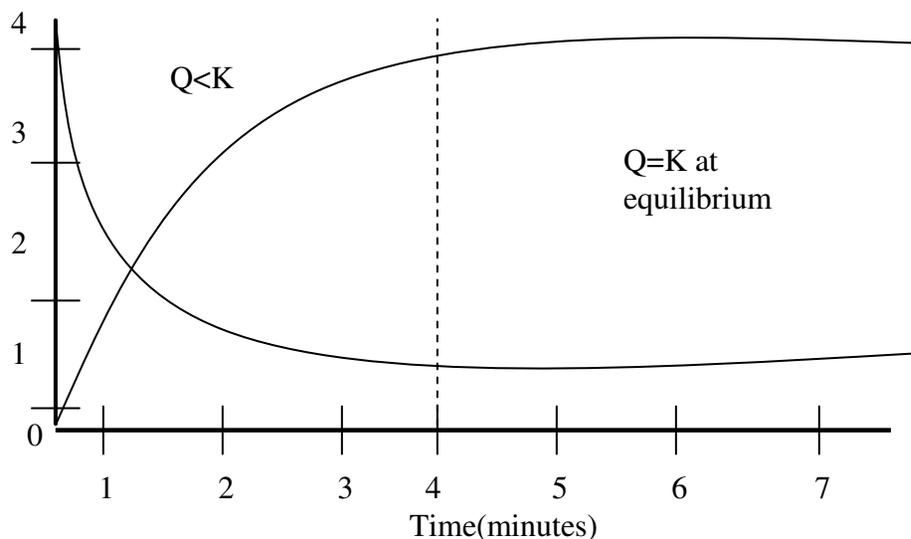


Lecture 7: Chemical Equilibria--a bit more detail and some additional kinds of problems.

Lecture Overview: We get even more involved in the details by equilibria by

- relating ΔG to K
- relating K_c to K_p
- comparing Q to K to figure out the direction of a reaction
- developing LeChatelier's principle to explain system stress

But first, a reminder of how to calculate Q and K from data. Why do I seem to start every lecture this way? Because it is the essence of how you should view chemical equilibria. What is the ratio of materials in a system and at what point do their rates stop changing so that $Q = K$.



Calculate Q at:

Note that $Q=K$ during this interval

Time 0 minutes

$$Q = \frac{B}{A} = \frac{0}{4} = 0$$

Time 2 minutes

$$Q = \frac{B}{A} = \frac{2}{2} = 1$$

Time 4 minutes

$$Q = \frac{B}{A} = \frac{3}{1} = 3 = K$$

Time 6 minutes

$$Q = \frac{B}{A} = \frac{3}{1} = 3 = K$$

Time out for a few interesting thoughts on K

Interesting thought 1. Solids and pure liquids are not included in equilibrium expression calculations

When you construct an equilibrium expression from the chemical reaction, you put the materials on the right in the numerator and the materials on the left on the denominator.



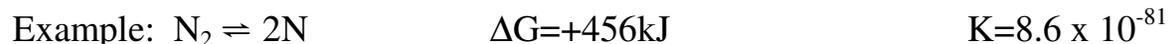
But these values are concentrations, and while the concentration of a gas can change (with pressure) and the concentration of a solute in a solvent can change, what about the concentration of pure liquids and solids? They don't change—they are constant which means there is no reason to include these constant values in the equilibrium expression.

So as a rule, for all solids and pure liquids, assume $[] = 1$. Here with $[\text{H}_2\text{O}]$, which has a constant concentration of 55.4 M (do the calculation yourself), we set $[\text{H}_2\text{O}] = 1$ and the equilibrium expression for water dissociation is actually



Interesting thought 2. K can have very large and very small values—get used to using the exponent button on your calculator

Although I emphasized the point that reactions never go to completion and that there are always both product and reactant in a closed system at equilibrium, this doesn't mean that there aren't a lot of reactions that go nearly to completion and produce very large equilibrium constants. Consider the reaction for the dissociation of diatomic nitrogen to make atomic nitrogen:



or the solubility product for silver sulfide



What about reactions that produce really large values of K, are there any of those? Sure, what about the reverse of these reactions:



Interesting thought 3: In the RICE calculation, how do you know which signs to put in the Δ row of the array

Consider the RICE expression. When you are doing calculations, either the stuff on the left is getting smaller and the stuff on the right is getting larger

$$3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$$

-	-	+

Or the stuff on the right is getting smaller and the stuff on the left is getting larger:

$$3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$$

+	+	-

In other words, the reaction is either shifting to the right ($Q < K$) or the reaction is shifting left ($Q > K$)

You always have to make this determination when working a problem or your calculation will be incorrect.

Examples:

Example 1: Start with all stuff on the left and none on the right, so clearly $Q < K$ and the reaction shifts right with the signs as below:

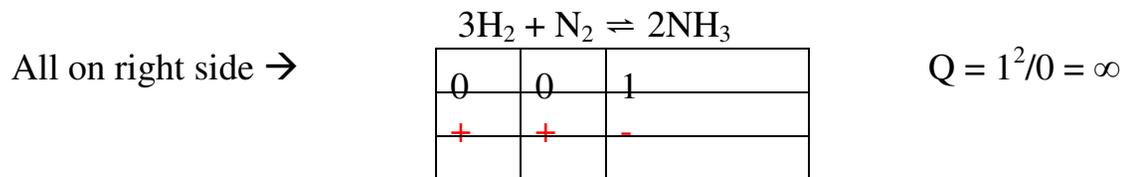
All on left side $\rightarrow Q =$

$$3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$$

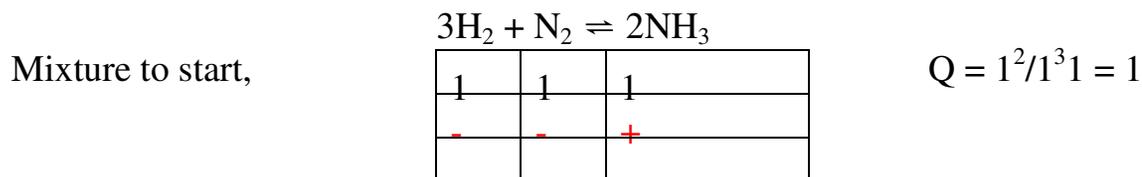
1	1	0
-	-	+

$$0^2/(1)^3(1)^2 = 0$$

Example 2: Start with all stuff on the right and none on the left, so clearly $Q > K$ and the reaction shifts left with the signs as below:



Example 3: Here you have some of everything to start so you have to do a Q vs K calculation. In this case, $Q = 1$ which is less than $K = 3/8$ so the reaction shifts right with the signs as below:



Time in.

Calculating K from ΔG° (a problem on quiz). As we have seen, equilibria is just another way of expressing thermodynamics concepts about the extent of a reaction and there is a simple mathematical relationship between ΔG and K that requires a simple plug and chug effort. By the way, this means that for every free energy in the tables in the back of the text book, you can instantly determine an equilibrium constant values for the reaction.

$$\Delta G^\circ = -RT \ln K$$

Example: At 298K for the reaction for the formation reaction: $2\text{C} + 3\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH}$

If $\Delta G^\circ = -168.6 \text{ kJ/mole}$, what is K ? First, stick the values in, second, rearrange for K and third, fix the units

Step 1: $-168.6 \text{ kJ} = (-8.3 \text{ J}) (298) \ln K$

Step 2: $\Delta G^\circ = -RT \ln K \quad \rightarrow \quad \left(\frac{\Delta G^\circ}{-RT}\right) = \ln K$
 $\exp\left(\frac{-\Delta G^\circ}{RT}\right) = K \quad \leftarrow \quad \exp\left(\frac{\Delta G^\circ}{-RT}\right) = \exp(\ln K)$ (multiple through by e^x)

Step 3: Now inserting values and changing kJ to J

$$K = \exp\left(\frac{-168.6 \times 10^3}{-(8.3)(298)}\right) = 3.5 \times 10^{29}$$

Note that as expected, a reaction with a high negative free energy will produce a very large positive exponent for K.

Another Time Out.

Know your exponent math!!!

1) You will see exp, ln, log, and 10^x functions a lot in CH302. You must be able to effortlessly move between values inside functions using inverse function concepts.

$$\begin{aligned} \ln(\exp x) &= x \\ \log(10^x) &= x \end{aligned}$$

$$\begin{aligned} \exp(\ln x) &= x \\ 10^{(\log x)} &= x \end{aligned}$$

(note we just used this trick in the ΔG to K problem above when we multiplied through by exp x)

2) You need to remember the simple math involving exponents and be able to do it in your head—remember the joke about how snakes do it by logs because they are adders? Well even if it isn't funny, you still need to be able to add exponents when working problems. For example, in the problem below, note that we add -5 and -1 to get -6 for the multiplication of the two exponents, and then we perform a square root by dividing by two to get -3 which is the power of the answer to the calculation below.

$$\text{Example} \quad x = [(10^{-5}) (.1)]^{1/2} = 10^{-3}$$

This is something you should be something you can do **without** a calculator, or you have no chance of working tests in the allotted time in this class.

Time in.

Converting between K_p and K_c : How you can report K values for both gases in both pressures and concentrations.

Note that gases often are described in atmospheres rather than molarity. How do we get from a K in molarity units to K in atmospheres? First a quick rearrangement of the ideal gas law to see that pressure and molarity are related by the constant RT .

$$PV = nRT \Rightarrow P = \frac{n}{v} RT \quad \text{and since } \frac{n}{v} = M = [] \text{ then } P = []RT$$

So this means that the equilibrium expression written in terms of gas pressures can be related to the equilibrium expression written for concentrations by RT values.

$$\text{Given } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

the relationship is simple $K_p = K_c (RT)^{\Delta n}$ All you need to do is find Δn of gases in a reaction and perform a simple multiplication.

Example, for $\text{CO}_g + \text{Cl}_{2g} \rightleftharpoons \text{COCl}_{2g}$ assuming an equilibrium constant values of $K_c=20$

$$K_p = 20 (RT)^{\Delta n} \quad \Delta n = -1,$$

$$\text{so } K_p = 20 [(0.082)(298)]$$

$$K_p = 0.82$$

As an aside, note that if $\Delta n = 0$, then $K_p = K_c$

LeChatelier's Principle: Problems based on how systems respond to external stress

First a profound thought on how chemical reactions are much more boring than people.

Although like people, chemical systems need to find a way to respond to stress, unlike people, who respond to stress by doing everything from shopping to simply lying on a couch watching the Cartoon Network, chemical systems can respond to stress in only one of two ways:

they can shift to the right or they can shift to the left.

Keep this in mind and LeChatelier's principle is easy.

So what LeChatelier's Principle tells us is how it reacts to relieve the stress. And since systems can only shift left or right, when you think about solutions to LeChatelier's principle problems, all you have to do is follow three simple steps:

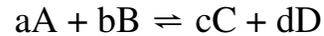
1. Find the external stress (either a change in concentration, pressure, or temperature)
2. Assume the system will do the opposite
3. Determine whether this happens by shifting the reaction left or shifting it right.

For example,

- if the external stress is increased temperature, the system will try to decrease the temperature
- if the external stress is decreased pressure, the system will try to increase the pressure
- if the external stress is increased the amount of a chemical, the system will try to decrease the amount of chemical

We will look at 3 kinds of stress to a system: concentration, pressure, temperature.

Concentration stress:



for the above reaction, if we add A or B, remove A or B, add C or D or remove C or D, we need to shift to get back to equilibrium. As rules of thumb:

add compound A or B to left side \rightarrow the reaction shift right to decrease A or B

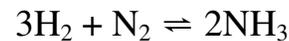
remove compound A or B from left side \rightarrow the reaction shift left to increase A or B

add compound C or D to right side \rightarrow the reaction shift left to decrease C or D

remove compound C or D from right side \rightarrow the reaction shift right to decrease C or D

Sample problem:

In the reaction to produce ammonia below, what happens to the concentration of H₂ as NH₃ is removed from the system?



Answer: The amount of H₂ decreases because the reaction shifts right to counter the stress from losing NH₃.

Pressure stress:

Pressure affects only gases so this stress occurs only in systems with gas.

So for $NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$ changing the pressure has no effect on equilibrium.

But in gas systems, you find the answer by shifting the reaction left or right so that the Δn gas relieves stress. For example:



If increase P then system shifts to make fewer gas molecules (to the left).

If decrease P then system shifts to make more gas molecules (to the right).

The general rules for how the system responds to pressure changes are:

$P\uparrow$ or $V\downarrow$ if Δn is + then the reaction shifts left

$P\downarrow$ or $V\uparrow$ if Δn is + then the reaction shifts right

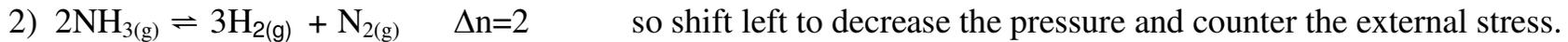
$P\uparrow$ or $V\downarrow$ if Δn is - then the reaction shifts right

$P\downarrow$ or $V\uparrow$ if Δn is - then the reaction shifts left

and for $\Delta n = 0$ there is no shift in the equilibrium as the pressure changes.

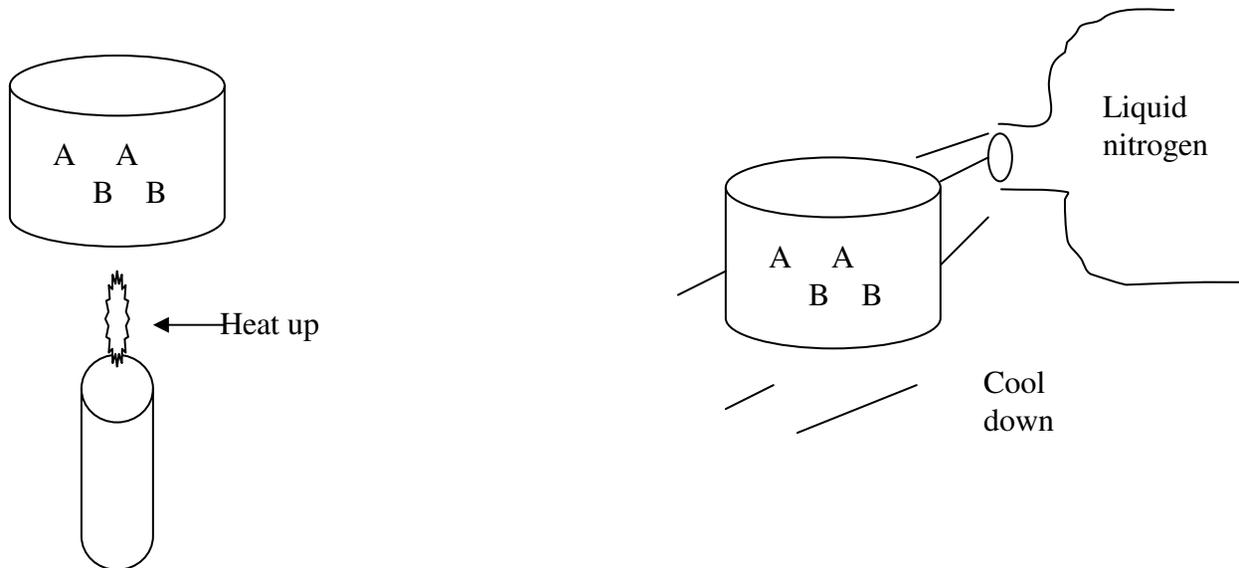
Examples.

Increase the pressure on the following two systems. What happens to the reaction?



Temperature Stress:

It is easy to add or remove heat from a system with an external stress:



So how does the system respond? The system will react to shift away from the heat or cold. This is done based upon whether reaction is endo or exothermic. Consider the following two reactions and their enthalpy values. Note that each is capable of changing the heat of the system by shifting left or right. And now, two cool real life applications of LeChatelier's Principle to wow your friends:

heat + NaCl \rightleftharpoons Na⁺ + Cl⁻ endothermic and will shift left to get warmer and right to get colder

O_{2(g)} \rightleftharpoons O_{2(ag)} + heat exothermic and will shift right to get warmer and left to get colder

So if a reaction evolves heat (it is exothermic), the system shifts left if heat is applied and shifts right if it gets colder.

O_{2(g)} \rightleftharpoons O_{2(ag)} + heat if you heat up reaction it shifts to the left.

Referring back to the last lecture, this is why warming the oceans shifts the equilibrium left and oxygen leaves water so fish die.

On the other hand:

if a reaction absorbs heat (is endothermic), the system shifts right if heat is added and shifts left if it gets colder.

Heat + NaCl_(s) \rightleftharpoons Na⁺ + Cl⁻ if you heat up the reaction it shifts to the right.

This is why when you want to dissolve more NaCl in H₂O you heat the solution up.