THERMODYNAMICS

Remember some terms from last time

System

Surroundings

Heat

Work

Joule

Calorie

Energy

Enthalpy

Bond Energy

First Law

Exothermic

Endothermic

State Function

How do we calculate the changes associated with State Functions?

What is Thermodynamics?

Thermodynamics is a funny subject,
the first time you go through the subject you don't understand it at all.
The second time you go through it you think you understand it
except for one or two small points.
The third time through it you know you don't understand it,
but by that time you are so used to it that doesn't bother you any more.

Arnold Sommerfeld

Our Guiding Question:

Spontaneity: (Webster's Ninth New Collegiate)The quality or state of being spontaneous.

A spontaneous process is one that will proceed on its own without further input from the rest of the universe, one that is thermodynamically stable. Spontaneity has nothing to do with time.

Example of temperature dependence:
Consider three identical beakers containing identical amount of water and ice. The only difference is the temperature of each beaker

What happens spontaneously in each of the three beakers?

An ordered state is not generally going to occur spontaneously.
It needs help, namely work!
You must do the work!

Piggy bank analogy.
Disorder increases spontaneity. So we developed a way to measure disorder.

Entropy

When a reaction occurs there is a change in energy, but there are also other properties changing. Entropy is one of these.

Exothermic Reactions are often spontaneous, but not necessarily.
Endothermic Reactions are often non-spontaneous, but not necessarily.

The big S

For a chemical reaction:

$$aA + bB \leftrightarrows cC + dD$$

Consider the following reaction:

$ZnS(s)$ +	$3/2O_2(g)$	$\leftrightarrows$	$ZnO(s)$ +	$SO_2(g)$
13.8	49.0		10.5	59.4

all in calories/mole degree

What is the entropy change for the overall reaction?

Why is the entropy of ZnS bigger then ZnO?

Why is the entropy of ZnS smaller then O_2?

Why is the entropy of SO_2 bigger then O_2?

Why is the overall change negative?

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The Second Law of Thermodynamics

What happens when you try to clean up your room?

General Statement

Clausius Statement

Kelvin Statement

Andrews Statement

How can we put this into an equation?

If an amount of heat is added to a system irreversibly the entropy of the system increases by:

The Statistical View of Nature

Ludwig Boltzman

Walter Nernst

Max Planck

Linus Pauling

How many ways can you put a crystal together?

The Third Law of Thermodynamics

The Zeroth Law of Thermodynamics

Why Zeroth?

Now let's answer our question

Free Energy

Josiah Willard Gibbs

When is a reaction spontaneous?

How do we calculate it? Two considerations:

1) State function 2) From other data

Conditions other then normal. The two delta G's

How does this relate to equilibrium?

What about phase changes?

Enthalpy	**Entropy**	**Free Energy**	**Best Conditions for Spontaneity**

Calculating Thermodynamic Functions from Standard Data Tables

State functions can always be calculated using products minus reactants.
Lets practice from tabulated data: Calculate the enthalpy, entropy, and free energy change for the following reactions from standard data tables.

1. __$Br_2(g)$ + __$I^-(aq)$ ⇆ __$I_2(s)$ + __$Br^-(aq)$

2. __$CH_4(g)$ + __$O_2(g)$ ⇆ __$CO_2(g)$ + __$H_2O(g)$

3. __$NO_2(g)$ ⇆ __$N_2O_4(g)$

4. __$Zn(s)$ + __$HCl(aq)$ ⇆ __$Zn^{2+}(aq)$ + __$H_2(g)$ + __$Cl^-(aq)$

5. __ $Na_2CO_3(s)$ + __$HCl\ (aq)$ ⇆ __$CO_2(g)$ + __$H_2O(g)$ + __$NaCl(s)$

Predicting Thermodynamic Change

With out doing any calculations make the following predictions:

The following reaction is spontaneous:

$CaO(s) + SO_2(g) \leftrightarrows CaSO_4(s)$

What are the signs of:

ΔG ΔS ΔH

The following phase change at 298 Kelvin:

$H_2O(l) \leftrightarrows H_2O(g)$

What are the signs of:

ΔG ΔS ΔH

The following phase change at 298 Kelvin:

$CO_2(s) \leftrightarrows CO_2(g)$

What are the signs of:

ΔG ΔS ΔH

The following reaction is highly endothermic and very spontaneous:
$Ba(OH)_2{\cdot}8H_2O_{(s)} + 2\ NH_4SCN_{(s)} \leftrightarrows Ba^{2+} + 2\ SCN^- + 2\ NH_{3(g)} + 10\ H_2O_{(l)}$

ΔG ΔS ΔH

How can both the enthalpy be what it is and the free energy what it is?

What drives this reaction?

Mathematical Examples

1. Gallium undergoes a solid/solid phase change at 275.6 K for which $\Delta H = 2100.$ J/mol. Calculate ΔS.

2. The heat of formation of gaseous HBr is - 36.40 kJ/mol and the entropy of formation is 57.183 J/K mol. Calculate the free energy change of formation for HBr at 25° Celsius.

3. At what temperature is this reaction spontaneous:

$$Br_2(l) \leftrightarrows Br_2(g)$$

if $\Delta H^o = 31.0$ kJ/mol and if $\Delta S^o = 93.0$ J/K mol.

What is the normal boiling point of Br_2?

4. The equilibrium constant for the dissociation of acetic acid at 298K is 1.75×10^{-5}. Write the equation for the reaction and calculate the free energy change associated with it.

5. Use the following thermochemical equations:

$CH_4(g) + 2O_2(g) \leftrightarrows CO_2(g) + 2H_2O(l)$ $\Delta G^o = -817$ kJ

$CH_3OH(l) + \frac{3}{2} O_2(g) \leftrightarrows CO_2(g) + 2H_2O(l)$ $\Delta G^o = -702$ kJ

To calculate the ΔG° for:

$CH_4(g) + \frac{1}{2} O_2(g) \leftrightarrows CH_3OH(l)$ $\Delta G^o = ?$

6. At 25°C, $\Delta G^o = -95.3$ kJ/mol for the formation of HCl (g).

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \leftrightarrows HCl(g)$$

What is the value of ΔG for the process if the partial pressures of $H_2 = 3.5$ atm, $Cl_2 = 1.5$ atm, and HCl = 0.31 atm?

7. For the reaction:

$$2NO_2(g) \leftrightarrows N_2O_4(g)$$

$\Delta G^o = -4.77$ kJ/mol at 25°C. Calculate K at 25°C for this reaction.

8. Calculate ΔG^o for the reaction that makes one mole of $N_2O_4(g)$ from $NO_2(g)$. Using the following data:

ΔH^o NO_2 = 33.2 kJ/mol

ΔH^o N_2O_4= 9.16 kJ/mol

S^o NO_2 = 239.9 J/K mol

S^o N_2O_4= 304.2 J/K mol

9. The overall reaction for the rusting of iron is:

$$4Fe(s) + 3O_2(g) \leftrightarrows 2Fe_2O_3(s)$$

Calculate the equilibrium constant for this reaction at 25°C using the following thermochemical data:

	ΔH°_f kJ/mol	S^o_f J/K mol
Fe_2O_3 (s)	−826	90
Fe (s)	0	27
O_2(g)	0	205

10. Consider the first ionization of sulfurous acid:

$$H_2SO_{3(aq)} \leftrightarrows H^{+}_{(aq)} + HSO_3^{-}{}_{(aq)}$$

Certain related thermodynamic data are provided below:

	$H_2SO_{3(aq)}$	$H^{+}_{(aq)}$	$HSO_3^{-}{}_{(aq)}$
H_f° kilojoules/mole	–608.8	0	–635.5
S° joules/mole K	234.3	0	108.8

Calculate the value of ΔG° at 25°C for the ionization reaction.

Calculate the value of K at 25°C for the ionization reaction.

Account for the signs of ΔS° and ΔH° when one mole turns into two moles?