CRITERIA FOR SPONTANEOUS REDOX REACTIONS

At Standard Conditions	At Non-standard Conditions	Spontaneity of Reaction
<i>E</i> ^o _{cell} > 0	<i>E_{cell}</i> > 0	The reaction occurs spontaneously.
$E^{o}_{cell} = 0$	$E_{cell} = 0$	The reaction is at equilibrium.
<i>E</i> ^o _{cell} < 0	<i>E_{cell}</i> < 0	The reaction is non-spontaneous.

PREDICTING SPONTANEITY OF A REDOX REACTION

Determination of E_{cell} and predict spontaneity of a cell reaction at standard conditions

Example 1

By calculating the E°, determine whether Brion can reduce I₂ under standard conditions.

$$2Br^{-}(aq) + I_2(s) \longrightarrow Br_2(l) + 2I^{-}(aq)$$

$$I_2(s) + 2e^- \rightarrow 2I^-(aq)$$
 $E^\circ = +0.53 \text{ V}$
 $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$ $E^\circ = +1.07 \text{ V}$

Note:

In predicting the spontaneity of a reaction, anode and cathode is based on equation given, not based on E°.

Solution:

$$2Br^{-}(aq) + I_{2}(s) \xrightarrow{\text{red /cathode}} Br_{2}(I) + 2I^{-}(aq)$$

cathode (red):
$$I_2(s) + 2e^- \rightarrow 2I^-(aq)$$

anode (ox):
$$2Br^{-}(aq) \rightarrow Br_{2}(I) + 2e^{-}$$

Overall:
$$2Br^{-}(aq) + I_{2}(s) \longrightarrow Br_{2}(l) + 2I^{-}(aq)$$

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

$$= E^{\circ}_{l_2/l^{-}} - E^{\circ}_{Br_2/Br^{-}}$$

$$= 0.53 - 1.07$$

$$= -0.54 \text{ V}_{p}$$

$$E^{o}_{cell} < 0$$

∴ The Br- ions will not reduce I₂ spontaneously.

Determination of E_{cell} and predict spontaneity of a cell reaction at non-standard conditions

Example

Mg(s) + 2Fe³⁺(aq, 5.0 M)
$$\longrightarrow$$
 Mg²⁺(aq, 10.0 M) + 2Fe²⁺(aq,1.0 M)
anode (ox): Mg(s) \longrightarrow Mg²⁺(aq) + 2e-
cathode (red): Fe³⁺(aq) + e⁻ \longrightarrow Fe²⁺(aq) \times 2
2Fe³⁺(aq) + 2e⁻ \longrightarrow 2Fe²⁺(aq)

Overall:
$$Mg(s) + 2Fe^{3+}(aq) \longrightarrow Mg^{2+}(aq) + 2Fe^{2+}(aq)$$

Nernst equation:

$$E_{cell} = E_{cell}^{o} - \frac{0.0592}{n} \log Q$$

$$n = 2$$

$$E_{cell} = E_{cell}^{o} - \frac{0.0592}{2} \log \frac{[Mg^{2+}][Fe^{2+}]^{2}}{[Fe^{3+}]^{2}}$$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$= E^{o}_{Fe}^{3+}/_{Fe}^{2+} - E^{o}_{Mg}/_{Mg}^{2+}$$

$$= +0.77 - (-2.37)$$

$$= +3.14 \text{ V}$$

Nernst equation:

$$E_{cell} = E_{cell}^{o} - \frac{0.0592}{2} \log \frac{[Mg^{2+}][Fe^{2+}]^{2}}{[Fe^{3+}]^{2}}$$

$$E_{cell} = 3.14 - \frac{0.0592}{2} \log \frac{(10.0)(1.0)^{2}}{(5.0)^{2}}$$

$$= + 3.153 \text{ V}$$

$$E_{cell} > 0$$

... The reaction occurs spontaneously.