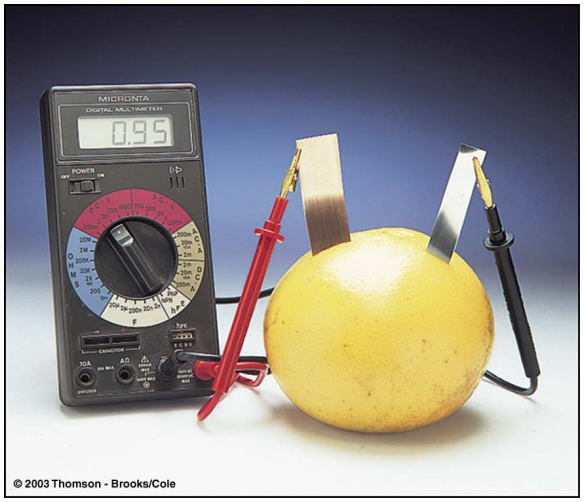
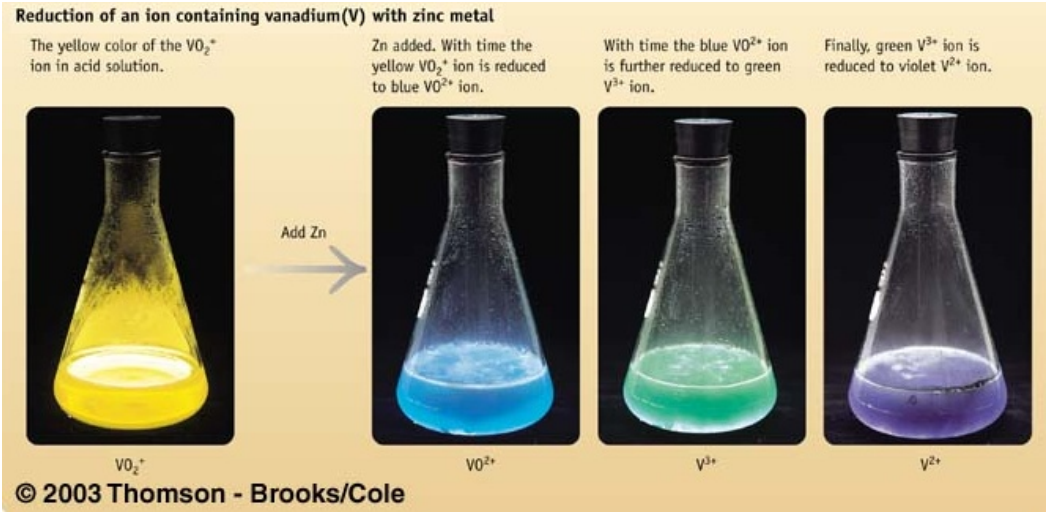




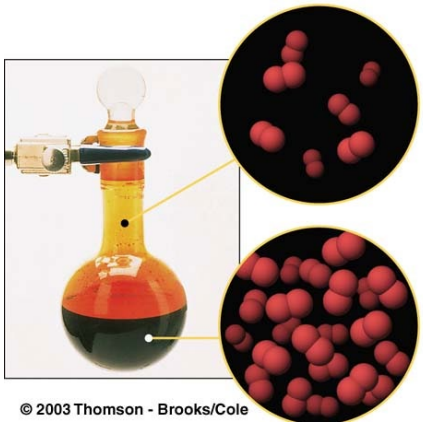
CHEMISTRY 2000

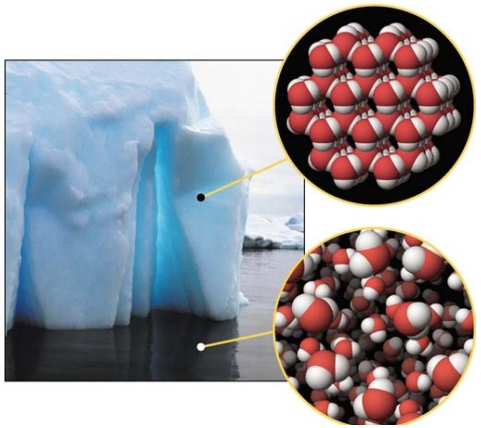
Topic #2: Thermochemistry and Electrochemistry –
What Makes Reactions Go?

Fall 2020

Dr. Susan Findlay

See Exercises 6.5 and 6.6





The Laws of Thermodynamics (Review)

1. The internal energy* of an isolated system is constant. There are only two ways to change internal energy – heat and work.

$$\Delta U = q + w$$

2. The entropy of the universe increases in any spontaneous process.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

3. The entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.

* Internal energy (U) is the energy stored in a system. It includes the energy of chemical bonds and intermolecular forces as well as kinetic energy.

2nd Law: Gibbs Free Energy

- At constant temperature, we saw that entropy change could be measured as:

$$\Delta S = \frac{q_{rev}}{T}$$

- Since, at constant pressure, $q_{system} = \Delta H_{system}$ that means that at constant pressure and constant temperature:

$$\Delta S_{system} = \frac{\Delta H_{system}}{T}$$

- The heat absorbed by the system will be the same as the heat released by the surroundings (and vice versa), so we can also say that:

$$\Delta S_{surroundings} = -\frac{\Delta H_{system}}{T}$$

2nd Law: Gibbs Free Energy

- Returning to the Second Law of Thermodynamics, we can say that if:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

Then:

Therefore:

Which can be restated as:

- For any spontaneous reaction, $-T\Delta S_{universe}$ will be _____

2nd Law: Gibbs Free Energy

- Since $-T\Delta S_{universe}$ can now be defined in terms of the system alone, a new term, the **Gibbs free energy** (G), is defined for the system:

$$G = H - TS$$

- At constant temperature and pressure,

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

(recall that enthalpy is only meaningful at constant pressure).

- For any spontaneous reaction, ΔG will be _____.

- Like entropy (from which it is derived), Gibbs free energy is a state function.

2nd Law: Gibbs Free Energy

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

- What do we know about ΔG for each of the following reactions?

	$\Delta H < 0$ **(exothermic)**	$\Delta H > 0$ **(endothermic)**
$\Delta S > 0$		
$\Delta S < 0$		

Gibbs Free Energy and the Standard State

- Changes in Gibbs free energy are quite sensitive to different reaction conditions. As such, if we want to make comparisons of free energy values, we have to define a **standard state**.

- We define a standard temperature and pressure as
  - T = 25 °C
  - P = 1 bar (100 kPa)

- In addition to being at the standard temperature and pressure,
  - A gas is in the standard state if it behaves ideally and has a partial pressure of 1 bar.
  - A dissolved substance is in the standard state if it behaves ideally and has a concentration of 1 mol/L.

Gibbs Free Energy and the Standard State

- **Standard molar Gibbs free energy of formation** ($\Delta_f G°$) is generally tabulated alongside standard molar enthalpy of formation and standard entropy *(see Appendix B of Silberberg)*. It refers to the free energy change when one mole of a compound is made from pure elements in their standard states:

$$\mathrm{Br_{2(l)}} \rightarrow \mathrm{Br_{2(g)}} \qquad \Delta_f G°(Br_{2(g)}) = 82.40\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

$$\mathrm{Na_{(s)}} + \frac{1}{2}\mathrm{Br_{2(l)}} \rightarrow \mathrm{NaBr_{(s)}} \qquad \Delta_f G°(NaBr_{(s)}) = -349.0\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

- If a substance *is* a pure element in its standard state, this means that its standard molar Gibbs free energy of formation must therefore be zero:

$$\mathrm{Br_{2(l)}} \rightarrow \mathrm{Br_{2(l)}} \qquad \Delta_f G°(Br_{2(l)}) = 0\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Gibbs Free Energy and Predicting Spontaneity

- As a general rule:

$$\Delta_r G° = \sum \Delta_f G°(\text{products}) - \sum \Delta_f G°(\text{reactants})$$

Note the similarity to Hess's Law (for enthalpy) and to using standard entropies to determine reaction entropy change.

- A few general notes:
  - As we saw when looking at $Br_{2(g)}$ vs. $Br_{2(l)}$, state of matter counts!
  - Only one allotrope of any element can have $\Delta_f G° = 0$. For most elements, it is the one that is most stable under standard conditions ($O_{2(g)}$, graphite, etc.; $P_{4(s)}$ is the exception to this rule).
  - Since it impossible to actually make ions without counterions, standard state $H^+_{(aq)}$ ($1\frac{mol}{L}$ @25°C) is used as the reference for ions. So, $\Delta_f G°\left(H^+_{(aq)}\right) = 0$.

Gibbs Free Energy and Predicting Spontaneity

- A reaction that we know is spontaneous occurs when potassium metal is added to water. *(Remember the purple sparks?)* What is the free energy change for this reaction under standard conditions?

e.g. $K_{(s)} + H_2O_{(l)} \rightarrow K^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(g)}$ $\Delta_r G° = ???$

$\Delta_f G°(H_2O_{(l)}) = -237.1 \frac{kJ}{mol}$

$\Delta_f G°(K^+_{(aq)}) = -283.3 \frac{kJ}{mol}$

$\Delta_f G°(OH^-_{(aq)}) = -157.2 \frac{kJ}{mol}$

Gibbs Free Energy and Predicting Spontaneity

- A reaction that we know doesn't proceed so easily is the reaction of hydrogen and nitrogen to make ammonia (for which our noses say thanks!). What is the free energy change for this reaction under standard conditions? What are the pressure, heat, and catalyst accomplishing in the Haber-Bosch process?

  e.g.

$$\Delta_f G^\circ(NH_{3(g)}) = -16.45 \frac{kJ}{mol}$$

Gibbs Free Energy and Activity

- To be fair, the Haber-Bosch process isn't performed under standard conditions so that free energy value doesn't apply to it. In fact, many reactions are run under nonstandard conditions.

- To deal with reactions under nonstandard conditions, we need to consider the **activity** ***(a)*** of the substances involved.

- Activity is a measure of a substance's deviation from the standard state:
  - Any substance in the standard state will have $a = 1$. *(Recall that the standard state requires that gases and solutes behave ideally!)*
  - Activity is dimensionless and therefore has no units.

Gibbs Free Energy and Activity

- For ideal substances, activity is relatively straightforward:
  - Pure solids have $a = 1$
  - Ideal gases have $a = P/P^\circ$ where $P^\circ = 1$ bar
  - Ideal solutes have $a = c/c^\circ$ where $c^\circ = 1$ mol/L
  - Ideal solvents have $a = X$ where X is the mole fraction of solvent molecules:

- For nonideal substances, activity must be modified by an activity coefficient (γ):
  - Nonideal solutes have $a = \gamma\ c/c^\circ$ where $c^\circ = 1$ mol/L
  - Activity coefficients are concentration-dependent as they account for such "nonideal" behaviours as intermolecular forces between different particles of solute. Thus, the activity coefficient will tend toward 1 as the concentration of a solute decreases *(since any solute will behave ideally if the concentration is low enough).*

Gibbs Free Energy & Nonstandard Conditions

- To calculate the free energy of a reaction under nonstandard conditions, we need to know the free energy under standard conditions and the amount of deviation from the standard state:

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

where $\Delta_r G_m$ is the molar Gibbs free energy change under the given conditions, R is the ideal gas constant, T is the given temperature (in K) and Q is the reaction quotient:

$$Q = \frac{\text{product of activities of products}}{\text{product of activities of reactants}}$$

- There is a similarity between the formula for reaction quotient (Q) and the formula for equilibrium constant (K). The difference is that the equilibrium constant only describes the system at equilibrium. A reaction quotient can be calculated for any conditions – not just equilibrium!

Gibbs Free Energy & Nonstandard Conditions

- It can be helpful to build an equation map to help you navigate through thermochemistry calculations. Let's start building one using the equations we know so far…

Gibbs Free Energy & Nonstandard Conditions

- Our strategy for solving thermochemistry problems will be:
  1. Make sure we have a balanced chemical equation.
  2. Identify where we are on the equation map. What do we know or can we easily find out?
  3. Identify where we're going on the equation map. What is the question is asking?
  4. Find a path from what we know to what the question is asking.
  5. Follow the path from what we know to what the question is asking.

Gibbs Free Energy & Nonstandard Conditions

- Calculate the molar Gibbs free energy change for the rusting of iron under atmospheric conditions.

$$\Delta_f G°(Fe_2O_{3(s)}) = -742.2 \frac{kJ}{mol}$$

$$P_{O_2} = 0.21 \text{ bar}$$

$$T = 25 °C$$

Gibbs Free Energy & Nonstandard Conditions

Gibbs Free Energy & Nonstandard Conditions

- Calculate the molar Gibbs free energy change for dissolving carbon dioxide in a soft drink under atmospheric conditions.

$$\Delta_f G°(CO_{2(g)}) = -394.4\,\frac{kJ}{mol}$$

$$\Delta_f G°(H_2O_{(l)}) = -237.1\,\frac{kJ}{mol}$$

$$\Delta_f G°(H_2CO_{3(aq)}) = -623.1\,\frac{kJ}{mol}$$

$$P_{CO_2} = 0.038\ \text{bar}$$

$$[H_2CO_3] = 0.1\ \text{M}$$

$$[\text{sugar}] = 0.6\ \text{M}$$

$$[H_2O] = 55.33\ \text{M}$$

$$T = 25\ °\text{C}$$

Gibbs Free Energy & Nonstandard Conditions

The activity of water in the soft drink was not significantly different from 1. Because the solution was relatively dilute, we would have been safe to approximate its activity as a = 1

Gibbs Free Energy & Nonstandard Conditions

- Repeat the calculation for dissolving carbon dioxide in a soft drink with a higher pressure for carbon dioxide (5.0 bar).

$$\Delta_f G°(CO_{2(g)}) = -394.4\,\frac{kJ}{mol}$$

$$\Delta_f G°(H_2O_{(l)}) = -237.1\,\frac{kJ}{mol}$$

$$\Delta_f G°(H_2CO_{3(aq)}) = -623.1\,\frac{kJ}{mol}$$

$P_{CO_2} = 5.0$ bar

$[H_2CO_3] = 0.1$ M

$[\text{sugar}] = 0.6$ M

$[H_2O] = 55.33$ M

$T = 25$ °C

Gibbs Free Energy & Nonstandard Conditions