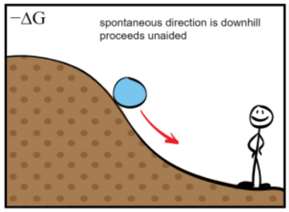
N5 – Spontaneity

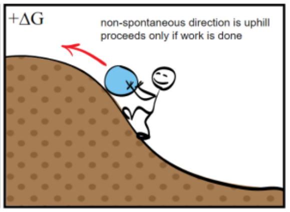
THERMODYNAMICS:
Will the reaction happen under these conditions?

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

FAST or **SLOW**

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





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

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

N6 – Entropy

Key Concepts About Entropy
#1 - a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components increases, S.
#2 – Random systems have more energy dispersal and are more energetically stable, lower energy, than ordered systems
#3 – Increase in entropy of the universe is the driving force for spontaneous reactions.
#4 – Nature proceeds toward the states that have the highest probabilities of existing.

Practice Problem:

For the Rx: $\mathbf{2NO(g) + O_2(g) \rightarrow 2NO_2(g)}$

$\Delta S°_{rxn} = -146.5$ J/mol•K

Calculate the standard molar entropy of $O_2(g)$.

$\Delta S°_{NO(g)} = 210.8$ J/mol•K , $\Delta S°_{NO2(g)} = 240.1$ J/mol•K

Some Changes that Increase Entropy
#1 - Products are in a more dispersed arrangement.
#2 - Larger numbers of product molecules than reactant molecules.
#3 - Rxn’s that have an increase in temperature (exothermic).
#4 – Products that have more degrees of movement.
#5 – Products that have more molecular complexity.

N7 – Gibbs Free Energy

Gibbs free energy, *G* - the maximum amount of work energy that can be released to the surroundings by a system for a constant temp and pressure system.

Gibbs free energy is often called the **chemical potential** because it is similar to the storing of energy in a mechanical system.

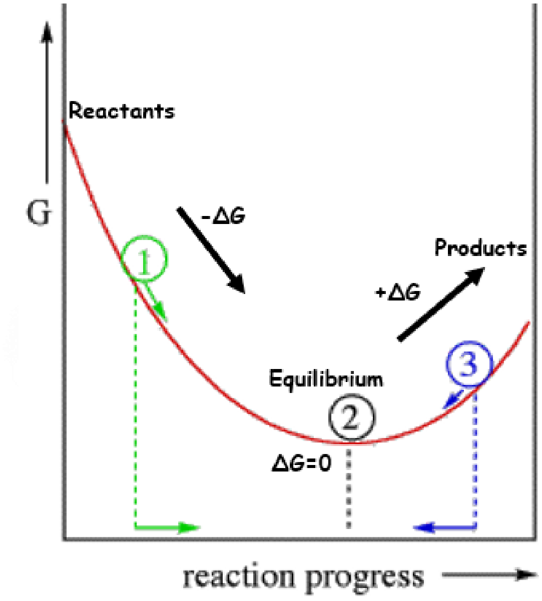
Gibbs Mental Math

$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$

ΔH	ΔS	ΔG	At…
− *exothermic*	+ *more disorder*	− *ALWAYS spont.*	Any temp
+ *endothermic*	− *less disorder*	+ *NEVER spont.*	Any temp
− *exothermic*	− *less disorder*	− *spont.*	Low Temp
− *exothermic*	− *less disorder*	+ *NOT spont.*	High Temp
+ *endothermic*	+ *more disorder*	− *spont.*	High Temp
+ *endothermic*	+ *more disorder*	+ *NOT spont.*	Low Temp

N7 – Gibbs Free Energy – Continued…

	ΔH<0	ΔH>0
ΔS>0	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
ΔS<0	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)



ΔG	K vs Q	
ΔG = 0	K = Q	@ equilibrium
ΔG < 0	K > Q	Shift right
ΔG > 0	K < Q	Shift left

N7 – Gibbs Free Energy – Continued…again…

A Variety of Helpful Equations

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S_{surr} = -\Delta H_{sys} / T$$

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

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

$$\Delta G° = -RT\ln(K)$$
$$\text{where } R = 8.314 J/mol \bullet K$$

$$\Delta G = \Delta G° + RT\ln(Q)$$

$$-RT\ln(K) = \Delta H° - T\Delta S°$$

$$\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

$$= -\frac{\Delta H^0}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^0}{R}$$

$$\begin{array}{ccccccc} \downarrow & & \downarrow & & \downarrow & & \downarrow \\ y & = & m & & x & + & b \end{array}$$

1st - Graph ln(K) vs $\left(\frac{1}{T}\right)$
2nd - Find line of best fit (Excel or graphing calculator)
3rd - Slope = $-\frac{\Delta H°}{R}$ Intercept = $\frac{\Delta S°}{R}$

N7 – Gibbs Free Energy – still…sorry…not sorry ☺

Practice Problems

#1 - For the following Rx:
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
Calculate the standard Free Energy, ΔG° for the rxn at 25°C.
ΔH°= -264kJ/mol ΔS°= -278 J/mol•K

#2 - Calculate the Boiling Point of BCl_3.
$BCl_{3(l)} \leftrightarrow BCl_{3(g)}$. Given:

	H_f kJ/mol	S J/mol k
BCl_3 (*l*)	-418	209
BCl_3 (g)	-395	290

#3 - Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, what substance(s) will be formed?
(ΔG° = 33.4 kJ)
$2\,NH_3(g) \rightarrow N_2(g) + 3\,H_2(g)$

#4 - Calculate the equilibrium constant for this reaction at 298 K.
$2\,NH_3(g) \rightarrow N_2(g) + 3\,H_2(g)$ (ΔG° = 33.4 kJ)