Notes for Chemical Equilibrium (Thermodynamics)

Chemical Equilibrium
Understanding how to work problems for chemical equilibrium is one of the most important concepts in second-semester chemistry. In fact, we will spend much of the rest of the course discussing aspects of this concept.

The previous section discussed chemical kinetics, which tells how fast chemical reactions proceed to form products. Chemical kinetics tells us how fast we get products but nothing about how much products to expect. Chemical equilibrium tells us how much product(s) we can expect if we wait long enough. Chemical equilibrium, a branch of thermodynamics, tells us how much products to expect, but nothing about how long it might take to get those products.

One goal of our discussions in chemistry so far has been to discover and to predict which chemical reactions are product favored. With a product-favored system, the reactants disappear, and new substances form, sometimes very quickly (fast kinetics). If you were to try an experiment by mixing pairs of chemicals (reactants) together and observe what happens, nothing would happen in many cases. These systems may do one of several things: react very slowly, not react appreciably (reactant favored), or react to give products with similar appearance to the reactants. Chemists have developed equilibrium models to help predict product-favored reactions.

Our observations so far have been to classify the reaction types that tend to be product favored. These include: acid-base reactions (H^+ with OH^-), precipitation reactions (solubility rules), redox reactions (when favored according to the activity series of metals: metals above replacing ions below), gas-forming reactions, and reactions that release heat to the surroundings (exothermic). More classifications will be added to this list.

Relationship between Kinetics and Thermodynamics (Equilibrium)
Is there any relationship to kinetics and equilibrium? Yes. At equilibrium, the rates of the forward reaction and the reverse reactions are the same for a reversible reaction, so no net changes occur to reactant or product concentrations. The reaction still occurs in the forward direction and in the reverse direction, but the relative amounts of reactants and products stay constant. Experiments have verified that reactions still occur at equilibrium, and such systems are in dynamic equilibrium. Chemists expect products and reactants to remain at equilibrium. Chemists expect a system to continue reacting in the forward and reverse directions even though the reaction appears to be complete. Do all reactions continue reacting in the forward and reverse directions at equilibrium? In principle, yes. In a measurable way, no, for several reasons. Some reactions have an energy barrier (activation energy, Ea) that is too high to occur in the forward, reverse, or both directions (a kinetic problem). Some reactions have a different set of products/ reactants that are more stable than the target products/reactants (a thermodynamic problem). Some reactions have both problems at the same time, so the products obtained depend on the reaction conditions. Are these hypothetical or real problems?

These are real problems. In organic chemistry, you will talk about reactions under thermodynamic and/or kinetic control. These are the models that you will need to predict what happens.

Develop the Equilibrium Model
To build our model further, we need to know that chemical reactions move toward a final state that has a certain mathematical ratio of products to reactants (this is the equilibrium model). The state where the concentrations of reactant and product remain fixed is called chemical equilibrium.

Reactant ↔ Product
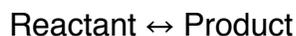
Reversible reactions at equilibrium get represented by a double-headed arrow to show that they can proceed forwards and backwards. (To know how fast reactions go (or how long they take) requires kinetics.) Equilibrium methods tell us the favored direction for a chemical system. A system that has too much reactant moves to form product in order to attain the equilibrium ratio, so the rate of the forward reaction is faster than the rate of the reverse reaction until equilibrium is attained. Likewise, a system that has too much product moves to form reactant to attain the equilibrium ratio, so the rate of the reverse reaction is faster than the rate of the forward reaction until equilibrium is attained. (To know how fast requires kinetics). The equilibrium ratios of product and reactants for each chemical system must be determined experimentally.

Meaning of the Equilibrium Constant, K
The reaction below shows hydrogen gas reacting with iodine gas to produce hydrogen iodide gas. The equilibrium constant (K) for the reaction was found to be 0.50 at 298K. (Note that we use a capital K for equilibrium constant and a small k for rate constant, so be careful with your labeling as you work problems.) This means that a mathematical ratio of products divided by reactants equals 0.50. Because K is less than 1, we expect more reactants than products at equilibrium, so the reaction of hydrogen gas with iodine gas is a reactant-favored reaction. Both products and reactants would be present when this reaction reaches equilibrium.

$H_2(g) + I_2(g) ↔ 2HI(g)$ K=0.50 at 298K

Given an equilibrium constant of 3.2 (K=3.2), reacting diamond to form elemental carbon is a product-favored reaction at room temperature. When K>1, this means a product-favored reaction. Though we might expect some amount of carbon to form from diamonds, this reaction is not kinetically favored at room (or ordinarily accessible) temperatures and pressures. The reason that the reaction does not proceed is that there is not enough energy available at room temperature to break the bonds holding diamond together. Raising the temperature of the reaction could provide that energy.

C(diamond) ↔ C(s)   K=3.2 at 298K

Changes of state (solid to liquid to gas) are examples of dynamic and reversible chemical equilibria.

Writing Expressions for the Equilibrium Constant, K, from Chemical Reactions
Below appears a general chemical reaction where A and B represent reactants, C and D represent products, and a, b, c, and d are their stoichiometric coefficients.

$$aA + bB \leftrightarrow cC + dD$$
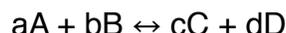
To write an equilibrium constant from this general chemical reaction, multiply the product concentrations (in units of molar) at equilibrium together, where each product concentration is raised to the power given by its stoichiometric coefficient. Next, divide by the product of the equilibrium reactant concentrations where each reactant is raised to its stoichiometric power. Below appears the equilibrium constant expression for the general reaction above. The square brackets indicate that the units of concentration are molarity. When the units of K are molarity, K is called Kc, where the small letter 'c' stands for concentration.

$$K = \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$$

Only reactant and product species that are gases and aqueous solutions appear in expressions for K. For this class, solids and liquids never appear in equilibrium constant expressions. (For now, presume that solids and liquids always have a constant concentration when some remains, so they would be part of the numerical value of K.)

Example: Write the equilibrium constant expression for this general reaction:
$$aA(s) + bB(g) \leftrightarrow cC(l) + dD(aq)$$

Using the information from the previous paragraph, only D and B appear in the expression for K. At equilibrium,

$$K = \frac{[D]^d}{[B]^b}$$

Write the equilibrium constant expression for this reaction: $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$. At equilibrium,

$$K = \frac{[HI]^2}{[H_2] \, [I_2]}$$

Write the equilibrium constant expression for this reaction:
$$NaHCO_3(s) \leftrightarrow NaOH(s) + CO_2(g)$$

At equilibrium, K = [CO_2].

Write the equilibrium constant expression for this reaction: C(s) ↔ C(diamond) at 298K.

For this class, K=1. Neither carbon nor diamond appears in the expression for K because they are solids. (The K value for the reaction above was found by another method using standard free energies of formation, but you will have to wait until a later thermodynamics discussion to learn how it was done.) The equilibrium method here teaches that K = 1 because the concentrations (activities) of solids do not change appreciably over the course of the reaction (as long as some solid remains). Due to kinetic barriers, this reaction requires temperatures substantially higher than 298K and pressures substantially higher than 1atm to be able to reach equilibrium. (We would need to recalculate K for the conditions of temperature and pressure where the reaction occurs). The reaction does not proceed in a measurable way at room temperature and pressure.

Calculating the Reaction Quotient (Q) from Concentrations at Different Points During a Chemical Reaction
If we measured the concentrations of reactants and products present at any time in a chemical reaction, how would we know whether or not that chemical system has reached equilibrium? The answer is to compare the ratios of products to reactants, exactly like we did for K. When we are not certain if the reaction is at equilibrium, we call this calculated ratio the reaction quotient (Q). We compare Q to the known value for K to see if the system has reached equilibrium. Q has exactly the same mathematical form as K. If you learned how to write the expression for K for a chemical reaction, you can write the correct expression for Q. For the general reaction,

$$aA + bB ↔ cC + dD$$

The reaction quotient is:

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

As before, solids and liquids do not appear in the expression for Q (only gases and aqueous solutions appear).

If Q is larger than K, the product concentrations, [C] and [D], are too high compared to the reactant concentrations, [A] and [B]. The reaction must shift back to reactants, causing [C] and [D] to go down and [A] and [B] to go up until Q=K. Likewise if we calculate Q and it's smaller than K, product concentrations must increase and reactant concentrations must decrease. The reaction must shift to products. If we calculate Q and it is equal to K, then the system is at equilibrium. At equilibrium, no net change to reactant or product concentrations occurs.

Now for some practice calculating Q. The example reaction is:
$$H_2(g) + I_2(g) ↔ 2HI(g) \qquad\qquad K=0.50 \text{ at } 298K$$
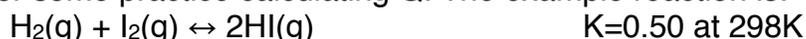
Example: Is the reaction at equilibrium when $[H_2]$=1.0M, $[I_2]$=1.0M, and [HI]=0 at 298K? If not which direction does the reaction go to reach equilibrium?

Answer: Calculate Q= 0^2/ (1 * 1) = 0. Because Q (0) < K (0.50), the reaction shifts to products.

Example: Is the reaction at equilibrium when $[H_2]$=0.592M, $[I_2]$=0.592M, and [HI] =0.814M at 298K? If not which direction does the reaction go to reach equilibrium?

Answer: Calculate Q= 0.814^2/ (0.592 * 0.592) = 1.89. Because Q (1.89) > K (0.50), the reaction shifts to reactants.

The graph below shows what happens to the reactant and product concentrations as the reaction approaches equilibrium. Initially (which is at time 0), the H_2 and I_2 concentrations are 2.0M (blue curve), while the concentration of HI is 0M (green curve). Q is zero initially (yellow curve). The reaction proceeds to form products with time (on the x or horizontal axis), where time is given in arbitrary units (a.u.). At a time of approximately 40 on the graph below, $[H_2]$=01.49M, $[I_2]$=1.49M, and [HI]=1.03M, which gives Q=0.476. As more and more time passes, the reaction gets closer and closer to where Q=0.50=K.

H2 + I2 --> 2HI
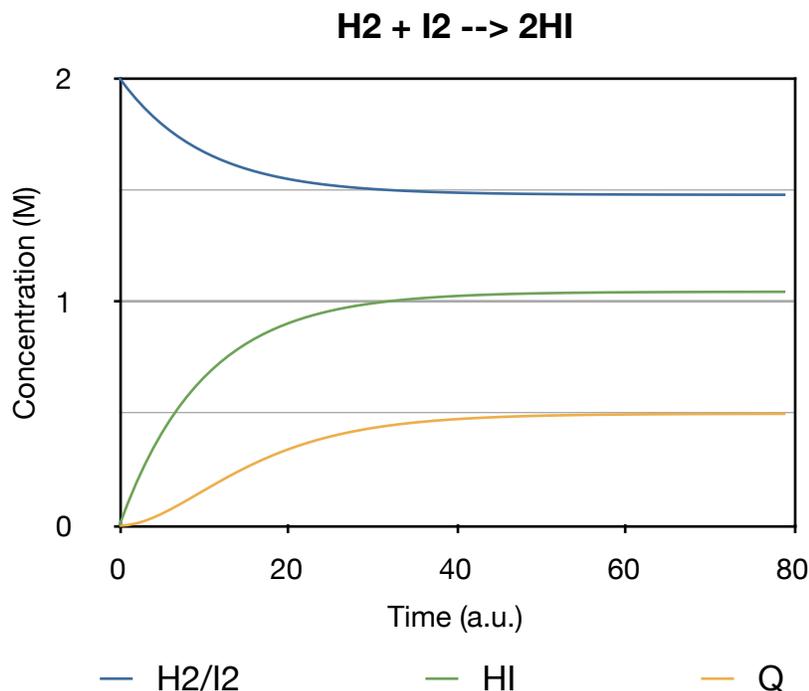
Using the expression for Q, we can test any concentrations at any time to see if a system is at equilibrium, not just the concentrations used in the example and the graph.

Example: Is the reaction, $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$, at equilibrium when $[H_2]=0.9M$, $[I_2]$ $=1.1M$, and $[HI]=2.1M$ at 298K? If not which direction does the reaction go to reach equilibrium?

Answer: Calculate $Q = 2.1^2 / (0.9 * 1.1) = 4.45$. Because Q (4.45) > K (0.50), the reaction shifts back from products to form reactants.

Example: Is the reaction, $2SO_2(g) + 2Cl_2(g) \leftrightarrow O_2(g) + 2SOCl_2(g)$, K=0.91 at 298K, at equilibrium when $[SO_2]=0.10M$, $[Cl_2]=0.80M$, $[O_2]=0.15M$, and $[SOCl_2]=0.73M$, at 298K? If not which direction does the reaction go to reach equilibrium?

Answer: Write the expression for Q. Calculate $Q = ([O_2] * [SOCl_2]^2) / ([SO_2]^2 * [Cl_2]^2) = (0.15 * 0.73^2) / (0.10^2 * 0.80^2) = 12.4$. Compare Q to K. Because Q (12.4) > K (0.91), the reaction must shift to the reactant side (and products must decrease in concentration while reactants increase in concentration) to reach equilibrium.

Calculate K from Concentration Data at Equilibrium
You can also calculate K using experimental concentrations at equilibrium. Calculating K from data can also be part of a more complex question. The steps to solve these types of problems include:
    (1) Balance the chemical reaction.
    (2) Write the expression for the equilibrium constant from the balanced chemical reaction, where only aqueous solutions and gases appear in the expression for K.
    (3) Set up an initial-change-equilibrium (ICE) table to calculate the molar concentrations for each species that appears in the expression for K at equilibrium. If some concentrations are not at equilibrium, you need to calculate equilibrium concentrations based on one that is known at equilibrium. Note: if the volume of the system changes, you also need to calculate the new concentrations after dilution.
    (4) Solve the expression for K after using the calculated equilibrium molar concentrations from Step 3. (Verify your answer.)

Example: A 2.00L flask is found to contain 2.00g of S, 2.00g of O_2, and 0.300g of SO_3 at equilibrium after the following reaction occurred: $S(s) + O_2(g) \leftrightarrow SO_3(g)$. Calculate the equilibrium constant from these data.

Answer: Balance the reaction first: $2S(s) + 3O_2(g) \leftrightarrow 2SO_3(g)$. Write the expression for the equilibrium constant, $K=[SO_3]^2 / [O_2]^3$. Calculate molar concentrations for the species that appear in the equilibrium constant. For O_2, 2.00g * (1 mol O_2 / 31.998g O_2) * (1 / 2.0L) = 0.03125M O_2. For SO_3, 0.300g SO_3 * (1 mol SO_3 / 80.063g SO_3) * (1 / 2.0L) = $1.8735 \times 10^{-3}M$. Calculate K from the equilibrium concentrations. $K = (1.8735 \times 10^{-3})^2/(0.03125)^3 = 0.115$.

Example: A 3.00L flask initially contains 1.00 mol of SO_2, 1.00 mol of of Cl_2 and 0.00 mol of SO_2Cl. After the reaction $SO_2(g) + Cl_2(g) \leftrightarrow SO_2Cl(g)$ reaches equilibrium, 0.75mol of Cl_2 remains in the flask. Calculate K from these data.

Answer: First, balance the chemical reaction: $2SO_2(g) + Cl_2(g) \leftrightarrow 2SO_2Cl(g)$. Second, write the mathematical expression for $K=[SO_2Cl]^2/[SO_2]^2[Cl_2]$. Third, set up an initial-change-equilibrium (ICE) table to get the concentrations of chemicals present at equilibrium (You could work in the mole, but it is equivalent to work directly in molarity when the volume of the system does not change). The entries in the ICE table are molar concentrations.

$$2SO_2(g) + Cl_2(g) \leftrightarrow 2SO_2Cl(g)$$

I	0.33	0.33	0
C			
E		0.25	

To reach equilibrium, the change in Cl_2 concentration was 0.25-0.33=-0.08M. Because of its 2 coefficient, the decrease in SO_2 concentration must have been twice the drop in Cl_2 concentration or -0.16M. Similarly, the increase in SO_2Cl concentration must have the same magnitude as the decrease in SO_2 concentration (or twice that of Cl_2 decrease).

$$2SO_2(g) + Cl_2(g) \leftrightarrow 2SO_2Cl(g)$$

I	0.33	0.33	0
C	-0.16	-0.08	+0.16
E		0.25	

Calculate the equilibrium concentrations by adding the initial concentration and the change together.

$$2SO_2(g) + Cl_2(g) \leftrightarrow 2SO_2Cl(g)$$

I	0.33	0.33	0
C	-0.16	-0.08	+0.16
E	0.17	0.25	0.16

Fourth, place the equilibrium molar concentrations (E) into the expression for K, and solve to get the answer. $K=[0.16]^2/[0.17]^2[0.25] = 3.54$.

Use K to Calculate Equilibrium Concentrations
When the equilibrium constant is known (from looking it up in a table or by it being given in the problem), you can solve for the concentrations of species at equilibrium, as long as you know the initial concentration. Solving for the equilibrium concentration tells how much of each species to expect after the reaction reaches equilibrium. The steps to solve these types of problems include:
      (1) Balance the chemical reaction.
      (2) Write the expression for the equilibrium constant from the balanced chemical reaction, where only aqueous solutions and gases appear in the expression for K.
      (3) Use an initial-change-equilibrium (ICE) table to calculate the molar concentrations for each species that appears in the expression for K at equilibrium,

which in this case, will involve an unknown, x, in the change (C) line of the ICE table. Note: if the volume of the system changes, you also need to calculate the new concentrations after dilution to the new volume.

      (4) Solve the expression for K for the unknown, x. The mathematics may involve solving a quadratic equation (or higher-order polynomial) for x.

      (5) Calculate the equilibrium concentrations using x. (Verify your answer.)

Example: Calculate the equilibrium concentrations for this reaction at 298K:
      $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ K=0.50 at 298K

The initial concentration of H_2 and I_2 are 0.50M.

Answer: The reaction is balanced, so the equilibrium constant expression is:

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

Initial concentrations are given in the problem, and the initial concentration of HI is presumed to be zero because it is not given. Use this data to set up an ICE table using the molar concentrations (If you calculate Q=0 for the initial conditions, you will see that the reaction must shift to the right to form products to get Q=K. The change to get to the equilibrium position, defined in terms of x, must be a positive number when we solve the math.):

      $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ K=0.50 at 298K

I	0.50	0.50	0
C	-x	-x	+2x
E	0.50-x	0.50-x	2x

Place the equilibrium concentrations (E) back into the mathematical expression for K, and solve for x. This gives: $0.50 = (2x)^2 / (0.50-x)(0.50-x)$. Normally, this expression simplifies algebraically to a quadratic equation of the form $ax^2 + bx + c = 0$. In this case there is a mathematical simplification that avoids the need to solve the quadratic equation: $0.50 = (2x)^2 / (0.50-x)^2$. Taking the square root of both sides gives $0.7071 = 2x / (0.50-x)$. Collect like terms in the form ax=b to solve for x: $0.3536-0.7071x = 2x$, $0.3536 = 2.707x$, and $x=0.13$. (Resist the temptation to report x , the change (C), as the answer. Instead report the equilibrium concentrations.) Using x with the equilibrium line of the ice table (E), the calculated equilibrium concentrations are $[H_2] = 0.37M$, $[I_2] = 0.37M$, and [HI]= 0.26M. There is opportunity to make a logical or mathematical mistake, so verify your answer by substituting the equilibrium concentrations back into the expression for K. This gives $0.50 = (0.26)^2 / (0.37)(0.37)$, and $0.50 = 0.49$. The answer is correct to significant digits (0.50=0.50), so the answer is a mathematically correct solution.

A change to one of the initial concentrations in the previous example requires the quadratic equation.

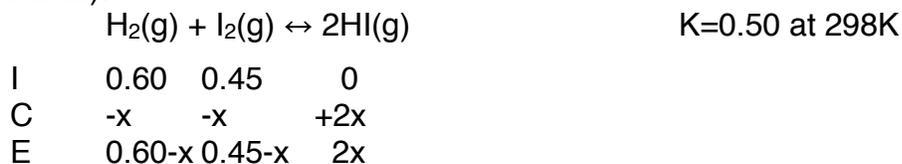Example: Calculate the equilibrium concentrations for this reaction at 298K:
      $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ K=0.50 at 298K

The initial concentration of H_2 is 0.60M, and the initial concentration of I_2 is 0.45M.

Answer: The steps to solve this example are exactly the same as for the previous example. In this case, though, we need to solve the quadratic equation to get the change, x. The reaction is balanced as it is written, so the equilibrium constant expression is:

$$K = \frac{[HI]^2}{[H_2]\,[I_2]}$$

Initial concentrations are given in the problem, and the initial concentration of HI is presumed to be zero because it is not given. Use this data to set up an ICE table using the molar concentrations (If you calculate Q=0 for the initial conditions, you will see that the reaction must shift to the right to form products to get Q=K. The change to get to the equilibrium position, defined in terms of x, must be a positive number when we solve the math.):

$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ $\qquad\qquad$ K=0.50 at 298K

| I | 0.60 | 0.45 | 0 |
| C | -x | -x | +2x |
| E | 0.60-x | 0.45-x | 2x |

Substitute the equilibrium concentrations back into the mathematical expression for K, and solve. This gives: $0.50 = (2x)^2 / (0.60-x)(0.45-x)$. Collect like terms in the form of a quadratic equation $ax^2 + bx + c = 0$ to solve for x: $0.50*(0.60-x)(0.45-x) = 4x^2$, $0.135-0.525x+0.50x^2 = 4x^2$, $3.5x^2 + 0.525x - 0.135 = 0$. Use the quadratic equation, $x=[-b + sqrt(b^2-4ac)]/(2a)$ and $x=[-b - sqrt(b^2-4ac)]/(2a)$ to solve, where a=3.5, b=0.525, and c=-0.135. This gives x= (-0.525 + 1.471) / 7 and x= (-0.525 - 1.471) / 7. In this case, keep the positive root (or the root that leads to physically meaningful equilibrium concentrations) because x, the change, must be a positive number. The two values for x are: x= 0.135 and x= -0.285. (The question asked for the equilibrium concentrations, so resist any urge to report x as the answer. Instead calculate the equilibrium concentrations using the equilibrium line of the ICE table.) Using the positive value for x (or the root that leads to answers that are physically possible), the calculated equilibrium concentrations are $[H_2]$ = 0.465M, $[I_2]$ = 0.315M, and [HI]= 0.270M. There is ample opportunity to make a logical or mathematical mistake, so verify your answer by substituting the calculated equilibrium concentrations back into the expression for K. This gives $0.50 = (0.270)^2 / (0.465)(0.315)$, and 0.50 = 0.50. The verification is correct to significant digits, so the answer is correct.

Note: if the math evaluates to polynomial that is a higher order than quadratic, then it will not be easily possible for you to solve it without the use of a computer. Should this happen on an exam, show the setup for the higher order polynomial. Mention that you would solve it for x to be able to calculate the equilibrium concentrations. Then stop.
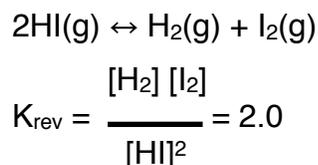
Relationships among K Values by Reversing a Reaction
There is a relationship between the equilibrium constant for a reaction written in the forward direction and a reaction written in the reverse direction. When a reaction is

reversed, products become reactants and reactants become products. In the equilibrium constant expression, the numerator becomes the denominator and the denominator becomes the numerator. In other words, $K_{forward} = 1/K_{reverse}$. You can also show this relationship by writing the equilibrium constants for a reaction in the forward and reverse directions. In the forward direction, the equilibrium constant expression for this reaction is the same as the one that we obtained before.

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

$$K_{fwd} = \frac{[HI]^2}{[H_2]\,[I_2]} = 0.50$$
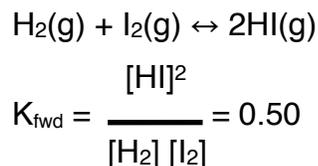
The reaction in reverse and its equilibrium constant appear below. By comparing K_{fwd} to K_{rev}, you can see that the mathematical relationship is $K_{fwd}=1/K_{rev}$. (Take $1/K_{rev}$, and it equals K_{fwd}.)

$$2HI(g) \leftrightarrow H_2(g) + I_2(g)$$

$$K_{rev} = \frac{[H_2]\,[I_2]}{[HI]^2} = 2.0$$

Relationships among K Values when Multiplying a Reaction by a Constant
Because coefficients in a chemical reaction appear as powers in the equilibrium constant, doubling a chemical reaction results in a squaring of the equilibrium constant compared to the original reaction. Tripling a chemical reaction results in a cubing of the equilibrium constant compared to the original reaction. In general, multiplying a chemical reaction by n raises its K to the "n" power. You can also show this relationship by writing the equilibrium constants for a reaction (K_1) and a reaction multiplied by a constant (K_2). The equilibrium constant expression for this reaction is the same as the one that we obtained before.

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

$$K_1 = \frac{[HI]^2}{[H_2]\,[I_2]} = 0.50$$
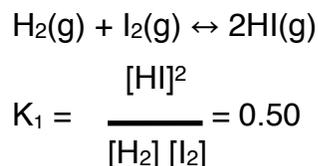
After multiplying the reaction through by a coefficient, n, we obtain the following reaction and equilibrium constant.

$$nH_2(g) + nI_2(g) \leftrightarrow 2nHI(g)$$

$$K_2 = \frac{[HI]^{2n}}{[H_2]^n\,[I_2]^n} = 0.50^n$$
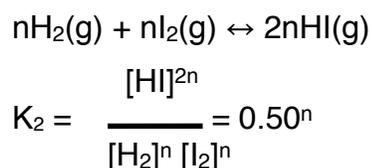
The relationship between K_1 and K_2 is $K_2=K_1{}^n$ (or you could write that the nth root of K_2 equals K_1, or $K_1=K_2{}^{(1/n)}$). When you multiply a reaction by a constant, it raises the original equilibrium constant for the reaction to the power of that constant.

Relationships among K Values when Adding Reactions
When adding two (or more) reactions, you multiply the equilibrium constants for the two (or more) reactions to obtain the equilibrium constant for the reaction that is the sum of the others. Given that the reaction for K_3 is the sum of the reactions for K_1 and K_2, then $K_3= K_1*K_2$.

Example: Calculate K_3 for the this reaction in terms of K_1 and K_2: $SO(g) + Cl_2(g) \leftrightarrow$

$SOCl_2(g)$, $K_3=?$, given the data below.

$2SO_2(g) + 2Cl_2(g) \leftrightarrow O_2(g) + 2SOCl_2(g)$	$K=K_1$
$2SO_2(g) \leftrightarrow 2SO(g) + O_2(g)$	$K=K_2$

Answer: Because the products and reactants for K_1 and K_2 are not the same as those for K_3, check whether adding the two reactions (perhaps using a constant or reversing the reactions for K_1 and K_2) can add up to the reaction for K_3.

$SO(g) + Cl_2(g) \leftrightarrow SOCl_2(g)$	$K_3=?$

Next, attempt to line up products and reactants on the correct sides. Notice that the reaction for K_1 has $SOCl_2(g)$ as a product and that $SOCl_2(g)$ is a product in the reaction for K_3. The coefficient for $SOCl_2(g)$ is 2 in K_1 and 1 in K_3, so we will multiply the reaction for K_1 by a constant (1/2) to obtain the following.

$SO_2(g) + Cl_2(g) \leftrightarrow 1/2O_2(g) + SOCl_2(g)$	$K_4=(K_1)^{1/2}$

The equilibrium constant for reaction K_4 above is the square root of K_1 (or to the 1/2 power) because we multiplied K_1 through by the coefficient 1/2. Now, look at the reaction for K_2 to see if we can add it to the reaction for K_4 (perhaps reversing the reaction for K_2 or perhaps multiplying it by a constant) to get the reaction for K_3. Looking at the reaction for K_4, $SOCl_2(g)$ and $Cl_2(g)$ are on the correct side with the correct coefficient. We also need $SO(g)$ as a reactant and the following species to cancel in the reaction for K_4: $SO_2(g)$ as a reactant and $1/2O_2(g)$ as a product. The reaction for K_2 has all of these species, but $SO_2(g)$ is a product in K_2 (and a reactant in K_3). Reverse K_2 and determine the new $K=K_5$ value as $1/K_2$.
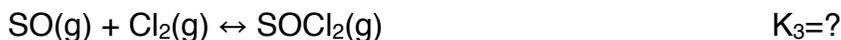
$2SO(g) + O_2(g) \leftrightarrow 2SO_2(g)$	$K_5= 1/K_2$

Looking at the reaction for K_4, $SO_2(g)$ has a 1 coefficient, while the coefficient of $SO_2(g)$ is 2 in K_5. In order to get $SO_2(g)$ to cancel after adding reaction K_5 to K_4, we need to multiply reaction K_5 by 1/2, giving K_6:
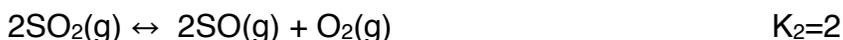
$SO(g) + 1/2O_2(g) \leftrightarrow SO_2(g)$	$K_6= (1/K_2)^{1/2}$

Adding reaction K_6 and K_4 gives the reaction for K_3 as follows:

$SO_2(g) + Cl_2(g) \leftrightarrow 1/2O_2(g) + SOCl_2(g)$	$K_4=(K_1)^{1/2}$
+ $SO(g) + 1/2O_2(g) \leftrightarrow SO_2(g)$	$K_6= (1/K_2)^{1/2}$

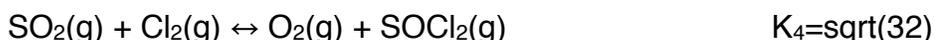$$SO(g) + Cl_2(g) \leftrightarrow SOCl_2(g) \qquad\qquad K_3 = ?$$

Adding reactions means multiplying the equilibrium constants, so $K_3 = (K_1)^{1/2} *(1/K_2)^{1/2}$, or $K_3 = (K_1/K_2)^{1/2}$.

Example: Calculate K for this reaction $SO(g) + Cl_2(g) \leftrightarrow SOCl_2(g)$, $K_3 = ?$, given the data below:

$$2SO_2(g) + 2Cl_2(g) \leftrightarrow O_2(g) + 2SOCl_2(g) \qquad\qquad K_1 = 32$$
$$2SO_2(g) \leftrightarrow 2SO(g) + O_2(g) \qquad\qquad K_2 = 2$$

Answer: This is the same question as the previous one, except that we have numbers for the equilibrium constants K_1 and K_2 instead of symbols. Follow the steps outlined above above to solve (Do not memorize or use the outcome from above because that will not help you on an exam). The reaction for K_1 needs to be multiplied by a constant 1/2, which raises K_1 to the 1/2 power. The reaction for K_2 needs to be reversed and multiplied by 1/2 before adding the previous reaction, which gives $1/K_2$ to the 1/2 power. (If do not attempt this on your own, it is unlikely that you will learn it.)

$$SO_2(g) + Cl_2(g) \leftrightarrow O_2(g) + SOCl_2(g) \qquad\qquad K_4 = sqrt(32)$$
$$2SO_2(g) \leftrightarrow 2SO(g) + O_2(g) \qquad\qquad K_6 = 1/sqrt(2)$$

$$SO(g) + Cl_2(g) \leftrightarrow SOCl_2(g) \qquad\qquad K_3 = ?$$

Adding the reactions for K_4 and K_6 to get reaction K_3 while and multiplying the equilibrium constants for K_4 and K_6 to get the K_3 gives $K_3 = (32/2)^{1/2} = 4$, $K_3 = 4$.

Write Equilibrium Constants in Terms of Pressure and Its Relation to Kc
Instead of molar concentration for Kc, you can use pressures in atmospheres for gases that behave ideally, then write the expression for Kp. This gives the equilibrium constant in terms of pressure.
Write the equilibrium constant expression, Kp, for this reaction: $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$.

At equilibrium,

$$Kp = \frac{P(HI)^2}{P(H_2)P(I_2)}$$

Use the partial pressures of each gas at equilibrium in the expression for Kp in order to calculate Kp. For an Ideal Gas, PV=nRT, the partial pressure of gas (P) is directly proportional to the number of moles of gas (n) present.

Write the equilibrium constant expression for Kp for this reaction:
$$NaHCO_3(s) \leftrightarrow NaOH(s) + CO_2(g)$$

At equilibrium, $Kp = P(CO_2)$, the partial pressure of CO_2.

The numerical value of K_c may different from, but related to K_p through the Ideal Gas Law. The relationship between K_c and K_p is given by: $K_p = K_c(RT)^{\Delta n_{gas}}$, where K_p is the equilibrium constant in terms of pressure, K_c is the equilibrium constant that uses molar concentration, R is the gas law constant in L atm/mol K, T is the temperature in Kelvin, and Δn_{gas} is the change in the total number of moles of gas between the reactant side and the product side of a chemical reaction. When $\Delta n_{gas} = 0$, $K_p = K_c$ because the other portion of the equation equals 1, $(RT)^0 = 1$. To determine Δn_{gas}, count the total number of moles of gas species on the reactant side and on the product side of the balanced chemical reaction. $\Delta n_{gas} = n_{gas(product)} - n_{gas(reactant)}$. For the reaction $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$, $\Delta n_{gas} = (2-2) = 0$, so $K_p = K_c$. For the reaction $NaHCO_3(s) \leftrightarrow NaOH(s) + CO_2(g)$, $\Delta n_{gas} = (1-0) = 1$, so $K_p = K_c(RT)^1$. If the value of K_c is known, the value of K_p can be calculated at a given temperature.

LeChatelier's Principle
A system in equilibrium will respond to counteract changes that affect the equilibrium. This is a statement of LeChatelier's principle. Using LeChatelier's principle, you can determine the effect of many external stimuli on chemical reactions. The stimuli to be considered here include temperature, pressure by changing the volume of the system, catalyst, and concentration. These stimuli are like levers that can control how much product you can get from a chemical reaction.

Effect of Concentration on K
Changing the concentrations of reactants and/or products in a chemical reaction does not change the value of K. Instead, the reaction shifts according to LeChatelier's Principle to establish a relative ratio of concentration according to K. K is unchanged. This technique is used frequently to obtain more products from a chemical reaction. There are two basic ways to form more product by changing concentrations:
  Add more reactants. Form more products.
  Take away products. Form more products.
To obtain more reactants, remove reactants or add products.

Effect of Temperature on K
The effect of temperature depends on whether a reaction is exothermic ($\Delta H_{rxn} < 0$) or endothermic ($\Delta H_{rxn} > 0$), so you must first calculate or be given ΔH_{rxn}. (Using standard conditions this would be ΔH°_{rxn}) An exothermic reaction has a negative ΔH_{rxn} value, and heat comes off as a product from the chemical reaction. Recall that you can increase the heat available by increasing the temperature.

 $A \leftrightarrow B + heat$ exothermic reaction ($\Delta H_{rxn} < 0$)

According to LeChatelier's Principle, adding heat pushes the reaction to form more reactants, which reduces the value of K at the higher temperature. The opposite holds for endothermic reactions where heat is a reactant. In this case, heat forms more products causing K to increase at the higher temperature.

Effect of Pressure on K
There are two methods to change the pressure on a system at equilibrium. Each method of changing pressure leads to a different analysis. When a system at equilibrium is squeezed to higher pressure by decreasing the volume, LeChatelier's Principle predicts that a reaction will shift to the side with fewer moles of gas. If both sides have the same number of moles of gas, there is no predicted change in K by increasing the pressure. Increasing the pressure on the reaction below by decreasing the volume results in a shift (according to LeChatelier's Principle) to form more reactants (the side with fewer moles of gas). This results in a decrease in equilibrium constant, K, at the higher pressure.

$$NaHCO_3(s) \leftrightarrow NaOH(s) + CO_2(g)$$

For a second example, consider liquifying oxygen gas from the atmosphere as shown in the reaction below. If you wanted more liquid oxygen, you would increase the pressure on the atmosphere by decreasing the volume. This increases the partial pressure of oxygen, forming more products.

$$O_2(g) \leftrightarrow O_2(l)$$
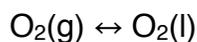
You may recognize the the reaction to liquify oxygen is an exothermic phase change. Removing heat by decreasing the temperature would also shift the reaction (by increasing K) to form more products (that is getting more liquid oxygen from the atmosphere).

Another method to increase the pressure is to pump an inert gas (neither a reactant nor a product) into the system. Use the example for liquifying oxygen shown above. (Note: if the added gas is a reactant or product the reaction will shift according to LeChatelier's Principle based on the effect of concentration on K. Consider this effect first. Adding oxygen gas shifts the reaction to products because the partial pressure of $O_2(g)$ increases. The value of K may also be changed by applying the analysis for effect of pressure above, but consider this effect secondary and only if the equilibrium data to determine the new K value have been provided.) Adding an inert gas to a fixed volume of the atmosphere does increase the total pressure, but it leaves the partial pressure of oxygen gas unaffected. If the partial pressure of oxygen gas is unaffected, the equilibrium position would also be unaffected. Finally, there is not a straightforward method to predict a change in K, unless data have been provided to calculate K.

Effect on Catalyst on K
Catalysts do not change the value of the equilibrium constant, K. Catalysts change the rate (or speed) of approach to equilibrium based on the activation energy of the slow step in the mechanism. Catalysts can make it faster for a system to reach equilibrium. Catalysts, in an ideal sense, affect the kinetics of reaction, not the thermodynamics.

Example

A system, $2SO_2(g) + Cl_2(g) \leftrightarrow 2SO_2Cl(g)$, is at equilibrium with $[SO_2Cl]= 0.16$, $[Cl_2]= 0.25$, and $[SO_2]= 0.17$. In which direction (right toward products or left toward reactants) does the reaction proceed to establish equilibrium with each of the following perturbations from the initial equilibrium conditions?

> A. Increase the $[SO_2Cl]$ to 0.20
> B. Decrease the $[SO_2]$ to 0.11
> C. Decrease the to $[Cl_2]$ to 0.20
> D. Increase the pressure by decreasing the volume of the reaction
> E. Increase the temperature
> F. Add a catalyst

Answers

A. Increasing the concentration of product causes reactant to form, a shift to the left. Also, $Q=5.53$ is greater than $K=3.54$, so the reaction forms more reactants.
B. Decreasing the concentration of reactant causes reactant to form, a shift to the left. Also, $Q=8.46$ is less than $K=3.54$, so the reaction forms more reactants.
C. Decreasing the concentration of reactant causes reactant to form, a shift to the left. Also, $Q=4.43$ is greater than $K=3.54$, so the reaction forms more reactants.
D. Increasing the pressure causes the reaction to form more products, the side with fewer moles of gas. (There are 3 moles of gas on the reactant side and two on the product side.)
E. Cannot tell without the enthalpy of reaction. If the reaction were exothermic, it would shift to reactants with increasing temperature. If the reaction were endothermic, it would shift to products with increasing temperature.
F. There is no shift by adding catalyst because catalysts do not affect the equilibrium condition.

Keep Trying...

It may be tempting to disregard the material in this section as too difficult; however, much of the remainder of the class depends on your understanding of setting up and solving chemical problems at equilibrium. Be sure that you can set up and work the problems in this section independently before you attempt to learn the next material. We will soon discuss acid-base reactions/pH, precipitation reactions/solubility, and redox reactions/voltage (all discussed generally in CHEM I) using the equilibrium model that is being developed in CHEM II. The equilibrium model will also be related to thermodynamics so that you can use calculations from thermodynamics to make predictions at equilibrium and vice versa.