

**Faculty of science** 

# **Cell Potential**

# 2<sup>nd</sup> Year Students-General, Science

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# **Electrochemical Cell**

A galvanic (voltaic) cell uses a <u>spontaneous</u> redox reaction ( $\Delta G < 0$ ) to generate electrical energy. -The system does work on the surroundings.

An electrolytic cell uses electrical energy to drive a nonspontaneous reaction ( $\Delta G > 0$ ).

-The surroundings do work on the system.

Both cell types are fabricated using <u>two electrodes</u> placed in an <u>electrolyte solution</u>.

The <u>anode</u> is the electrode at which <u>oxidation</u> occurs. The <u>cathode</u> is the electrode at which <u>reduction</u> occurs.

# **Electrochemical Cell: Types**

#### **1. Reversible cell**

- The reaction and the current may be made in the reverse direction by applying a greater external potential opposite to that of the cell.
- As in Daniell cell, Zn ion will be deposited at its electrode and copper would go into solution.

#### **2. Irreversible cell**

- The cell in which the electrode reactions can not be reversed.
- Such as evolution of  $H_2$  accompanies the chemical reaction.

# **Concentration Cells**

A cell made of the <u>same materials</u>, but with <u>different</u> <u>concentrations</u>, will produce a potential difference.

As the concentrations of the solutions are Cu plates e $e_{-}$ onto cathode different, the cell potential is > 0 and the Cu dissolves from anode cell can do work. What is standard cell potential More Less F° for this cell? What is the cell conc. conc. 0.01M CuSO J 1M CuSO₄ potential E? What is the cell potential at equal Cu is exidized to Cu<sup>24</sup> half-cell concentrations? Cu<sup>24</sup> is reduced to Cu Making this half-cell Making this half-cell more concentrated more dilute

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# **Concentration Cells**, continued

 $Cu(s)|Cu^{2+}(0.001 \text{ M})||Cu^{2+}(1.00 \text{ M})|Cu(s)$ 

 $Cu(s) \rightarrow Cu^{2+}(0.001 M) + 2e^{-}$  $Cu^{2+}(1.00 M) + 2e^{-} \rightarrow Cu(s)$ 

 $Cu^{2+}(1.00 M) \rightarrow Cu^{2+}(0.001 M)$ 

 $Cu^{2+}(1 \text{ M}) + 2e^{-} \rightarrow Cu(s) E^{0}_{Red} = +0.34 \text{ V}$ 

 $Cu(s) \rightarrow Cu^{2+}(1 \text{ M}) + 2e^{-} E^{0}_{Oxd} = -0.34 \text{ V}$ 

[anode; oxidation] [cathode; reduction]

> At standard conditions: The standard cell potential in this cell must be 0.0 V for the two electrodes

$$E^{0}_{Cell} = 0.0 V$$

$$E = E^{0} - \frac{0.0592}{n} \log \left( \frac{\left[Cu^{2+}\right]_{anode}}{\left[Cu^{2+}\right]_{cathode}} \right)$$

$$= 0 - \frac{0.0592}{2} \log \left( \frac{0.001}{1.00} \right) = +0.089V$$
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# A concentration cell: Cu/Cu<sup>2+</sup> half-reaction



 $E_{cell} > 0$  as long as the half-cell concentrations are different. Once the concentrations are equal, the cell is no longer able to do work

# **Electrolytic Cell**

#### What about running the cell in reverse?

- •Apply an external voltage of opposite polarity.
- •The magnitude must exceed the +1.10 V that the cell produces on its own.
- •Cu electrode now dissolves and Zn now plates out on its electrode.



# **Electrolytic Cell**, continue

An electrolytic cell *uses electrical energy* from an external source to drive a *nonspontaneous* redox reaction.

 $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ [oxidation at anode] $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ [reduction at cathode]

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

As in the Galvanic cell, <u>oxidation occurs at the anode</u> and <u>reduction takes place at the cathode</u>.

An external source supplies the cathode with electrons, which is *negative*, and the anode, is *positive*. <u>Electrons flow from anode to cathode</u>.

### **Comparison of (A) Galvanic and (B) Electrolytic Cells**





A galvanic cell converts the  $\Delta G$  of a spontaneous redox reaction into the kinetic energy of electrons.

The *cell potential* ( $E_{cell}$ ) of a galvanic cell depends on the *difference* in electrical potential between the two electrodes.

Cell potential is called the *voltage* of the cell or the *electromotive forces (emf)*.

### $E_{\text{cell}} > 0$ for a spontaneous process.

## **Voltages of Some Voltaic Cells**

Voltaic Cell	Voltage (V)
Common alkaline flashlight battery	1.5
Lead-acid car battery (6 cells $\approx$ 12 V)	2.1
Calculator battery (mercury)	1.3
Lithium-ion laptop battery	3.7

### Measuring the standard cell potential of Daniell cell



The standard cell potential is designated  $E^{\circ}_{cell}$  and is measured at a specified temperature with no current flowing and all components in their standard states (I M concentrations).

# **Standard Reduction Potentials**

The standard electrode potential ( $E^{\circ}_{half-cell}$ ) = the potential of a given half-reaction when all components are in their standard states.

By convention, all standard electrode potentials refer to the half-reaction written as a *reduction*.

The standard cell potential equals to the *difference* between the <u>abilities of the two electrodes to act as reducing agents</u>.



# **Single Electrode Potential**

When a strip of metal e.g. Zn is placed in 1 M solution of its ions an equilibrium reaction develops between the metal and its ions  $Zn \rightarrow Zn^{2+} + 2e$ 

- Only the E of a cell, resulting from combination of 2 electrodes is measured.
- To measure and evaluate potential difference between various electrodes (half cells).

**Solution:** connect to a Reference Electrode.

# **Measuring Standard Electrode Potential**

- Use a cell consisting of the <u>H<sub>2</sub> electrode and the electrode</u> whose potential is unknown (standard state, unit activity).
- Connect the 2 half cells by a salt bridge containing a concentrated solution of KCI with an agar plug at the end.
- The potential of the reference electrode is subtracted from the e.m.f. of the cell to get the E<sup>o</sup> value of the half cell under test.
- The H<sub>2</sub> electrode may serve as an anode or cathode.

# **Reference electrode**

#### **Requirements for reference electrodes**

- Easy to construct
- Show reversible behavior
- Give constant and reproducible potentials for a given set of conditions.

For example: Standard hydrogen electrode (SHE)

# **Standard Hydrogen Electrode**

- •It is assigned a potential of zero.  $E^{\circ} = 0.00 \text{ V}$
- •The electrode consists of a piece of Pt connected with a wire and immersed in a solution of H<sup>+</sup> ions (1M).
- •The Pt electrode is covered with finely divided platinum.
- •H<sub>2</sub> (1 atm) is bubbled over the platinized Pt electrode.

The finely divided platinum adsorbs  $H_2$  exists in equilibrium with  $H^+$  ions

The half reaction for the electrode.

Pt,H<sub>2</sub> (1 atm) |H<sup>+</sup> (1 M)

 $2H_{2}^{+}(ag; 1 M) + 2e^{-} \rightarrow H_{2}(g; 1 atom)$ 



## **Standard Electrode as a Reference**

Since SHE potential is assigned the value of 0.00 V, the potential difference measured experimentally is attributed to the other electrode.

The cells are formed by connecting the SHE as the anode and the other half-cell as the cathode.

Any potential we measure will be its cathodic or reduction potential.

#### Example:

```
Pt | H<sub>2</sub> (1.00 atm) | H<sup>+</sup> (1.00 M) | Cu<sup>2+</sup> (1.00 M) | Cu
```

```
Measured potential = +0.340 V
```

will be the **STANDARD REDUCTION POTENTIAL** of the Cu<sup>2+</sup>/Cu couple, as the activity of components in the Cu cell are standard.

# **Determining an unknown** *E*°<sub>half-cell</sub> with SHE



# **Standard as a Reference**, continued

Consider the half-cell of  $Zn^{2+}/Zn$ .

Pt | H<sub>2</sub> (1.00 atm) | H<sup>+</sup> (1.00 M) | Zn<sup>2+</sup> (1.00 M) | Zn Measured Cell Potential = -0.7626 V

This is the **<u>Standard Reduction Potential</u>** for this couple.

The fact that it is negative means that in reality in our test cell, Zn was being oxidized.

#### to make it easier, use of tables.

## **Determining an unknown** $E^{\circ}_{half-cell}$ with SHE



Problem: A galvanic cell houses the reaction between aqueous bromine and zinc metal:

Br<sub>2</sub>(*aq*) + Zn(*s*) → Zn<sup>2+</sup>(*aq*) + 2Br<sup>-</sup>(*aq*)  $E^{\circ}_{cell}$  = 1.83 V. Calculate  $E^{\circ}_{bromine}$ ,? given that  $E^{\circ}_{zlnc}$  = -0.76 V

#### Answer

As  $E_{cell}^{\circ}$  is positive, so the reaction is spontaneous as written. By dividing the reaction into half-reactions, we found that  $Br_2$  is being reduced and Zn is being oxidized. So, the zinc is the anode electrode. Then we can use the equation for  $E_{cell}^{\circ}$  to calculate  $E_{bromine}^{\circ}$ .  $Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$  [reduction; cathode]

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$  [oxidation; anode]  $E^{\circ}_{zinc} = -0.76 V$ 

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$
  
1.83 =  $E^{\circ}_{bromine} - (-0.76)$   
1.83 + 0.76 =  $E^{\circ}_{bromine}$ 

$$E^{\circ}_{\text{bromine}} = 1.07 \text{ V}$$

# **Comparing** *E*<sup>o</sup><sub>half-cell</sub> **values**

Standard electrode potentials refer to the half-reaction as a reduction.

 $E^{\circ}$  values therefore reflect the ability of the reactant to act as an *oxidizing agent*.

The *more positive* the *E*° value, the more readily the *reactant* will act as an *oxidizing agent*.

The *more negative* the *E*° value, the more readily the *product* will act as a *reducing agent*.

# **Standard Potential Tables**

At equilibrium, electrochemical data is presented in **Standard Reduction Potential** tables (**Electrochemical Series**).

$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$2H^+ + 2e^- \rightarrow H_2$	0.0000
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^+ + e^- \rightarrow Au$	+1.69	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$\ln^{3+} + 3e^- \rightarrow \ln$	-0.34
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$V^{2+} + 2e^- \rightarrow V$	-1.19
$AgCI + e^- \rightarrow Ag + CI^-$	+0.22	$Cs^+ + e^- \rightarrow Cs$	-2.92
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15	$Li^+ + e^- \rightarrow Li$	-3.05

**Table 20.1** • Standard Reduction Potentials in Aqueous Solution at 25 °C\*

	Reduction Half-Reaction		<i>E</i> ° (V)	
	$F_2(g) + 2 e^-$	$\longrightarrow$ 2 F <sup>-</sup> (aq)	+2.87	
	H <sub>2</sub> O <sub>2</sub> (aq) + 2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ 2 H <sub>2</sub> O( $\ell$ )	+1.77	
	PbO <sub>2</sub> (s) + SO <sub>4</sub> <sup>2-</sup> (aq) + 4 H <sup>+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow PbSO_4(s) + 2 H_2O(\ell)$	+1.685	
	MnO4 <sup>-</sup> (aq) + 8 H <sup>+</sup> (aq) + 5 e <sup>-</sup>	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(\ell)$	+1.52	
	Au <sup>3+</sup> (aq) + 3 e <sup>-</sup>	$\longrightarrow Au(s)$	+1.50	
	Cl <sub>2</sub> (g) + 2 e <sup>-</sup>	$\longrightarrow 2 \ Cl^{-}(aq)$	+1.360	
	Cr <sub>2</sub> 0 <sub>7</sub> <sup>2-</sup> (aq) + 14 H <sup>+</sup> (aq) + 6 e <sup>-</sup>	$\longrightarrow$ 2 Cr <sup>3+</sup> (aq) + 7 H <sub>2</sub> O ( $\ell$ )	+1.33	
	0 <sub>2</sub> (g) + 4 H <sup>+</sup> (aq) + 4 e <sup>-</sup>	$\longrightarrow 2 H_2O(\ell)$	+1.229	
	Br₂(ℓ) + 2 e <sup>-</sup>	$\longrightarrow$ 2 Br <sup>-</sup> (aq)	+1.08	
	$NO_3^{-}(aq) + 4 H^+(aq) + 3 e^-$	$\longrightarrow NO(g) + 2 H_2O(\ell)$	+0.96	
nts	$OCl^{-}(aq) + H_2O(\ell) + 2 e^{-}$	$\longrightarrow$ Cl <sup>-</sup> (aq) + 2 OH <sup>-</sup> (aq)	+0.89	nts
age	Hg <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ Hg( $\ell$ )	+0.855	age
bii	$Ag^{+}(aq) + e^{-}$	$\longrightarrow Ag(s)$	+0.80	Бu
idi	$Hg_2^{2+}(aq) + 2 e^{-}$	$\longrightarrow$ 2 Hg( $\ell$ )	+0.789	duci
š	$Fe^{3+}(aq) + e^{-}$	$\longrightarrow Fe^{2+}(aq)$	+0.771	Fre
5	I <sub>2</sub> (s) + 2 e <sup>-</sup>	$\longrightarrow$ 2 I <sup>-</sup> (aq)	+0.535	h of
ngt	$0_2(g) + 2 H_20(\ell) + 4 e^-$	$\longrightarrow$ 4 OH <sup>-</sup> (aq)	+0.40	ngt
stre	Cu <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow Cu(s)$	+0.337	stre
Ē	Sn <sup>4+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ Sn <sup>2+</sup> (aq)	+0.15	Ē
easi	2 H <sup>+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow H_2(g)$	0.00	easi
ncĩ	Sn <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow$ Sn(s)	-0.14	L L
	Ni <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow Ni(s)$	-0.25	<b>*</b>
	$V^{3+}(aq) + e^{-}$	$\longrightarrow V^{2+}(aq)$	-0.255	
	PbSO <sub>4</sub> (s) + 2 e <sup>-</sup>	$\longrightarrow Pb(s) + SO_4^{2-}(aq)$	-0.356	
	$Cd^{2+}(aq) + 2 e^{-}$	$\longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2e^{-}$	$\longrightarrow$ Fe(s)	-0.44	
	$Zn^{2+}(aq) + 2 e^{-}$	$\longrightarrow$ Zn(s)	-0.763	
	2 H₂O(ℓ) + 2 e <sup>-</sup>	$\longrightarrow$ H <sub>2</sub> (g) + 2 OH <sup>-</sup> (aq)	-0.8277	
	Al <sup>3+</sup> (aq) + 3 e <sup>-</sup>	$\longrightarrow Al(s)$	-1.66	
	Mg <sup>2+</sup> (aq) + 2 e <sup>-</sup>	$\longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^-$	$\longrightarrow$ Na(s)	-2.714	
	K <sup>+</sup> (aq) + e <sup>-</sup>	$\longrightarrow K(s)$	-2.925	
	$Li^+(aq) + e^-$	$\longrightarrow$ Li(s)	-3.045	

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\*In volts (V) versus the standard hydrogen electrode.

**Using half-reactions to write a Spontaneous Redox Reaction:** 

Sn<sup>2+</sup>(aq) + 2e<sup>-</sup> → Sn(s)  $E^{\circ}_{tin} = -0.14 \text{ V}$ Ag<sup>+</sup>(aq) + e<sup>-</sup> → Ag(s)  $E^{\circ}_{silver} = 0.80 \text{ V}$ 

**Step 1:** Reverse one of the half-reactions into an oxidation step so that the difference between the E° values will be positive.

Here the Ag<sup>+</sup>/Ag half-reaction has the more positive *E*° value, so it must be oxidizing agent (the reduction). This half-reaction remains as written.

We reverse the Sn<sup>2+</sup>/Sn half-reaction, <u>but we do *not* reverse the</u> sign:

$$Sn(s) \rightarrow Sn^{2+}(aq) + 2e^{-}$$
  $E^{\circ}_{tin} = -0.14 \text{ V}$ 

**Step 2:** Multiply the half-reactions if necessary so that the number of  $e^{-1}$  lost is equal to the number or  $e^{-2}$  gained.

$$2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s) \quad E^{\circ}_{silver} = 0.80 \text{ V}$$

Note that we multiply the equation but *not* the value for  $E^{\circ}$ .

**Step 3:** Add the reactions together, cancelling common species. Calculate  $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$ .

Sn(s)  $\rightarrow$  Sn<sup>2+</sup>(aq) + 2e<sup>-</sup> 2Ag<sup>+</sup>(aq) + 2e<sup>-</sup>  $\rightarrow$  2Ag(s)  $E^{\circ}_{silver} = 0.80 \text{ V}$ 

 $Sn(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Sn^{2+}(aq) \qquad E^{\circ}_{cell} = 0.94 V$ 

$$E^{\circ}_{cell} = E^{\circ}_{silver} - E^{\circ}_{tin} = 0.80 - (-0.14) = 0.94 V$$

#### Example 1

Consider the following two half reactions

$$Fe^{2+} + 2e^- \rightarrow Fe$$
 $E= -0.44 V$  $V^{2+} + 2e^- \rightarrow V$  $E= -1.19 V$ 

- 1.Let the more negative (least positive) reaction be that for the anode. That means that its direction will be reversed.
- 2. Balance the number of electrons but scaling the reactions appropriately, but DO NOT modify their cell potentials.

To get a final positive cell potential, consider the more negative halfreaction (V) as the anode.

$$Fe^{2+} + V \rightarrow Fe^{} + V^{2+}$$
  
 $E_{cell} = -0.44 - (-1.19) = +0.75 V$ 

### Example 2

 $Sn^{2+} + 2e^- \rightarrow Sn$  -0.14 (Anode, more negative )

 $Ag^+ + e^- \rightarrow Ag$  +0.80 (cathode, more postive)

Consider the more negative potential reaction as the anode (Sn<sup>2+</sup>).

Multiply the Ag reaction by 2, but don't modify the cell potential.

2 Ag<sup>+</sup> + Sn 
$$\rightarrow$$
 2 Ag + Sn<sup>2+</sup>  
E<sub>cell</sub> = +0.80 - (-0.14) = +0.94 V

#### Using the Tables

$F_2 + 2e^- \rightarrow 2F^-$	+2.87	<ul> <li>choose one reaction for reduction</li> </ul>
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	<ul> <li>choose another for oxidation</li> </ul>
$Au^+ + e^- \rightarrow Au$	+1.69	$\Delta u^+ + \rho^- \longrightarrow \Delta u$
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$Cu \rightarrow Cu^{2+} + 2e^{-}$
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	Overall Reaction:
$Ag^+ + e^- \rightarrow Ag$	+0.80	$2Au^+ + Cu \rightarrow Cu^{2+} + 2Au$
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	Cell potential E:
AgCl + $e^- \rightarrow Ag + Cl^-$	+0.22	E = +1.69 - 0.34 = +1.35 V
$Sn^{4+} + 2e^- \rightarrow Sn^{2+} +0.15$		

•The cell constructed using a Au and a Cu electrode and solutions of Au(I) and Cu(II) ions, when at unit activity (1.00 M) has a potential of +1.35 V.

•This indicates that the Au electrode is the cathode and the Cu electrode is the anode.

#### Using the Tables <sub>continued</sub>

$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81
$Au^+ + e^- \rightarrow Au$	+1.69
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
AgCl + $e^- \rightarrow Ag + Cl^-$	+0.22
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15

choose one reaction for reduction

choose another for oxidation

 $Ce^{4+} + e^- \rightarrow Ce^{3+}$  $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$ 

Overall Reaction:

 $Ce^{4+} + Sn^{2+} \rightarrow 2Ce^{3+} + Sn^{4+}$ 

Cell potential E:

E = 1.61-0.15= +1.46 V

#### **Problems**

1. A concentration cell consists of two Ag/Ag<sup>+</sup> half-cells. In halfcell A, the electrolyte is 0.01 *M* AgNO<sub>3</sub>; in half-cell B, it is  $4.0x10^{-4} M$  AgNO<sub>3</sub>. What is the cell potential at 298.15 K?

2. Lead can displace silver from solution, and silver occurs in trace amounts in some ores of lead.

 $Pb(s) + 2Ag^{+}(aq) \rightarrow Pb^{2+}(aq) + 2Ag(s)$ 

As a consequence, silver is a valuable byproduct in the industrial extraction of lead from its ore. Calculate K and  $\Delta G^{\circ}$  at 298.15 K for this reaction.

3. Rank the relative strengths of the oxidizing and reducing agents.

(1) 
$$NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-} \rightarrow NO(g) + 2H_2O(l) = E^{\circ} = 0.96 V$$

- (2)  $N_2(g) + 5H^+(aq) + 4e^- \rightarrow N_2H_5^+(aq)$   $E^\circ = -0.23 V$
- $(3)_{2020-03-18} MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) E^\circ = 1.23 V$

4. Given the E° for the following half-reactions:

 $Cu^+ + e^- \rightarrow Cu^\circ$  $E^{\circ}red = 0.52 V$  $Cu^{2+} + 2e^{-} \rightarrow Cu^{\circ}$   $E^{\circ}red = 0.34 V$ What is E° for the reaction:  $Cu^+ \rightarrow Cu^{2+} + e^-$ 

5. For each pair of species, choose the better reducing agent.

(a) Ag(s) or Sn(s), given:  $Ag+(aq) + e^{-} \rightarrow Ag(s)$  $Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$   $E^{\circ}red = -0.136 V$ (b) Br<sup>-</sup>(aq) or Cl-(aq), given:  $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ (c) Zn(s) or Co(s), given:  $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$  $Co^{2+}(aq) + 2e^{-} \rightarrow Co(s)$ (d) Au(s) or  $I^{-}(aq)$ , given:  $Au^{3+}(aq) + 3e^{-} \rightarrow Au(s)$  $I_2(s) + 2e^- \rightarrow 2I^-(aq)$ 

E°red = 0.799 V E°red = 1.065 V E°red = 1.359 V E°red = -0.763 V  $E^{\circ}red = -0.277 V$ E°red = 1.420 V  $E^{\circ}red = 0.540 V$ 

6) Calculate the cell potential for the following two half reactions

(a)  $\operatorname{Sn}^{2+} + 2e^- \rightarrow \operatorname{Sn} \quad E^\circ = -0.14 \text{ V}$ 

 $Ag^+ + e^- \rightarrow Ag$   $E^\circ = +0.80 V$ 

(b)  $\text{Li}^+ + e^- \rightarrow \text{Li}$   $E^\circ = -3.05 \text{ V}$  $\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$   $E^\circ = +1.81 \text{ V}$ 

**7)** Calculate the cell potential at 25°C for a cadmium concentration cell in which the Cd<sup>2+</sup> concentration in one half-cell is equal to 0.050 M and the Cd<sup>2+</sup> concentration in the other half-cell is equal to 1.5 M.

# Interrelation of E <sub>Cell</sub>, ΔG<sup>°</sup> and *K*

### Consider the cell

Pt | I<sup>-</sup> (1 M), I<sub>2</sub> (s) | Fe<sup>3+</sup> (1 M), Fe<sup>2+</sup>(1 M) | Pt

Standard Cell Potential is (see tables) = 0.771 V - 0.536 V = +0.235 V

$$\Delta G^{o} = -nFE^{o} = -2(96285)(0.235) = -45,348 \frac{J}{mol}$$

This is the free energy change. It leads to the equilibrium constant for the reaction.

$$\Delta G = -RT \ln K_{eq} \implies \ln K_{eq} = -\frac{\Delta G^{\circ}}{RT} = -\frac{\left(-45348 \frac{J}{mol}\right)}{\left(8.314 \frac{J}{K mol}\right)(298 \text{ K})} = 18.3034$$

$$K_{eq} = e^{18.3034} = 8.89 \times 10^7$$
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## The interrelationship of $\Delta G^{\circ}$ , $E^{\circ}_{cell}$ , and K



Reaction Parameters at the Standard State			
ΔG°	К	E° <sub>cell</sub>	Reaction at standard-state conditions
< 0	>1	> 0	spontaneous
0	1	0	at equilibrium
> 0	< 1	< 0	Non spontaneous

**Example**: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a  $Zn/Zn^{2+}$  half-cell and an  $H_2/H^+$  half-cell under the following conditions:

 $[Zn^{2+}] = 0.010 \text{ M}$   $[H^+] = 2.5 \text{ M}$   $P_{H_2^-} 0.30 \text{ atm}$ Calculate  $E_{cell}$  at 298 K.

#### **Solution**

We write the equation for the spontaneous reaction and calculate  $E^{\circ}_{cell}$  from standard electrode potentials then apply Nernst equation.

We must convert the given pressure to Molarity in order to have consistent units.

(1)  $2H^{+}(aq) + 2e^{-} \rightarrow H_{2}(g)$ (2)  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$   $E^{\circ} = -0.76 V$   $2H^{+}(aq) + Zn(s) \rightarrow H_{2}(g) + Zn^{2+}(aq)$  $E^{\circ}_{cell} = 0.00 - (-0.76) = 0.76 V$ 

#### Converting pressure to molarity:

$$\frac{n}{V} = \frac{P}{RT} = \frac{0.30 \text{ atm}}{0.0821 \text{ atm} \cdot \text{L}} = 1.2 \times 10^{-2} M$$

$$\frac{1.2 \times 10^{-2} M}{\text{mol} \cdot \text{K}}$$

$$Q = \frac{[\text{H}_2][\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.012 \times 0.010}{(2.5)^2} = 1.9 \times 10^{-5}$$

Solving for  $E_{cell}$  at 25°C (298.15 K), with n = 2:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q$$
  
= 1.10 V -  $\left[ \frac{0.0592 \text{ V}}{2} \log(1.9 \times 10^{-5}) \right] = 0.76 - (-0.14 \text{ V}) = 0.90 \text{ V}$ 

# **Formal Potentials**

- Standard states are impossible to achieve
- Theoretical calculations of activity coefficients possible below 10<sup>-2</sup> M.
- For more concentrated solutions, no theory available to do the calculation.
- One way around this problem is to use Formal Potentials.
- The formal potential is the reduction potential applies under a specified set of conditions (pH and ionic strength)
- Solution of high concentration of inert electrolyte, activity coefficients are constant.
- Often specified as occurring in 1.0 M HClO<sub>4</sub>, 1.0 M HCl, or 1.0  $M H_2 SO_4$ . 2020-03-18

#### Example

$$a = \gamma \frac{C}{C^{\circ}}$$

Consider the Fe(III)/Fe(II) couple. The Nernst equation

$$\begin{split} E &= E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right) = E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{2+}}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{2+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{2+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{2+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right) \\ &= E_{Fe^{3+}/Fe^{3+}}^{\circ} - \frac{RT}{F} \ln \left( \frac{\gamma_{Fe^{3+}}}{\gamma_{Fe^{3+}}} \right) - \frac{RT}{F} \ln \left( \frac{Fe^{3+}}{Fe^{3+}} \right)$$

When the Q is 1, the last term is 0. This defines the new formal potential (read "E zero prime") as

$$E^{\circ'} = E^{\circ}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F} \ln\left(\frac{\gamma_{Fe^{2+}}}{\gamma_{Fe^{3+}}}\right)$$

This new reference potential is constant, because the activity coefficients are constant at huge excess of inert ions.

## **Example** continued

The standard reduction potential for the Fe(III)/Fe(II) couple is  $E^{\circ} = 0.771 \text{ V}$ 

In 1.0 M HClO<sub>4</sub> it is  $E^{\circ}(1.0 \text{ M HClO}_4) = 0.732 \text{ V}$ 

In 1.0 M HCl it is  $E^{\circ}(1.0 \text{ M HCl}) = 0.700 \text{ V}$ 

- In the HClO<sub>4</sub> solution, the potential is 39 mV lower than the standard potential.
- As the ionic strength is controlled by the huge excess of inert electrolyte, changes in the dilute concentrations of the iron species, do not lead to changes in their activity coefficients.
- So the Reference Formal Potential is constant, and measurements can be used to accurately calculate ion concentrations.

#### The Relation Between *E*<sub>cell</sub> and Log *Q* for the Zinc-copper Cell



If the reaction starts with  $[Zn^{2+}] < [Cu^{2+}] (Q < 1)$ ,  $E_{cell}$  is higher than the standard cell potential.

As the reaction proceeds,  $[Zn^{2+}]$  decreases and  $[Cu^{2+}]$  increases, so  $E_{cell}$  drops. The system reaches equilibrium and the cell can no longer do work.

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### **Reference**

Daniel Harris, (2007), "Quantitative Chemical Analysis" 7th Edition, New York, chapters 17&18.