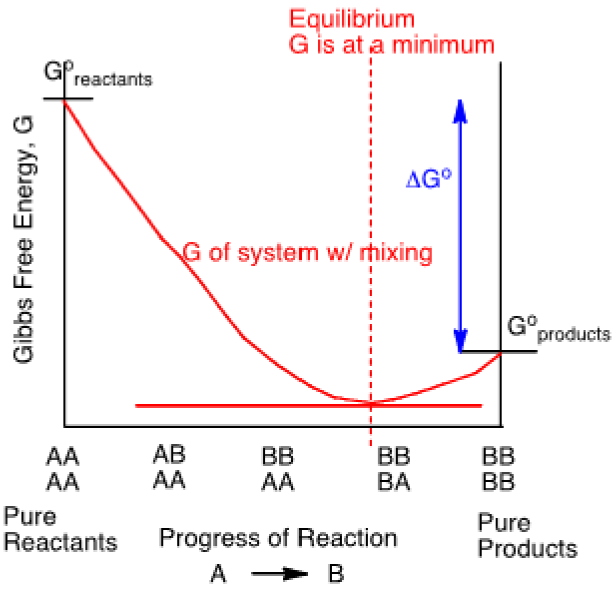
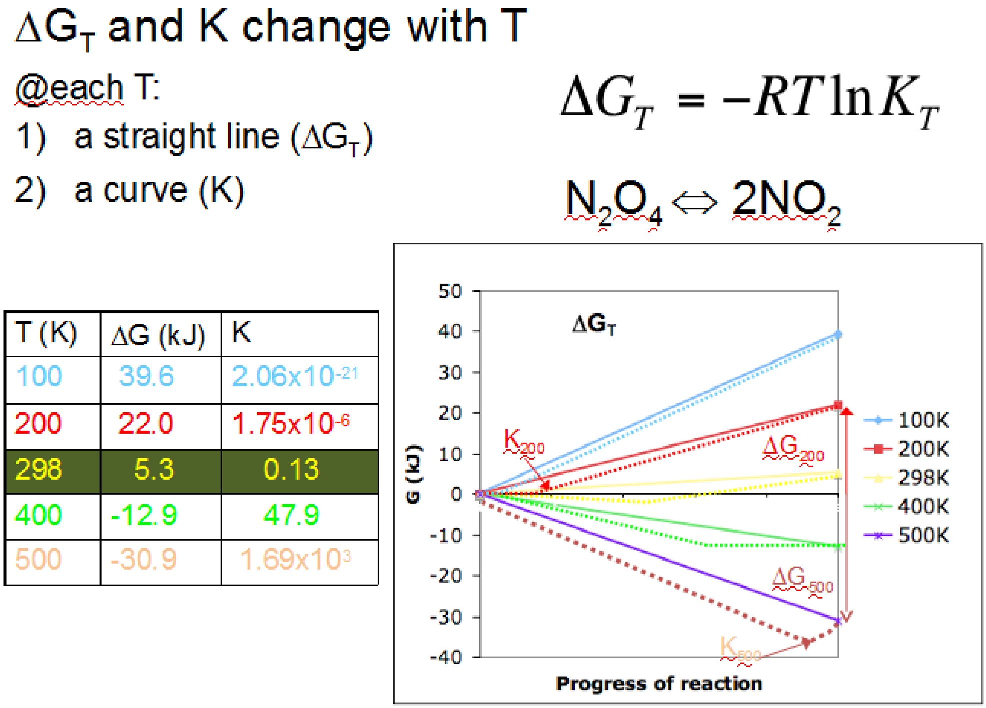
- Mixing
  - Entropy increases with mixing.
  - Mixing results in a lowering of G. The system will spontaneously act to minimize G. The very minimum G is **equilibrium**.

Gibbs free energy as the reaction takes place if mixing is considered.



- Gibbs free energy and product to reactant ratios
  - A reaction with $\Delta G^{\circ} < 0$ does not go to completion but makes more products than reactants; the more negative ΔG°, the more products that are made.
  - A reaction with $\Delta G^{\circ} > 0$ will form some product; the more positive ΔG°, the smaller the quantity of products made. More reactants are left over than product made.
- Law of mass action
  - **The law of mass action** states that at equilibrium (the minimum Gibbs free energy of a reaction), the composition of the reaction mixture can be expressed in terms of an equilibrium constant (K).
  - Given the equation: $a\,A_{(g)} + b\,B_{(g)} \Leftrightarrow c\,C_{(g)} + d\,D_{(g)}$
    - The equilibrium constant $K = \dfrac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$ where "a" is an activity.
    - **Activities** are unitless. They account for deviations from ideality and for intermolecular forces.
    - A simplified form can be used for ideal gases and for solutes in dilute solutions.
      - For ideal gases, activity = pressure in atm. The equilibrium constant for gases is called $\mathbf{K_p}$.
      - For solutes in dilute solutions, activity = concentration in molarity. The equilibrium constant for solutes in solutions is called $\mathbf{K_c}$.
    - Solids and pure liquids are never factored into these calculations. Only take gases or aqueous solutes into account.

- Gibbs free energy and equilibrium
  - Gibbs free energy and the equilibrium constant relates as follows: $\Delta G = -RT \ln K_{298K}$ where R = 8.314 $\frac{J}{mol * K}$ and T = 298 K.
  - Note that it is K_{eq} at 298K and not K_c or K_p.
  - This equation tells us, the more negative ΔG is, the greater the value of K is and the more positive ΔG is, the smaller the value of K is.
  - ΔG varies with temperature in a linear fashion. Keq varies with temperature in a curve fashion.



ΔG_T and K change with T

@each T:

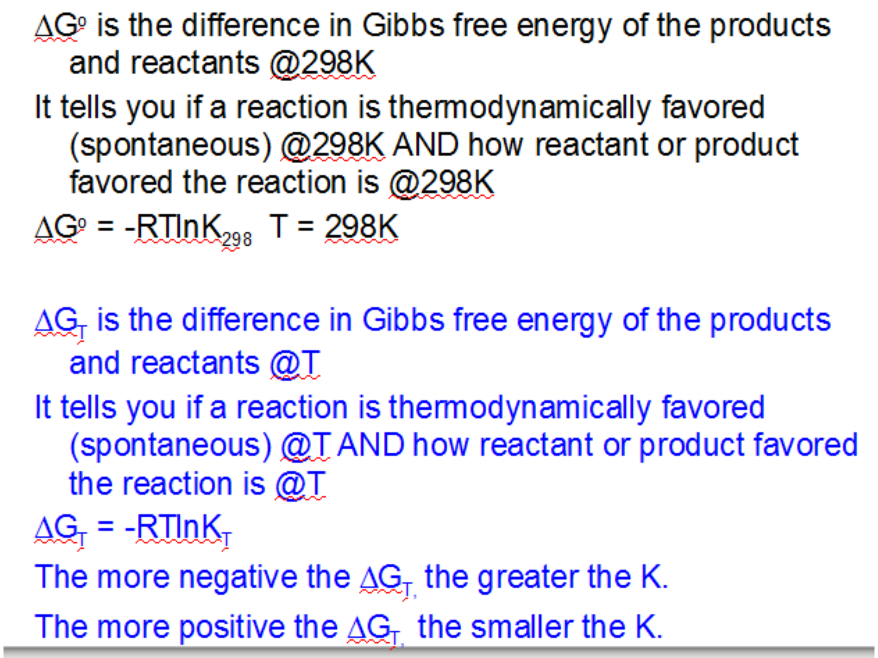
1) a straight line (ΔG_T)
2) a curve (K)

$$\Delta G_T = -RT \ln K_T$$

$N_2O_4 \Leftrightarrow 2NO_2$

T (K)	ΔG (kJ)	K
100	39.6	2.06×10^{-21}
200	22.0	1.75×10^{-6}
298	5.3	0.13
400	-12.9	47.9
500	-30.9	1.69×10^{3}

- K and temperature
  - The equilibrium constant (K) is constant at constant temperature.
  - Varying temperature is the only way to change K for a given reaction!
- Great summary slide regarding Gibbs and Equilibrium:



ΔG^o is the difference in Gibbs free energy of the products and reactants @298K

It tells you if a reaction is thermodynamically favored (spontaneous) @298K AND how reactant or product favored the reaction is @298K

$\Delta G^o = -RT\ln K_{298}$ T = 298K

ΔG_T is the difference in Gibbs free energy of the products and reactants @T

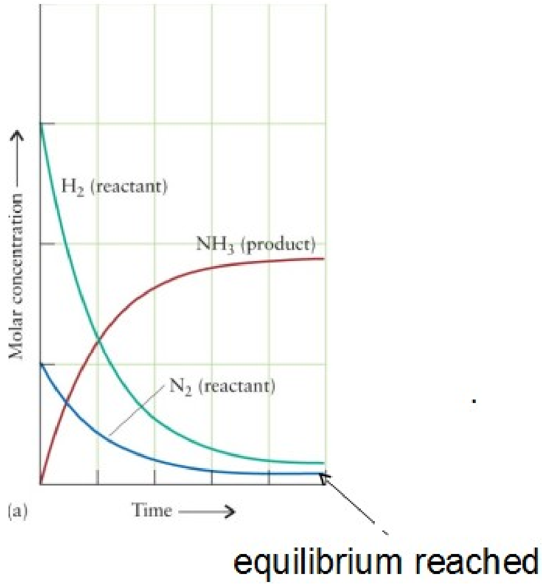
It tells you if a reaction is thermodynamically favored (spontaneous) @T AND how reactant or product favored the reaction is @T

$\Delta G_T = -RT\ln K_T$

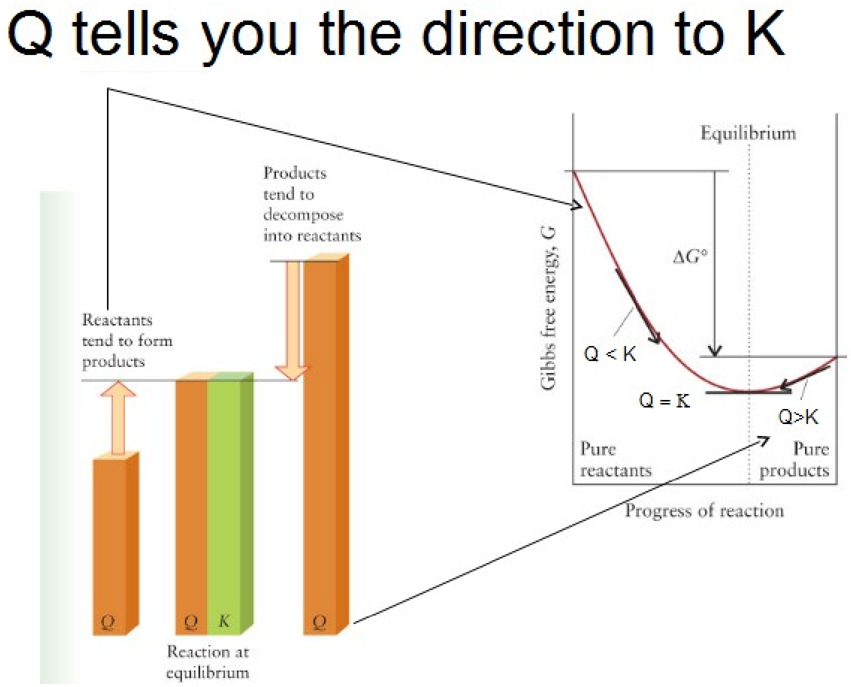
The more negative the ΔG_T, the greater the K.

The more positive the ΔG_T, the smaller the K.

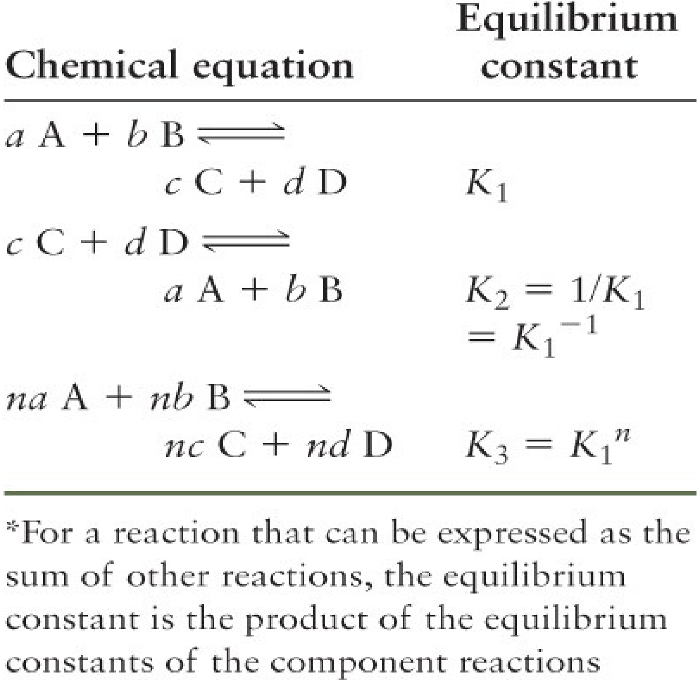
- Meaning of equilibrium
    - When equilibrium is reached, the rates of the forward and reverse reactions are equal (not necessarily zero).
        - This means that the concentrations of the products and reactants stay constant. This does NOT necessarily mean [reactants] = [products] at equilibrium.
        - K tells you the ratio of products to reactants!



- Reaction Quotient (Q)
    - **The reaction quotient**, Q, is the law of mass action applied to a reaction at some given point in time. This means that Q may or may not be equal to K as you may be finding Q when the reaction is not yet at equilibrium.
    - If Q = K, then the system is at equilibrium.
    - If Q > K, there are too many products and the reverse reaction will be **favored** (meaning that it is spontaneous) whereas the forward reaction **will not be favored** (meaning that it is nonspontaneous). ΔG < 0 for reverse reaction, and ΔG > 0 for forward reaction.
    - If Q < K, there are not enough products and the forward reaction will be favored whereas the reverse reaction will not be favored. ΔG < 0 for forward reaction, and ΔG > 0 for reverse reaction.


Q tells you the direction to K

- Gibbs to equilibrium
    - **Gibbs to equilibrium** (ΔG_{toeq}) is the difference in Gibbs energy between where the reaction is and gibbs at equilibrium (the minimum gibbs of the system).
    - $\Delta G_{toeq} = -RTln(\frac{Q}{K})$
        - R = 8.314 $\frac{J}{mol*K}$
        - $\Delta G_{toeq} > 0$ is same as Q > K.
        - $\Delta G_{toeq} < 0$ is same as Q < K.
        - $\Delta G_{toeq} = 0$ is at equilibrium.
- Hess's law and Keq
    - Hess's law also applies to K_{eq}, but the ***rules are different***:
        - When you reverse an equation, you invert its equilibrium constant.
        - When you multiply an equation by a coefficient, raise the K value to the power of the coefficient.
        - When you combine equations, multiply the equilibrium constants.

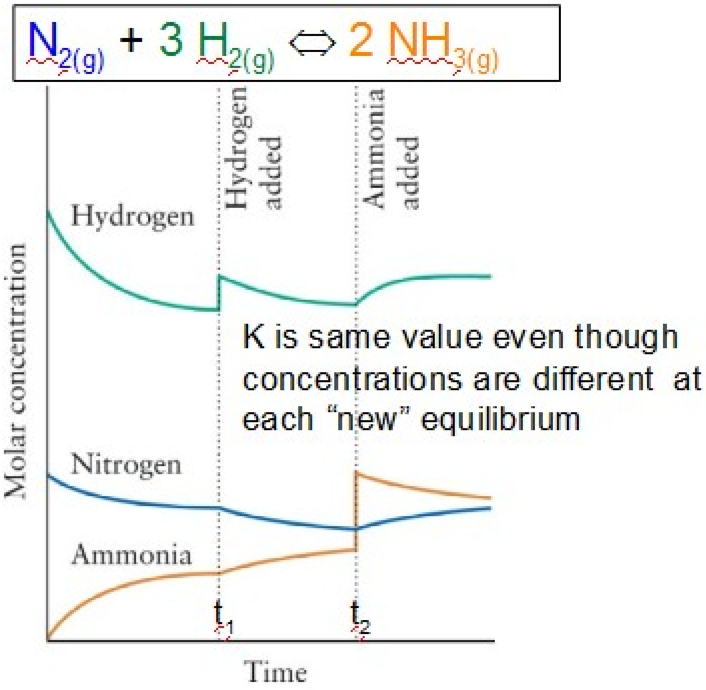


Chemical equation	Equilibrium constant
$a\,A + b\,B \rightleftharpoons c\,C + d\,D$	K_1
$c\,C + d\,D \rightleftharpoons a\,A + b\,B$	$K_2 = 1/K_1 = K_1^{-1}$
$na\,A + nb\,B \rightleftharpoons nc\,C + nd\,D$	$K_3 = K_1^{n}$

*For a reaction that can be expressed as the sum of other reactions, the equilibrium constant is the product of the equilibrium constants of the component reactions

- Le Chatelier's principles
    - NOTE: only by changing temperature you can change the value of K_{eq}.
    - Temperature and K:
        - Endothermic reaction ($\Delta H > 0$): “add heat to reactants”
            - Temperature <u>increase</u> favors products.
            - Temperature <u>decrease</u> favors products.
        - Exothermic reaction ($\Delta H < 0$): “add heat to products”
            - Temperature increase favors reactants.
            - Temperature decrease favors products
        - Enthaltipically neutral reaction (($\Delta H = 0$), temperature has no effect.
        - Quantitative changes in K with T: $\ln\frac{K_2}{K_1} = \frac{\Delta H^o_{rxn}}{R}(\frac{1}{T_1} - \frac{1}{T_2})$

    - R = 8.314 $\frac{J}{mol*K}$ and Temperatures in kelvin.
- Adding/removing reactant or product to the system:
  - Remove reactant or product = shift in the direction of the removed reactant/product.
  - Add reactant or product = shift in opposite direction of the added reactant/product.
  - Adding/taking away solids or pure liquids have no effect on shift unless its H_2O or completely removed.



- Change in volume/pressure
  - Increase in pressure, decrease in volume; side with the fewer moles of gas is favored to minimize pressure increase.
  - Decrease in pressure, increase in volume; side with more moles of gas is favored to minimize pressure decrease.
  - For aqueous ions, H_2O is like volume!!!!!
- Inert gases
  - Inert gases only affects the reaction if it causes change in the volume meaning the reaction must be in a flexible container.
- Adding a catalyst changes how reacts form products (the rate) but does not effect K!
- ICE boxes
  - An **ICE** (**I**nitial, **C**hange, **E**quilibrium) **table** is simple matrix formalism that used to simplify the calculations in reversible equilibrium reactions (e.g., weak acids and weak bases or complex ion formation).
  - ICE is an acronym for the titles of the first column of the table:
    - **I** stands for initial concentration. This row contains the initial concentrations of products and reactants.
    - **C** stands for the change in concentration. This is the concentration change required for the reaction to reach equilibrium. It is the difference between the equilibrium and initial rows. The concentrations in this row are, unlike the other rows, expressed with either an appropriate positive (+) or negative (-) sign and a variable; this is because this row

    - represents an increase or decrease (or no change) in concentration.
    - **E** is for the concentration when the reaction is at equilibrium. This is the summation of the initial and change rows. Once this row is completed, its contents can be plugged into the equilibrium constant equation to solve for K_c.
- Use this link to learn how to solve ice problems (<u>learn how to do each type of problem</u>): http://www.chem.purdue.edu/gchelp/howtosolveit/Equilibrium/ICEchart.htm