Lecture 2 on Equilibria: An introduction to RICE calculations

An introduction to how to do equilibrium calculations using the RICE set up will be introduced. This method will be used for the next two months in every conceivable chemical system to calculate system concentrations and K values. Sadly, you will get so used to this kind of calculation, and the approximations that simply its application, that you will not remember the young lasses and lads you were when I first introduced this material. But trust me, no matter how sophisticated you get in working equilibrium calculations, it all is based on the concepts in this lecture.

But first, time out for a big picture reminder that equilibria is just thermodynamics.

$$-nFE° = \Delta G° = -RT\ln K$$

Ch 12   Ch7   Ch 9-11

In comparing these formulas, think of a reaction as falling down a free energy hill, a gradient of energy release or concentration change that drives toward an equilibrium at the bottom of the hill.

$$A \rightleftharpoons B$$
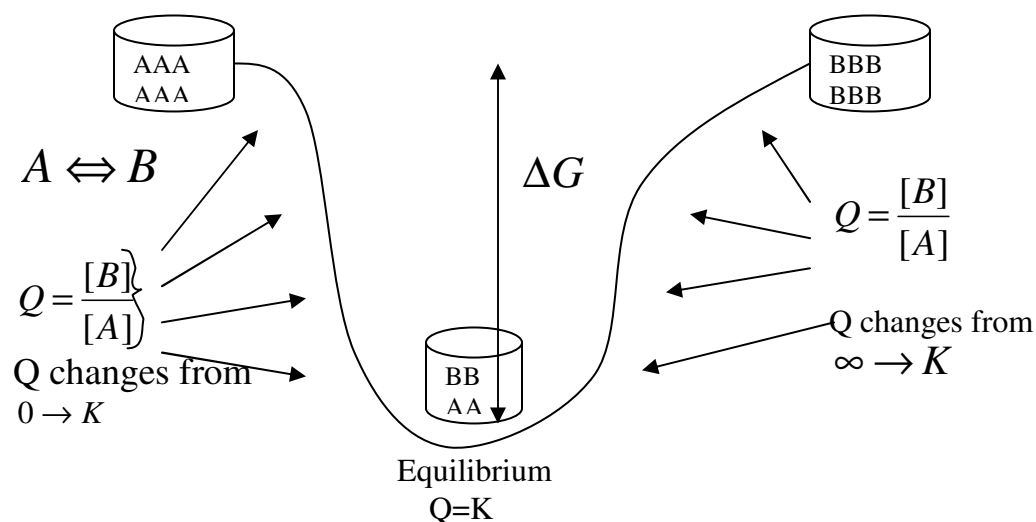
In the picture, note that whether you start with all A or all B, or somewhere in between, you can find a Q value. When Q is less than K, the reaction shifts from left to right. When Q is greater than K, the reaction shifts from right to left Q. When Q reaches K, you are at equilibrium.

Another way to present this concept is by graphing the relative amounts of the reactants, A and B in this case, to show:
- on the left side, the values when A is in excess and Q<K
- in the middle, the time during which Q=K and there is no change in the rate of A or B forming
- on the right side, the values when B is in excess and Q>K
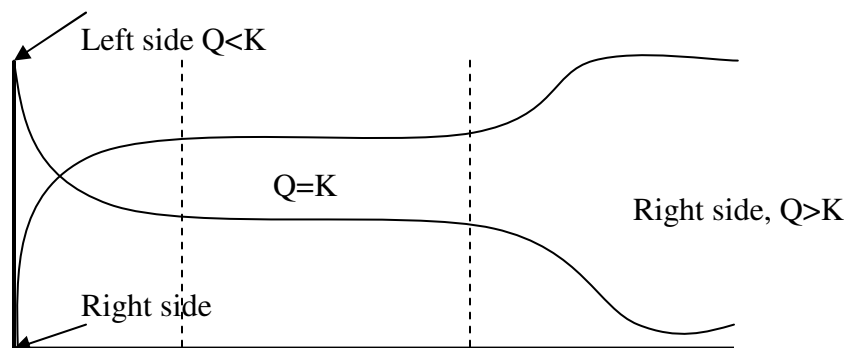
You will learn that finding whether Q is greater or less than K is a useful trick to understand what a reaction is doing.

Generalized treatment of equilibrium calculations: The RICE diagram

Rather than draw a graph of concentrations, why not put them in an array. Shown below is the general form of a reaction in which compounds A and B react to form compounds C and D.

Underneath the reactions, a matrix is created in which we can put various concentrations at different times. The RICE expression, in which RICE is an acronym for the following

R   Reaction
I   Initial Concentration (the non-equilibrium or Q values)
C   Change in concentration from initial to equilibrium
E   Equilibrium concentration (the values used to calculate K)

Reaction:	aA	+	bB	⇌	cC	+	dD	
Initial	C_A		C_B		C_C		C_D	← data used to calculate Q
Change	$C_A \pm [A]$		$C_B \pm [B]$		$C_C \pm [C]$		$C_D \pm [D]$	
Equilibrium	[A]		[B]		[C]		[D]	← data used to calculate K

Note that by convention,

       we let C values be the concentrations **not** at equilibrium

  and

       we let [ ] = concentration at equilibrium

Also note that we can use the values in the boxes to calculate Q and K

$$K_{eq} = [C]^c[D]^d / [A]^a[B]^b \qquad Q = C_C{}^c C_D{}^d / C_B{}^b C_A{}^a$$

And the game we play for the rest of the semester is to make up chemistry questions in which we are provide numbers for K, Q and parts of the array, and then solve for unknowns.

Below are some general categories of equilibrium problems.

We will use the following equilibrium as an example:

    A famous reaction $3H_2 + N_2 \rightleftharpoons 2NH_3$ and form the RICE expression below with a given K value.

Reaction:	3H₂	+	N₂	⇌	2NH₃	
Initial	C_{H2}		C_{N2}		C_{NH3}	← data used to calculate Q
Change	$C_{H2} \pm [H_2]$		$C_{N2} \pm [N_2]$		$C_{NH3} \pm [NH_3]$	
Equilibrium	$[H_2]$		$[N_2]$		$[NH_3]$	← data used to calculate K

    With $K = [NH_3]^2/[H_2]^3[N_2] = 3.8$

Problem Type 1. The simplest case. Everything is already at equilibrium.

What is K_{eq} if $[N_2] = 0.1M$, $[H_2] = 0.5M$ and $[NH_3] = 0.057M$?

How do you do this problem? Stick the values into the RICE expression where they belong, at equilibrium and then substitute them into the equilibrium expression K and solv.

Reaction: $3H_2$ + N_2 $\rightleftharpoons$ $2NH_3$

	C_{H2}	C_{N2}	C_{NH3}	
Initial	C_{H2}	C_{N2}	C_{NH3}	$\leftarrow$ data used to calculate Q
Change	$C_{H2} \pm [H_2]$	$C_{N2} \pm [N_2]$	$C_{NH3} \pm [NH_3]$	
Equilibrium	0.5M	0.1M	0.057M	$\leftarrow$ data used to calculate K

$$K = (0.057)^2/(0.5)^3(0.1) = 3.8$$

Guess what, you get to do this really simple kind of problem once on a quiz to feel good about yourself. And then never again (high school is over.)

Problem Type 2. How to manipulate your way around the RICE array.

A fun kind of problem to see how well you can deal with the stoichiometric relationships and the use of change of concentration in the middle row.

Given K = 3.8 and $[N_2] = 0.3$, $[H_2] = 0.2$, $C_{NH3} = 0.04$, fill in rest of chart.

Step 1: find the $[NH_3]$ from K calculation

Reaction: $3H_2$ + N_2 $\rightleftharpoons$ $2NH_3$

	C_{H2}	C_{N2}	
Initial	C_{H2}	C_{N2}	0.04
Change	$C_{H2} \pm [H_2]$	$C_{N2} \pm [N_2]$	$C_{NH3} \pm [NH_3]$
Equilibrium	0.2	0.3	Step 1, find from K

$\leftarrow$ $K = 3.8 = x^2/(0.3*0.2)^3 = 0.035$

Step 2: Find the $C_{NH3} \pm [\ NH_3\ ]$ term which is 0.04 – 0.0035

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	C_{H2}	C_{N2}	0.04
Change	$C_{H2} \pm [\ H_2\ ]$	$C_{N2} \pm [\ N_2]$	.0005
Equilibrium	0.2	0.3	.0035

Step 3: Use Stoichiometry to find the rest of the second row

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	C_{H2}	C_{N2}	0.04
Change	.0075	.0025	.0005
Equilibrium	0.2	0.3	.0035

Step 4: Perform a little math to find the starting concentrations for C_{H2} and C_{N2}.

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	.1925	.2975	0.04
Change	.0075	.0025	.0005
Equilibrium	0.2	0.3	.0035

A few things to note:
- Because NH3 was decreasing in amount in the first step, the H_2 and N_2 must have been increasing, in other words, the reaction was going in reverse and must have started with Q>K

- This kind of problem rarely shows up on tests, but if you can understand it, you are going to be a whiz at working RICE problems.

Problem Type 3. The real problem. Given all of the initial concentrations and K, find the equilibrium concentrations.

Why is this the "real" problem? Because it is what you would do in real life. You know the initial concentrations because you are the one who put the stuff in the container, and K values are constants found in tables just like thermodynamics values.

If I start with 0.1M NH_3, how much N_2 do I have at equilibrium?

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	0	0	0.1M
Change	$C_{H2}\pm[H_2]$	$C_{N2}\pm[N_2]$	$C_{NH3}\pm[NH_3]$
Equilibrium	$[H_2]$	$[N_2]$	$[NH_3]$

← note that we assume 0 for the concentrations not mentioned

← what we want to calculate

So what to do now? How about replacing the six unknowns in the second and third rows with values that are all related to each other through stoichiometry.

So let x = $[N_2]$ which is the quantity we want to know.

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	0	0	0.1M
Change	$C_{H2}\pm[H_2]$	$C_{N2}\pm[N_2]$	$C_{NH3}\pm[NH_3]$
Equilibrium	$[H_2]$	x	$[NH_3]$

← note that we assume 0 for the concentrations not mentioned

← what we want to calculate

And then assign the other unknown values based upon stoichiometry arguments.

Reaction: $3H_2$ + N_2 ⇌ $2NH_3$

	$3H_2$	N_2	$2NH_3$
Initial	0	0	0.1M
Change	+3x	+x	-2x
Equilibrium	3x	x	0.1 – 2x

← note that we assume 0 for the concentrations not mentioned

← what we want to calculate

So put everything in terms of x = $[N_2]$ and substitute into the equilibrium expression.

$$K = 3.8 = (0.1 – 2x)^2/(3x)^3(x)$$

Yikes, how do we solve a quartic (fourth order polynomial.

1. a fancy calculator
2. substitution of correct answers from multiple choice exam question
3. simplify (which we do in Ch. 10-11)
4. beg Dr. Laude not to put this on a test.

Actually the fastest way is probably back substitution which will no doubt come in handy on tests and also allow you to avoind buying or learning to use a fancy calculator.

But my favorite, of course, is method 3, learn to simplify the equation by approximations.