Nernst equation

Using thermodynamics of equilibrium for the given rxn

aA bB $\rightleftharpoons$ cC dD

From law of mass action,

$$K_{eq} = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}}$$

At equilibrium

Q<K ; rxn shift to right
Q>K ; rxn shift to left
Q = K ; no reaction

$$Q = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

Not equilibrium

Using this Q for above reaction, we can write
Change in Gibbs free energy for any reaction, thermodynamically

$$\Delta G = \Delta G^{0} + RT \ln Q \quad \ldots\ldots\ldots\ldots\ldots(1)$$

For galvanic cell work is done by the cell
And this work done is electrical work done which can be given by

$$W_{max} = -\text{ charge} \times V$$
$$= -nFE$$

This work done is equal to ΔG of reaction
Ie., $\Delta G = -nFE_{Cell}$

Also, $\Delta G^0 = -nFE^0_{Cell}$ ………….(2)

Putting this value in eq 1,

$-nFE_{Cell} = -nFE^0_{Cell} + RT \ln Q$
Dividing this equation by – nF

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q} \quad \text{…………(3)}$$

E_{Cell} = EMF of cell (or electrode potential) at non standard condition
E^0_{Cell} = EMF of cell (or electrode potential) at standard condition
R= Universal gas constant = 8.314 J/mol-K
T = Absolute Temperature in Kelvin
N = Number of electron take part in redox reaction
F = Faraday constant = 96500 C/mol
Q = reaction quotient similar to equilibrium constant in reversible reaction

Temperature is generally taken 25^0C (298K)

$$\boxed{E_{cell} = E^o_{cell} - \frac{0.0257}{n}\ln Q} \quad \ldots\ldots\ldots\ldots(4)$$

In chemistry common log is used and Since; ln (x)= 2.303 log (x)

We have,

$$\boxed{E_{cell} = E^o_{cell} - \frac{0.0592}{n}\log Q} \quad \ldots\ldots\ldots\ldots(5)$$

Q1. Calculate the emf of given cell at 30^oC

$Mg/Mg^{++}(0.1M)//HCl(0.2M)/H_2(g,1\ atm)/Pt$

Given, $E^0_{Mg^{++}/Mg} = -2.37$ V

Solution; At anode (oxidation)

$Mg \longrightarrow Mg^{++} + 2e$, $E^0_{Mg/Mg^{++}} = +2.37V$

At cathode (reduction

$2H^+ + 2e \rightarrow H_2$, $E^0_{Anode} = 0$ V

Net rxn, $Mg + 2H^+ \rightarrow Mg^{++} + H_2$, $E^0cell = 2.37$ V

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q}$$

$= 2.37 - (8.314 \times 303/2 \times 96500)\ \ln\ ([Mg^{++}][H_2])\ /\ [Mg][H^+]^2$

$= 2.37 - 0.01305\ \ln\ 0.1/(0.2)^2$

$= 2.37 - 0.012$

$= 2.35$ V

Q2. From the given reaction, calculate the emf of cell at 25^0 C

$CuCl_2$ (0.2M)+ H_2 Cu + 2HCl (0.5M)

Solution, $CuCl_2 + H_2 \rightarrow Cu + 2HCl$

At anode (oxidation)

$H_2 \rightarrow 2H^+ + 2e$, $E^0 = 0$ V

At cathode (reduction

$Cu^{++} + 2e \rightarrow Cu$, $E^0_{Cu^{++}/Cu} = 0.34$ V

Net rxn, $Cu^{++} + H_2 \rightarrow Cu + 2H^+$, $E^0cell = 0.34$ V

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q}$$

= 0.34- (0.0592/2) log10 ($[H^+]^2$ / $[Cu^{++}]$)

= 0.34- 0.0296 log10 $(0.5)^2$ /0.2

= 0.34-0.0028

= 0.312 V

Q3. From the given data (I and ii) at 25^0 C, answer the following questions

i. Fe^{++} (0.1M) $\longrightarrow$ Fe^{+++} (1M) + e , E^0= - 0.77 V

ii. Cu^{++} (0.2M) + 2e $\rightarrow$ Cu E^0 = 0.34V

a. Write down electrode reactions
b. What is net cell reaction?
c. Calculate EMF of cell
d. Reaction is spontaneous or not
e. Write down the cell notation

Solution; to find out anode and cathode, the electrode potential should be in terms of reduction

i. Fe^{++} (0.1M) → Fe^{+++} (1M) + e , $E^0_{Fe^{++}/Fe^{+++}}$ = - 0.77 V, $E^0_{Fe^{+++}/Fe^{++}}$ = + 0.77 V

ii. Cu^{++} (0.2M) + 2e → Cu $E^0_{Cu^{++}/Cu}$ = 0.34V

At anode (oxidation)

Cu ⟶ Cu^{++} (0.2M)+ 2e, E^0 = - 0.34 V

At cathode (reduction

2 Fe^{+++} (1M) + 2e → 2 Fe^{++} (0.1M), $E^0_{Fe^{+++}/Fe^{++}}$ = 0.77 V

Net cell rxn, Cu + 2 Fe^{+++} (1M) → Cu^{++} + 2 Fe^{++} (0.1M), E^0cell = 0.43 V

$$\boxed{E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q}$$

= 0.43- (0.0591/2) log10 ($[Fe^{++}]^2$ $[Cu^{++}]$)/$[Fe^{+++}]^2$

= 0.43- 0.0296log10 $(0.1)^2$ x 0.2/ $(1)^2$

= 0.43-(-0.079)

= 0.50V

Since, emf of cell is +ve, the redox reaction towards forward direction is spontaneous

Cell notation; Cu/Cu $^{++}$(0.2M)//Fe^{+++}(1M)/Fe^{++}(0.1M)/Pt

Will give you TUTORIAL next week

1) The following reaction takes place in a cell.

$Zn + Co^{+2} \longrightarrow Co + Zn^{+2}$

$E^0_{Zn/Zn^{+2}} = 0.76V$

$E^0_{Co/Co^{+2}} = 0.18V$

Write the cell notation and calculate the EMF of the cell.

2) From the given cell notation at 20^0C

- $Fe/Fe^{++}(0.2M)//Ag^{+}(0.1M)/Ag$ +

$E^0_{Fe/Fe++} = -0.44v$

$E^0_{Ag+/Ag} = 0.8V$

3) What is non-standard electrode potential? Calculate the emf of cell obtained from given electrode reactions.

$Fe^{++}(0.2M) \longrightarrow Fe^{+++}(1M) + e^-$ $E^0 = -0.77V$

$Cu^{++}(0.1M) + 2e^- \longrightarrow Cu$ $E^0 = +0.34V$

4) What is single electrode potential? Calculate the emf of cell obtained by following electrode reactions at 30^0C

$Sn^{++}(0.2M) + 2e^- \longrightarrow Sn$ $E^0 = -0.14V$

$Ag \longrightarrow Ag^{+}(0.1\ M) + e^-$ $E^0 = -0.80V$