ENGINEERING CHEMISTRY

Department of Science and Humanities

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Electrochemical equilibria

Class content:

- *Cell potential*

- *Nernst Equation*

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Electrochemical equilibria

Cell potential
- The difference in electrode potentials of the electrodes constituting the cell
- It is denoted by E_{cell}

Standard cell potential
- E_{cell} depends on concentration of the ions in the cell, temperature and the partial pressures of any gases involved in the cell reaction.
- When all the concentrations are 1M, all partial pressures of gases are 1atm and temperature is 298K, the emf is called Standard cell potential, E^{o}_{cell}

Calculation of E_{cell}

$$E_{cell} = E_{rhs} - E_{lhs} = E_{cathode} - E_{anode}$$

- E_{cell} represents the driving force for the cell reaction to take place

$$\Delta G = - nFE_{CELL}$$

- If reaction is spontaneous ΔG is negative, thus E_{CELL} should be positive
- If reaction is non spontaneous ΔG is positive, thus E_{CELL} should be negative

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Electrochemical equilibria

Electrochemical Series:

- In order to predict the electrochemical behavior of an electrode – electrolyte system, elements are arranged in the order of their standard reduction potentials.
- This arrangement is known as electrochemical series.
- A negative value indicates oxidation tendency while a positive value indicates a reduction tendency.

Electrochemical series

Equilibrium (Oxidants ↔ Reductants)	E° (volts)
Lithium: Li$^+$(aq) + e$^-$ ↔ Li(s)	-3.03
Potassium: K$^+$(aq) + e$^-$ ↔ K(s)	-2.92
Calcium: Ca^{2+}(aq) + 2e$^-$ ↔ Ca(s)	-2.87
Sodium: Na$^+$(aq) + e$^-$ ↔ Na(s)	-2.71
Magnesium: Mg^{2+}(aq) + 2e$^-$ ↔ Mg(s)	-2.37
Aluminum: Al^{3+}(aq) + 3e$^-$ ↔ Al(s)	-1.66
Zinc: Zn^{2+}(aq) + 2e$^-$ ↔ Zn(s)	-0.76
Iron: Fe^{2+}(aq) + 2e$^-$ ↔ Fe(s)	-0.44
Lead: Pb^{2+}(aq) + 2e$^-$ ↔ Pb(s)	-0.13
Hydrogen: 2H$^+$(aq) + 2e$^-$ ↔ H$_2$(g)	0.00
Copper: Cu^{2+}(aq) + 2e$^-$ ↔ Cu(s)	+0.34
Silver: A$^+$(aq) + e$^-$ ↔ Ag(s)	+0.80
Gold: Au^{3+}(aq) + 3e$^-$ ↔ Au(s)	+1.50

Metal Reducing Activity Increasing

Metal Oxidizing Activity Increasing

Source:https://www.syedgilanis.com/2019/04/electrochemicalseries.html

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Electrochemical equilibria

Nernst equation for a single electrode

A quantitative relationship between electrode potential and concentration of species with which the electrode is reversible

The reaction at the electrode is

$$M^{n+} + ne^- \rightleftharpoons M$$

The maximum work that can be obtained is

$$-\Delta G = W_{max}$$

For an electrochemical system, maximum work done is

$$W_{max} = \text{Total charge available} \times \text{Energy available per unit charge}$$

- **Total charge available** , i.e., No. of moles of electrons exchanged in redox reaction (n) multiplied by charge carried per mole of electrons ,F(96,500 C/mol) = nF

- **Energy available per unit charge**, i.e., electrode potential because

    electrode potential = energy/unit charge = E

Therefore , $W_{max} = nFE$; $\Delta G = -nFE$

Under standard conditions, $\Delta G^o = -nFE^o$

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Electrochemical equilibria

$$M^{n+} + ne^- \rightleftharpoons M$$

A thermodynamic equation which relates reaction quotient and decrease in free energy is given by,

$$\Delta G = \Delta G^o + RT\ln Q \text{ , where Q is the reaction quotient}$$

The reaction quotient for the reaction is, $Q = [M]/[M^{n+}]$

Substituting for ΔG, ΔG^o and Q , we get

$$-nFE = -nFE^o + RT\ln\left(\frac{[M]}{[M^{n+}]}\right)$$

Where , E^o = Standard electrode potential, n = number of electrons exchanged in the redox reaction, R = Gas constant. 8.314 JK^{-1} mol^{-1} , T = temp in Kelvin,

F = Faraday 96500 C mol^{-1}

dividing throughout by –nF, $E = E^o - \dfrac{RT}{nF}\ln\left(\dfrac{[M]}{[M^{n+}]}\right)$

Electrochemical equilibria

since [M] = 1 for pure substances,

$$E = E^o + \frac{RT}{nF}\ln([M^{n+}])$$

at 298K,

$$E = E^o + \frac{0.0591}{n}\log([M^{n+}])$$

Nernst equation may also be used to calculate. emf of electrochemical cells. For the cell reaction

$$aA + bB \rightleftharpoons cC + dD$$

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

Nernst equation is

$$E = E^o - \frac{0.0591}{n}\log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

n= no. of e⁻s transferred, E^o_{cell} = std. emf of the cell

THANK YOU

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