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

What is Thermodynamics?

Our Guiding Question:

Spontaneity

The quality or state of being spontaneous (Webster's Ninth New Collegiate Dictionary)

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.

What are the three factors that will determine spontaneity?

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?

Entropy

An ordered state is not generally going to occur spontaneously. You must do work!

Piggy Bank analogy.

Disorder favors spontaneity. So we developed a way to measure disorder.

Absolute Entropy

What is our reference point?

What about a negative number?

For the three states of matter:

Entropy is a State Function!

For a chemical reaction:

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

The Second Law of Thermodynamics

What happens when you try to clean up your room?

General Statement

Clausius Statement

It is impossible to have a natural process whose sole outcome is the transfer of heat from a colder body to a hotter body.

Kelvin Statement

It is impossible to have a natural process whose sole outcome is the transfer of energy, as heat, perfectly to work.

Andrews Statement

The properties of an isolated system eventually quit changing.

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

It is acceptable to define the entropy of a perfect crystal to be zero at absolute zero.

The Zeroth Law of Thermodynamics

If system A is in thermal equilibrium with system B and system B is in thermal equilibrium with system C, than system A is in thermal equilibrium with system C.

Why Zeroth?

Now let's answer our question! Did you remember that we had a guiding question?

Free Energy

Josiah Willard Gibbs

When is a reaction spontaneous?

Free Energy is a state function.

The Gibbs Equation

Conditions other than normal.

Can an equilibrium constant predict spontaneity?

Return of conditions other than normal.

What about phase changes?

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

What favors a chemical reaction being spontaneous?

Do you need to do any work to heat up a Tea Kettle?

Do you need to do any work to let a Tea Kettle cool off?

Do you have to do work to clean your room?

Do you have to do work to let your room get messy?

Who is going to do the work?

The single most important table in all of chemistry.

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

Predicting Thermodynamic Change

With out doing any calculations make the following predictions:

The following phase change at 298 Kelvin:

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

What are the signs of:

ΔG ΔS ΔH

Now consider the reverse reaction at 298 Kelvin:

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

What are the signs of:

ΔG ΔS ΔH

The following phase change at 298 Kelvin:

$H_2O(s) \leftrightarrows H_2O(l)$

What are the signs of:

ΔG ΔS ΔH

Now what if we changed the temperature:

The following phase change at 271 Kelvin:

$H_2O(s) \leftrightarrows H_2O(l)$

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 chemical change at 25°C:

$H_2(g) \leftrightarrows 2H(g)$

ΔG ΔS ΔH

The following chemical change at 25°C:

$2N(g) \leftrightarrows N_2(g)$

ΔG ΔS ΔH

The following reaction is spontaneous:

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

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?

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. Finally check them using the Gibbs equation to see if you get the same answer.

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

Mathematical Examples

R= 8.31 J/mole K = 8.31 x 10^{-3} kJ/mole K = 1.987 calorie/mole K

1) Consider the following reaction:

$ZnS(s)$ +	$^3/_2\, O_2\,(g)$	$\leftrightarrows$	$ZnO(s)$ +	$SO_2(g)$
13.8	49.0		10.5	59.4

all in calories/mole degree formerly called the Entropy Unit (eu)

a) What is the entropy change for the overall reaction?

b) Why is the entropy of ZnS bigger then ZnO?

c) Why is the entropy of ZnS smaller then O_2?

d) Why is the entropy of SO_2 bigger then O_2?

e) Why is the overall entropy change negative?

2) Gallium undergoes a solid/solid phase change at 275.6 K for which ΔH = 2100. J/mol. Calculate ΔS.

3) 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.

4) Explain why the reaction below has such a strange entropy change:

$$H_2S(aq) \leftrightarrows H^+(aq) + HS^-(aq)$$

5) At what temperature is this reaction spontaneous:

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

if $\Delta H° = 31.0$ kJ/mol and if $\Delta S° = 93.0$ J/K mol. What is the normal boiling point of Br_2?

6) The equilibrium constant for the dissociation of acetic acid at 298K is 1.75×10^{-5} Calculate the free energy change associated with it.

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

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

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?

8) For the reaction:

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

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

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

$\Delta H°\ NO_2 = 33.2$ kJ/mol $\Delta H°\ N_2O_4 = 9.16$ kJ/mol

$S°\ NO_2 = 239.9$ J/K mol $S°\ N_2O_4 = 304.2$ J/K mol

10) The overall reaction for the rusting of iron is:

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

	ΔH°_f kJ/mol	ΔG°_f kJ/mol	S^o_f J/K mol
Fe_2O_3 (s)	−826	−743.6	?
Fe (s)	0	0	27
$O_2(g)$	0	0	205

Calculate ΔS°_{rxn} for this reaction.

Calculate the value of $S°_f$ for $Fe_2O_3(s)$