1st Law of Thermodynamics

- Used mainly for bookkeeping
- Does…
  1. Indicate energy flow into or out of the system
  2. Indicate how much energy is involved
- Doesn't indicate why the reaction occurs

Will a reaction be spontaneous?

Spontaneous Processes

- any process that occurs without outside intervention
  - gas fills a container uniformly, never collects at one end of the container
  - wood burns to form CO_2, H_2O and heat, wood doesn't form when CO_2 and H_2O are heated together
- a spontaneous reaction has a **direction**
- a process spontaneous in one direction...
  - is not spontaneous in the opposite direction

More Examples:

- egg is dropped and breaks, spontaneous
  - reverse reaction (egg leaps into hand intact) is not spontaneous
- ball rolls down a hill, but never up
- iron rusts if exposed to air and moisture, but rust doesn't change back to iron metal and oxygen

- Direction of a spontaneous reaction can depend on temperature
- Example:
  - ice changes to water spontaneously at T>0°C
  - water changes to ice spontaneously at T<0°C

Again, how do you know if a reaction is spontaneous or not?

And why in one direction and not the other?

Entropy, S

- reflects the degree of disorder in a system
  - the larger the S, the more disordered
- processes in which disorder increases tend to be spontaneous
  - Ex: melting, vaporizing, dissolving

- In general, S increases as:
  - solid → liquid → gas
  - number of gas particles increases
  - molar mass increases
  - number of atoms in the chemical formula
  - temperature increases
- associated with **probability**
  - more ways for things to be out of place than for them to be in place

- Ex: Which substance has higher entropy?

  solid CO_2 *or* gaseous CO_2
- Ex: Is the entropy increasing or decreasing?

  solid sugar added to water to make a solution

  $I_2(g)$ condenses on a cold surface to form crystals

So…
Is the reaction spontaneous?

2nd Law of Thermodynamics

- in any spontaneous process, the entropy of the universe increases.
  - entropy is *not* conserved

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

$\Delta S_{universe} > 0$, spontaneous

$\Delta S_{universe} < 0$, spontaneous in the opposite direction

OK…
How do you know if the entropy of the universe has increased?

Calculating ΔS for Chemical Reactions

- $\Delta S^\circ_{reaction} = S^\circ_{prod} - S^\circ_{react}$
- S° = standard molar entropy, J/K-mol
- use chart of thermodynamic properties for S° values

Ex: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$\Delta S^\circ = 2(192) - [1(192) + 3(131)]$
$= -201 J/K$

expect negative, because the # gas molecules decreases

Calculating ΔS for the Surroundings

$$\Delta S_{surr} = \frac{-\Delta H}{T}$$

- the sign of ΔS_{surr} depends on the direction of heat flow
  - + for exothermic reactions, - for endothermic reactions
- the magnitude of ΔS_{surr} depends on the temperature
  - greater impact at lower temperatures

- Ex: Calculate the ΔS_{surr} at 298K and 1 atm for the following:
  (Temperature must be in Kelvin… **K = °C + 273**)

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
S° for NH_3 = -46.19 kJ/mol

ΔH =

$\Delta S_{surr} = \frac{-\Delta H}{T} =$

So…is the reaction
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
spontaneous?

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

Remember:
Spontaneity of a process is determined by the entropy change it produces in the universe.

- If ΔS_{system} and ΔS_{surr} are positive, spontaneous
- If ΔS_{system} and ΔS_{surr} are negative, spontaneous in the opposite direction
- If ΔS_{system} and ΔS_{surr} have opposite signs, spontaneity depends on magnitude of each

Gibbs Free Energy, G

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

- $\Delta G < 0$, forward reaction spontaneous
- $\Delta G > 0$, reverse reaction spontaneous
- $\Delta G = 0$, reaction is at equilibrium
- If $\Delta H < 0$ and $\Delta S > 0$ then $\Delta G < 0$ ..... spontaneous
- If $\Delta H > 0$ and $\Delta S < 0$ then $\Delta G > 0$ ..... not spontaneous

- If ΔH and ΔS have the same sign, ΔG depends on…the magnitude of each and the temperature
- if ΔH and ΔS are both negative, spontaneous at low temps
- if ΔH and ΔS are both positive, spontaneous at high temps

- Calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$ for the following reaction:

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ at 25°C 1 atm

Given:	$\Delta H_f°$ (kJ/mol)	$S°$ (J/K mol)
$SO_2(g)$	-297	248
$SO_3(g)$	-396	257
$O_2(g)$	0	205

$\Delta H°$ =

$\Delta S°$ =

$\Delta G°$ =

(verify with $\Delta G_f°$, pg 1019: products – reactants = -140 kJ)

Another way to determine G…

$$\Delta G°_{rxn} = \Delta G°_{f\ prod} - \Delta G°_{f\ react}$$

($\Delta G°_f = 0$ for elements)

Ex: Calculate Gibbs Free Energy:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

-50.8 0 -394.4 -237

Spontaneous?

Ex: At what temperature is the following process spontaneous? $Br_2(l) \rightarrow Br_2(g)$

(i.e. What is the boiling point of bromine?)

$\Delta H = 31.0$ kJ/mol $\Delta S = 93.0$ J/K mol

$\Delta G = \Delta H - T\Delta S$ $0 = \Delta H - T\Delta S$ $\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{31000\ J/mol}{93.0 \frac{J}{K\ mol}} = 333\ K$$

Above 333 K, $T\Delta S > \Delta H$, and ΔG is negative

Above 333 K, this reaction (vaporization) is spont.

Coupled Reactions

- Using one spontaneous reaction to drive another non-spontaneous reaction
- Common in biological systems

- Ex: Metabolism of foods releases energy:
  $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
  $\Delta G° = -2880$ kJ
- This free energy is used to convert:
  ADP and phosphate $\rightarrow$ ATP
  (low energy) (high energy)
- When ATP $\rightarrow$ ADP, the energy released is used to drive other reactions

Whether or not a reaction is ***spontaneous***
says nothing about how ***fast*** a reaction will occur.

We need both ***thermodynamics*** and ***kinetics***
to describe a reaction fully.