## CHEM 116 Electrochemistry at Non-Standard Conditions, and Intro to Thermodynamics

Lecture 23 Prof. Sevian

Important announcement:

If you borrowed a clicker from me this semester, return it to me at the end of next lecture or at the final exam

If you do not return it, you will receive an INC for your grade



## Today's agenda

#### • Big picture of electrochemistry

- Redox reactions and oxidation numbers (last lecture)
- Charge flow in electrochemical cells and diagramming a cell
- Using the mathematical model to predict current and voltage under standard and non-standard conditions
- Important points of thermodynamics for general chemistry
  - Enthalpy change (+endothermic, -exothermic)
  - Entropy change (+more disorder, -more order)
  - Gibbs free energy (+non-spontaneous, -spontaneous)
  - Connection to equilibrium
  - Connection to electrochemistry

#### Announcements

• Final exam is Tuesday, Dec 16, 3:00-6:00pm in S-1-006

# Predicting voltage under standard conditions

- Voltage = cell potential (E<sup>o</sup><sub>cell</sub>) = related to ∆G, which is related to ∆H, T, and ∆S
- Table of reference voltages, all referenced to the hydrogen half-cell
- All reference voltages are reduction potentials, so if you need an oxidation potential you just take the opposite
- See table of standard reduction potentials
- Example of using standard reduction potentials to predict E<sup>o</sup><sub>cell</sub>

## Non-standard conditions: Nernst equation

Concentrations of solutions not at standard 1.0 M

$$E_{cell} = E_{cell}^{o} - \frac{0.0257}{n} \ln Q$$
  
=  $E_{cell}^{o} - \frac{0.0592}{n} \log Q$   
• Temperature not at standard 25 °C  
 $E_{cell} = E_{cell}^{o} - \frac{RT}{n\Im} \ln Q$   
Least common multiple of electrons exchanged in the redox reaction

where  $\mathcal{F}$  is the Faraday constant:  $\mathcal{F} = 96,500$  C/mol

http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem /voltaicCellEMF.html set up Cu|Cu<sup>2+</sup>(0.001M)||Ag<sup>+</sup>(2.0M)|Ag cell

## Electrolysis: electrochemical cell forced to run backwards (against its will)

- Note: sections 20.7 and 20.8 in the text book are fascinating reading, but they are not required reading. However, section 20.9 is required reading.
- <u>Electroplating</u>: The longer you run the cell, the more metal electroplate builds up
- Current means how many electrons pass by per second
- If you know how much metal electroplate you want to make, then stoichiometry tells you how many electrons are required
  - $\operatorname{Cu}^{2+}(aq) + 2 e^{-} \rightarrow \operatorname{Cu}(s)$
  - $\operatorname{Au}^{3+}(aq) + 3 e^{-} \rightarrow \operatorname{Au}(s)$
  - $\operatorname{Ag}^+(aq) + 1 e^- \rightarrow \operatorname{Ag}(s)$
- If you know what current is being applied (e.g., 0.800 amperes = 0.800 Coulombs/second), then you can figure out how much time you must run the cell for in order to build the amount of electroplated metal that you want

## **Electrolysis example**

Similar to Sample Exercise 20.14, pp. 885-886

Calculate the mass of  $O_2$  produced in the electrolysis of water, using a current of 0.445 A for a period of 45 minutes.



Adapted from "Key Concept Summary" in McMurray & Fay, Chemistry (3rd edn)

## Three laws of thermodynamics

- 1. The total energy of the universe is constant.
  - Energy is conserved in all processes
  - If a system gains/loses heat energy, then the surroundings must do the opposite
- 2. In processes that occur spontaneously, disorder in the universe increases.
  - Disorder (called "entropy") is a measure of how spread out matter is
  - If a system gains/loses disorder, then the surroundings must do so in a way such that both system and surroundings together net an increase in the universe's disorder
- 3. Zero disorder is defined as a perfect crystal at zero absolute temperature.
  - Zero absolute temperature is impossible to achieve

## Additional important implications

- If a chemical or physical change written in one direction is nonspontaneous, then written in the opposite direction it is spontaneous
  - "Spontaneous" means that once a process begins (after activation barrier is surmounted) it continues without intervention
  - Spontaneous and non-spontaneous are opposites
- Whether a given change is spontaneous depends on the experimental conditions (e.g., temperature, pressure)
  - A change that is spontaneous under one set of conditions may be nonspontaneous under a different set of conditions
- Spontaneous change always progresses toward a condition of equilibrium

## Enthalpy: what you have already learned

- Heat flow
  - Endothermic = into the system (at constant p,  $\Delta H$  is +)
  - Exothermic = out of the system (at constant p,  $\Delta H$  is –)
- System vs. surroundings
  - Together, system + surroundings = universe
  - Heat flows from one to the other
    - If heat flows out of system (exothermic), then it goes into surroundings
    - If heat flows into system (endothermic), it is because it comes from the surroundings
    - Total energy of the universe remains constant
- Closed system
  - Heat can go in and out of system, but matter cannot
- Can be measured by calorimetry
  - Using equation  $q = mC\Delta T$
  - At constant pressure,  $q = \Delta H$ 
    - When heat flows into the system, the temperature goes up
    - When heat flows out of the system, the temperature goes down

## Using Hess's law to calculate $\Delta H_{sys}$

<u>Hess's law</u>: enthalpy is a "state function" and as such its value does not depend on the path taken to get from initial to final state

<u>Reference state</u> has enthalpy change of zero – "reference state" defined to be elements in the states they exist in naturally at standard conditions (*e.g.*, hydrogen is  $H_2(g)$ , carbon is C (*s*), iron is

Fe (s)) initial state  $\rightarrow$  final state

$$\Delta H^{o} = \sum_{final \ components} \Delta H^{o}_{formation} - \sum_{initial \ components} \Delta H^{o}_{formation}$$

Example

 $\Delta H^{o}$  for H<sub>2</sub>O (*l*)  $\leftrightarrows$  H<sub>2</sub>O (*g*) can be predicted from tabulated values (see Appendix C, pp. 1123-1125 in text book)

$$H_{2}O(l) \rightarrow H_{2}O(g)$$
  

$$\Delta H^{o} = \sum_{\text{final components}} \Delta H_{f}^{o}(H_{2}O(g)) - \sum_{\text{initial components}} \Delta H_{f}^{o}(H_{2}O(l))$$
  

$$= \left[-241.83 \frac{kJ}{mol}\right] - \left[-285.83 \frac{kJ}{mol}\right] = +44.00 \frac{kJ}{mol}$$

## Absolute entropy (S)

- Entropy means disorder, or "spreadedness"
  - The more disordered or spread out a material is, the greater the absolute entropy (*S*)
  - The more ordered a material is, the lower the entropy
- Must always be a comparison
- Ultimate comparison is to absolute order, which is a perfect crystal lattice structure with no motion (zero absolute temperature)
- Impossible for absolute entropy to be zero (except at reference state of absolute order, which is unachievable)

Examples (comparison per mole of the chemical)

- Water in different states
- Homologous series of alkanes



Eek! Chaos!



## Comparing absolute entropy of water in different

### Comparing absolute entropy of different alkanes under standard conditions

- The more complex the molecular structure, the higher the absolute entropy of the substance
- More complicated molecules have more options for configurations, rotations, vibrations, etc.

(This is the same as Fig 19.15 in your text book, but the one here is a slightly nicer drawing.)

From Chemistry & Chemical Reactivity 5<sup>th</sup> edition by Kotz / Treichel, C 2003. Reprinted with permission of Brooks/Cole, a division of Thomson Learning: <u>www.thomsonrights.com</u>. Fax 800-730-2215.



## Molecular interpretation of entropy (S)

#### $S = k \ln W$

*W* is the number of microstates available, k is a constant So, as *W* increases, the absolute entropy (*S*) increases

Factors that influence W (for making qualitative comparisons)

- Temperature
- Volume
- Number of independently moving particles

## Compare absolute entropies

Arrange in order from lowest to highest <u>absolute</u> <u>standard</u> entropy  $(S^{\circ} \text{ not } \Delta S^{\circ})$ :

a)	$O_{2}\left(g ight)$	VS.	<b>O</b> <sub>3</sub>	(g)
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- b)  $NH_4Cl(s)$  vs.  $NH_4Cl(aq)$
- c)  $F_{2}(g), Cl_{2}(g), Br_{2}(l), I_{2}(s)$

d) NaCl (s) vs. MgO (s)

<b>O</b> <sub>2</sub> <b>O</b> <sub>3</sub>	205.1 J/mol·K 238.9
NH <sub>4</sub> C	I (s) 94.85 J/mol·K
NH <sub>4</sub> C	l (aq) 164.9
I <sub>2</sub> (s	) 116.1 J/mol·K
Br <sub>2</sub>	( <i>l</i> ) <b>152.2</b>
$\mathbf{F}_{2}(\mathbf{g})$	g) <b>202.8</b>
Cl <sub>2</sub>	(g) <b>223.1</b>
MgO (s) NaCl (s)	26.85 J/mol·K 72.11

## Entropy change

#### (Now we're talking about $\Delta S^{\circ}$ , not $S^{\circ}$ )

- The change from one state to another state (can be positive or negative)
- Difference between the final and initial entropy states
- Symbolized  $\Delta S$
- When ∠S > 0 it means disorder ("spreadedness") of the system increases during the change
- Hess's law applies because entropy is also a state function

#### Example





## Gibbs free energy

• Derives from the idea that the entropy change to the universe resulting from a change in a system and its surroundings, under conditions of constant temperature and pressure, is

$$\Delta S_{universe} = \Delta S_{surroundings} + \Delta S_{system}$$
  
(see pp. 822-823 in your text book)

- Measures absolute entropy change to the entire universe, which always increases for any change that occurs spontaneously
- Results in an equation in terms of the system of interest (at const. p):

$\Delta G$	$= \Delta H$	- $T \Delta S$
Gibbs free energy	Enthalpy change	Absolute Entropy temp- change erature

- Depends on both enthalpy change term (ΔH) and entropy change term (TΔS)
- Either term, or both, could drive the change to be spontaneous (spontaneous when  $\Delta G$  is negative)

## Example: $H_2O(l) \rightarrow H_2O(g)$ is a physical change

- <u>Enthalpy</u>: The change, in the forward direction written, is endothermic ( $\Delta H = 44 \text{ kJ/mol} > 0$ , the system requires energy input from the surroundings for the change to proceed)
- <u>Entropy</u>: The change, in the forward direction written, represents an increase in the system's disorder ( $\Delta S = 118.89 \text{ J/mol·K} > 0$ , gases are more disordered or "spread out" than liquids)

$$\Delta G = \Delta H - T \Delta S$$

Conditions: Conditions: Conditions:  $T = 90 \,{}^{\circ}\text{C}, p = 1 \text{ atm}$  $T = 100 \,^{\circ}\text{C}, p = 1 \text{ atm}$  $T = 110 \,{}^{\circ}\text{C}, p = 1 \text{ atm}$  $\Delta G = \Delta H - T \Delta S$  $\Delta G = \Delta H - T \Delta S$  $\Delta G = \Delta H - T \Delta S$ =44 - (90 + 273)(0.119)=44 - (110 + 273)(0.119)=44 - (100 + 273)(0.119) $=+0.80 \, kJ \, / \, mol$ = 0 kJ / mol $= -1.6 \, kJ \, / \, mol$ Non-spontaneous in Spontaneous in direction At equilibrium direction written written

## Summarizing the example of water's physical change from $H_2O(I)$ to $H_2O(g)$

• The spontaneity of the change depends on what temperature the change occurs at

	$\Delta G^o$ =	ΔH°	_	Т	ΔS°
Below normal b.p.	+0.80 kJ/mol = (non- spontaneous)	44 kJ/mol (endothermic)	_	( <mark>90</mark> +273 K)	(0.119 kJ/mol·K) (increasing disorder)
At normal boiling point	0 = (at equilibrium)	same	_	( <mark>100</mark> +273 K)	same
Above normal b.p.	-1.6 kJ/mol = (spontaneous)	same	_	(110+273 K)	same

## Magnitudes and signs of terms in free energy

TABLE	19.4	Effect of Temperature on the Spontaneity of Reactions		
$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T \Delta S$	Reaction Characteristics
-	+	-	_	Spontaneous at all temperatures
+	_	+	+	Nonspontaneous at all temperatures
-	_	+	+ or -	Spontaneous at low T; nonspontaneous at high T
+	+	-	+ or -	Spontaneous at high T; nonspontaneous at low T

About the mathematical terms in this table:

- ★  $\Delta H$  is the change of <u>enthalpy</u>. When  $\Delta H > 0$  (i.e.,  $\Delta H$  is positive), the change is endothermic. When  $\Delta H < 0$  (i.e.,  $\Delta H$  is negative), the change is exothermic.
- ★  $\Delta S$  is the change of <u>entropy</u>. When  $\Delta S > 0$  (i.e.,  $\Delta S$  is positive), the entropy increases during the process (the system becomes more disordered). And vice versa.
- T is the absolute temperature (i.e., Kelvin scale). It is always a number larger than zero.
- Therefore, the term  $-T\Delta S$  has the opposite sign of  $\Delta S$ .

### Effect of temperature on spontaneity

#### Similar to Exercise 19.8, p. 829

Metallic iron is produced in a blast furnace by reducing iron oxide (mined from the earth) using carbon. For the reaction,

$$2 \operatorname{Fe}_2 O_3(s) + 3 \operatorname{C}(s, \operatorname{graphite}) \rightarrow 4 \operatorname{Fe}(s) + 3 \operatorname{CO}_2(g)$$

the following information is available:  $\Delta H_{rxn}^{o} = +467.9 \text{ kJ}$ 

$$\Delta S_{rxn}^{o} = +560.7 \text{ J/K}$$

Show that it is necessary that this reaction be carried out at a high temperature.

## Relationship between $\Delta G$ and $K_{eq}$

 At a temperature (7) other than standard temperature (25°C = 298K), the Gibbs free energy is given by

 $\Delta G = \Delta G^{\circ} + RT \ln Q$ 

- At equilibrium,  $\Delta G = 0$
- Also at equilibrium,  $Q = K_{eq}$
- Substituting into the expression above, at equilibrium

 $0 = \Delta G^{\rm o} + RT \ln K_{\rm eq}$ 

• Therefore (rearranging):

 $\Delta G^{\circ} = -RT \ln K_{eq}$ 

## How $\Delta G$ indicates reaction extent

Similar to Exercise 19.11, p. 834 Determine the standard free energy change for the reaction

$$C(s) + CO_2(g) \rightarrow 2 CO(g)$$

from the following thermodynamic data.

C (s)	$\Delta G_f^o = 0 \text{ kJ/mol}$
$\operatorname{CO}_2\left(g\right)$	$\Delta G_f^o = -394.359 \text{ kJ/mol}$
CO (g)	$\Delta G_f^o = -137.168 \text{ kJ/mol}$

Then, use this result to calculate the equilibrium constant at 25 °C.

## What's left to cover this semester?

- Relating  $\Delta G$ ,  $E^{o}_{cell}$  and  $K_{eq}$
- Predicting free energy changes under non-standard conditions
- Next class (last lecture this semester) we will do this in the context of going over selected problems from Assignment 13
  - *Re-read chapter 19, and section 20.5, and attempt the homework before you come to the next lecture*
  - Doing thermochemistry problems brings together nearly all of the topics you have learned this semester, and is in this sense a review of the semester