

## Lecture Notes 5: Chemical Equilibrium

Chemical equilibrium is an important concept. It touches on what we will spend most of the rest of the semester dealing with. However, the basic concepts are universal such that if you can grasp the key ideas you see how they will apply over and over again in different situations. In many ways, you already have seen the key ideas look a physical equilibrium but I will try to emphasize those concepts again. Along with what is unique to chemical equilibria (the plural of equilibrium).

Why should we care?

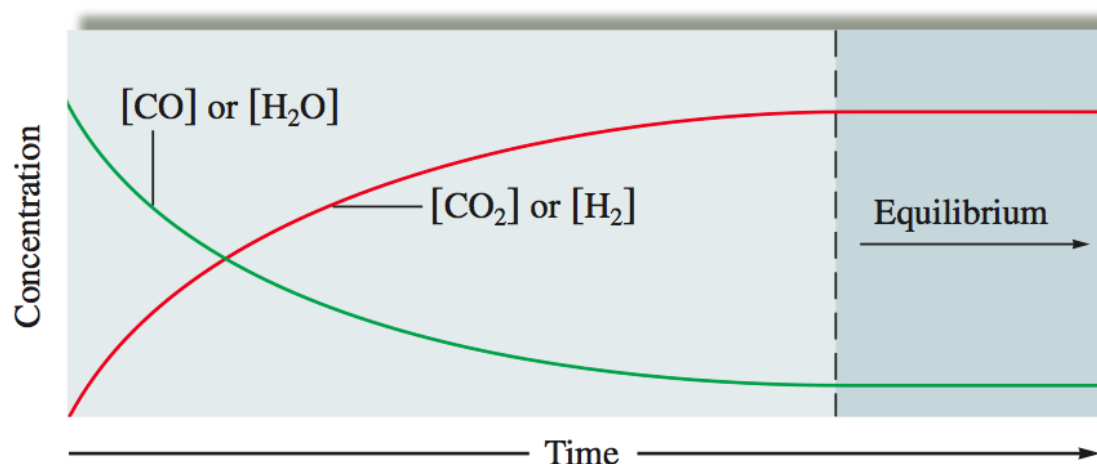
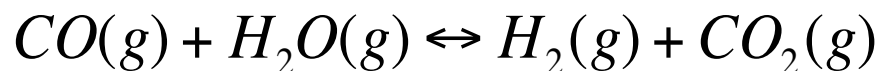
At its heart, the idea of equilibria is predictive. That is because it is derived from thermodynamics which is predictive. If I mix this and that can I make this other thing? It tells us the possibilities of chemical reactions.

Moreover, if we have a system at equilibrium we can easily predict how it will react to changes or “stresses” that we apply. What will happen if I add more of this? What will happen if I compress the system to increase the pressure? What will happen at a higher temperature?

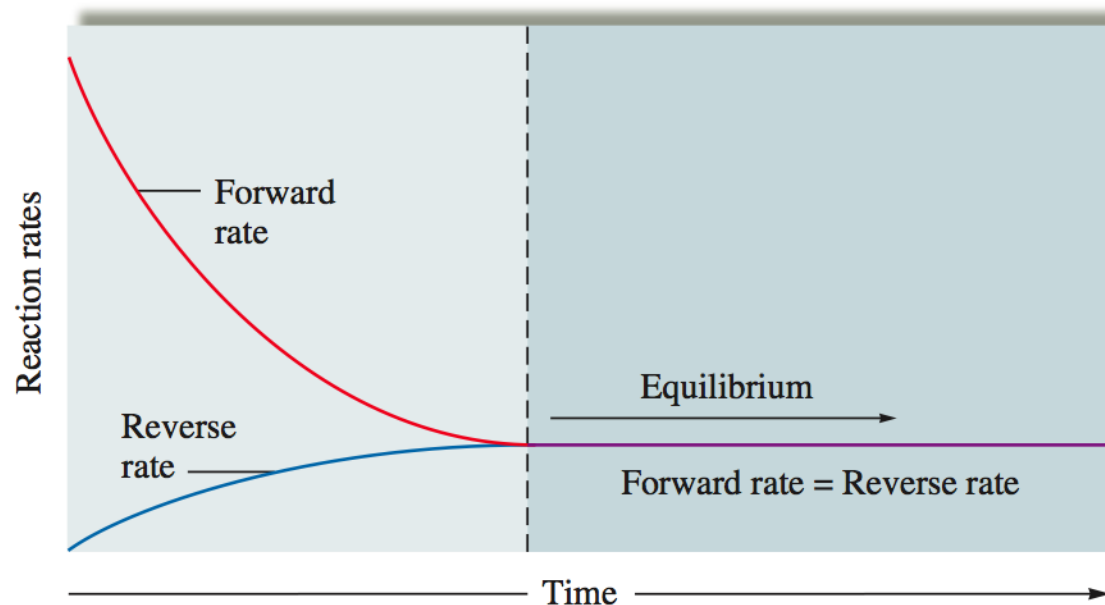
Finally, with the help of our knowledge that matter is composed of atoms and reactions are governed by balanced equations, equilibrium ideas lead to quantified measures of reactions.

## Equilibrium happens

Let's look at what happens during a reaction that is approaching chemical equilibrium. For my example, we can look at the reaction of carbonmonoxide and water to make hydrogen and carbondioxide.



As the reaction proceeds the concentrations of the reactants CO and H<sub>2</sub>O drop while the concentrations of the CO<sub>2</sub> and H<sub>2</sub> rise. While you may have in the past viewed all reactions as having “gone to completion”. This is not always the case. In fact, with the except of some heterogeneous reactions, technically they will never go absolutely 100% to completion. In many cases they don't even get close. Instead, at somepoint the concentrations level off and stop changing. Why is this? Has the chemistry stopped? In a sense it has as the net concentrations have stopped changing. However, the situation is very dynamic. Rather than all chemistry stopping, what has occurred is that the forward and backward chemical reactions are now proceeding at the same rate. This is dynamic equilibrium. This is seen in the graph on the next page that shows the rates as a function of time.



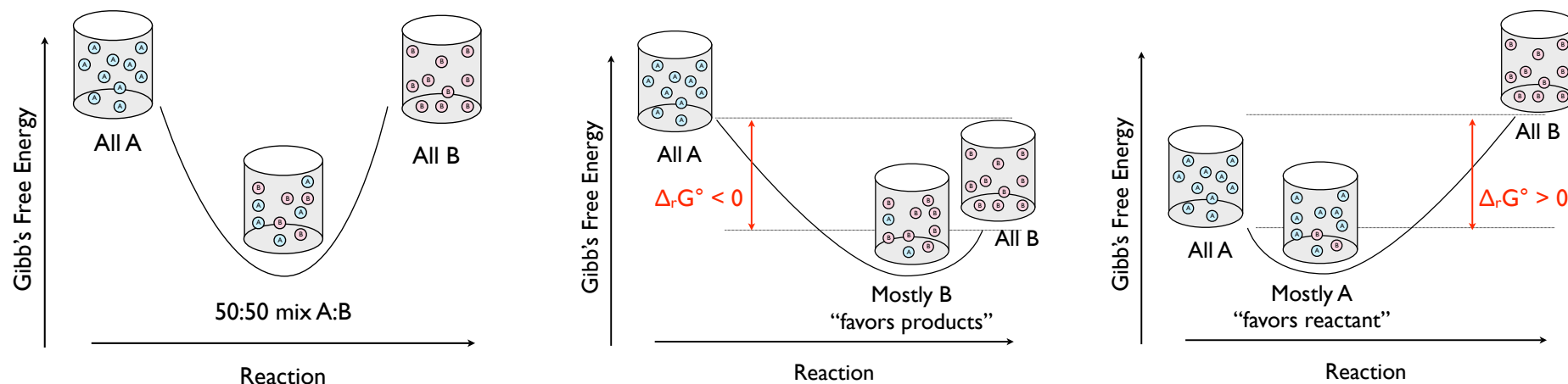
This graph assumes the previous reaction in which the initial concentrations are all reactant and the products are zero. When the reaction starts the forward rate is the fastest. It drops with time as the reactant concentrations are dropping. Also, at time = zero, the backward reaction is zero since there is nothing to react. However, as the products form, some of them react backward. The rate of the backward reaction increases until finally the forward and backward rates are equal. This is when we have reached equilibrium.

Key idea: At equilibrium we have a fixed ratio of the concentrations. We'll see more about this later.

## Free Energy and Equilibrium

First, what is happening with equilibrium? When you put a bunch of molecules together they will “react” in such a way to lower their free energy. One of the easiest ways to look at this is to imagine a situations in which we have only two molecules A and B. By chance these two molecules have identical free energies. If this is the case then the standard free energy of reaction  $\Delta_r G^\circ = 0$ . On this basis we would predict that A and B have identical stabilities? So what will happen if I start out with a system of pure A? Will any B form? What if everything is B? What about mixtures?

Let's look at a plot of free energy as a function of the reaction



The case where  $\Delta_r G^\circ = 0$  is on the left. The lowest free energy state is the state with equal number of molecules of A & B. This is the state with the highest entropy. Neither pure state has any entropy from mixing. Thus the even though A and B have identical free energies, the lowest free energy is in the 50/50 mixture. Higher entropy leads to lower free energy ( $G = H - TS$ ). So the equilibrium mixture will be right in the middle.

What happens if one side is lower in free energy. For example, let's say B is more stable than A. Then  $\Delta_r G^\circ < 0$ . Then the equilibrium point will be shifted from the middle over towards the product side. How much it depends on how the magnitude of  $\Delta_r G^\circ$ . If this is a very large negative number then the equilibrium point will be very close to the "goes to completion" side. If it is negative but not that big, then the equilibrium point will be somewhere between all the way and the 50/50 point. For these reactions, we say the "products are favored" since at equilibrium we have more products than reactants. This is to be expected since the products are more stable (lower free energy).

Similarly, when the reactants are more stable than the products  $\Delta_r G^\circ > 0$ , the equilibrium "favors the reactants" and we have mostly reactants at equilibrium. The larger  $\Delta_r G^\circ$  the closer to all reactants the equilibrium point will be.

How big is big? A good rule of thumb is that  $\Delta_r G^\circ$  which are larger than approximately  $10 \text{ kJ mol}^{-1}$  (either positive or negative) are close to being 100% reactant or product. However, there are many cases in which we are worried about very small fractions reacting. Acid/base chemistry is full of examples where very small amount of material reacting that have very large consequences.

How do we describe that point at the bottom of the free energy curve that where we end up at equilibrium?

You notice for  $\Delta_r G > 0$  we are on the "reactant" side, for  $\Delta_r G < 0$  we are on "product side", and for  $\Delta_r G = 0$  we are right in the middle. How do we quantify where the reaction comes to equilibrium?

It turns out that this point is described by a ratio of the concentrations or partial pressures of the different chemical compounds in the reaction. Specifically we define an equilibrium constant that is essentially the concentration of the product molecules divided by the concentration of the reactant molecules. This constant gets the symbol,  $K$ . Therefore for  $\Delta_r G > 0$  we "favor" the reactants. This means in essence more reactants than products and our equilibrium constant  $K$  will be less than one. When  $\Delta_r G < 0$  the reaction will favor the products. More products than reactant and  $K > 1$ . For the case of  $\Delta_r G = 0$ , products and reactants are the same and  $K = 1$ .

So what is K and how do we find it?

K is related to the balanced equation we write for our reaction. Technically it tells us about how the free energy is minimized relative to the standard states of the reactants and products. More on this later. We want to think of it as a ratio of concentrations.

Generically the equilibrium constant for some reaction



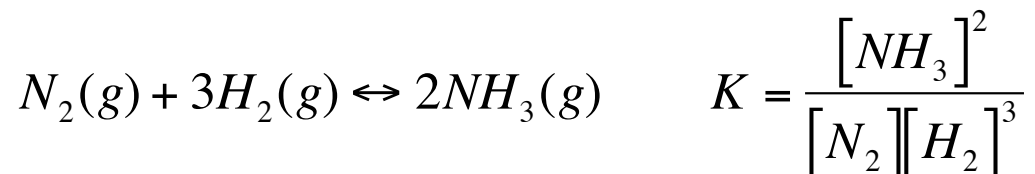
Where A & B are reactant molecules and C & D are product molecules. The stoichiometric coefficients a, b, c, and d are the numbers in the balanced equation that relate the ratios of the numbers of molecules in the reaction.

For this reaction the equilibrium constant is the concentration of the products raised to the power of their stoichiometric coefficient divided by the concentration of the reactants raised to the power of their stoichiometric coefficients.

Thus for the reaction given

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

Where the brackets [ ] denote the concentration of a particular species  
So for the following reaction



Let's look at this particular example. Below is a chart that shows several initial starting conditions for mixtures of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ . You note that at equilibrium each situation results in different concentrations. However, when all of these concentrations are plugged into the equilibrium constant expression we get the same number. Thus the name, equilibrium constant.

**TABLE 6.1** Results of Three Experiments for the Reaction  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
I	$[\text{N}_2]_0 = 1.000 \text{ M}$ $[\text{H}_2]_0 = 1.000 \text{ M}$ $[\text{NH}_3]_0 = 0$	$[\text{N}_2] = 0.921 \text{ M}$ $[\text{H}_2] = 0.763 \text{ M}$ $[\text{NH}_3] = 0.157 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$
II	$[\text{N}_2]_0 = 0$ $[\text{H}_2]_0 = 0$ $[\text{NH}_3]_0 = 1.000 \text{ M}$	$[\text{N}_2] = 0.399 \text{ M}$ $[\text{H}_2] = 1.197 \text{ M}$ $[\text{NH}_3] = 0.203 \text{ M}$	
III	$[\text{N}_2]_0 = 2.00 \text{ M}$ $[\text{H}_2]_0 = 1.00 \text{ M}$ $[\text{NH}_3]_0 = 3.00 \text{ M}$	$[\text{N}_2] = 2.59 \text{ M}$ $[\text{H}_2] = 2.77 \text{ M}$ $[\text{NH}_3] = 1.82 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$

How do we get K?

Option 1.

We measure it by doing an experiment and finding all the concentration at equilibrium.

Option 2

We calculate it knowing thermodynamics.

K is related to  $\Delta_r G^\circ$ . This is an equation you should keep with you

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

That is the standard free energy change for the reaction is equation to the natural log of the equilibrium constant times the temperature and the ideal gas constant.

From this you can see  $\Delta_r G^\circ > 0$  leads to  $K < 1$ ,  $\Delta_r G^\circ = 0$  give  $K = 1$ , and  $\Delta_r G^\circ < 0$  yields  $K > 1$ .

One key to this is knowing what the standard free energy of the reaction is. This is the free energy of pure products in their standard state minus the free energy of the pure reactants in their standard state. The equilibrium constant is a comparison of the free energy at equilibrium relative to this standard state.



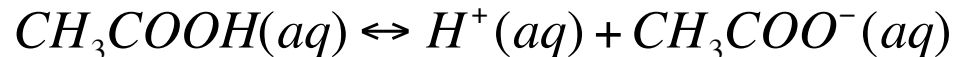
## TIME OUT FOR ACTIVITIES

Since we are comparing things at equilibrium to the “standard state” it is important to ask what is the standard state? It turns out this doesn't have an easy answer as we define different standard states for different substances. As such what goes into the equilibrium constant is different for different situations.

This ratio of equilibrium compared to the standard is called the activity.  
The activity is what we put in the equilibrium constant.

First solutions. We'll do a lot of solution chemistry. For solution we define the standard state of a solute as a solution with a concentration of 1 M. In our equilibrium constant we are always looking at a ratio of the equilibrium concentration to this concentration. However if we use units of Molarity then this subtlety goes away. Thus for ideal solutions the activity is simply the concentration.

Let's look at solution reaction



For this equilibrium constant should be

$$K = \frac{([CH_3COO^-]/[C]_0)([H^+]/[C]_0)}{[CH_3COOH]/[C]_0} = \frac{([CH_3COO^-]/1M)([H^+]/1M)}{[CH_3COOH]/1M} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The concentration are all relative to the standard concentration. Since the standard concentration is 1M, if we use the equilibrium concentration in molarity then we are simply dividing by 1 and the standard concentration all disappear. Who cares then? Units matter. It means that if we want to relate this K to  $\Delta_r G^\circ$  the concentration must be in Molarity.

What about things that aren't solution?

For pressures we have a different standard state.

For pressures the standard state is a pressure of 1 atm (or 1 bar depending on the data). Generally we'll use 1 atm as we are slow to change.

Here again the "thing" we put in the equilibrium constant is measured relative to the standard state. Now rather than concentrations we use partial pressures. Again if we use the correct units (atm) then the standard 1 atm disappears. Thus for ideal gases the activity is just the partial pressure

Take home lesson. For gas reaction if you want to relate  $K$  to  $\Delta_r G^\circ$  you must use pressures in the equilibrium constant and the pressures need to be in units of atm.

Finally, things that aren't mixtures. Pure solid and pure liquids. Here the standard state of the material is the same as the state of the material in the reaction. Its free energy is not changed compared to the standard state (no mixing).

Therefore when we compare it at equilibrium to its free energy in the standard state they are the same.

The activity is one. Thus pure solids and liquids don't seem to enter in to the equilibrium constant. They are there. But since they are always equal to one they don't matter.

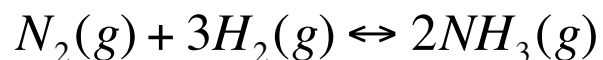
How tell if you are at equilibrium.

We can look at the concentrations or pressures of reactants and products in any given situation and figure out if we are at equilibrium.

To do this, we simply calculate something very much like the equilibrium constant but the activities (concentrations and pressures) that go into the calculation are what we HAVE RIGHT NOW rather than the concentration at equilibrium.

This is called the reaction quotient and it gets the symbol Q.

For example for the reaction



If the right now  $[N_2] = 0.5$  M,  $[H_2] = 2$  M, and  $[NH_3] = 2$  M is the system at equilibrium at a temperature at which  $K = 0.062$ ?

We need to calculate Q. What we have right now. And compare it to K. What we would have at equilibrium

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2)^2}{(.5)(2)^3} = 1$$

$Q > K$ . Therefore this is not equilibrium.

Which direction does the reaction need to “move” to reach equilibrium? Since Q is larger than K this means there are “too many products”. Therefore the reaction will shift back to the reactant side. Remember Q is just like K in that it is products divided by reactants. At equilibrium  $Q = K$ . So if Q is too big the only way to reduce it is to generate more reactants while reducing the products.

$Q > K$  to the reactant side “too many products”

$Q < K$  to the product side “too many reactants”

$Q = K$  you are at equilibrium.