

Unit 4, Lesson #4: Calculations using The Equilibrium Constant

For the general **homogeneous**, reversible chemical reaction: $aA + bB \leftrightarrow cC + dD$

At equilibrium, when the rate of the forward and reverse reactions are equal, we can write the general equilibrium expression:

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

If we know the amounts or concentrations of the reactants and products of a chemical system at equilibrium, we can calculate the value of the equilibrium constant K_{eq} .

Similarly, if we know the value of K_{eq} at a specified temperature, and the initial concentrations of the reactants, we can calculate the equilibrium concentrations of each species. The *stoichiometry* (molar coefficients) of the reaction is very important in these calculations.

eg. At 430 °C, the equilibrium constant, K_c , for the following reaction is 1.84×10^{-2} .



If 0.100 mol of hydrogen iodide is placed in a 1.00 L container and allowed to reach equilibrium at this temperature, find the concentrations of all the species at equilibrium.

Solution:

- Set up a chart called an “ICE” table. “I” stands for “initial”. “C” stands for “change” and “E” stands for equilibrium. Write the equation across the top of the table as your heading. Include the K_{eq} value.

	2 HI (g)	\leftrightarrow	H₂ (g)	+	I₂ (g)	$K_{eq} = 1.84 \times 10^{-2}$
I						
C						
E						

- Fill in any known initial **concentration** values. If you are given amounts that are not expressed as concentrations, convert to mol/L before you fill in the ICE table. For this example, we are told that there are 0.100 mol of HI in a 1.00 L flask. This is an initial concentration of 0.100 mol/L. Initially, there is no H_2 or I_2 , because the reaction has not started yet, so fill in 0.0 mol/L for these species.

	2 HI (g)	\leftrightarrow	H₂ (g)	+	I₂ (g)	$K_{eq} = 1.84 \times 10^{-2}$
I	0.100 mol/L		0.0 mol/L		0.0 mol/L	
C						
E						

- As the reaction occurs and the system reaches equilibrium, the amount of H_2 and I_2 will increase while the amount of HI will decrease. If H_2 increases by an amount “x” then, using the molar coefficients, I_2 will also increase by “x”. HI will decrease by “2x” because 2 moles of HI are used up for every one mole of H_2 and I_2 produced. Fill in these *changes* in molar concentration in the change row.

	2 HI (g)	\leftrightarrow	H₂ (g)	+	I₂ (g)	$K_{eq} = 1.84 \times 10^{-2}$
I	0.100 mol/L		0.0 mol/L		0.0 mol/L	
C	-2x		+x		+x	
E						

4. At equilibrium, the concentrations of each species will be equal to the initial concentration *plus* the change in concentration. Add the top two columns to get the equilibrium concentration for each species, and fill this in the equilibrium row.

	2 HI (g)	\leftrightarrow	H₂ (g)	+	I₂ (g)	$K_{eq} = 1.84 \times 10^{-2}$
I	0.100 mol/L		0.0 mol/L		0.0 mol/L	
C	-2x		+x		+x	
E	0.100 - 2x		x		x	

5. Now we have an expression with a single variable (x) that we can solve using the K_c equilibrium expression, because we know the value of K_c for the system at equilibrium.

- a) Write the K_c equation including only the species in the highest entropy phase:

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

- b) Substitute the concentration terms with the equilibrium values from the ICE table, and the value of K_c :

$$1.84 \times 10^{-2} = \frac{x \cdot x}{(0.100 - 2x)^2}$$

- c) Now, to solve for x. There are three possibilities:

- if the equation does not include any squared terms, then rearrange and solve for x
- if the equation includes squared terms that are perfect squares, take the square root of both sides of the equation, then rearrange and solve for x
- if the equation includes squared terms that are not perfect squares, you will need to expand out all terms and rearrange the equation into the form $ax^2 + bx + c = 0$. Solve for x using the quadratic formula.

For our example, it is a perfect square ($x \cdot x = x^2$), so we will take the square root of both sides (the square root is the same as the number raised to the power $\frac{1}{2}$):

$$(1.84 \times 10^{-2})^{1/2} = \frac{x}{(0.100 - 2x)}$$

Now rearrange and solve for x:

$$0.1356 = \frac{x}{(0.100 - 2x)}$$

$$0.1356(0.100 - 2x) = x$$

$$0.01356 - 0.2712x = x$$

$$0.01356 = 1.2712x$$

$$x = 0.0107$$

6. To find the equilibrium concentrations, substitute the value for “x” back into the equilibrium concentrations in the ICE table. Therefore:

$$\begin{aligned} [\text{HI}] &= 0.100 - 2x \\ &= 0.100 - (2 \times 0.0107) \\ &= 0.0786 \text{ mol/L} \end{aligned}$$

$$\begin{aligned} [\text{H}_2] &= [\text{I}_2] = x \\ &= 0.0107 \text{ mol/L} \end{aligned}$$

* the units for concentration are always the same as the initial units for concentration used in the ICE table.

Example #2: Solid ammonium chloride is heated to 400K in a closed one litre flask. The ammonium chloride decomposes to form ammonia and hydrogen chloride gas. The K_{eq} for this reaction at 400 K is 6.0×10^{-9} . What are the equilibrium concentrations of the gases?

Solution: The reaction is: $\text{NH}_4\text{Cl (s)} \leftrightarrow \text{NH}_3 \text{ (g)} + \text{HCl (g)}$ K_{eq} at 400K is 6.0×10^{-9}

1. This is a heterogeneous system. The species in the highest entropy phase are $\text{NH}_3 \text{ (g)}$ and HCl (g) , so we will not be including the concentration of $\text{NH}_4\text{Cl (s)}$ in the K_{eq} equation. Set up a chart called an “ICE” table. Write the equation across the top of the table as your headings. Include the K_{eq} value. We do not need a value for the NH_4Cl initial concentration. The concentration of the products will initially be zero.

	$\text{NH}_4\text{Cl (s)}$	\leftrightarrow	$\text{NH}_3 \text{ (g)}$	+	HCl (g)	K_{eq} at 400K is 6.0×10^{-9}
Initial	omit		0.0 mol/L		0.0 mol/L	
Change	omit					
Equilibrium	omit					

2. As the NH_4Cl decomposes, the concentration of $\text{NH}_3 \text{ (g)}$ and HCl (g) will increase. The molar coefficient for each gas is one, so if one mole of NH_3 forms, one mole of HCl will also form. Fill this into the change row of the ICE table. Let “x” be the increase in both gases.

	$\text{NH}_4\text{Cl (s)}$	\leftrightarrow	$\text{NH}_3 \text{ (g)}$	+	HCl (g)	K_{eq} at 400K is 6.0×10^{-9}
Initial	omit		0.0 mol/L		0.0 mol/L	
Change	omit		+ x		+ x	
Equilibrium	omit					

3. To find the equilibrium concentrations of both gases, add the initial and change values together. Enter this in the equilibrium row.

	$\text{NH}_4\text{Cl (s)}$	\leftrightarrow	$\text{NH}_3 \text{ (g)}$	+	HCl (g)	K_{eq} at 400K is 6.0×10^{-9}
Initial	omit		0.0 mol/L		0.0 mol/L	
Change	omit		+ x		+ x	
Equilibrium	omit		x		x	

4. Now we have an expression with a single variable (x) that we can solve using the K_{c} equilibrium expression, because we know the value of K_{c} for the system at equilibrium.

a) Write the K_{c} equation including only the species in the highest entropy phase:

$$K_{\text{c}} = [\text{NH}_3] [\text{HCl}]$$

b) Substitute the concentration terms with the equilibrium values from the ICE table, and the value of K_c :

$$6.0 \times 10^{-9} = x \cdot x$$

c) Solve for x by taking the square root of both sides:

$$6.0 \times 10^{-9} = x^2 \quad \text{and} \quad x = 7.7 \times 10^{-5} \text{ mol/L}$$

d) Therefore, the concentration of both NH_3 and HCl gases at equilibrium will be $7.7 \times 10^{-5} \text{ mol/L}$

Does this make sense? K_{eq} is very small, so the reaction will not proceed very far to the right, so the concentrations of the products will be small. Yes, this answer does make sense.

Example #3: How many moles of HI are present at equilibrium when 2.0 moles of H_2 is mixed with 1.0 mole of I_2 in a 0.50 L container and allowed to react at 448°C . At this temperature $K_{eq} = 50$.

Solution

The reaction is: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2 \text{HI}(\text{g})$

Then, we have been given the number of moles and volume of the container, so calculate the initial concentrations of each species:

$$\begin{array}{ll} [\text{H}_2] = n/V & [\text{I}_2] = n/V \\ = 2.0 \text{ moles}/0.50 \text{ L} & = 1.0 \text{ moles}/0.50 \text{ L} \\ = 4.0 \text{ moles/L} & = 2.0 \text{ moles/L} \end{array}$$

$[\text{HI}] = 0$ moles therefore 0 moles/L (the reaction has not started yet, so no product has formed).

Fill in the initial concentrations of each species in the ICE table:

	H₂ (g)	+	I₂ (g)	\leftrightarrow	2 HI (g)	$K_{eq} = 50$
I	4.0 mol/L		2.0 mol/L		0.0 mol/L	
C						
E						

As the reaction occurs, for every mole of H_2 that reacts, one mole of I_2 will also react, and two moles of HI will form. Let “ x ” represent the changes in each species, and fill in the change row of the ICE table:

	H₂ (g)	+	I₂ (g)	\leftrightarrow	2 HI (g)	$K_{eq} = 50$
I	4.0 mol/L		2.0 mol/L		0.0 mol/L	
C	- x		- x		+2 x	
E						

Add the first two rows together to find the equilibrium values of each species and complete the “E” row of the ICE table:

	H₂ (g)	+	I₂ (g)	\leftrightarrow	2 HI (g)	$K_{eq} = 50$
I	4.0 mol/L		2.0 mol/L		0.0 mol/L	
C	- x		- x		+2 x	
E	4.0 - x		2.0 - x		+2 x	

Substitute the equilibrium concentrations of each species and K_{eq} into the K_{eq} equation:

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{I}_2][\text{H}_2]}$$

$$50 = \frac{(2x)^2}{(4.0 - x)(2.0 - x)}$$

We're not so lucky this time. There are no perfect squares here. We will have to expand the equation by multiplying out and get the equation into standard form:

$$50 = \frac{4x^2}{8.0 - 6.0x + x^2} \quad (\text{Careful here- } (2x)^2 \text{ is equal to } 4x^2)$$

$$400 - 300x + 50x^2 = 4x^2$$

$$46x^2 - 300x + 400 = 0 \quad (\text{the standard form of } ax^2 + bx + c = 0)$$

Use the quadratic equation to solve for 'x'.

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

In this case $a = +46$, $b = -300$ and $c = +400$.

The quadratic equation is a mathematical relationship for solving the equation for a parabola to find its roots. In chemistry the 'roots' represent real life values. One will be realistic and the other will not be.

$$x = \frac{+300 \pm \sqrt{(-300)^2 - 4(46)(400)}}{2(46)}$$

$$x = \frac{+300 \pm \sqrt{90000 - 73600}}{92}$$

$$x = \frac{+300 \pm 127}{92}$$

$$x = 4.7 \text{ and } 1.9$$

Only one of these values will be possible. Looking back at our data, we started with only 4.0 mol/L of H_2 . If we subtract 4.7 mol/L, we will get a negative value for concentration, which is impossible. Therefore, $x=4.7$ is not a realistic answer, so $x=1.9$ mol/L.

Substitute ' $x=1.9$ mol/L' back up into the equilibrium concentration calculations of the ICE table and calculate the equilibrium *concentrations* of each species:

[HI] at equilibrium is $2x = 2(1.9 \text{ mol/L}) = 3.8 \text{ mol/L}$

But, the question asked us for the number of moles of HI, so to convert the concentration back to moles, use the equation $n = CV = 3.8 \text{ mol/L} \times 0.5 \text{ L} = 1.9 \text{ mol of HI}$

And [HI] equals $2x = 2(1.9 \text{ mol/L}) = 3.8 \text{ mol/L}$

The moles of HI present at equilibrium would be:

$$\begin{aligned} n &= CV = 3.8 \text{ moles/L} * 0.5 \text{ L} \\ &= 1.9 \text{ moles} \end{aligned}$$

Does this make sense? Yes, the K_{eq} for this reaction is large ($K_{eq} = 50.0$), so the reaction will go almost to completion, and it did.

Homework:

1. Read pages 339, 344 – 347 in McGraw-Hill.
2. Do the practice problems on page 347 in this order: 11, 15, 13, 14 and 12