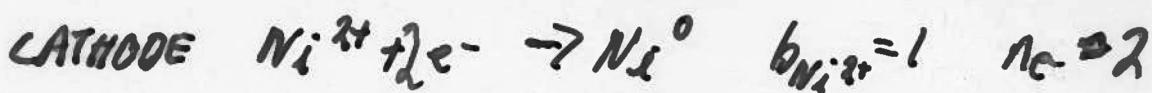
SET UP MASS BALANCE

$\underline{\underline{N_i^{2+}}}$ Ni^{2+} is generated at the anode

$\underline{\underline{N_i^{2+}}}$ is consumed at the cathode



$$\therefore \frac{r_{Ni^{2+}}}{\text{ANODE}} = \frac{I_{\text{ANODE}}}{n_e / b_{Ni^{2+}} F} = \frac{I_{\text{ANODE}}}{2F} > 0$$



$$\therefore \frac{r_{Ni^{2+}}}{\text{CATHODE}} = \frac{I_{Ni}}{n_e / b_{Ni^{2+}} F} = \frac{I_{Ni}}{2F} = -\frac{|I|}{2F} \quad \text{SINCE } I_{Ni} < 0$$

OVERALL Ni^{2+} generation ratio

$$\begin{aligned} r_{Ni^{2+}} &= r_{Ni^{2+}} \Big|_{\text{ANODE}} + r_{Ni^{2+}} \Big|_{\text{CATHODE}} \\ &= \frac{I_{\text{ANODE}}}{2F} - \frac{|I_{Ni}|}{2F} \end{aligned}$$

STEADY STATE BALANCE Ni^{2+}

$$\frac{V dC_{Ni^{2+}}}{dt} = 0 = q C_{Ni^{2+}} f - q C_{Ni^{2+}} + \frac{I_{\text{anode}}}{2F} - \frac{|I_{Ni}|}{2F} \quad \text{①}$$



$$\therefore I_{at} = \frac{I_{H_2}}{\frac{n_{e^-} F}{b_{H^+}}} = \frac{I_{H_2}/F}{-\frac{I_{H_2}}{F}} \quad \text{SINCE } I_{H_2} < 0$$

STEADY STATE BALANCE H^+

$$V \frac{dC_{H^+}}{dt} = q C_{H^+_f} - q C_{H^+_i} - \frac{(I_{H_2})}{F} = 0 \quad (2)$$

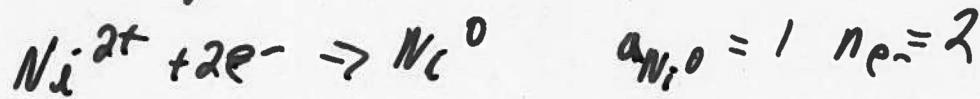
CURRENTS ARE RELATED AS FOLLOWS

$$I_{\text{ANODE}} = |I_{\text{CATHODE}}| \approx |I_{Ni}| + |I_{H_2}| \quad (3)$$

NOW CALCULATE CURRENTS FROM "GIVEN" INFO.

PRODUCTION RATE of Ni^0 at cathode.

$$= \frac{700 \text{ kg}}{\text{day}} \left| \frac{10^3 \text{ g}}{\text{kg}} \right| \frac{1 \text{ day}}{24 \text{ hours}} \left| \frac{1 \text{ hr}}{3600 \text{ sec}} \right| \frac{1 \text{ mol/Ni}}{58.71 \text{ g}} = 0.138 \text{ mol/sec}$$



PRODUCTION RATE Ni^0 at cathode =

$$= \frac{I_{Ni}}{-\frac{n_{e^-} F}{a_{Ni^0}}} = -\frac{I_{Ni}}{2F} = \frac{|I_{Ni}|}{2F} \quad I_{Ni} < 0$$

$$|I_{Ni}|/2F = 0.138 \text{ mol/sec}$$

$$(I_{Ni}) = 2 \left(96,485.31 \text{ C/mol} \right) (0.138 \text{ mol/sec}) = 26,629.52 \text{ C/sec}$$

$$= 26,629.52 \text{ A}$$

(3)

SINCE CURRENT EFFICIENCY for Ni⁺
DEPOSITION AT CATHODE IS 95%

$$\text{TOTAL CATHODIC CURRENT} = |I_{\text{CATHODE}}| = \frac{|I_{\text{Ni}}|}{0.95} = \frac{26,629.52 \text{ A}}{0.95} = 28,031.08 \text{ A}$$

$$\therefore |I_{H_2}| = |I_{\text{CATHODE}}| - |I_{\text{Ni}}| = 28,031.08 - 26,629.52 \\ = 1,401.55 \text{ A}$$

$$I_{\text{ANODE}} = 28,031.08 \text{ A}$$

REARRANGE EQUATION ①

$$q C_{\text{Ni},f} = q C_{\text{Ni}} - \frac{I_{\text{ANODE}}}{2F} + \frac{|I_{\text{Ni}}|}{2F}$$

(USE mol L⁻¹ OR mol m⁻³
UNITS FOR CONCENTRATION)

$$C_{\text{Ni},f} = C_{\text{Ni}} - \frac{I_{\text{ANODE}}}{2Fq} + \frac{|I_{\text{Ni}}|}{2Fq} = C_{\text{Ni}} - \frac{(I_{\text{ANODE}} - |I_{\text{Ni}}|)}{2Fq}$$

$$C_{\text{Ni},f} = \frac{70 \text{ g/L}}{58.7 \text{ g/mol}} - \frac{(28,031.08 \text{ A} - 26,629.52 \text{ A})}{2(96,485.31 \text{ C/mol})(2 \times 10^{-4} \text{ m}^3/\text{s})} 10^3 \text{ L/m}^3 \\ = 1.156 \text{ mol/L} = 67.9 \text{ g/L}$$

OUTLET CONCENTRATION
EXCEEDS INLET
ION
CONCENTRATION

∴ FEED CONCENTRATION OF $NiSO_4$ SOLUTION

$$= \left(1.156 \frac{\text{mol}}{\text{L}} \right) \left(\frac{154.7 \text{ g } NiSO_4}{\text{mol}} \right)$$

$$= 178.84 \text{ g } NiSO_4 / \text{L}$$

NOW H^+ REARRANGE (2)

$$q C_{H^+ f} = q C_{H^+} + \frac{|I_{H^+}|}{F}$$

$$C_{H^+ f} = C_{H^+} + \frac{|I_{H^+}|}{F q}$$

SS
∴ $V \frac{dC_{H^+}}{dt} = 0$

IDEAL SOLUTION $C_{H^+} = 10^{-pH} = 10^{-4.0} \text{ mol/L}$

$$\therefore C_{H^+} = 10^{-4} \text{ mol/L} + 1,401.55 A$$

$$\left(\frac{76,485.31 C}{\text{mol}} \right) 2 \times 10^{-4} \frac{\text{m}^3}{\text{s}} \left(10^3 \frac{\text{L}}{\text{m}^3} \right)$$

$$= 10^{-4} + 0.0726 \text{ mol/L}$$

$$= 0.0727 \text{ mol/L}$$

$$pH_f = -\log C_{H^+} = -\log (0.0727) = 1.14$$

∴ pH Feed 1.1 + 180 g/L $NiSO_4$

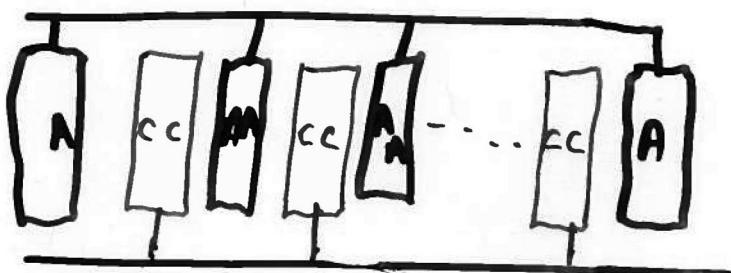
WHAT ABOUT THE ELECTRODE SIZE?

NOTE: CURRENT DENSITY THROUGH EACH CATHODE
WILL BE HIGHER THAN CURRENT DENSITY
THROUGH EACH ANODE.

$$\text{POWER} = V_{cell} I_{TOTAL} \quad \text{ENERGY} = \int_0^t V_{cell} I dt$$

(5)

Ni



61 ANODE ELECTRODES

60 CATHODE ELECTRODES

60 cathode plated two sides

 $60 \times 2 = 120$ cathode "faces"

59 ANODE DISSOLVED 2 SIDES = 118 faces

2 ANODES DISSOLVED 1 SIDE = 2 faces

61 ANODES TOTAL ELECTRODES = 120 ANODE FACES

\therefore 120 ANODE/CATHODE COUPLES
FOR 120 CELLS

$$\frac{I_{CATHODE}}{A_{area}_{CATHODE}} = i_{CATHODE} = \frac{28031 A}{\text{monopolar}} \Big| \frac{120 \text{ cells}}{0.8 \times 1.1 \text{ m}^2} = 265.1 \frac{A}{m^2}$$

$$\frac{I_{ANODE}}{A_{area}_{ANODE}} = i_{ANODE} = \frac{28031 A}{\text{monopolar}} \Big| \frac{120 \text{ CELLS}}{0.9 \times 1.2 \text{ m}^2} = 216.3 \frac{A}{m^2}$$

(6)

Ni-MONOPOLAR

$$I_{ANODE} = I_{CATHODE} = 28,031 \text{ A}$$

$$i_{CATHODE} = 265.4 \text{ A/m}^2$$

$$i_{ANODE} = 216.3 \text{ A/m}^2$$

$$I_{CELL} = \frac{I_{TOTAL}}{\# \text{ CELLS}} = \frac{28,031 \text{ A}}{120 \text{ CELLS}} = 233.6 \text{ A}$$

$$I_{CELL} = I_{ELECTROLYTE} = 233.6 \text{ A}$$

I to Each CATHODE ELECTRODE WITH
TWO CATHODE FACES = $2 \times I_{CELL} = 467.2 \text{ A}$

I to Each ANODE ELECTRODES $\approx 467.2 \text{ A}$
EXCEPT END ANODE = 233.6 A

$V_{CELL} = V_{TOTAL} = \underline{\text{UNKNOWN}}$
MONOPOLAR.



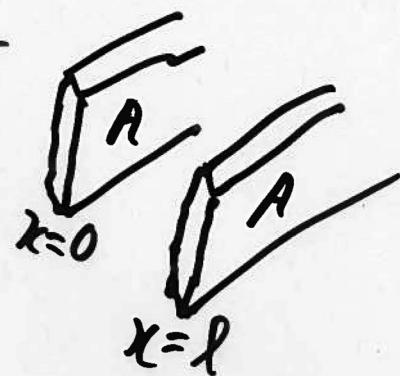
(1)

ANALOGY WITH OHM'S LAW FOR ELECTRIC CIRCUITS

CONSIDER 2 FLAT ELECTRODES

- CONCENTRATION OF ELECTROLYTE
IS UNIFORM

- i_{TOTAL} and K will be
UNIFORM



INTEGRATION OF (12) FROM $x=0$ TO $x=l$

$$\left\{ \begin{array}{l} \frac{d\phi}{dx} = -\frac{i_{\text{tot}}}{K} \\ \phi(0) \end{array} \right. \int_0^l dx$$

$$\phi(l) - \phi(0) = -\frac{i_{\text{tot}}}{K} l$$

\therefore MAGNITUDE OF VOLTAGE DROP BETWEEN
THE ELECTRODES

$$|\Delta\phi| = |\phi(l) - \phi(0)| = \frac{i_{\text{tot}}}{K} l$$

SINCE $|i_{\text{tot}}| = |I_{\text{TOT}}|/A$, the $|\Delta\phi| = \frac{|I_{\text{TOT}}| l}{A K}$ (13)

THink of the electrolyte as a resistor

(2)

THEN (13) is like Ohm's law for a simple resistor.

$$|\Delta\phi| = |I_{TOTAL}| R \quad (14)$$

R = effective ohmic resistance of electrolyte
of the resistance to ionic transport
through the electrolyte

CMPARE (13) & (14)

$$R = \frac{l}{AK} \quad (15)$$

RATIO l/A is defined as the cell constant

COMMENTS:

① How can R be minimized?

- decrease l (inter-electrode spacing)
- increase A (electrode A)
- increase K

② OHMIC or "IR" "DROP" ACROSS A CELL
(ASSUMING CARTESIAN GEOMETRY)

$$\text{"IR" DROP} = |\Delta\phi| = \frac{|I_{TOT}| l}{AK} = \frac{|I_{TOT}| l}{K}$$

③ IR DROP ALWAYS HAS A
NEGATIVE IMPACT

- ELECTROLYTIC CELL - raises input voltage
to operate at a given current

- galvanic cell - lower output VOLTAGE
to operate external load
at a given current

④ EQUATIONS ⑬ → ⑮ ARE BASIS OF
CONDUCTIVITY MEASUREMENTS IN
LAB

EXAMPLE ELECTRICAL CONDUCTIVITIES

- AT 25°C

MATERIAL

Ag, Cu

Molten NaCl (molten Na^+
 Cl^-)

0.1M KCl solution in H_2O

0.1M $\text{NaOH}_{(\text{aq})}$

0.1M HAc solution in H_2O

H_2O

Sulphur

κ (SIEMEN/m)

$\sim 5-6 \times 10^7$ metallic

~ 300 molten ionic

1.3 } MODERATE []
2.2 } STRONG ELECTROLYT

5×10^{-3} WEAK ELECTROLYT

4×10^{-6} NEUTRAL POLAR

1×10^{-14} NON-POLAR

DIFFERENCES IN CONDUCTIVITIES DUE TO DIFFERENCES
IN CONCENTRATION OF MOBILE CHARGE CARRIERS.

EXAMPLE

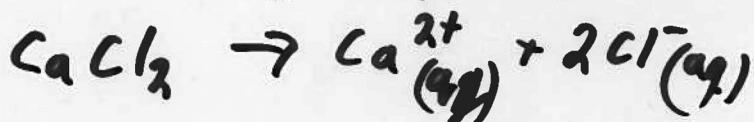
(1)

ESTIMATE κ for a 0.01 M CaCl_2 solution
(strong electrolyte) using KOHLRAUSCH's law

USE TABLE

for λ_j^{∞} values

ASSUME CaCl_2 completely dissociates



THUS $\text{CaCl}_2 = 0.01 \text{M} = 10 \text{ mol/m}^3$ Amount added
TO SOLUTION

$$C_{\text{Ca}^{2+}} = 0.01 \text{M} = 10 \text{ mol/m}^3$$

$$C_{\text{Cl}^-} = 0.02 \text{M} = 20 \text{ mol/m}^3$$

$$K_{\text{CaCl}_2} = C_{\text{Ca}^{2+}} \lambda_{\text{Ca}^{2+}}^{\infty} + C_{\text{Cl}^-} \lambda_{\text{Cl}^-}^{\infty}$$

$$= \frac{10 \text{ mol}}{\text{m}^3} \left(119.0 \times 10^{-4} \frac{\text{s} \cdot \text{m}^2}{\text{mol}} \right) + 20 \frac{\text{mol}}{\text{m}^3} \left(76.35 \times 10^{-4} \frac{\text{s} \cdot \text{m}^2}{\text{mol}} \right)$$

$$= 0.272 \text{ s/m}$$

NOTE EXPERIMENTAL RESULT FOR κ
 $= 0.241 \text{ s/m}$

EXAMPLE ①

2

YOU CAN COMBINE INDIVIDUAL IONIC MOBILITIES TO ESTIMATE CONDUCTIVITIES OF SOLUTIONS

GIVEN - EXPERIMENTAL MOLAR CONDUCTIVITIES

$$NaAc : \lambda_{NaAc}^{\infty} = 91.05 \times 10^{-4} \text{ S m}^2/\text{mol}$$

$$NaCl : \lambda_{NaCl}^{\infty} = 126.5 \times 10^{-4} \text{ S m}^2/\text{mol}$$

$$HCl : \lambda_{HCl}^{\infty} = 426.2 \times 10^{-4} \text{ S m}^2/\text{mol}$$

USE THESE VALUES TO ESTIMATE λ^{∞}
for HA_c (acetic acid).

λ_+ and λ_- are 1 in all cases

$$\lambda_{NaAc}^{\infty} = \lambda_{Na^+}^{\infty} + \lambda_{Ac^-}^{\infty} = 91.05 \times 10^{-4}$$

$$\lambda_{NaCl}^{\infty} = \lambda_{Na^+}^{\infty} + \lambda_{Cl^-}^{\infty} = 126.5 \times 10^{-4}$$

$$\lambda_{HCl}^{\infty} = \lambda_{H^+}^{\infty} + \lambda_{Cl^-}^{\infty} = 426.2 \times 10^{-4}$$

SUBTRACT ② from ① ADD ③

$$① - ② : \lambda_{Na^+}^{\infty} + \lambda_{Ac^-}^{\infty} - \lambda_{Na^+}^{\infty} - \lambda_{Cl^-}^{\infty} = -35.45 \times 10^{-4}$$

$$\lambda_{Ac^-}^{\infty} - \lambda_{Cl^-}^{\infty} = -35.45 \times 10^{-4}$$

$$ADD ③ \quad \lambda_{Ac^-}^{\infty} - \lambda_{Cl^-}^{\infty} + \lambda_{H^+}^{\infty} + \lambda_{Cl^-}^{\infty} = 426.2 \times 10^{-4} - 35.45 \times 10^{-4}$$

$$\lambda_{H^+}^{\infty} + \lambda_{Ac^-}^{\infty} = 390.8 \times 10^{-4} \text{ S m}^2/\text{mol}$$

$$G_D \quad \lambda_{HAc}^{\infty} = \lambda_{H^+}^{\infty} + \lambda_{Ac^-}^{\infty} = 390.8 \times 10^{-4} \frac{\text{S m}^2}{\text{mol}}$$

(1)

MOHAR & IONIC CONDUCTIVITIES

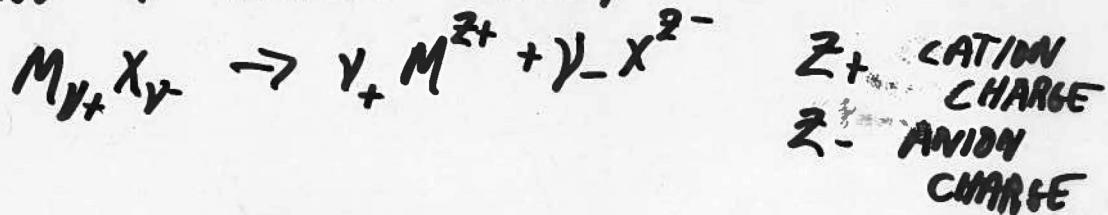
K is important BUT difficult to deal with
(i.e. reporting property values)

BECAUSE K is proportional to electrolyte
CONCENTRATION

∴ NEED A FUNDAMENTAL PROPERTY THAT
DEPENDS ON THE NATURE OF THE
ELECTROLYTE.

TWO APPROACHES.

1. CASE OF STRONG BINARY ELECTROLYTE



USE EQN (1)

$$K = F^2 (Z_+^2 u_+ c_+ + Z_-^2 u_- c_-)$$

u_+, u_- are the mobility of M^{2+} and X^{2-}

c_+, c_- are the concentration of M^{2+} and X^{2-}

c mol/litre of the salt $M_{Y+}X_{Y-}$ added to the solution

FROM THE STOICHIOMETRY

$$c_+ = v_+ c$$

$$c_- = v_- c$$

ASSUMES COMPLETE
DISSOCIATION OF
THE SALT

$$\therefore K = F^2 (z_+^2 u_+ v_+ + z_-^2 u_- v_-) c \quad (2)$$

DEFINE Λ as the molar conductivity
OR MOLAR CONDUCTANCE

$$\Lambda \equiv \frac{K}{c} = F^2 (z_+^2 u_+ v_+ - z_-^2 u_- v_-) \quad (17)$$

\leftarrow CONCENTRATION OF SALT ADDED
UNITS OF Λ $\left[\frac{\text{S}}{\text{m/mol/m}^3} \right]$ or $\left(\frac{\text{S m}^2}{\text{mol}} \right)$

ASSUME u_+ and u_- are independant of concentration
 $\therefore \Lambda$ is independant of concentration

Λ is a PROPERTY of SALT and SOLVENT

- BUT i) based on only 2 ions
 ii) COMPLETE DISSOCIATION
 iii) Λ experimentally does sometimes depend on concentration

(2) APPROACH #2

(3)

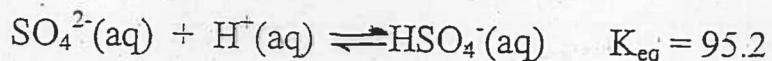
DEFINE INDIVIDUAL CONDUCTIVITIES FOR
EACH ION

$$\lambda_+ \equiv F^2 z_+^2 u_+$$

Example: Conductivity of $\text{Na}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ Solution

An electrolyte made up by dissolving Na_2SO_4 and H_2SO_4 in water is to be used in a cell operating at 300 A m^{-2} , pH 2.0 and 25°C . The cathode-anode spacing is 2 cm and the immersed area per face of each electrode is 0.4 m^2 .

At pH 2.0, all of the H_2SO_4 added has completely dissociated into SO_4^{2-} or HSO_4^- ions. The equilibrium between SO_4^{2-} and HSO_4^- is determined by the reaction:

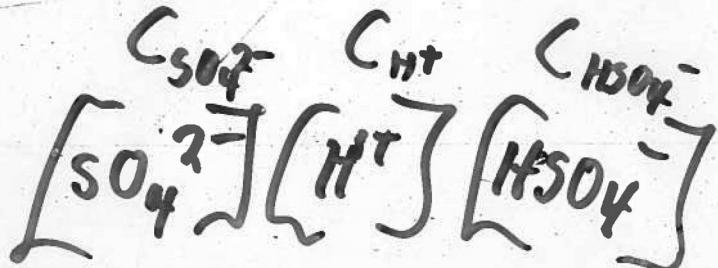


How many grams of Na_2SO_4 must be dissolved per litre of solution so that the ohmic drop is 0.3 volts during operation of the cell? Assume Kohlrausch's Law of independent mobilities can be used to determine κ . Use the table in the course notes to obtain the λ^∞ values. λ^∞ for HSO_4^- is $50.05 \times 10^{-4} \text{ S m}^2/\text{mol}$.

Assume solution thermodynamics behaves ideally.

STAT

3 UNKNOWNs



KNOWN RELATIONS

K_{eq}

OHMIC DROP $\rightarrow \kappa \rightarrow C_i$

ASSUME: ELECTRO NEUTRALITY

①

CONCENTRATION DEPENDENCE of N^{∞} in WEAK ELECTROLYTES

α is the degree of dissociation



$$\text{INITIAL} \quad C \quad 0 \quad 0$$

$$\text{EQUILIBRIUM} \quad (1-\alpha)c \quad \alpha c \quad \alpha c$$

EQUILIBRIUM CONSTANT K

$$K = \frac{(\alpha c)^2}{(1-\alpha)c} \quad ①$$

ARRHENIUS α and λ

$$\alpha = \frac{\lambda}{\lambda^\infty} \quad ②$$

COMBINE ① & ②

$$(\alpha c)^2 = (1-\alpha) c K$$

$$\left(\frac{\lambda}{\lambda^\infty}\right)^2 c^2 = \left(1 - \frac{\lambda}{\lambda^\infty}\right) c K$$

$$\frac{c \lambda^2}{\lambda^\infty (\lambda^\infty - \lambda)} = K \quad \text{OSTWALD DILUTION LAW}$$

Note

$$\frac{1}{\lambda} = \frac{1}{\lambda^\infty} + \frac{C \lambda}{K \lambda^\infty}$$

PLOT $c \lambda$ vs $\frac{1}{\lambda}$

SLOPE $\frac{1}{K \lambda^\infty}$

Intercept $\frac{1}{\lambda^\infty}$