Chapter 17

Chemical Equilibria

Chemical Equilibrium: **It is the condition of a chemical reaction in which the rate of formation of products (from reactants) equals the rate of formation of the reactants (from products).**

$$A + B \underset{rate_{-1}}{\overset{rate_1}{\rightleftharpoons}} C + D$$

Equilibrium occurs when $rate_1 = rate_{-1}$.

Although chemists usually want reactions to go completely to products (and ideally only to a single product), many do not. Theoretically all reactions are in equilibrium.

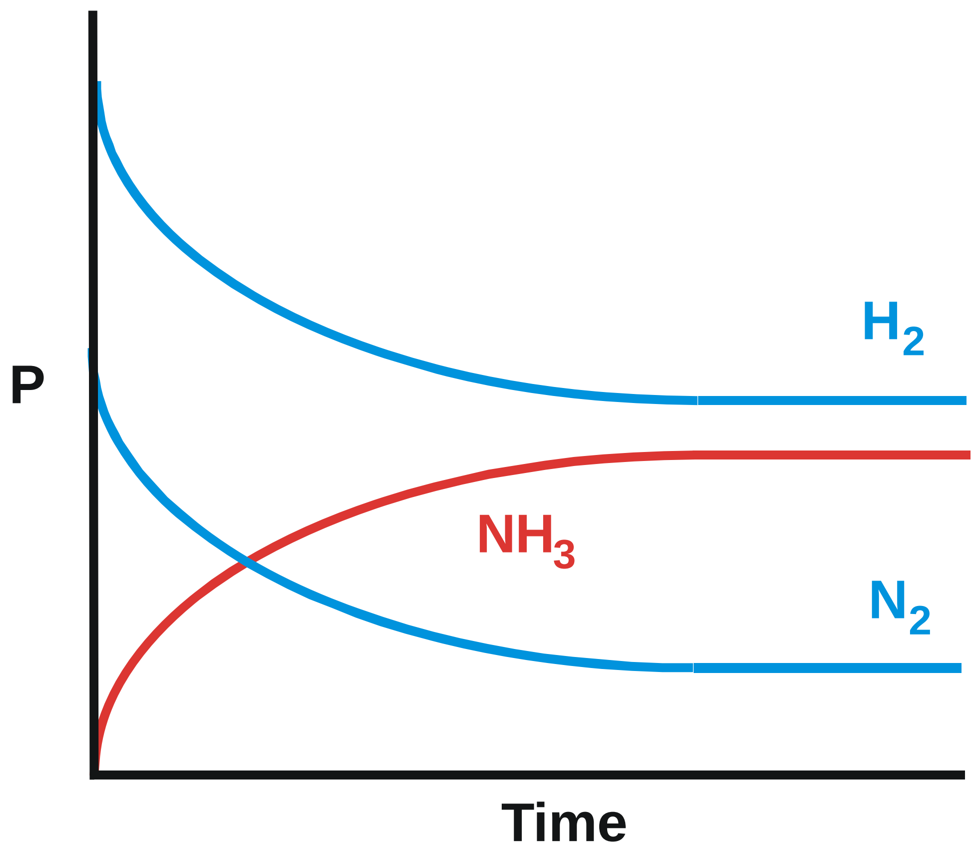
A reaction will *not* generally reach equilibrium if:

1) **The rxn is very exothermic (exoergic)**
2) **One (or more) of the products (or reactants) is removed from the rxn**
3) **One of the products (or reactants) is insoluble**

Consider the very important industrial reaction (the Haber process) of nitrogen and hydrogen to produce ammonia, which is used as a fertilizer:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

This is a very difficult reaction (large activation barrier) that requires high temperatures, pressures and a catalyst. At the high temperatures required to make the reaction proceed at a reasonable rate, the thermodynamics favors the $N_2 + H_2$ reactants producing the following behavior:



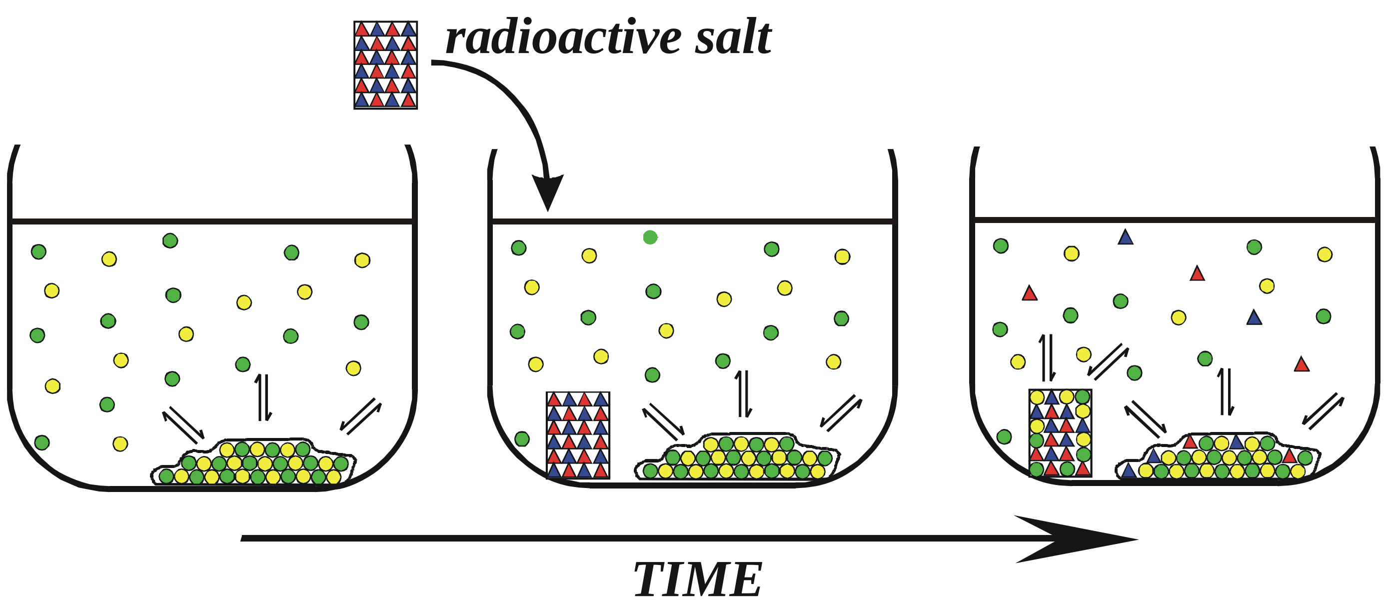
Note that the rxn does not go to completion, rather the forward and backward rxns reach a state of chemical equilibrium.

Equilibrium is a *dynamic* process. This means that when a reaction has reached a state of equilibrium, the forward and backward reactions making up the overall reaction *have not stopped*!! The equilibrium definition states that equilibrium is reached when the forward and backward reaction rates become equal!

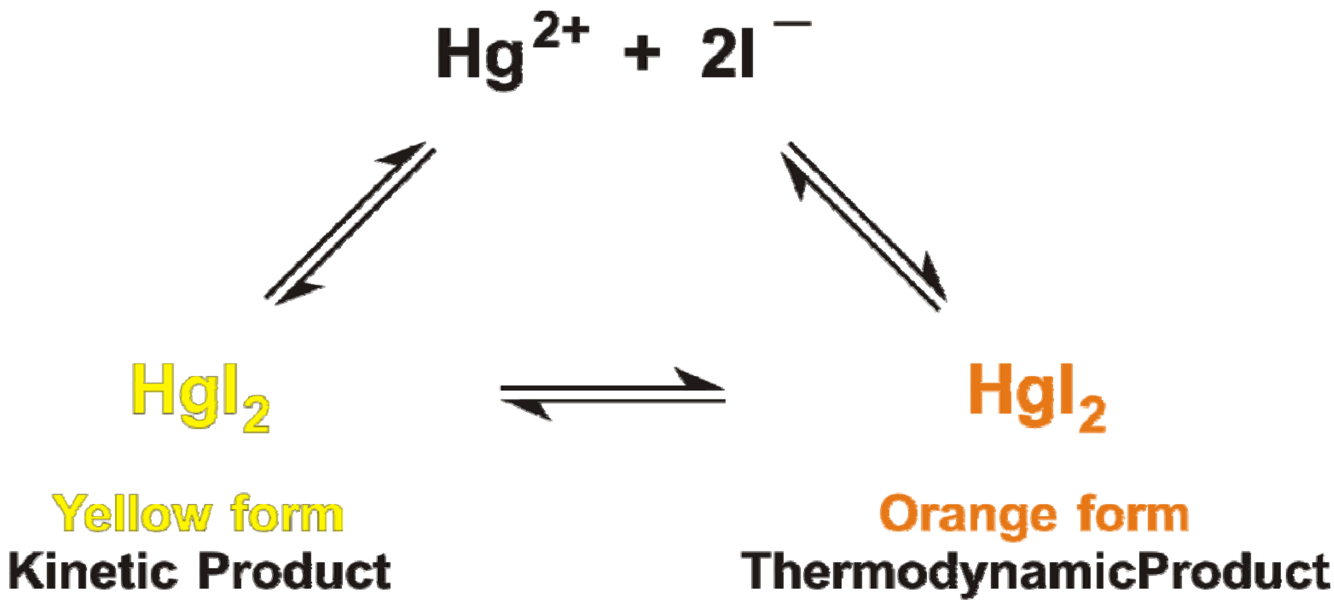
For example consider a *saturated solution* of NaCl (no additional salt will dissolve):

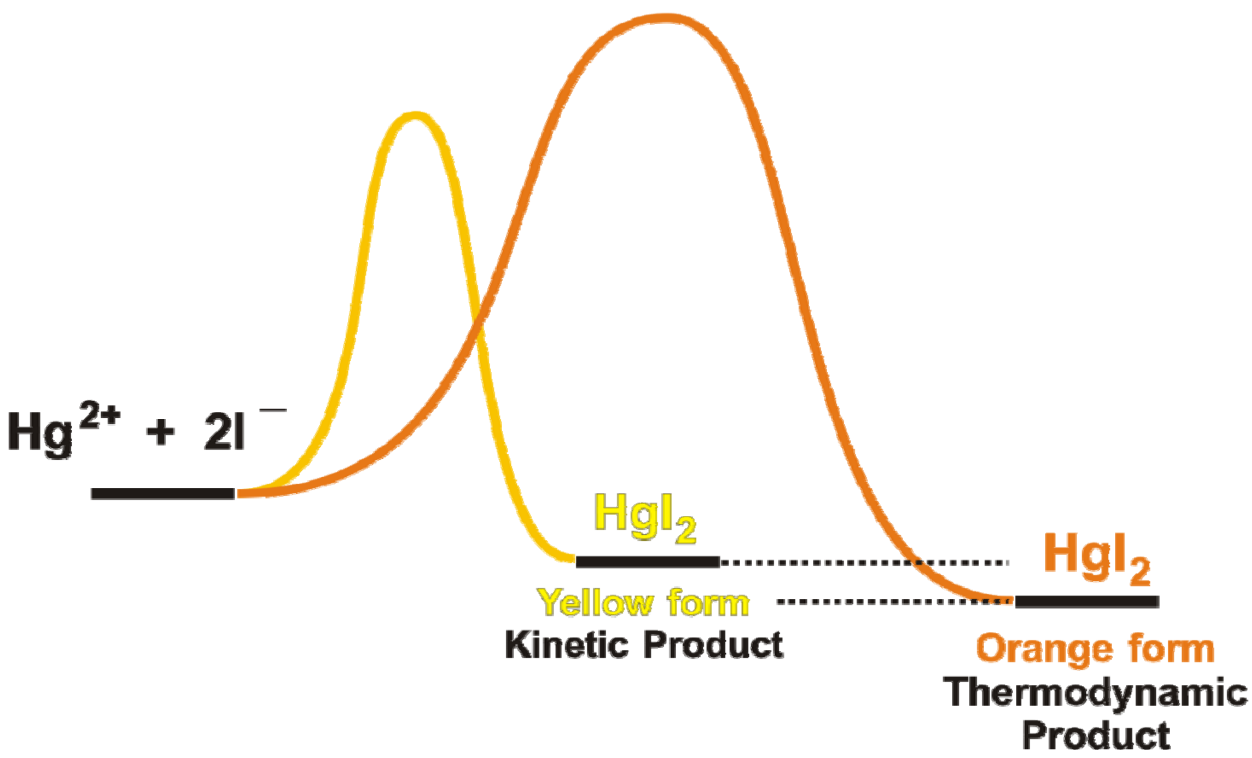
$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

If we add 5 g more NaCl(*s*) to this solution, the amount of solid NaCl in the container will increase by 5 g (that is, no additional solid NaCl will dissolve into solution). This does not mean, however that some of the new NaCl that we just added won't dissolve at all. Some of it will dissolve, while some $Na^+(aq)$ + $Cl^-(aq)$ in solution elsewhere will precipitate out! We could follow this by adding radioactive $^{24}Na^{38}Cl$ to the container:



Demonstration:





Law of Mass Action

One can set up a general mathematical expression to describe the following chemical equilibria:

$$wA + xB \rightleftharpoons yC + zD$$

$$K_{eq} = \frac{[C]^y [D]^z}{[A]^w [B]^x} \qquad \begin{matrix} \textit{products} \\ \textit{reactants} \end{matrix}$$

K_{eq} is called the equilibrium constant

The equilibrium expression for the Haber process reaction would be written as:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad \begin{matrix} \textit{products} \\ \textit{reactants} \end{matrix}$$

Consider, for example, the equilibrium between $N_2O_4(g)$ and $NO_2(g)$:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

Listed below is experimental data giving initial concentrations for $N_2O_4(g)$ and $NO_2(g)$. After some time the reaction reaches equilibrium and the concentrations listed.

Initial		@ Equilibrium		
N_2O_4	NO_2	N_2O_4	NO_2	K_{eq}
0.00	0.02	0.0014	0.017	0.21
0.00	0.03	0.0028	0.024	0.21
0.00	0.04	0.0045	0.031	0.21
0.02	0.00	0.0045	0.031	0.21

Note how K_{eq} is the same regardless of the initial concentrations. This is why it is called the equilibrium constant.

Some Features of Equilibrium Constants

- ✓ K_{eq} usually depends on temperature
- ✓ If one reverses the way a reaction is written the new K_{eq} is the inverse of the original value:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$$

$$K_{eq} = \frac{[H_2O]}{[H_2]\,[O_2]^{1/2}} = 10 \quad \text{(@ high temp)}$$

Reversing the above rxn we now write:

$$H_2O(g) \rightleftharpoons H_2(g) + \tfrac{1}{2}O_2(g)$$

$$K_{eq}^{*} = \frac{[H_2]\,[O_2]^{1/2}}{[H_2O]} = 0.1 = \frac{1}{K_{eq}}$$

- ✓ Multiplying a reaction by a constant factor results in raising K_{eq} to that power:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

$$K_{eq}^{\#} = \frac{[H_2O]^2}{[H_2]^2[O_2]} = 100 \quad \text{(@ high temp)}$$

Equilibrium constants have a number of very important functions:

1) **whether a rxn will be spontaneous under a given set of conditions (equilibrium constants are directly related to ΔG – Gibbs Free Energy, see end of this chapter)**

2) **in which direction a reaction is going to proceed to reach equilibrium**

3) **allow us to calculate the concentrations of products and reactants at equilibrium**

Qualitatively, the magnitude of K_{eq} should immediately tell you in what direction a reaction is going to proceed and how far it will go before reaching equilibrium. For example:

$K_{eq} >> 1$ **reaction will go mainly to products**

$K_{eq} \sim 1$ **reaction will produce roughly equal amounts of product and reactant**

$K_{eq} << 1$ **reaction will go mainly to reactants**

Problem: Will the following equilibria proceed mainly to products, reactants or produce an approximately equal amount of both?

a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_{eq} = 0.001$

b) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_{eq} = 2$

c) $2HBr(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + Br_2(g)$ $K_{eq} = 10^4$

d) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $K_{eq} = 10^{-28}$

e) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_{eq} = 1$

f) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ $K_{eq} = 10^{44}$

g) $PCl_3(sol) + Cl_2(sol) \rightleftharpoons PCl_5(sol)$ $K_{eq} = 0.1$

h) $2HCl(g) + Br_2(g) \rightleftharpoons 2HBr(g) + Cl_2(g)$ $K_{eq} = 10^{-4}$

Units on K_{eq}

There are typically no units on equilibrium constants. This is because one is formally supposed to use the activities of compounds instead of their concentrations. The activity of a compound in an ideal mixture is the ratio of its concentration (or partial pressure) to a standard concentration (or pressure). Since the activity is defined as a ratio, the units cancel out.

Despite the fact that we should use dimensionless activities, most chemists still refer to equilibrium concentrations in terms of *M* or pressure units (atm).

One does need to watch out when one is working with gases. An equilibrium constant calculated with gas pressures (atm is the standard unit for gases) will not have the same numerical value as one calculated using molarity values if there are different # of gas molecules on each side of the equilibrium. This is because of the relationship between pressure and molarity as defined by the ideal gas law.

Chemists use various subscripts on the equilibrium constant K to indicate different types of equilibria: K_p = gases (pressure), K_c = solutions (molarity), K_a = acids, K_b = bases, K_{sp} = solubility product (slightly soluble solids).

Reaction Quotient

If a reaction is at equilibrium, then the equilibrium relationship will hold true:

$$wA + xB \rightleftharpoons yC + zD$$

$$K_{eq} = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

But, what if one is *NOT* at equilibrium? Then we find that the equilibrium expression is redefined as the reaction quotient, Q:

$$K_{eq} \neq \frac{[C]^y [D]^z}{[A]^w [B]^x} = Q$$

this will not be equal to K_{eq} if the reaction is not at equilibrium

when this occurs, the equilibrium expression is defined as being equal to Q, the Reaction Quotient

By comparing Q to K_{eq}, one can tell in which direction a reaction will go to reach a state of equilibrium:

$$wA + xB \rightleftharpoons yC + zD$$

More products?

$$K_{eq} \stackrel{?}{=} \frac{[C]^y [D]^z}{[A]^w [B]^x} = Q$$

More reactants?

$Q > K_{eq}$ **reverse reaction will be spontaneous**

$Q = K_{eq}$ **reaction @ equilibrium**

$Q < K_{eq}$ **forward reaction will be spontaneous**

EXAMPLES:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

$$\frac{[CO][H_2O]}{[CO_2][H_2]} = K_{eq} = 4.4$$

If the initial concentrations of all species are 1 M, which way will the reaction proceed to reach equilibrium?

$$\frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{(1)\,(1)}{(1)\,(1)} = 1 = Q$$

$$K_{eq} = 4.4$$

$$Q = 1$$

$Q < K_{eq}$ } ***therefore, the rxn will go FORWARD to reach equilibrium***

What if we *increase* the [CO] concentration to 10 M?

$$\frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{(10)\,(1)}{(1)\,(1)} = 10 = Q$$

$$K_{eq} = 4.4$$

$$Q = 10$$

$Q > K_{eq}$ } ***therefore, the rxn will go BACKWARD to reach equilibrium***

If you are ever given a problem where the product and reactant concentrations are all non-zero, you *MUST* calculate Q and compare it to K_{eq} in order to figure out which way the reaction has to go to reach equilibrium.

DANGER!! Common mistake!!

Problem: Are the following rxns @ equilibrium? If not, which way must they proceed to reach a state of equilibrium?

a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\quad K_{eq} = 1$

5M $\quad$ 1M $\quad$ 5M

b) $CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\quad K_{eq} = 4$

1M $\quad$ 2M $\quad$ 2M $\quad$ 3M

c) $Br_2(g) + I_2(g) \rightleftharpoons 2BrI(g)$ $\quad K_{eq} = 1 \times 10^{-4}$

0.2 M $\quad$ 0.2 M $\quad$ 0.1 M

d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\quad K_{eq} = 9$

2 M $\quad$ 0.0001 M $\quad$ 2 M

Numerical Problems -- Using K_{eq}

EXAMPLE: **Consider the following rxn. The initial concentrations are $[I_2] = [H_2] = 2M$, $[HI] = 0M$, and $K_{eq} = 16$. What will be the various concentrations when the reaction reaches equilibrium?**

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

Step 1: ***Write out your initial and @ equilibrium conditions:***

Initial cond: $[I_2] = [H_2] = 2M$

$[HI] = 0M$

note that since [HI] = 0M, the reaction must proceed to the right to make more product. Thus, for this example, we will lose reactants and gain product. What we don't know is how much. Therefore, we will setup an algebraic expression to solve for **x*****, the amount of product being produced and the amounts of reactant that we are losing. It is CRITICAL to remember to multiply*** **x** ***by the appropriate coefficient from the balanced chemical equation.***

@ Equilibrium:

$[I_2] = [H_2]$ = (initial conc.) – (coefficent)(x)

= 2 – x

[HI] = (initial conc.) + (coefficent)(x)

= 0 + 2x

= 2x

DANGER!! Common mistake!!

Step 2: ***Write out your equilibrium expression:***

$$K_{eq} = \frac{[HI]^2}{[H_2]\,[I_2]} = 16$$

now substitute in the @equilibrium conditions:

$$\frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(2x)^2}{(2-x)\,(2-x)} = 16$$

now solve for x:

$$\frac{(2x)^2}{(2-x)\,(2-x)} = \frac{(2x)^2}{(2-x)^2} = 16$$

DANGER!!
Common mistake!!

make sure that you don't miss common algebraic simplifications!!

take the square root of each side:

$$\sqrt{\frac{(2x)^2}{(2-x)^2}} = \sqrt{16} \longrightarrow \frac{(2x)}{(2-x)} = 4$$

$$2x = (4)\,(2-x) \longrightarrow 2x = 8 - 4x$$

$$6x = 8 \longrightarrow x = 8/6 \qquad x = 1.33$$

Step 3: ***Substitute the value for x that you solved back into the equilibrium conditions that you wrote out in Step 1 above:***

@ Equilbrium: $[I_2] = [H_2] = 2 - x = 2 - 1.33 = 0.66\ M$

$[HI] = 2x = 2.66\ M$

$[I_2] = [H_2] = 0.66\ M$
$[HI] = 2.66\ M$

Step 4: ***Substitute the equilibrium concentrations you just found back into the equilibrium expression to see if you calculate the correct value for K_{eq}:***

$$K_{eq} = \frac{[HI]^2}{[H_2]\,[I_2]} = 16$$

substitute in the calculated equilibrium concentrations and see if you get K_{eq}

$$\frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(2.66)^2}{(0.66)\,(0.66)} = 16$$

Step 5: ***Carefully read the question and make sure that you are picking the right answer. Note that what you solve for x may <u>not</u> be the answer (make sure you do Step 3!)!!***

DANGER!! Common mistake!!

Problem:

Starting with $[CO_2]$ = 2 M, $[H_2]$ = 2 M, [CO] = 0 M and $[H_2O]$ = 0 M, what will be the various concentrations @ equilibrium. K_{eq} = 9.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

More Difficult *EXAMPLE*: Calculate K_{eq} for the following reaction. Initial concentrations are: $[SO_2]$ = 4 M, $[O_2]$ = 4 M, $[SO_3]$ = 6 M. At equilibrium $[SO_2]$ = 3 M.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Solution:

This is really just a stoichiometry problem. Given the initial concentrations and a single equilibrium concentration (along with some algebra) one can solve for the other equilibrium concentrations. Once you have obtained all the equilibrium concentrations, one can put them into the equilibrium expression to solve for K_{eq}.

First one must figure out which way the reaction is going to go in order to reach equilibrium. We can't use the *Reaction Quotient*, *Q*, because we don't know K_{eq}. We do, however, have our initial and one final equilibrium condition to tell us which way the reaction will shift: initial $[SO_2]$ = 4 M, @ equilib $[SO_2]$ = 3 M. So we are losing $[SO_2]$, therefore, the reaction will go to make more product and to lose reactant.

Now we can setup and solve for the other equilib values:

initial:	4	4	6
	$2SO_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2SO_3(g)$
@ equilib:	4-2x	4-x	6+2x

Normally we would substitute our x values into the equilibrium expression and solve for x. Here, however, we actually *know one of the equilibrium values*:

@ equilib: (given)	3	?	?

So we can let 4-2x = 3 and solve for x:

$$4-2x = 3 \longrightarrow 2x = 1 \longrightarrow x = 0.5$$

Now, substitute x into our @ equilibrium formulas:

@ equilib:	4-2x	4-x	6+2x
	3 M	3.5 M	7 M

Finally, substitute the final values into the equilibrium expression to solve for K_{eq} :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(7)^2}{(3)^2(3.5)} = 1.6$$

Problem:

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Initially we start with [CO] = 10 M and [H_2] = 11 M. When the reaction reaches equilibrium there is 5 M [CH_3OH]. Calculate K_{eq} for this reaction.

As Tough as We Get *EXAMPLE*: Calculate equilibrium concentrations for the following reaction. Initial values are: $[CO_2]$ = 1 M, $[H_2]$ = 2 M, [CO] = 6 M, and $[H_2O]$ = 6 M. K_{eq} = 2.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

Solution:

First we need to determine in which direction the reaction will shift to reach equilibrium because none of the concentrations are zero. To do this we use the *Reaction Quotient*, *Q*, and the initial concentrations:

$$\frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{(6)\,(6)}{(1)\,(2)} = 18 = Q$$

$$K_{eq} = 2$$

$$Q = 18$$

$Q > K_{eq}$ } ***therefore, the rxn will go BACKWARDS to reach equilibrium***

Now we can write out our initial and (most importantly) @ equilibrium values using x's:

Initial cond:	**$[CO_2]$ = 1 M**	**$[H_2]$ = 2 M**
	[CO] = 6 M	**$[H_2O]$ = 6 M**
@ Equilibrium:	**$[CO_2]$ = 1 + x**	**$[H_2]$ = 2 + x**
	[CO] = 6 - x	**$[H_2O]$ = 6 - x**

$$K_{eq} = \frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{(6-x)\,(6-x)}{(1+x)\,(2+x)} = 2$$

$$\frac{(x^2 - 12x + 36)}{(x^2 + 3x + 2)} = 2$$

$$x^2 - 12x + 36 = 2x^2 + 6x + 4$$

$$x^2 + 18x - 32 = 0$$

} *this is a quadratic equation*

solve by using quadratic formula:

$$ax^2 \pm bx \pm c = 0$$

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

$$x = \frac{-18 \pm \sqrt{(18)^2 - 4(-32)}}{2} = \frac{-18 \pm \sqrt{(324) + (128)}}{2}$$

$$x = \frac{-18 \pm \sqrt{452}}{2} = \frac{-18 \pm 21.3}{2} = 1.7 \text{ or } -19.7$$

~~-19.7~~ *physically impossible*

$$x = 1.7$$

Note that x is NOT OUR ANSWER!!!!

DANGER!! Common mistake!!

@ Equilibrium: $[CO_2] = 1 + x$ $[H_2] = 2 + x$
$[CO] = 6 - x$ $[H_2O] = 6 - x$

Substituting in x = 1.7 we can get the equilibrium values:

@ Equilibrium: $[CO_2] = 2.7$ M $[H_2] = 3.7$ M
$[CO] = 4.3$ M $[H_2O] = 4.3$ M

Double-check that these numbers are correct by recalculating K_{eq} **and comparing to the value given to you in the problem:**

$$\frac{[CO][H_2O]}{[CO2][H_2]} = \frac{(4.3)(4.3)}{(2.7)(3.7)} = 1.85 \approx 2$$

You don't get exactly 2.0 due to round-off error (I only carried one decimal point in my calculation)

A Simple EXAMPLE (but looks really hard if you don't think): **If 2 moles of H_2O are placed into a 5L container, what will be the equilibrium concentration of H_2, O_2 and H_2O?**

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \quad K_c = 6.0 \times 10^{-28}$$

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = 6.0 \times 10^{-28}$$

initial cond: $[H_2O]$ = 2.0 moles/5 L = 0.40 M

$[H_2]$ = $[O_2]$ = 0 M

@ equilibrium: $[H_2] = 2x$

$[O_2] = x$

$[H_2O] = 0.40 - 2x$

substituting into our equilibrium expression we get:

$$\frac{[2x]^2[x]}{[0.4 - 2x]^2} = 6.0 \times 10^{-28}$$

$$4x^3 - 24.0 \times 10^{-28}x^2 + 9.6 \times 10^{-28}x - 0.96 \times 10^{-28} = 0$$

But this is a cubic equation!!! Almost impossible for you to solve!!!

OH MY GOD, WHAT DO I DO NOW!!
What is this idiot Professor doing to me!!

HOWEVER, consider the *physical reality* of the situation. K_c = 6.0 x 10^{-28} is *extremely* small, this means that *very little* H_2O will decompose to form H_2 or O_2!! That means that the amount of H_2 or O_2 forming will be *very, very small*. That means that *x* will be *very, very small*. Small enough that we can *ignore* it in the $[H_2O] = 0.40 - 2x$ expression. This considerably simplifies the math:

$$\frac{[2x]^2[x]}{[0.4]^2} = 6.0\times10^{-28}$$

$$\frac{4x^3}{0.16} = 6.0\times10^{-28}$$

$$x^3 = 0.24\times10^{-28}$$

$$x = 2.9\times10^{-10} M$$

Since *x* is indeed *much, much smaller* than 0.40, the approximation was *a very good one*. So our concentrations at equilibrium are:

@ equilibrium: $[H_2]$ = 5.8 x 10^{-10} M
$[O_2]$ = 2.9 x 10^{-10} M
$[H_2O]$ = 0.40 M

Actually, one didn't have to do any calculations for this problem!

Because K_c is so very small, you should know that virtually no products will be produced. Therefore:

@ equilibrium: $[H_2]$ = $[O_2]$ = 0 M
$[H_2O]$ = 0.40 M

For this course and this kind of problem, there isn't much difference between 5.8 x 10^{-10} M and 0 M!!

Heterogeneous Equilibria

So far all the equilibrium examples we have used have involved gases or solutions. What happens if we have other states of matter present -- such as solids or pure liquids?? How do they affect the equilibrium??

It turns out that as long as some solid or liquid is present, the equilibrium will be independent of the amount of that solid or liquid that is present!

EXAMPLE:

$$Br_2(l) \rightleftharpoons Br_2(g)$$

$$K_{eq} = \frac{[Br_2(g)]}{[Br_2(l)]}$$

What is the concentration of $[Br_2(l)]$?

$$M = \frac{\text{moles of } Br_2(l)}{\text{volume}}$$

The density of $Br_2(l)$ is 3.12 g/mL, so the # of moles is:

 # moles = (3.12 g/mL) / (159.8 g/mol)

 # moles = 0.0195

The M can now be calculated for liquid bromine:

$$M = \frac{\text{moles of } Br_2(l)}{\text{volume}} = \frac{0.0195 \text{ moles of } Br_2(l)}{0.001 \text{ L}}$$

M = 19.5 mol/L

Now we can look at our equilibrium expression:

$$K_{eq} = \frac{[Br_2(g)]}{[Br_2(l)]} = \frac{[Br_2(g)]}{19.5 \text{ M}}$$

note that this is a constant concentration -- it is independent of the amount of liquid bromine present, as long as some is there!!

Because the $[Br_2(l)]$ concentration is a constant value we can multiply the equilibrium expression by that amount and incorporate it into K_{eq} :

$$(K_{eq})\,(19.5 \text{ M}) = [Br_2(g)]$$

$$K^{*}_{eq} = [Br_2(g)]$$

DANGER!! VERY Common mistake!!

Therefore, one should *NOT* include *solids* or *pure liquids* in equilibrium expressions!!

A more technical, but simpler explaination is that we are actually using activities instead of concentrations (see section on units), and the activity of a solid or pure liquid is defined as being = 1. Thus it factors out of the equilibrium expression.

Problem: **Write out equilibrium expressions for the following reactions:**

a) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

b) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

c) $Br_2(l) + Ni(CO)_4(l) \rightleftharpoons NiBr_2(s) + 4CO(g)$

d) $H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$

e) $HCl(g) + H_2O(l) \rightleftharpoons H^+(aq) + Cl^-(aq)$

Numerical Example: What is the equilibrium concentration for $[Ag^+]$ in the following reaction:

$$Ag_2(SO_4)\,(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq) \qquad K_{sp} = 4 \times 10^{-9}$$

Answer: K_{sp} refers to equilibria involving *solubility products*, that is, solids that are slightly soluble in water (or other solvents). Note that the reactant in this problem is a solid and, as such, will NOT appear in the final equilibrium expression. We also usually do NOT give the amount of the solid and assume that there is excess present, since only a little bit will dissolve in solution. Otherwise, set it up and solve just like a regular equilibrium problem:

	$Ag_2(SO_4)\,(s)$	$\rightleftharpoons$	$2Ag^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	*excess solid*		0M		0M
@Equilib:	*less excess solid*		2x		x

The equilibrium expression for this rxn is:

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

(the solid Ag_2SO_4 doesn't appear in the equilibrium expression because it is a solid!). Plug in the @equilb values and solve for x:

$[2x]^2[x] = 4 \times 10^{-9}$

$4x^3 = 4 \times 10^{-9}$

$x^3 = 1 \times 10^{-9}$

$x = 1 \times 10^{-3}$

BUT, watch out, x is *NOT* our answer!! → ***DANGER!! Common mistake!!***

$[Ag^+] = 2x$, so $[Ag^+] = 2 \times 10^{-3}$ M.

Problems:

a) What is the equilibrium concentration for OH^- in the following reaction:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = 4 \times 10^{-6}$$

b) What is the equilibrium concentration for Ag^+ for the following system:

$$Ag_3(AsO_4)_3(s) \rightleftharpoons 3Ag^+(aq) + AsO_4^{3-}(aq) \quad K_{sp} = 1 \times 10^{-22}$$

K_p – K_c Relationship

When the number of equivalents of gas phase reactants and products is *not* equal the following relationship relates K_c (concentration in *M*) and K_p (concentration in *pressures - atm*). This is true even if we technically use dimensionless activities due to the relationship between molarity and pressure (even when units are factored out).

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = K_p(RT)^{-\Delta n} \quad \text{-or-} \quad K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$\Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

No gas molecules? Then $\Delta n = 0$.

Equal number of gas molecules on reactant & product side? Then $\Delta n = 0$.

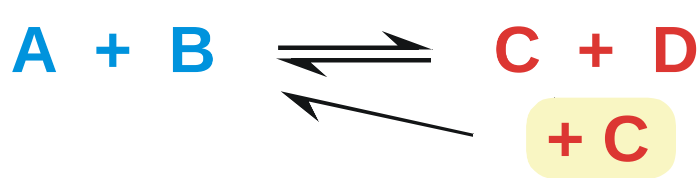
Pressures must be expressed in atmospheres (atm).

Le Chatelier's Principle

When a system in a state of equilibrium is acted upon by some outside stress, the system will, if possible, shift to a new equilibrium position to oppose the effect of the stress.

What do we mean by *"stress"*? Stress means that we are *disturbing* the reaction by: adding or removing reactants or products; increasing or decreasing the temperature; and increasing or decreasing the pressure (if gases are involved). Once we do one of these things, the reaction will (usually) no longer be in equilibrium and will have to shift to make more reactants or products to reattain a state of chemical equilibrium.

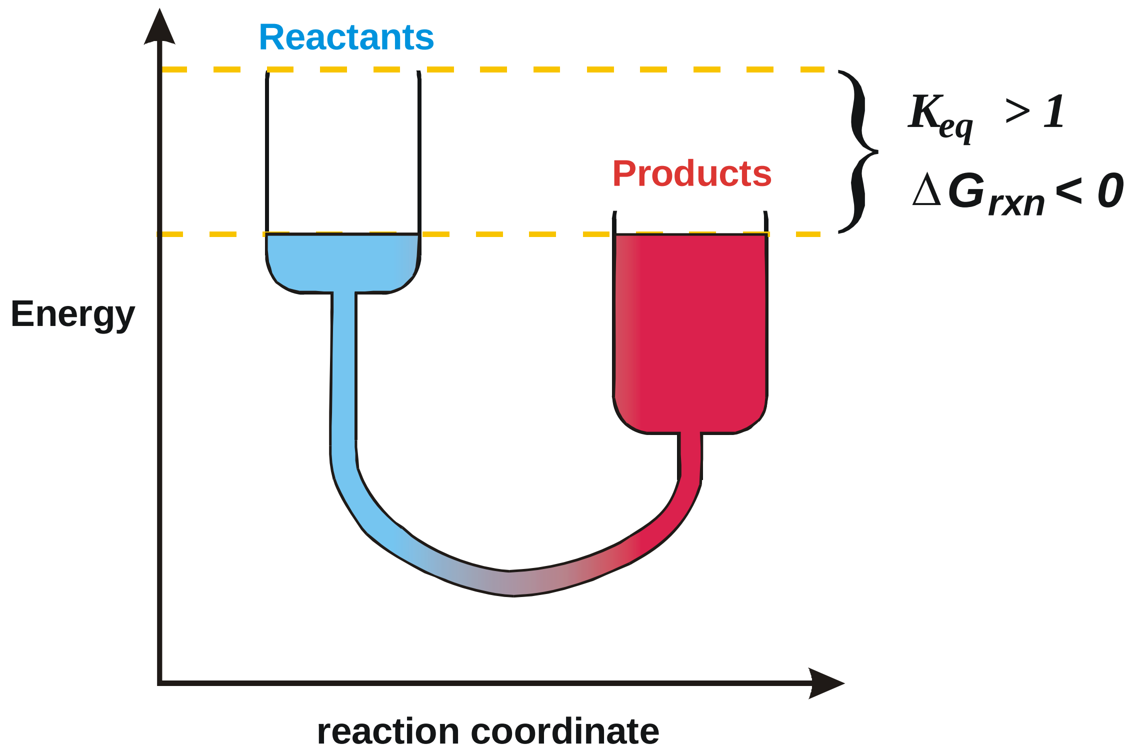
original rxn in equilibrium



but now we have added more product C and there is too much product

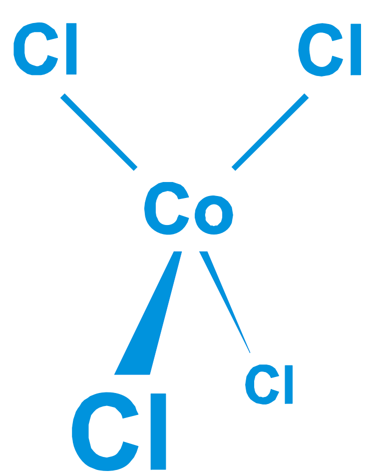
the reaction has to shift backwards to consume some of the products and make more reactants!

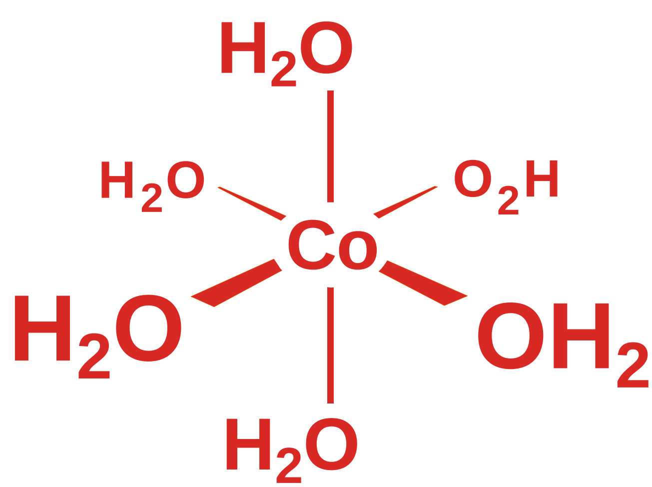
Concept Demonstration:



Chemical Demonstration:

$$CoCl_4^{2-}(sol) + xH_2O \rightleftharpoons Co(H_2O)_6^{2+}(sol) + 4Cl^-(sol)$$





Listed below are how various *"disturbances"* affect equilibria:

1) **Adding *products* (unless one of the products is a solid!) to a reaction will cause the equilibrium to shift back to produce more *reactants*.**

2) **Adding *reactants* (unless one of the reactants is a solid!) to a reaction will cause the equilibrium to shift forward to produce more *products*.**

3) **Removing *reactants* (unless one of the reactants is a solid and as long as there is some left) will cause the equilibrium to shift back to produce more *reactants*.**

4) **Removing *products* (unless one of the products is a solid and as long as there is some left) will cause the equilibrium to shift forward to produce more *products*.**

5) **The effect of temperature on a reaction is dependent on whether the reaction is *exothermic* (ΔH_{rxn} = negative) or *endothermic* (ΔH_{rxn} = positive):**

Exothermic rxn:

$$A + B \rightleftharpoons C + \boxed{\text{heat}}$$

} *heat is one of the products*

a) increasing the temperature (adding heat) will cause the equilibrium to shift back to make more reactants

b) decreasing the temperature (removing heat) will cause the equilibrium to shift forward to make more products

Endothermic rxn:

heat is one of the reactants

$$A + B + \boxed{\text{heat}} \rightleftharpoons C$$

a) increasing the temperature (adding heat) will cause the equilibrium to shift forward to make more products

b) decreasing the temperature (removing heat) will cause the equilibrium to shift back to make more reactants

6) The effect of changing pressure depends on the number of gasous reactants and products present:

a) if there are NO gas phase species present then pressure will have NO effect on the equilibrium (actually, there is an effect at very high pressures -- but we won't worry about this).

b) if there are gas phase species present, but there are the same number of gaseous molecules on each side of the reaction, pressure will have NO effect on the equilibrium.

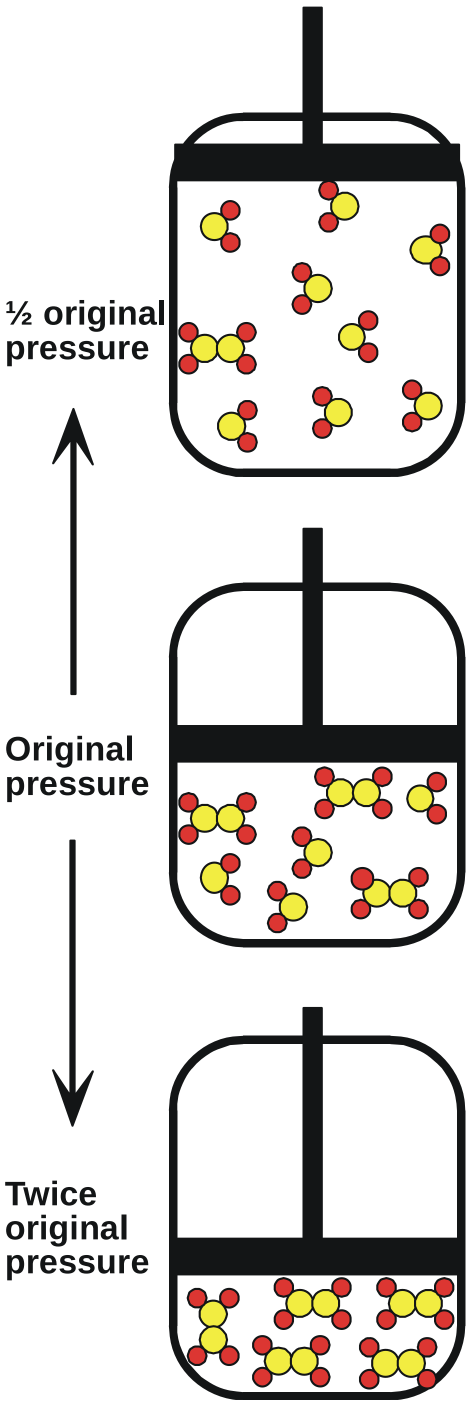
c) if there are different numbers of gas phase species present on the reactant and product sides of the equilibrium, then:

- ***i*) increasing the pressure will favor the side of the equilibrium with the smaller number of gas phase molecules.**
- ***ii*) decreasing the pressure will favor the side of the equilibrium with the larger number of gas phase molecules.**

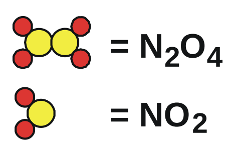
Qualitative EXAMPLE:

Consider the following equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



Note how the N_2O_4 molecules have dissociated in order to produce more NO_2 molecules. These more efficiently fill up the "empty" space present in this system.



Note how the NO_2 molecules have combined in order to produce fewer N_2O_4 molecules. These more efficently save space, which is in short supply in this compressed system.

Mathematical EXAMPLE: **Effect of doubling the pressure (halving the volume) on $N_2O_4(g) \rightleftharpoons 2NO_2(g)$**

original equilib { N_2O_4 (*0.0045 M*) $\rightleftharpoons$ $2NO_2$ (*0.031 M*) $K_{eq} = 0.21$

compress ↓

N_2O_4 (*0.009 M*) $\overset{?}{\rightleftharpoons}$ $2NO_2$ (*0.062 M*) } *is this in equilibrium?*

Calculate *Q* the *reaction quotient* to determine the direction of the reaction to reach equilibrium:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.062)^2}{(0.009)} = 0.427$$

since $Q > K_{eq}$ the rxn has to go *backwards* to reach equilibrium. That means that some of the NO_2 has to disappear.

@ equilibrium: $[N_2O_4] = 0.009 + x$ } **we are gaining N_2O_4**

$[NO_2] = 0.062 - 2x$ } **we are losing NO_2**

substituting $[N_2O_4] = 0.009 + x$ and $[NO_2] = 0.062 - 2x$ into our equilibrium expression we can solve for x:

$$\frac{(0.062 - 2x)^2}{0.009 + x} = 0.21$$

$$4x^2 - 0.458x + 0.0019 = 0$$

[solve using quadratic equation]

$$x = 0.004, 0.106$$

x = 0.106 M is *physically unreasonable* *(that would give us a negative concentration, which is impossible)*, we can forget it.

So x = 0.004 M. Substituting this back into our equilibrium conditions we can find the final equilibrium concentrations:

$[N_2O_4]$ = 0.009 + x = 0.013 M

$[NO_2]$ = 0.062 - 2x = 0.054 M

So the N_2O_4 concentration has increased and the NO_2 concentration has decreased: exactly what one would qualitatively predict from Le Chatilier's principle!!

Problem: **What are the various things that one can do to the following reactions to shift the equilibria to a) favor the reactants; b) favor the products? (you can add or remove products and reactants; change the temperature; change the pressure)**

a) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

$\Delta H_{rxn} = -179$ kJ/mol

b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

c) $Ca^{+2}(aq) + 2Cl^-(aq) \rightleftharpoons CaCl_2(s)$

$\Delta H_{rxn} = +95$ kJ/mol

d) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

e) $Br_2(l) + Ni(CO)_4(l) \rightleftharpoons NiBr_2(s) + 4CO(g)$

f) $H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$

g) $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$

Le Chatelier's Principle II: Common Ion Effect

The common ion effect is Le Chatelier's principle – just under a different name. You will see another variant of this at the end of the Acid/Base chapter when we discuss Buffer solutions.

Consider the following equilibrium:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$$

$$K_{sp} = 1.8 \times 10^{-10}$$

What happens to the $Ag^{+}(aq)$ concentration if we add enough NaCl to raise the $Cl^{-}(aq)$ concentration to 0.1 M?

Qualitatively, of course, from Le Chatelier's principle, adding product (Cl^{-}) to the solution will push the equilibrium backwards to produce more reactant (AgCl(*s*)). This will decrease the free $Ag^{+}(aq)$ concentration in solution. The Na^{+} cations will not have any effect, so we can pretty much ignore them (spectator ions).

In this case the Cl^{-} anion is the *<u>Common Ion</u>* between the NaCl and AgCl.

Let's set this up and mathematically solve for the concentration of Ag^+ after adding 0.1 M Cl^-.

Initial:	*solid*	0	0.1
	$AgCl(s) \rightleftharpoons$	$Ag^+(aq)$ +	$Cl^-(aq)$
@ equilib:	*less solid (-x)*	x	$0.1 + x$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$(x)(x + 0.1) = 1.8 \times 10^{-10}$$

$$x^2 + 0.1x - 1.8 \times 10^{-10} = 0$$

solve via the *quadratic equation* to get:

$$x = 1.8 \times 10^{-9} \quad \text{-- or --} \quad -0.1000000003$$

Physically impossible!!

$$x = [Ag^+] = 1.8 \times 10^{-9}\ M$$

But, there is a simple approximation we can use to make our math a lot easier. *Before* we add any extra Cl^-, let's show that the concentrations of $[Ag^+]$ and $[Cl^-]$ present are very small:

Initial:	*solid*	**0**	**0**
	$AgCl(s) \rightleftharpoons$	$Ag^+(aq)$ +	$Cl^-(aq)$
@ equilib:	*less solid (-x)*	*x*	*x*

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$(x)(x) = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

$$x = \boxed{[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}\ M}$$

Concentrations with no extra Cl- anion added to the solution!

So the Ag^+ and Cl^- concentrations in solution from AgCl(s) are 1.3×10^{-5} M. Le Chatelier's principle tells us that adding more Cl^- will decrease the Ag^+ and Cl^- (*x* values) from the AgCl(s) dissociation even further. Small enough that we can make the approximation that 0.1 + *x* in the original problem is essentially 0.1. This will reduce our *quadratic expression* down to a very simple algebra problem:

Initial:		*solid*	**0**	**0.1**
		$AgCl(s) \rightleftharpoons$	$Ag^{+}(aq)$ +	$Cl^{-}(aq)$
@ equilib:		*less solid (- x)*	*x*	0.1 + *x*

Simplify to just 0.1 because x is very small

$$K_{sp} = [Ag^{+}][Cl^{-}] = 1.8 \times 10^{-10}$$

$$(x)(0.1) = 1.8 \times 10^{-10}$$

Approximation!

divide through by 0.1

$$x = [Ag^{+}] = 1.8 \times 10^{-9}\ M$$

Note that this is the same as what we calculated from the quadratic equation ($[Ag^{+}] = 1.8 \times 10^{-9}$ M). And it is a LOT quicker and easier to calculate!

So using this approximation, when *appropriate*, will save you a lot of time. Typically it is OK to drop *x* in a (# + *x*) or (# – *x*) algebraic expression when *x* is going to be more than an order of magnitude smaller than the # it is being added or subtracted to *AND* it will simplify the algebra.

You will see similar approximations a lot in Acids & Bases for *weak* acid and base equilibrium calculations.

Problem: **What is the concentration of Ag^+ in a 0.01 M K_2SO_4 solution to which excess $Ag_2(SO_4)$ is added. K_{sp} ($Ag_2(SO_4)$) = 4 x 10^{-9}**

Initial:

$$Ag_2(SO_4)\,(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

@Equilib:

Problem: **What is the concentration of H^+ in a 0.1 M acetic acid (HOAc) solution to which 0.1 M Na^+OAc^- is added. K_{eq} (HOAc) = 2 x 10^{-5}**

	HOAc(aq)	⇌	H^+(*aq*)	+	OAc^-(*aq*)
Initial:	0.1		0		0.1
@Equilib:	0.1 – x		x		0.1 + x

Note: This is called a Buffer Solution (see Acids/Bases)

ΔG^o & the Equilibrium Constant

As I've mentioned during the first part of this chapter, the equilibrium constant is directly related to the Gibbs Free Energy, ΔG.

ΔG^o = negative ⟶ $K_{eq} > 1$ (spontaneous)

ΔG^o = zero ⟶ $K_{eq} = 1$ (rare)

ΔG^o = positive ⟶ $K_{eq} < 1$ (non-spontaneous)

The mathematical relationship for calculating ΔG^o, given K_{eq} is:

$$\Delta G^o = -RT \ln K_{eq}$$

R = 8.314 J/K (gas constant) T = Temp in ^{o}K

Given the value of ΔG^o, we can rearrange the above equation to solve for K_{eq}:

$$K_{eq} = e^{-(\Delta G^o/RT)}$$

Thus, given ΔG^o (or ΔH^o and ΔS^o) we can calculate K_{eq} at a given temperature. Similarly, given K_{eq}, we can calculate ΔG^o.

ΔG^o vs. ΔG: Standard vs. Non-Standard Conditions

Remember that the º ("not") on ΔG^o indicates that the numerical value of ΔG^o is based on the reaction at standard conditions (1 M solution concentration, 1 atm gas pressure). Temperature is NOT part of standard conditions!

As soon as one has a concentration different than 1 M or 1 atm pressure, the º "not" goes away and one has ΔG.

Consider the reaction:

Initial:	**1 atm**	**1 atm**	**1 atm**

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$\Delta G^o_{rxn} = -142 \text{ kJ/mol}$$

The ΔG^o_{rxn} of –142 kJ/mol is for when each gas is present with a concentration of 1 atm. This indicates that the reaction under these conditions will proceed to make products (spontaneous).

As the reactants start reacting, however, their concentrations decrease (SO_2 twice as fast as O_2) and ΔG^o turns into ΔG and becomes less negative.

When ΔG = 0 the reaction has reached equilibrium.

Example: **A reaction has a ΔG^o value of –40 KJ/mol at 25°C. What is the K_{eq} for this reaction?**

First convert the temperature from °C to K:

Temp (K) = 25°C + 273 = 298 K

Now we can use the formula for calculating K_{eq}:

$$K_{eq} = e^{-(\Delta G^o / RT)}$$

Don't forget to carry along the sign on ΔG°

$$K_{eq} = e^{-((-40000\ J/mol) / (8.314\ J/mol\ K)(298K))}$$

Important Note: **R the gas constant has units of J/molK, while we usually express ΔG° in KJ/mol. The units must match!!! The easiest thing is to multiply the ΔG° value in KJ/mol by 1000 to give J/mol.**

DANGER!! Common mistake!!

$$K_{eq} = e^{(16.14)}$$

$$K_{eq} = 1.02 \times 10^7$$

The negative ΔG^o represents a *spontaneous* reaction. See how this converts over to a large positive K_{eq} value, indicating that the reaction goes mainly to products. Note also how there are no units when you calculate K_{eq} this way.

Example: **A reaction has a K_{eq} value of 0.01 at 25°C. What is ΔG^{o} for this reaction?**

First convert the temperature from °C to K:

Temp (K) = 25° + 273 = 298 K

Now we can use the formula for calculating ΔG^{o}:

$$\Delta G^{o} = -RT \ln K_{eq}$$

$$\Delta G^{o} = -(8.314 \text{ J/mol K})(298\text{K}) \ln(0.01)$$

$$\Delta G^{o} = -(2477 \text{ J/mol})(-4.6)$$

$$\Delta G^{o} = +11{,}394 \text{ J/mol} \quad \text{-- or --} \quad \boxed{+11.4 \text{ KJ/mol}}$$

Don't forget to convert J/mol to KJ/mol for the ΔG^{o} value!!

DANGER!! Common mistake!!

Problem: **A reaction has a K_{eq} value of 10 at 25°C. What is ΔG^o for this reaction?**

Catalysts

Catalyst: **a material that speeds up the *RATE* of a reaction without being consumed in the reaction.**

A catalyst will *NOT* change an equilibrium, only the speed (rate) at which equilibrium is reached!

Remember that equilibrium is directly related to thermodynamics. Catalysts never affect the thermodynamics of a reaction. They only lower the energy of activation (kinetics) of a reaction.

Chemical Demonstration:

Oscillating Iodine Reaction