Unit 5, Lesson 09: Le Chatelier's Principle, Quantitative Approach

We have seen that if an equilibrium system is "stressed" by the addition or removal of a reactant or product, a change in pressure or volume, or a change in temperature, the system will shift in such a way as to reduce the effect of that stress.

But, as always, this is not good enough for most chemists- they want to know "How much?"

We can build on our earlier Keq calculations to figure out exactly how, and how much, a chemical system will shift to counteract a stress.

To do these types of problems, you will need to know which direction the equilibrium will shift. You should be able to predict the direction of the shift using Le Chatelier's principle.

- if it shifts to the right, the concentration of the products will increase, and reactants will decrease
- if it shifts to the left, the concentration of reactants will increase, and products will decrease

Once we know the direction that the system will shift, we can complete an ICE table and calculate the new values for the concentrations of each species. Let's look at some example questions.

(These questions are kind of like limiting factor questions in stoichiometry, there is a lot to keep track of. It is good idea to lay your work out clearly, and find a pattern for approaching the problems that suits you. Always follow the same pattern, and it will reduce the number of mistakes that you make.)

Example #1: The following reaction takes place in a 1.00 L vessel at 500ºC:

$$2\ HI\ (g) \leftrightarrow H_2\ (g) + I_2\ (g) \qquad Keq = ?$$

At equilibrium, the concentrations of each species are found to be [HI] = 1.76 mol/L, $[H_2]$ = 0.20 mol/L and $[I_2]$ = 0.20 mol/L. If an additional 0.500 moles of HI gas is introduced to the system when it is at equilibrium, how will the system respond and what will the concentrations of each species be when the system regains equilibrium?

Step 1: We can't do anything unless we know the value of K_{eq}. We can calculate this from the concentrations of each species at the original equilibrium:

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

$$= \frac{(0.20)(0.20)}{(1.76)^2}$$

$$= 0.0129$$

Step 2: We need to know which direction the equilibrium will shift in order to set up our ICE table. This question is pretty straight-forward. Because reactant is being added, the equilibrium will shift to the right. After the additional HI (g) is added, the reaction will shift to decrease the amount of HI and this will increase the amounts of both H_2 and I_2.

Step 3: Now that we know which direction the equilibrium will shift, set up an ICE table. This will be a little different from our other ICE tables, because we need a row to record the original equilibrium concentrations of each species. Call this row the E' (equilibrium prime, which means the first equilibrium).

a) In the E' row, fill in the concentrations of each species at the first equilibrium:

	2 HI (g)	↔	**H_2 (g)**	+	**I_2 (g)**	K_{eq} = 0.0129
E'	1.76 mol/L		0.20 mol/L		0.20 mol/L	
I						
C						
E						

b) In the I (Initial) row, write what the new concentrations of each species will be, after the stress has been applied, but before the equilibrium has shifted:

	2 HI (g)	↔	**H_2 (g)**	+	**I_2 (g)**	K_{eq} = 0.0129
E'	1.76 mol/L		0.20 mol/L		0.20 mol/L	
I	(1.76 + 0.500) mol/L		0.20 mol/L		0.20 mol/L	
C						
E						

c) In the C (change) row, use the variable "x" to record how the concentration of each species will respond to the stress. In this case, the concentration of HI will decrease after the stress has been applied, and it has a molar coefficient of 2, so it's change will be –2x. The concentration of both H_2 and I_2 will increase after the stress has been applied, and they both have molar coefficients of one, so they will both increase by +x.

	2 HI (g)	↔	**H_2 (g)**	+	**I_2 (g)**	K_{eq} = 0.0129
E'	1.76 mol/L		0.20 mol/L		0.20 mol/L	
I	(1.76 + 0.500) mol/L		0.20 mol/L		0.20 mol/L	
C	(2.26 –2x) mol/L		(0.20 + x) mol/L		(0.20 + x) mol/L	
E						

d) Add together the I and the C rows to find the concentrations of each species at equilibrium:

	2 HI (g)	↔	**H_2 (g)**	+	**I_2 (g)**	K_{eq} = 0.0129
E'	1.76 mol/L		0.20 mol/L		0.20 mol/L	
I	(1.76 + 0.500) mol/L		0.20 mol/L		0.20 mol/L	
C	–2x mol/L		+ x mol/L		+ x mol/L	
E	(2.26 –2x) mol/L		(0.20 + x) mol/L		(0.20 + x) mol/L	

Step #4: From here on in, the problem is identical to our previous problems. When the system reaches the new equilibrium, it will have the same K_{eq} value as before the stress. Substitute the expressions in the "E" row into the K_{eq} equation, and solve for "x".

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

$$0.0129 = \frac{(0.20 + x)(0.20 + x)}{(2.26 - 2x)^2}$$

Yes!! This equation is a perfect square. Take the square root of both sides.

$$(0.0129)^{1/2} = \frac{(0.20 + x)}{(2.26 - 2x)}$$

$$0.1136\ (2.26 - 2x) = 0.20 + x$$

Now, solve for x.

$$0.2567 - 0.2272x = 0.20 + x$$

$$0.0567 = 1.2272x$$

$$x = 0.046$$

Step #5: To find the new concentrations of each species at equilibrium, substitute the value for x into the last line of the ICE table.

$[HI] = (2.26 - 2x)$ mol/L $= 2.26 - 2(0.046)$ mol/L $= 2.17$ mol/L	$[H_2] = (0.20 + x)$ mol/L $= (0.20 + 0.046)$ mol/L $= 0.246$ mol/L	$[I_2] = (0.20 + x)$ mol/L $= (0.20 + 0.046)$ mol/L $= 0.246$ mol/L

Double check: sub the new values into the K_{eq} equation. If you have done the math correctly, the new concentrations will give you the K_{eq}.

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

$$= \frac{(0.246)\ (0.246)}{(2.17)^2}$$

$= 0.0129$ so we have done the problem correctly. Cool, huh?

Example 2. For the reaction: **$SO_2(g)$ + $NO_2(g)$ ↔ $SO_3(g)$ + $NO(g)$**

Suppose we add SO_2 to the system. The reaction must shift to the right and increase to yield of products.
At 200°C analysis of the equilibrium mixture shows:
$[SO_2] = 4.0$ M, $[NO_2] = 0.50$ M
$[SO_3] = 3.0$ M, $[NO] = 2.0$ M
What is the new equilibrium concentration of NO when 1.5 moles of NO_2 is added to the equilibrium mixture above?

Solution
Step #1: Find the value of K_{eq} first. Since it's a constant at this temperature then it will be valid for the equilibrium mixture and the stressed mixture.

$$K_{eq} = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(3.0\,M)(2.0\,M)}{(4.0\,M)(0.50\,M)} = 3.0$$

Step 2: We need to know which direction the equilibrium will shift in order to set up our ICE table. This question is pretty straight-forward. Because reactant is being added, the equilibrium will shift to the right. After the additional NO_2 (g) is added, the reaction will shift to decrease the amount of both SO_2 (g) and NO_2 (g). The amounts of SO_3 (g) and NO (g) will increase.

Step #3: Fill out an E'ICE chart

	$SO_2(g)$	+	**$NO_2(g)$**	↔	**$SO_3(g)$**	+	**$NO(g)$**	$K_{eq} = 3.0$
E'	4.0 mol/L		0.50 mol/L		3.0 mol/L		2.0 mol/L	
I	4.0 mol/L		(0.50 + 1.5) mol/L		3.0 mol/L		2.0 mol/L	
C	– x mol/L		- x mol/L		+ x mol/L		+ x mol/L	
E	(4.0 – x) mol/L		(2.0 + x) mol/L		(3.0 + x) mol/L		(3.0 + x) mol/L	

Step #4: Now we will fill in these factors in the K_{eq} equation and solve for 'x'.

$$K_{eq} = \frac{[SO_3][NO]}{[SO_2][NO_2]}$$

$$3.0 = \frac{(3.0 + x)(2.0 + x)}{(4.0 - x)(2.0 - x)}$$

Ugh. This is not a perfect square. Expand and rearrange.

After a few multiplications and additions we get:
$2.0x^2 - 23x + 18 = 0$

After using the quadratic equation on this formula we get a value for x = 0.75 mol/L

Step #5: Calculate the new concentration of NO (g).
$[NO] = 2.0 + x = 2.75$ mol/L

Double Check: Sub the new equilibrium values into the expression for Keq and solve. Yes, these new equilibrium values are correct.