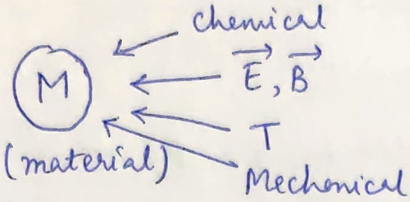
CORROSION AND DEGRADATION [MLL452]

Prof. Suryanarayan Vikrant Karra

LECTURE 1 — CORROSION AND DEGRADATION

05/01/2023

1] **Material degradation** : factors that lead to this are :



exposure to all these causes damage

If it is the case of both : $\underbrace{\text{Chemical + Electrical}}$

↓ we call this

Electrochemical

↓

if this leads to damage of material (degradation)

↓

then this is called

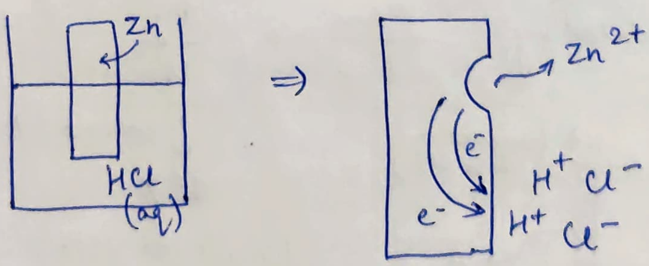
* Corrosion

LECTURE 2

06/01/2023

2] $Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow$

$Zn \rightarrow Zn^{2+} + 2e^-$



Oxidation :

$Zn \rightarrow Zn^{2+} + 2e^-$ (Anode)

Reduction :

$2H^+ + 2e^- \rightarrow H_2 \uparrow$ (Cathode)

NOTE: (eg: If we provide e^-

↓

by Le Châtelier's principle, cathodic rxn. rate increases & anodic rxn. rate decreases)

3] **Water** :

$2H_2O + 2e^- \rightarrow H_2 + OH^-$

(Similar to $2H^+ + 2e^- \rightarrow H_2$)

In the presence of O_2:

Neutral solⁿ: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Acidic solⁿ: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

4] For the case of: $\boxed{Fe} + H_2O + O_2$:

Anodic (one possible rxn.) $Fe \rightarrow Fe^{2+} + 2e^-$

Cathodic: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Also it is possible: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

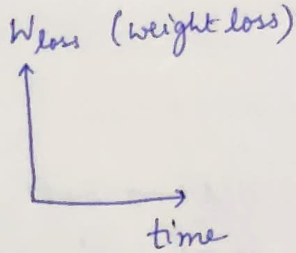
$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$

$\downarrow$ decomposes to

$Fe_2O_3 + H_2O$

5] An Experiment we will perform:

$\longrightarrow$ We will plot



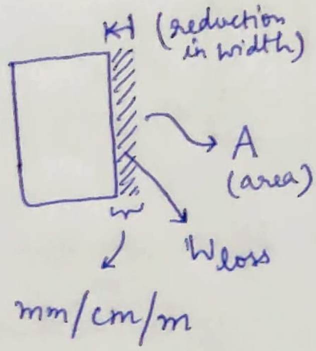
* NOTE: Corrosion rate calculated by: $\frac{W_{loss}}{time} \xrightarrow{\text{units}} \frac{mg}{s}$

* { 1 mil = 0.001 inch }

$\downarrow$ converted to instead

MPY

(mils per year)



* NOTE: $MPY = \frac{534\,W}{DAT}$ — W → mg; D → g/cm^3; A → sq. inch; T → hours

and, $\frac{\mu m}{year} = \frac{87600\,W}{DAT}$ — A here: sq. cm

LECTURE 3

10/01/2023

6] First Law of Thermodynamics

$$dU = \delta Q + dW$$

and we also know:

$$dS = \frac{\delta Q}{T} \quad , \quad dW = -P\,dV$$

$$= \underbrace{\overleftrightarrow{\sigma} : d\overleftrightarrow{\varepsilon}_e}_{\text{mechanical/electrical energy}}$$

$$\Rightarrow \delta Q = T\,dS$$

In general, the work dW will have other contributions as well:

$$dW = \underbrace{-P\,dV}_{\substack{\text{mechanical}\\ \text{work}}} + \underbrace{\phi}_{\substack{\text{electrostatic}\\ \text{potential}}} \underbrace{dq}_{\text{charge}} + \underbrace{\mu}_{\substack{\text{chemical}\\ \text{potential}}} \underbrace{dn}_{\text{no. of moles}}$$

mechanical work (PV work)

electrostatic potential → electrical work

chemical potential → chemical work

Thus, we can relate each intensive property in this eqn. to a corresponding extensive property:

Intensive	Extensive
T	S
P	V
ϕ	q
μ	n

We can write using the First law:

$$dU = \delta Q + dW$$

Thus, $$dU = T\,dS - P\,dV + \phi\,dq + \mu\,dn$$

$$\therefore U = U(S, V, q, n)$$

In general, we will write: $\phi\,dq \longrightarrow \sum_{i=1}^{n} \phi_i\,dq_i$

$$\mu\,dn \longrightarrow \sum_{i=1}^{n} \mu_i\,dn_i$$

* To find the max^m/min^m of function U

we say $dU = 0$

thus, this means it will happen when T, P, ϕ and μ are all zero

(NOTE: If dS, dV, dq and dn are zero then only single phase will occur)

Later on, we will see!

eg: $dU^{total} = \underbrace{(T^{\alpha} - T^{\beta})}_{\text{this will be zero for min}^m/\text{max}^m} dU^{\alpha} + \ldots$

7] Similarly, $dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\phi}{T} dq - \frac{\mu}{T} dn$
(by rearrangement)

thus, $S = S(U, V, q, n)$

* NOTE! It turns out (and it can be derived) that minimization of U leads to maximization of S.

8] Let's say, we have two phases: α and β, in equilibrium.

$$dU^{\alpha} = T^{\alpha} dS^{\alpha} - P^{\alpha} dV^{\alpha} + \mu^{\alpha} dn^{\alpha}$$
$$dU^{\beta} = T^{\beta} dS^{\beta} - P^{\beta} dV^{\beta} + \mu^{\beta} dn^{\beta}$$

NOTE! We can also write α and β in subscripts

$\therefore$

Now: $U_T = U_{\alpha} + U_{\beta} = \text{constant} \Rightarrow dU_{\alpha} = -dU_{\beta}$

$V_T = V_{\alpha} + V_{\beta} = \text{Constant} \Rightarrow dV_{\alpha} = -dV_{\beta}$

$n_T = n_{\alpha} + n_{\beta} = \text{Constant} \Rightarrow dn_{\alpha} = -dn_{\beta}$

(and thus also, $dS_{\alpha} = -dS_{\beta}$)

Thus, we get:

$$dS_{\alpha} = \frac{dU_{\alpha}}{T_{\alpha}} + \frac{P_{\alpha}}{T_{\alpha}} dV_{\alpha} - \frac{\mu_{\alpha}}{T_{\alpha}} dn_{\alpha}$$

$$dS_{\beta} = \frac{dU_{\beta}}{T_{\beta}} + \frac{P_{\beta}}{T_{\beta}} dV_{\beta} - \frac{\mu_{\beta}}{T_{\beta}} dn_{\beta}$$

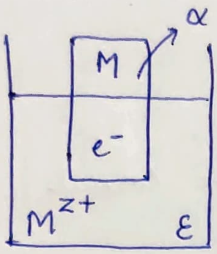
Hence, we have:

$$dS_T = dS_\alpha + dS_\beta$$
$$= \left(\frac{1}{T_\alpha} - \frac{1}{T_\beta}\right) dU_\alpha + \left(\frac{P_\alpha}{T_\alpha} - \frac{P_\beta}{T_\beta}\right) dV_\alpha - \left(\frac{\mu_\alpha}{T_\alpha} - \frac{\mu_\beta}{T_\beta}\right) dn_\alpha$$

$\therefore$ for equilibrium:

$T_\alpha = T_\beta$, $P_\alpha = P_\beta$, and $\mu_\alpha = \mu_\beta$

(Thermal eqbm.) (Mechanical eqbm.) (Chemical eqbm.)

9] 

$$M \longrightarrow M^{z+} + ze^-$$

We know:

$$dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \sum \phi_\alpha dq_\alpha + \sum \mu_\alpha dn_\alpha$$

This can be written as:

$$dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \phi_\alpha^M dq_\alpha^M + \phi_\alpha^e dq_\alpha^e + \mu_\alpha^M dn_\alpha^M + \mu_\alpha^e dn_\alpha^e$$

LECTURE-4

13/01/2023

10] We have: $dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \sum_{i=1}^{n} \mu_i^\alpha dn_i^\alpha + \sum_{i=1}^{n} \phi_i^\alpha dq_i^\alpha$

$$\Rightarrow dU_\alpha = T_\alpha dS_\alpha - P_\alpha dV_\alpha + \mu_M^\alpha dn_M^\alpha + \mu_e^\alpha dn_e^\alpha + \phi_M^\alpha dq_M^\alpha + \phi_e^\alpha dq_e^\alpha$$

Similarly, for electrolyte ε:

$$dU_\varepsilon = T_\varepsilon dS_\varepsilon - P_\varepsilon dV_\varepsilon + \mu_{M^{z+}}^\varepsilon dn_{M^{z+}}^\varepsilon + \phi_{M^{z+}}^\varepsilon dq_{M^{z+}}^\varepsilon$$

NOTE: By Faraday's First Law, we know:

$$q = ZFn$$

q → charge; Z → given by valency of metal (or in general, the change in oxid^n state); n → mass

Thus, we will get:

$$n_M^{\alpha} + n_{M^{Z+}}^{\varepsilon} = \text{constant}$$

$$\Rightarrow dn_M^{\alpha} = -dn_{M^{Z+}}^{\varepsilon}$$

and, $$q_M^{\alpha} + q_{M^{Z+}}^{\varepsilon} = \text{constant}$$

$$\Rightarrow dq_M^{\alpha} = -dq_{M^{Z+}}^{\varepsilon}$$

We will also get:

$$q_{M^{Z+}}^{\varepsilon} = ZF\, n_{M^{Z+}}^{\varepsilon}$$

and, $$q_e^{\alpha} = -F n_e^{\alpha}$$

Putting this in the charge conservation formula:

$$ZF\, dn_M^{Z+} = F\, dn_e^{\alpha}$$

(and also thus, $dn_e^{\alpha} = -Z\, dn_M^{\alpha}$)

11] Going back to the original two phase problem:

$$dS_{\varepsilon} = -dS_{\alpha}$$

$$dV_{\varepsilon} = -dV_{\alpha}$$

Now, $$dU_{Total} = dU_{\varepsilon} + dU_{\alpha}$$

$$= \cancel{(T_{\alpha} - T_{\varepsilon})}^{0}\, dS_{\alpha} - \cancel{(P_{\alpha} - P_{\varepsilon})}^{0}\, dV_{\alpha}$$

$$+ (\mu_M^{\alpha} - Z\mu_e^{\alpha} - \mu_{M^{Z+}}^{\varepsilon})\, dn_M^{\alpha}$$

$$+ (\phi_e^{\alpha} - \phi_{M^{Z+}}^{\varepsilon})(ZF\, dn_M^{\alpha})$$

*{NOTE: $\phi_M^{\alpha} dq_M^{\alpha} = 0$ always since $q_M^{\alpha} = 0$ (bcz M has no charge)}

This gives us finally:

$$\mu_M^{\alpha} - Z\mu_e^{\alpha} - \mu_{M^{Z+}}^{\varepsilon} = -(\phi_e^{\alpha} - \phi_{M^{Z+}}^{\varepsilon})\, ZF$$

Lecture 7

(20/01/2023)

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \Delta\phi^\circ = 0.342\ V$$

$$\mu^{\varepsilon}_{Cu^{2+}} + 2\mu^{\alpha}_{e} - \mu^{\alpha}_{Cu} + 2F\left(\phi^{\varepsilon}_{Cu^{2+}} - \phi^{\alpha}_{e}\right) = 0$$

$$\Rightarrow \left(\phi^{\alpha}_{e} - \phi^{\varepsilon}_{Cu^{2+}}\right) = \frac{\left(\mu^{\varepsilon}_{Cu^{2+}} + 2\mu^{\alpha}_{e} - \mu^{\alpha}_{Cu}\right)}{2F}$$

$$\Rightarrow \underbrace{\left(\phi^{\alpha,0}_{e} - \phi^{\varepsilon,0}_{Cu^{2+}}\right)}_{0.342} = \frac{\mu^{\varepsilon,0}_{Cu^{2+}} + 2\mu^{\alpha,0}_{e} - \mu^{\alpha,0}_{Cu}}{2F}$$

NOTE:

This can be written as

$\phi_{Cu} - \phi_{Cu^{2+}}$ (as given in some textbooks)

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \Delta\phi^\circ = 0.0\ V$$

$$\Delta\phi_{H^+/H_2} = \phi^{\varepsilon}_{H^+} - \phi^{\alpha}_{e} = \frac{2\mu_{H^+} + 2\mu_e - \mu_{H_2}}{2F}$$

$$= \Delta\phi^\circ_{H^+/H_2} + \frac{RT}{2F}\ln\left[\frac{(a_{H^+})^2 (a_e)^2}{a_{H_2}}\right]$$

Here, $pH = -\log[H^+]$

$a_{H^+} = [H^+]$

$a_e = 1$

$a_{H_2} = P_{H_2} = 1\ atm$

$*\{\ln() = 2.303\log_{10}()\}$

$$\Rightarrow \Delta\phi_{H^+/H_2} = \Delta\phi^\circ_{H^+/H_2} + \frac{RT\,(2.303)}{F}\log[H^+]$$

$$= \Delta\phi^\circ_{H^+/H_2} - 0.059\ pH$$

$$= 0 - 0.059\ pH$$

$*\left\{\text{NOTE: } \frac{2.303RT}{F} = 0.059\right\}$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad \Delta\phi^\circ = -0.826 \text{ V}$$

Here, $a_{H_2O} = 1$

$a_{H_2} = p_{H_2} = 1$ atm

Also, we know, $pH + pOH = 14$

Thus, $$\Delta\phi = \Delta\phi^\circ + \frac{RT}{2F} \ln\left[\frac{[a_{H_2O}]^2 [a_e]^2}{[a_{H_2}][a_{OH^-}]^2}\right]$$

$$= \Delta\phi^\circ + \frac{RT}{2F}(2.303) \log_{10}\left[\frac{1}{(a_{OH^-})^2}\right]$$

$$= \Delta\phi^\circ + 0.059 \, pOH$$

$$= -0.826 + 0.059\,(14 - pH)$$

$$= -0.059 \, pH$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad \Delta\phi^\circ = 0.401 \text{ V}$$

$$\Rightarrow \Delta\phi = \Delta\phi^\circ + \frac{2.303\,RT}{4F} \log\left[\frac{p_{O_2}(a_{H_2O})^2}{[OH^-]^4}\right]$$

Taking $p_{O_2} = 1$, $a_{H_2O} = 1$

$$\Rightarrow \Delta\phi = \Delta\phi^\circ + 0.059 \, pOH$$

$$= 0.401 + 0.059\,(14 - pH)$$

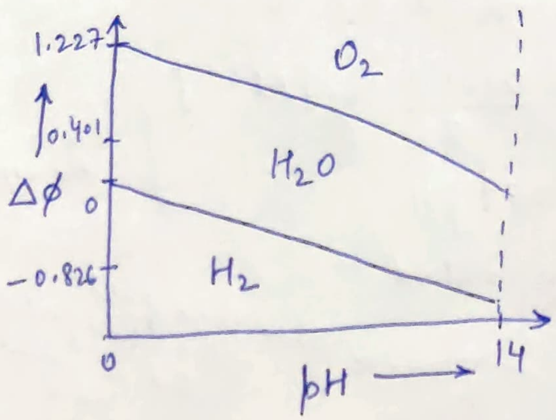
$$= 1.227 - 0.059 \, pH$$

Thus, we have seen:

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$, $\Delta\phi = -0.059 \, pH$

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$, $\Delta\phi = 1.227 - 0.059 \, pH$

Hence we get:

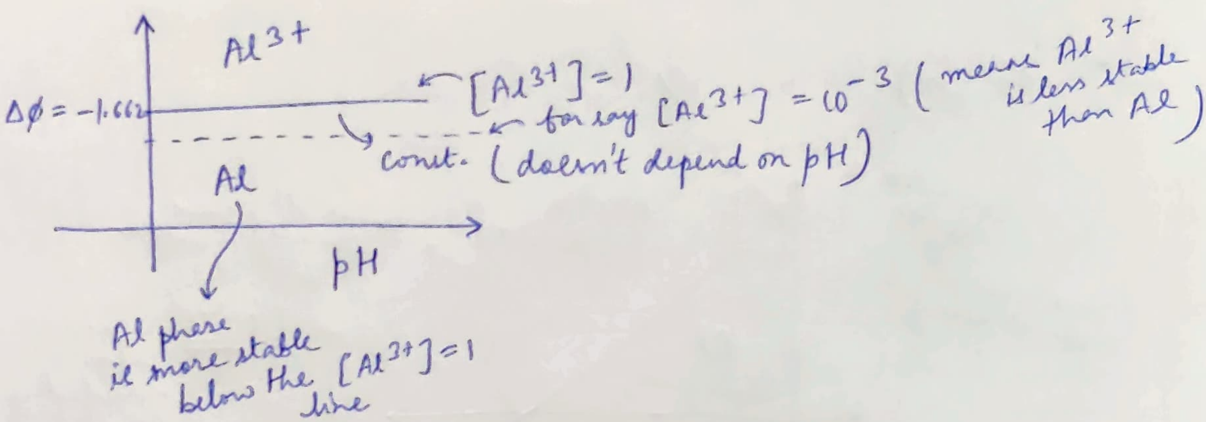


This is called a POURBAIX DIAGRAM

LECTURE-8 (24/01/2023)

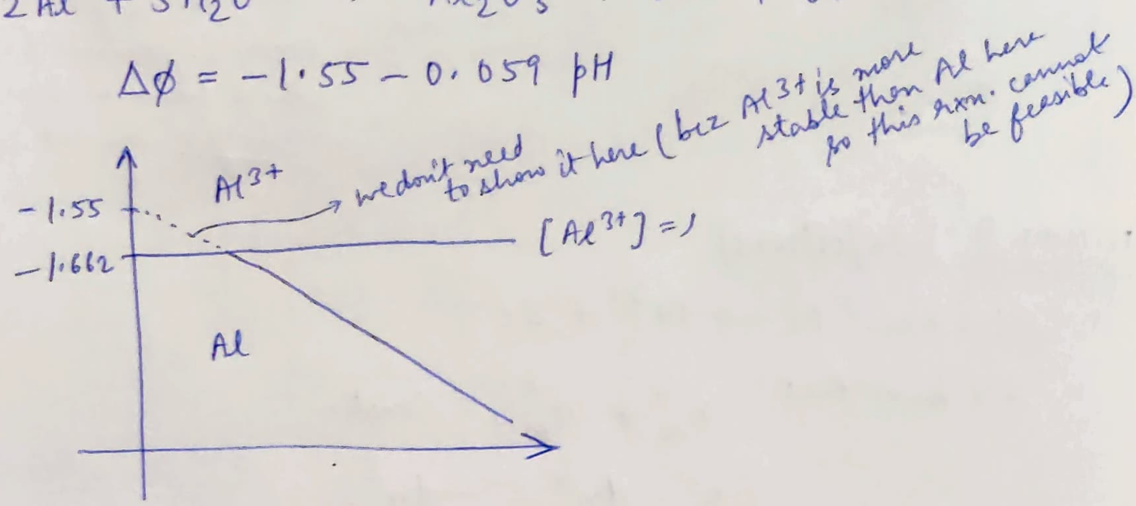
$Al^{3+} + 3e^- \longrightarrow Al \qquad \Delta\phi^\circ = -1.662$

$$\Delta\phi = -1.662 + \frac{0.059}{3} \log [Al^{3+}]$$



$2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e^-$

$\Delta\phi = -1.55 - 0.059\ pH$

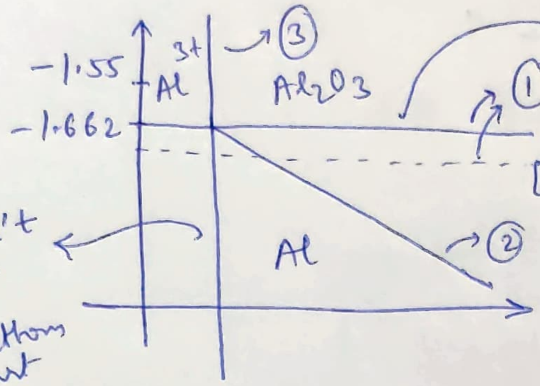


For the equation:

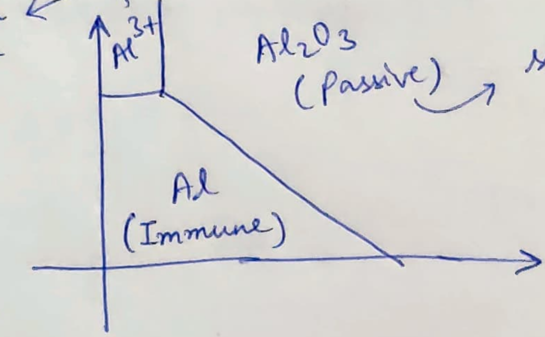
$$2Al^{3+} + 3H_2O \longrightarrow Al_2O_3 + 6H^+$$

we have:
$$-0.11 + \frac{0.059}{3} \log [Al^{3+}] = -0.059\, pH$$
this is the equation

$\Rightarrow$ ∴ the pH is constant:



$\Downarrow$



* (NOTE: This is also corroded of course
↓
but we call this "passive" bcz sometimes this region contains oxides/hydroxides/etc. which form a protective layer against corrosion)

* Immune: i.e. No corrosion happens

LECTURE 9 (25/01/2023)

For a Rxn.: $M \longrightarrow M^{z+} + ze^-$

We know that: $n_M^\alpha + n_{M^{z+}}^\varepsilon = \text{Const.}$

i.e. $dn_M^\alpha = -dn_{M^{z+}}^\varepsilon$

Also, we have:

$$q^{\varepsilon}_{M^{z+}} = zF\, n^{\varepsilon}_{M^{z+}}$$

Thus, $$\frac{dq^{\varepsilon}_{M^{z+}}}{dt} = zF\left(\frac{dn^{\varepsilon}_{M^{z+}}}{dt}\right)$$

$$\therefore\ I = \frac{dq^{\varepsilon}_{M^{z+}}}{dt} = -zF\left(\frac{dn^{\alpha}_{M}}{dt}\right)$$ ← Hence the weight loss can be directly related to current

{ NOTE: $q^{\alpha}_{e} + q^{\varepsilon}_{M^{z+}} = \text{Const.}$

$$\Rightarrow I = -\frac{dq^{\alpha}_{e}}{dt} = \frac{dq^{\varepsilon}_{M^{z+}}}{dt}$$ }

LECTURE-10 (27/01/2023)

In other words, we can say:

$$It = -zF\, \underbrace{\Delta n^{\alpha}_{M}}_{\text{gives idea of weight gain}}$$

Now, $$\Delta n^{\alpha}_{M} = \frac{\Delta m}{M} = \frac{It}{zF}$$ ← taking magnitude here (so Δm can be either weight gain or loss)

$$\Rightarrow \Delta m = \frac{It}{zF} M$$

Taking corrosion rate as: $i = \frac{I}{A}$ (A/m²) unit; → equivalent to: mpy

$$\Rightarrow \frac{\Delta m}{A} = i\,\frac{tM}{zF}$$

$$\Rightarrow \boxed{i = \frac{\Delta m}{A}\,\frac{zF}{tM}}$$

eg: For SS 304:

Cr → 19% (0.19)
Ni → 9.25% (0.0925)
Fe → 71.75% (0.7175)

The reactions:

$$Cr \rightarrow Cr^{3+} + 3e^-$$
$$Ni \rightarrow Ni^{2+} + 2e^-$$
$$Fe \rightarrow Fe^{2+} + 2e^-$$

NOTE: Equivalent weight is defined by:

$$\frac{1}{E.W.} = \sum_i \frac{f_i}{\left(\frac{M_i}{Z_i}\right)}$$

We use this E.W. to solve for this material.

$$2H^+ + 2e^- \longrightarrow H_2$$

At equilibrium, we can say equal current flows both forward and backward
(i.e. Net current is zero)

$$\underset{\substack{\downarrow \\ \text{exchange current density}}}{i} = i_f = i_b = \frac{\Delta m}{A} \frac{ZF}{tM}$$

and, $I_{total} = I_f - I_b = 0$ (or $i_{total} = i_f - i_b = 0$)