Class 10.2
Electrochemistry

CHEM 102H
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Standard Reduction Potentials

Reduction Half-reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$2\ H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00 (by defn.)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn\ (s)$	-0.76

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don’t depend on that choice.

From Red. Potentials to Cell Potentials

Reduction Half-reaction	$E°$ (V)
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	[-0.76]
$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$	1.10

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don’t depend on tis choice.

Using the Electromotive Series - "Recipe" for Evaluating Redox Rxns' Spontaneity

- Find the appropriate half-reactions
- Write the half-reactions with the most positive (or "least negative") value first.
- Write the other half-rxn as an oxidation and write its oxidation potential (= **–** reduction Potential)
- Balance the half-rxns. with respect to e^- transfer. (Don't multiply the potentials by the multiplicative constant used in balancing.)
- Add half-rxns and $E°$'s to get $\boldsymbol{E°_{cell}}$, if > 0, it's spontaneous.

Examples

- Can MnO_4^- oxidize Cl^- to Cl_2 to form Mn^{2+} in acidic solution (all species 1.0 M)?

Examples

- Can Ag(s) reduce $Mg^{2+}(aq)$ to metallic Mg (with formation of $Ag^+(aq)$)?

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\qquad E° = 0.799$

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $\qquad E° = -2.38$

More Definitions and Concepts

- Faraday: the "amount of electricity" in one mole of electrons:

1 Faraday = $N_A e$ =

$(6.022 \times 10^{23}\ \text{mol}^{-1})(1.6022 \times 10^{-19}\ \text{C})$

1 F = 96,485 Coulombs/mol

- Ampere: current flow equal to the passage of 1.0 C per second:

1 A = 1 C/s

More ...

- With the definitions above, we can quickly see that:
- If s amperes of current flow for t seconds, then

st Coulombs of charge have passed through the circuit, and

$(st)/96{,}485$ = # of moles of electrons that have passed through the circuit

Key Relationship between ΔG_{rxn} and E

In Chap. 7 of your book, you will see that ΔG_{rxn} is equal to the maximum amount of nonexpansion work that a reaction can do at const. T and P. In an electrical cell, this is the electrical work, w_{elec}, that can be done:

$$\Delta G_{rxn} = w_{elec}$$

The electrical work to move a particle of charge q through a potential difference E is just qE. To move n moles of electrons (nN_A electrons, each with charge $-e$) through a potential difference E, $w_{elec} = nN_A(-eE) = -nFE$

$$\mathbf{\Delta G_{rxn} = -nFE}$$

n is number of moles of electrons in the half-reactions of a cell reaction.

Some checks on units

From electricity, we know Ohm's Law, V = IR

$^{J}/_{s}$ ~ Power (Watts) ~ I^2R = IV ~ Amps • Volts

$^{J}/_{s}$ = Amps • Volts = $^{C}/_{s}$ • V $\quad\therefore$ J = C • V

Joules = Coulombs • Volts

$$\Delta \mathbf{G}_{\mathbf{rxn}} = -\boldsymbol{nFE}$$

Check: Joules ~ mol • $^{\text{Coulombs}}/_{\text{mol}}$ • Volts

$E°_{cell}$ and $\Delta G°_{rxn}$

Very often, we refer to standard conditions for a cell reaction:

$$\Delta \mathbf{G}°_{\mathbf{rxn}} = -\boldsymbol{nFE}°_{\mathbf{cell}}$$

$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$ $\qquad E°_{cell} = 1.10$ V

All conditions are standard:

T = 298 K, P = 1 atm, $[Cu^{2+}] = [Zn^{2+}] = 1.0$ M

$\Delta G°_{rxn} = -nFE°_{cell} =$

(-2)(96,485 C)(1.10 V) = - 212.3 kJ

Going to Equilibrium from Standard Conditions

$$\Delta \mathbf{G} = \Delta \mathbf{G}°_{\mathbf{rxn}} + \mathbf{RTln}\boldsymbol{Q}$$

(see Chap. 9) Starting at standard conditions,

$Q = 1, \quad \Delta G = \Delta G°_{rxn}$

As we approach equil.,

$Q \rightarrow K_{eq}, \Delta G \rightarrow 0$

we recover,

$\Delta G°_{rxn} = -RT\ln K_{eq}$

$$\Delta \mathbf{G}_{\mathbf{rxn}} = -\boldsymbol{nFE}_{\mathbf{cell}}$$

Substitution gives the famous Nernst Eqn:

$$\boldsymbol{E}_{\mathbf{cell}} = \boldsymbol{E}°_{\mathbf{cell}} - \frac{\boldsymbol{RT}}{\boldsymbol{nF}}\ln \boldsymbol{Q}$$

as $Q \rightarrow K_{eq}, E_{cell} \rightarrow 0$

$$E°_{cell} = \frac{RT}{nF}\ln K_{eq}$$

Nernst Equation

- The Nernst Eqn., using base 10 logarithm:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - 2.303\frac{RT}{nF}\log Q$$

Often, $\dfrac{2.303RT}{F}$ is combined (T = 298 K)

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n}\log Q$$

Example 1

- What is the initial potential, E_{cell}?
- What will happen as the cell goes to equilibrium?