Chemical Equilibrium

∗ Most chemical reactions are reversible: they can go in the forward or reverse direction.

∗ Equilibrium is the idea that reversible reactions will proceed to some point and then for every forward. event there will be a reverse event. The reaction doesn't stop. It's just that the forward rate = reverse rate, and the concentration of all species becomes constant.

∗ The equilibrium constant is a number that relates the concentrations of reactants and products at equilibrium.

∗ The formal way of writing out the equilibrium constant is pretty ugly, but I'm gonna write it out and try and learn ya somethin'...

$$K_C = \frac{\prod [\text{products}]^{v_i}}{\prod [\text{reactants}]^{v_j}}$$

⟵ This is the complicated way of writing the expression for the equilibrium constant. Mathematically, the Π symbol is like the Σ symbol only instead of meaning "the sum of" it means "the product of." So, this expression says that the equilibrium constant is equal to the product of the concentrations of the products raised to their stoichiometric coefficients divided by the product of the concentration of the reactants raised to their stoichiometric coefficients.

It's easier to see by example:

Let's look at any old generic reaction:

$$aA + bB \rightleftharpoons cC + dD$$
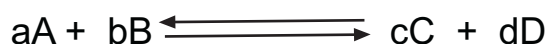
The equilibrium constant expression is:

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$ (remember, [ ] means molarity)

Rules for writing K_C expressions:

1. K_C is a function of temperature even though it's not shown in the above expression.

2. It's not a function of original concentrations, volume, or pressure.

3. Don't put solids or pure liquids in the K_C expression (pay attention to s, g, l subscripts).

4. K_C reverse = $\dfrac{1}{K_{C \text{ forward}}}$ -- easy algebra.

5. Also if you multiply any chemical equation through by a factor it raises K_C to that power.

6. If you add chemical reactions to get a final rxn, multiply the K_C's to get the final reaction's K_C

7. Reactions that go to completion do not have an equilibrium constant. In this case, the concentration of reactants would go to zero and therefore K_C goes off to infinity.

Equilibrium Problems

These are just little algebra problems that you have to be good at setting up. After that they are all kind of the same problem.

* Understand that starting, initial, or changes from equilibrium concentrations **are all nonequilibrium states** and that the system will react until equilibrium is established or re-established.

* If you are given some concentrations and you don't know which way a reaction will proceed, use Q_C, **the reaction quotient**, to figure out which way it will go. Q_C is algebraically the same expression as K_C You are just plugging in nonequilibrium concentration values.

> $Q_C = K_C$ means you are at equilibrium
> $Q_C < K_C$ means not enough products, the rxn will go forward
> $Q_C > K_C$ means too many products, the rxn will go reverse

* Now you do these problems by introducing one unknown, x, the concentration of a species, of your choice, reacted or formed and then set up an algebraic expression for K_C. (Remember to relate x to the other reactants and products with the stoichiometry of the chemical equation.)

* Okay, here is an example of a problem in which you are given Kc and asked to find the equilibrium concentrations of all speices from some given initial concentrations. (This example won't use numbers; its kind of a template):

Always make the "ICE" Table

$$A + B \rightleftharpoons 2\,C$$
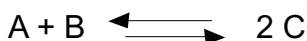
Obviously there are no numbers from which to determine the initial direction of the reaction so, I just assumed it to be forward--thus the -x.

	[A]	[B]	[C]
Initial	$[A]_o$	$[B]_o$	$[C]_o$
Change	-x	-x	2x
Equililbrium	$[A]_o - x$	$[B]_o - x$	$[C]_o + 2x$

This is a number given in the problem statment.

$$K_C = \frac{([C]_o + 2x)^2}{([A]_o - x)([B]_o - x)}$$

Multiply everything out and you will get a quadratic in x: use your calculator to solve it

$$ax^2 + bx + c = 0$$

Now, strictly speaking, you should use the quadratic equation to solve for x:

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

* In some problems, when you start with all reactants and no products, and when $K_C < 10^{-6}$, you can ignore the -x's in the denominator terms because not much of the initial reactants gets used up. When you do this and multiply everything out, you end up just having to take a square root instead of using the quadratic equation.

Kp, Gas Phase Equilibrium Problems

Very similar to K_c problems except you are using partial pressures instead of concentrations.

1. K_p is a function of temperature even though it's not shown in the above expression.

2. It's not a function of original concentrations, volume, or pressure.

3. Don't put solids or pure liquids in the K_p expression (pay attention to s, g, l subscripts).

4. K_p reverse = $\dfrac{1}{K_{p\ forward}}$ -- easy algebra if you look at it.

5. Also if you multiply any chemical equation through by a factor it raises K_p to that power.

6. If you add chemical reactions to get a final rxn, multiply the K_p's to get the final reaction's K_p

7. Reactions that go to completion do not have an equilibrium constant. In this case, the partial pressure of reactants would go to zero and therefore K_p goes off to infinity.

For example:

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$
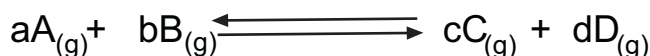
$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

P is the partial pressure of each species
Notice from the ideal gas law that at constant temperature and volume, partial pressure is proportional to molar concentration.

$$P_A = \frac{n_A}{V} RT = [A]\ RT$$

The relationship between K_c and K_p is an easy derivation from the ideal gas law: $PV = nRT$

just substitute the ideal gas law for each species into the Kp expression:

$$K_p = \frac{([C]\ RT)^c ([D]\ RT)^d}{([A]\ RT)^a ([B]\ RT)^b}$$

pull out the expression for K_c $\quad K_p = K_c (RT)^{\Delta n}$

"Δn" just equals the sum of the stoichiometric coeffiecients of the products minus the sum of the stoichiometric coefficients of the reactants (like, c + d - a - b).

So you can relate K_p to K_c as a function of temperature and change in number of moles between products and reactants.

To do these problems, just algebraically proceed in the same way as K_c. Set up the "ICE" table using partial pressures and solve for x. You can always convert to molar concentration using the ideal gas law.