

Chapter 9: Introduction to Chemical Equilibrium

This lecture is outside the confines of the textbook development of chemical equilibrium and is intended as a sweeping introduction to chemical equilibrium (a topic that will engage us for much the rest of the semester.) I hope you will see just how easily equilibrium concepts can be applied to other areas of endeavor in and outside of the sciences. In class today, for example, we will have a house party and see that the same stresses that drive chemical reactions one direction or another, quite logically drive the actions of young adults engaged in an activity I have heard young people call “partying.” Having never “partied” myself, I take it at your word this is an enjoyable exercise.

Some of the big picture concepts that you should appreciate by the end of the lecture:

- Just like thermodynamics, equilibrium theory can tell you about whether a reaction occurs, not by evaluating the flow of energy but rather by following the flow of chemical compounds
- The equilibrium constant, K , is a very simple ratio of stuff on one side of an equation to stuff on the other—it is the mathematical structure used in equilibrium theory to tell you at a glance whether a reaction happened or not.
- Stress is a concept that both chemical reactions and students hate, and both chemical reactions and you respond to it in exactly the same way—you run from it.

Following chemical concentrations to determine if a reaction happens.

Most of you have a prejudiced and incorrect view that a chemical reaction starts with a bunch of reactants you pull off of a shelf that are allowed to react to completion—at completion only product remains. For example, consider this reaction below for the combustion of a hydrogen balloon:

For example:	2H_2	$+ \text{O}_2$	$\rightleftharpoons 2 \text{H}_2\text{O}$
Initial amounts	100	50	0
Final amounts	0	0	100

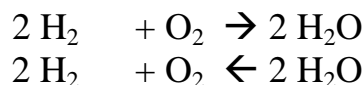
This little bit of fiction even uses the exact ratio of reactants so that when completed, every last bit of reactant is used up (there is no “limiting reagent”. But in fact, this fiction never happens. Not only do we always have stuff “left over” but the reaction **never goes to completion**. Instead **it goes to an equilibrium concentration** in which that amount of H_2 , O_2 and H_2O are together in amounts such that the rate of forward and reverse reactions is equal so that there is no overall change in the system concentrations.

So here is the truth of a reaction:

	2H_2	$+ \text{O}_2$	$\rightleftharpoons 2 \text{H}_2\text{O}$
Initial amounts	100	50	0
equilibrium amounts	2	1	98

What can we say about this final concentration:

- It is at “equilibrium”
- At equilibrium, for every forward reaction
there is a reverse reaction
- The fact that there are a lot more molecules on the left side of the reaction than the reaction would suggest that the reaction “happened” and that ΔG is negative (spontaneous)



No matter where you start, you end up at equilibrium.

It doesn't matter whether we start with all H_2 and O_2 or all H_2O or somewhere in between, the reaction has a driving force toward the equilibrium concentration.

For example, for the starting amounts below, the reaction shifts left to equilibrium:

	2H_2	$+ \text{O}_2$	$\rightleftharpoons 2 \text{H}_2\text{O}$
Initial amounts	0	0	100
Final amounts	2	1	98

Or for example, the reaction starts with some of everything and shifts right to equilibrium:

	2H_2	$+ \text{O}_2$	$\rightleftharpoons 2 \text{H}_2\text{O}$
Initial concentrations	60	30	40
Final concentrations	2	1	98

The equilibrium constant, K —one number tells us everything.

There is a simple math expression that ratios the stuff on the right to the stuff left to give us a single number, the equilibrium constant, which tells us if a reaction happens (goes to the right as written).

For the hydrogen balloon exploding, at equilibrium the amount on the right divided by the amount on the left

$$K = 49 = \frac{[98]}{[1][2]}$$

is the equilibrium constant.

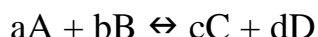
And get this.

If $K > 1$ the reaction “happened” and ΔG is negative
and

if $K < 1$ the reaction “didn’t happen” and ΔG is positive

Generalizing the idea of K to all reactions—the law of mass action

Consider a generic chemical reaction

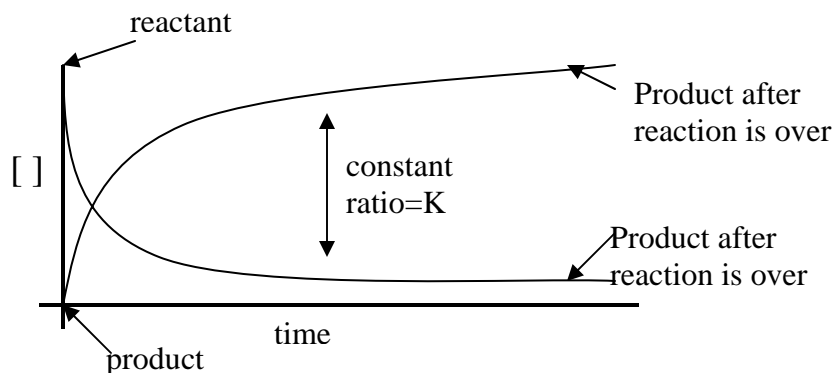


We can always create a quotient, Q , that is a ratio of the compounds on the right divided by the compounds on the left.

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

Things to notice:

- Note the brackets: $[]$ refers to concentration of the compounds in molarity units (moles per liter of solution)—we can also present them as pressures if they are gases
- Note the stoichiometric coefficients (a, b, c, d) that are exponents in Q simply shorthand to indicate that if you have two of the same compound you can write more easily as a power
- The value of Q changes over the course of a reaction—for example, the examples of Q for the reaction of H_2 and O_2 included $Q = 0$ when there was no H_2O to start, $Q = (40)/((60)(30)) = 0.022$ when we started with some of each substance, and $Q = \text{infinity}$ when we started with all stuff on the right side of the equation $Q = 100/(0)(0)$
- If you were to imagine a plot of reactant and product concentrations as a function of time beginning with all reactant and no product, it might look something like the plot below for a reaction that happened. Note that $Q = 0$ to start and gradually increases over time.



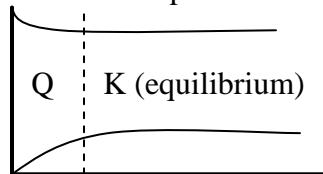
- Finally, note that as Q increases and then levels off at a constant value when the reaction is over. At this point we have a new and exciting special name for the quotient, because $Q \rightarrow K$ which is the equilibrium constant when the rates of the forward and reverse reactions are equal.

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

K and ΔG

Look at two examples of the plot of concentrations versus time to see Case 1 in which the reaction doesn't happen (little change in initial concentration) and Case 2 in which there is a lot of change in concentration. You can see in this that the value of K is related to whether a reaction happens, and thus to the spontaneity, ΔG .

Case 1 – non spontaneous

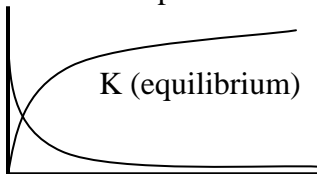


Reactant stays big,
product small, so:

$$K = \frac{\text{prod}}{\text{reac}} = \text{small number } (<1)$$

when ΔG is +

Case 2 – spontaneous



Reactant disappears,
product grows, so:

$$K = \frac{\text{prod}}{\text{reac}} = \text{large number } (>1)$$

when ΔG is -

So is there a quantitative relationship between the equilibrium constant, K , and the thermodynamic equilibrium value, ΔG ? Yes, as we will learn to derive soon,

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

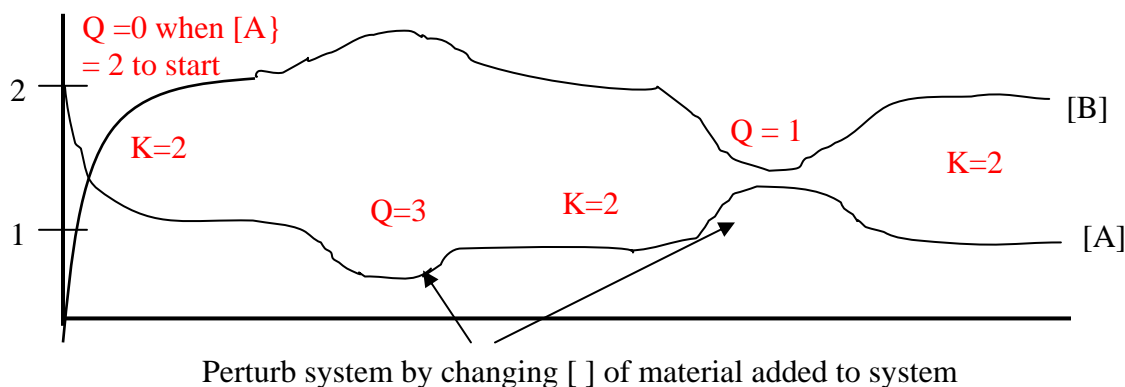
Which is a simple way to relate every value in CH 7 on thermodynamics to every value in CH 9 through 12 on equilibria.

For example: consider $K=10^3$ when $\Delta G = -17.2 \text{ KJ}$ in a spontaneous process
and $K=10^{-5}$ when $\Delta G = +28.7 \text{ KJ}$ for a non-spontaneous process

The relationship between Q and K as stress is applied to a system.

As we will learn, the value of K does not change at constant temperature. However I can do all kinds of things to put stress on a system that will shift the concentration values away from K to a non-equilibrium Q value. Example of ways we put stress on a system are to change P or V or add or remove material from the system. However wants this stress occurs, the system has a driving force that carries it back to K .

Consider the system below for a reaction $A \rightarrow B$ starting with $[A] = 2$, $[B] = 0$ and $K = 2$.



Note that in this reaction the system drives toward equilibrium and is then perturbed two times, always returning to $K = 2$. We will study this idea of stressing a system in some depth when we discuss LeChatelier's Principle.

Equilibrium House Party—your chance to perform equilibrium calculations in real life.

To begin, consider a reaction of one boy + one girl to make a couple.



Let's create a system in a two room house:

singles	couples
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Our rules are to be discrete—let's always put single B and G in the front room and BG (couples) in the bedroom.

Front Room

Bedroom

The reaction quotient, Q, is $Q = \frac{[BG]}{[B][G]}$ (couples in back room) / (singles in the front room)

(Understand the couples in the bedroom are being chaperoned by a TA who makes sure there is only handholding and no kissing!!)

Now on the night in question, it is a balmy 60°C and the K value for the party is $K = 0.5$. We will examine nine different points on the party curve that occur over the course of the evening into the next day. For each case, calculate either a Q or K as a ratio of BG to B and G.

Point 1: the night is young, the first 4B and 4G arrive at party. Calculate Q.

Snoop
Dogg and
Dr.Dre are
on radio

B	G	B
B		G
G	B	G

$$Q = \frac{[BG]}{[B][G]} = \frac{0}{(4)(4)} = 0 \neq K$$

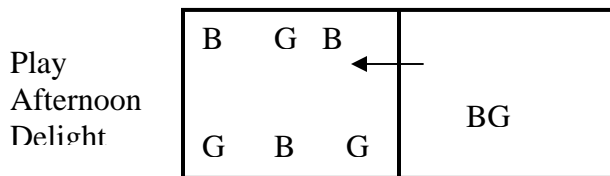
Case 2: Reach equilibrium for the first time with K = 0.5 reached

Marvin
Gaye plays

B	G	→	BG
G	B		BG

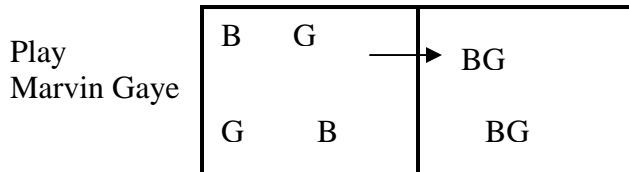
$$K = \frac{(2)}{(2)(2)} = \frac{1}{2}$$

Case 3: System perturbed—almost no one can stand intimacy with the worst song every played on the radio



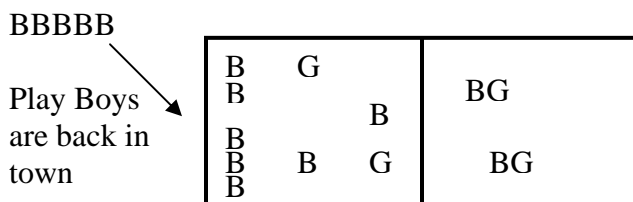
$$Q = \frac{(1)}{(3)(3)} = \frac{1}{9}$$

Case 4: Back to K= 0.5 as young men and women regroove to Marvin



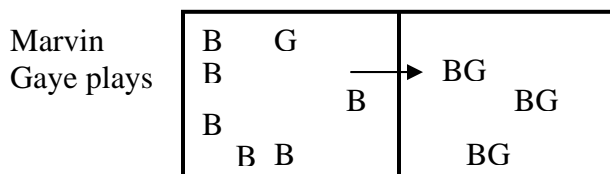
$$K = \frac{(2)}{(2)(2)} = \frac{1}{2}$$

Case 5: Party Crashers. 5 boys show up. Not at equilibrium.



$$Q = \frac{(2)}{(7)(2)} = \frac{1}{7}$$

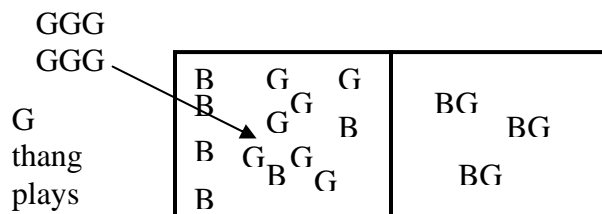
Case 6: New Equilibrium, K still 1/2



$$K = \frac{(3)}{(6)(1)} = \frac{1}{2}$$

Note K can equal 1/2 many ways $\frac{(2)}{(2)(2)}$ and $\frac{(3)}{(6)(1)}$ are examples

Case 7: 6 girls crash the party which move away from equilibrium to a new Q value



$$Q = \frac{(3)}{(6)(7)}$$

Case 8: Everyone gets comfortable and moves back to the equilibrium K still 1/2

Marvin Gaye plays	B	G	G	BG	BG
	B	G		BG	BG
	B		G	BG	BG

$$K = \frac{(6)}{(3)(4)} = \frac{1}{2}$$

Case 9: It is near dawn and has suddenly gotten colder—there is a K=4 because it is colder and everyone feels the need to snuggle.

Let It Snow plays	B			BG	BG	BG
		G		BG	BG	BG
		G		BG	BG	BG

$$K = \frac{(8)}{(2)(1)} = 4$$

Case 10: everyone crashes and wakes up around 4 pm. It is hot out and a new K=1/72 results because everyone is hot and sticky and hasn't showered and feels really cheap and can't believe who they are holding hands with

Summer in the City plays	B	GG	BG
	BB	GG	
	BB	GG	
	B	GG	
	BB	GG	

$$K = \frac{(1)}{(8)(9)} = \frac{1}{72}$$

The End.

It is important to note that this counting game we are playing is exactly the same strategy you use when determining the interplay between Q and K in chemical reactions. Always remember this when you grow hazy on the relationship between the math to calculate K and Q and what is taking place physically in a chemical system. It is just the ratio of the amount of material on one side of a chemical reaction to another.