N5 - THERMODYNAMICS

Spontaneity

Link to YouTube Presentation: https://youtu.be/M__SVaI0jhI

N5 - THERMODYNAMICS

Spontaneity

Target: I can explain what makes a reaction spontaneous, and can predict if a reaction is driven by enthalpy and/or entropy.

Spontaneous Processes

Spontaneous: When a process occurs without outside intervention.

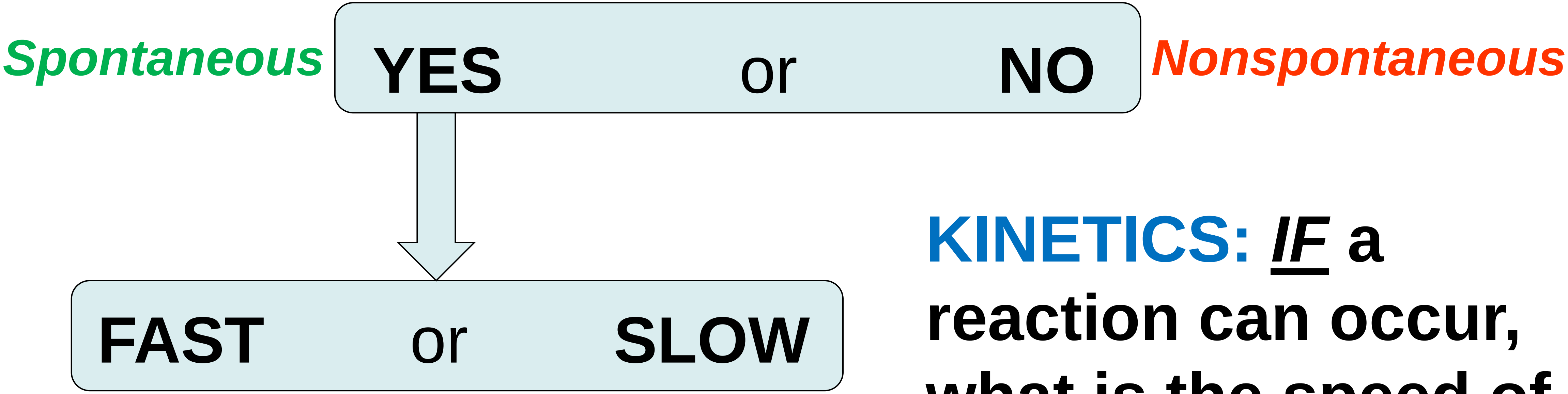
Can be fast or slow

- Just because it *can* happen, doesn't mean it will be fast! It could be very very slow!
- Most combustion is fast.
- Converting diamond into graphite is very slow.

Thermodynamics vs. Kinetics

THERMODYNAMICS:

Will the reaction happen under these conditions?



Spontaneous **YES** or **NO** *Nonspontaneous*

FAST or **SLOW**

KINETICS: ***IF*** **a reaction can occur, what is the speed of the reaction?**

What determines spontaneity?

Less chemical potential energy after the reaction means the reaction is **thermodynamically favorable**

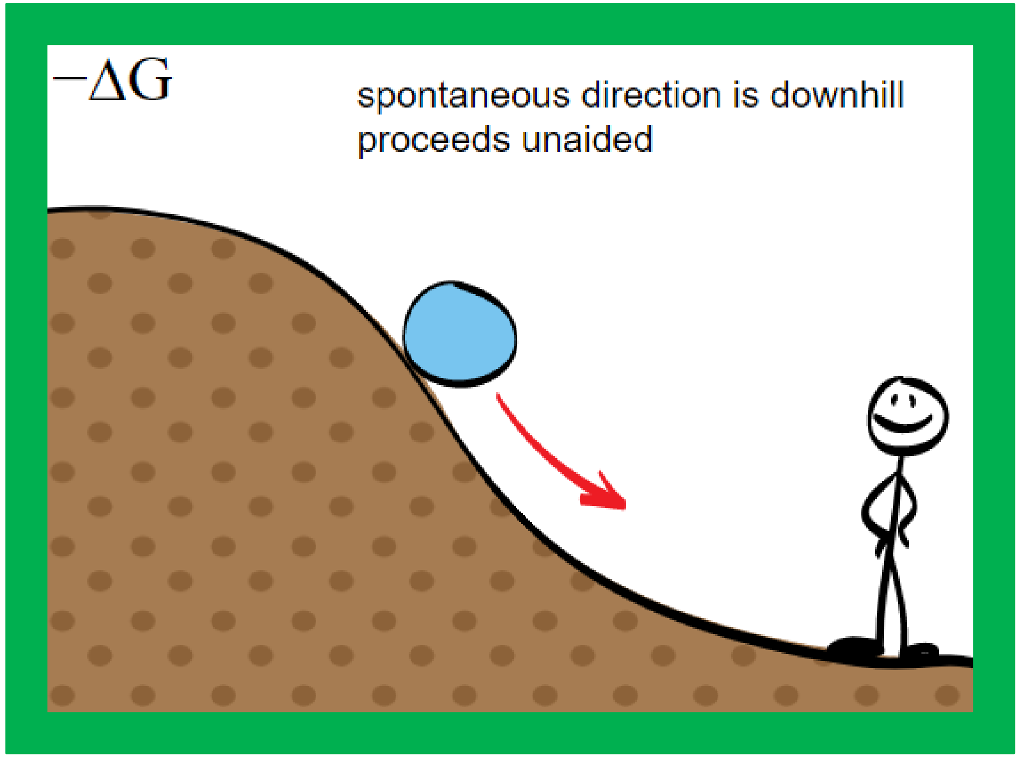
Determined by comparing the chemical potential energy of the system before and after the reaction. This difference in energy is called:

Gibbs Free Energy (ΔG)

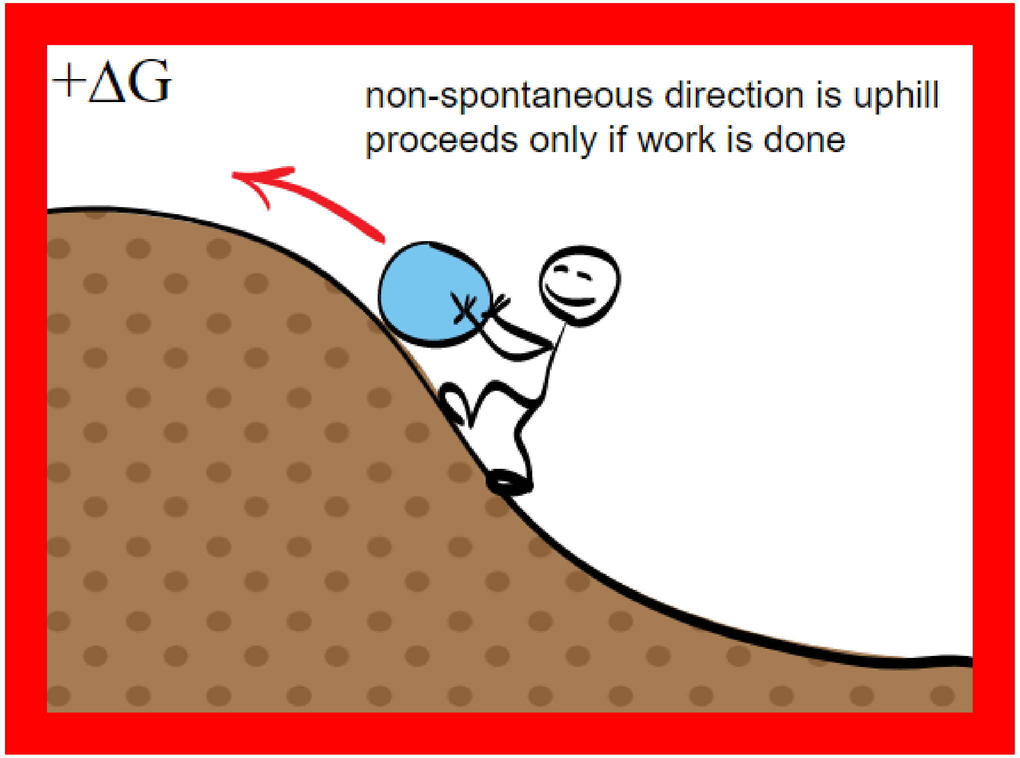
What determines spontaneity?

$\Delta G°$ = negative = spontaneous

$\Delta G°$ = positive = non-spontaneous


$-\Delta G$

spontaneous direction is downhill
proceeds unaided


$+\Delta G$

non-spontaneous direction is uphill
proceeds only if work is done

Spontaneity Based on $\Delta G°$

$\Delta G° > 0$, positive → non-spontaneous,
NOT "thermodynamically favorable"

$\Delta G° < 0$, negative → spontaneous
YES "thermodynamically favorable"

Remember!

Spontaneity ≠ Fast or Slow

Thermodynamics Kinetics

NOTE **-** Sometimes a reaction may be spontaneous, but you cannot see it happening at any “observable rate” – that might be due to having a huge activation energy! It might be very hard to get over the activation barrier even though it is technically spontaneous. We call this **“being under kinetic control.”**

What Factors into ∆G° ?

There are two factors that determine whether a reaction is spontaneous.

Enthalpy change , ∆H°
Entropy change , ∆S°

Enthalpy Contribution

Enthalpy change, ΔH

You already know this one!

Difference in total heat content of a system.

(The difference in the sum of the internal energy and pressure/volume work energy of the reactants to the products.)

****Important****

ΔH usually in **kJ**/mol

Enthalpy Considerations

Spontaneous processes occur because they release energy from the system.

So which would be more favorable for spontaneity?

Endothermic or Exothermic?

EXOTHERMIC! A release of energy to the system!

Favorability of Enthalpy Change

Enthalpy change is favorable for exothermic rxns and unfavorable for endothermic rxns

Enthalpy Considerations

Most spontaneous processes are:

Exothermic

But there *are* some spontaneous processes that are:

Endothermic

THINK…How can something absorb heat energy, yet have a net release of Gibbs Free Energy?!

Because there are other things to consider!

You can’t just consider enthalpy!

You must also consider **ENTROPY!**

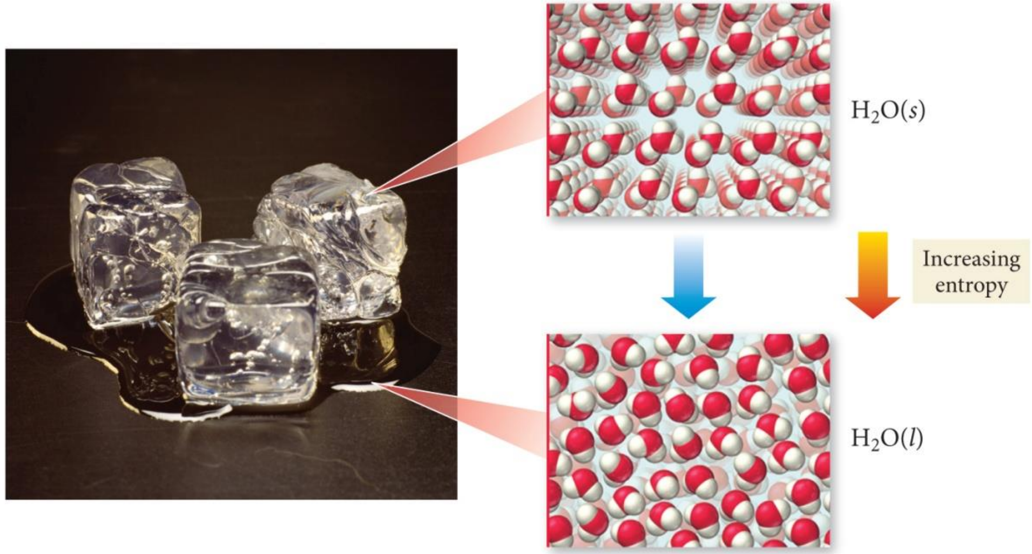
Most people think of entropy as the amount of “randomness” in the system. **Bad definition...**

“The number of microstate arrangements” or the degree of “energy dispersal” is a better phrase than “amount of randomness.”

Think About Melting Ice…

Melting is an endothermic process, yet ice *will* spontaneously melt above 0 °C.

Even though it is endothermic which lends itself towards non-spontaneous, the **increase in *ENTROPY* overcomes this problem**, causing the reaction to end up spontaneous!



Entropy of Ice Melting...

When a solid melts, the particles spread apart and have more freedom of movement.

More freedom of motion increases the number of ways the particles can be arranged, and how spread out all the energy is.

So liquid water has more entropy than solid ice does. It has **“more microstate arrangements.”**

Entropy Contribution

Entropy change, ΔS

Difference in the number of possible "microstate arrangements" of the reactants compared to the products. More "disorder" means there are more ways to arrange the particles – more microstate arrangements, more energy dispersal.

****Important****

ΔS usually in J/K

Entropy Contribution

Remember permutations in math class? The number of unique combinations you could make out of things like flipping coins? Similar idea!

Now think about an ice cube versus gas particles – those gas particles will be able to arrange themselves in WAY more combinations in 3-dimensional space than the solid particles could in their little cube.

Algebraic Sign on Entropy

Positive (+) ΔS

Increase in the “microstate arrangements”

Negative (-) ΔS

Decrease in the “microstate arrangements”

Favorability of Entropy Change

Entropy change is favorable for increase in entropy and unfavorable for decrease in entropy

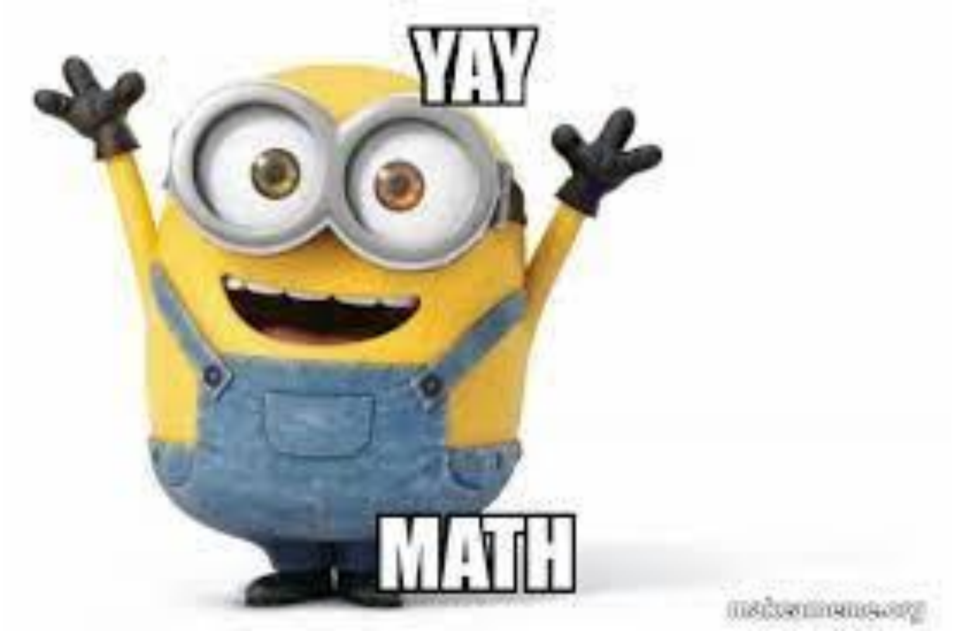
What "Drives" the Reaction?

What is Driving the Spontaneity?		
Enthalpy driven	Enthalpy change overcomes decrease in entropy	$\Delta H^\circ = -$
Entropy driven	Entropy change overcomes endothermic enthalpy	$\Delta S^\circ = +$
Both	Enthalpy and entropy both favorable	$\Delta H^\circ = -$ AND $\Delta S^\circ = +$
Neither	Never spontaneous b/c enthalpy and entropy are both unfavorable.	$\Delta H^\circ = +$ AND $\Delta S^\circ = -$

Summary Chart

Favorable		
Enthalpy	Entropy	Gibbs Free Energy
$\Delta H^\circ = -$ Exothermic	$\Delta S^\circ = +$ Increase in entropy	$\Delta G^\circ = -$ Spontaneous Thermodynamically Favorable
NOT Favorable		
Enthalpy	Entropy	Gibbs Free Energy
$\Delta H^\circ = +$ Endothermic	$\Delta S^\circ = -$ Decrease in entropy	$\Delta G^\circ = +$ Non-spontaneous NOT thermodynamically Favorable

Yes…there will be math…yay!



Calculating ΔG°

$$\Delta G^0 = \sum n_p \Delta G^0_{f\,(\text{products})} - \sum n_r \Delta G^0_{f\,(\text{reactants})}$$

Just like you have done with ΔH°
Have to have the ΔG° values for products and reactants to do it this way.

Gibbs-Helmholtz Equation

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

BE CAREFUL WITH YOUR UNITS!
Look out for J vs kJ

One Last Tidbit - Reversibility

Doesn’t mean the same thing in chemistry as in day-to-day life.

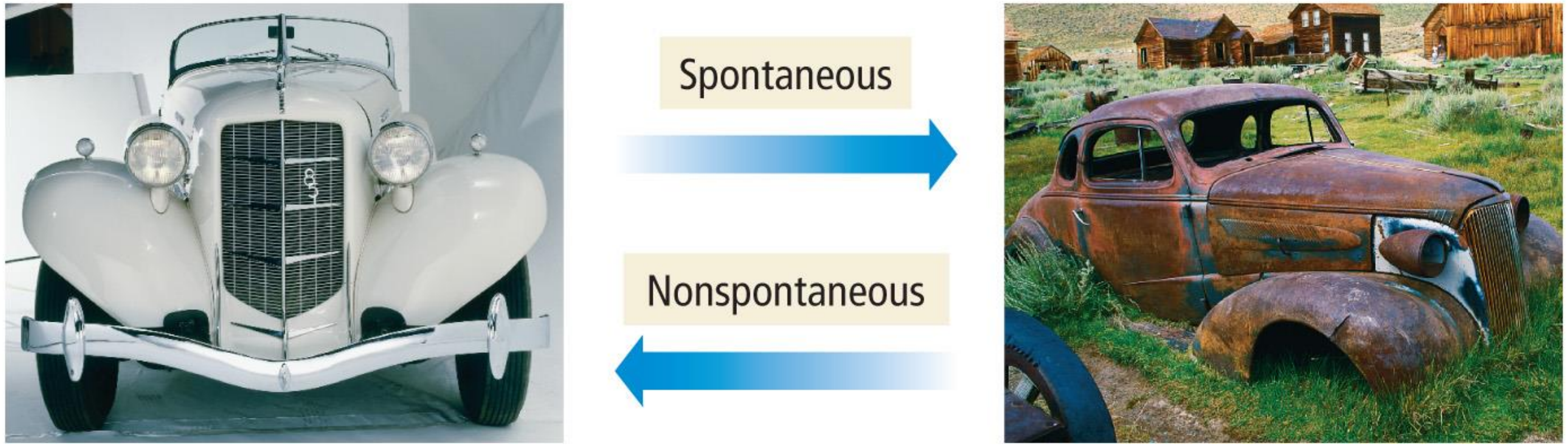
ALL spontaneous rxns = IRREVERSIBLE

Can’t go backwards *without outside intervention*.

Because there is a net release of energy when it proceeds in the forward direction!

Reversibility

If a process is spontaneous in one direction, it MUST be non-spontaneous in the opposite direction.



Reversibility – not what you think it is...

A REVERSIBLE process will proceed back and forth between the two end conditions.

Any reversible process is at equilibrium!

This results in no change in free energy ($\Delta G=0$).

YouTube Link to Presentation

https://youtu.be/M__SVaI0jhI