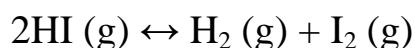


## The Law of Chemical Equilibrium

Le Châtelier established that a system in equilibrium will respond to a disturbance in a predictable way. Other chemists (Guldberg and Waage) studied this at a mathematical level - a mathematical constant must exist for any system at equilibrium. They came up with the **law of chemical equilibrium** which states:

**For a system at equilibrium at a specific temperature, a special relationship exists between the concentrations of the products and the concentrations of the reactants.**

We can see the relationship by examining a system:



Trial	[HI]	[H <sub>2</sub> ]	[I <sub>2</sub> ]
1	0.0177	0.00183	0.00313
2	0.0165	0.00291	0.00171
3	0.0135	0.00456	0.000740
4	0.00353	0.000480	0.000480
5	0.00841	0.00114	0.00114

Note: even though the system is at equilibrium, it does **not** mean the concentrations of reactants and products are equal, remember equilibrium means the forward reaction rate and the reverse reaction rate are equal.

For each of the trials, calculate  $\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$

No matter what the initial concentrations of the species, the equilibrium constant expression yields a constant,  $K$  or  $K_{eq}$  which equals:

**THE PRODUCT OF THE CONCENTRATIONS OF THE PRODUCTS RAISED TO THE POWER OF THEIR COEFFICIENTS, DIVIDED BY THE PRODUCT OF THE CONCENTRATIONS OF THE REACTANTS RAISED TO THE POWERS OF THEIR COEFFICIENTS.**

When writing equilibrium constant expressions there are very important things to keep in mind:

1. **Only aqueous species and gases** are included in the expression.
2. **Coefficients** of the balanced equation become the **powers** in the expression, but you don't need to use the power of 1.
3. The value of  $K$  will change with changes in temperature, often in Kelvin rather than degrees Celsius
4. The value of  $K$  is affected by the way the chemical equation is written, because now the positions of the products and reactants are reversed.

**General Equation:  $aA + bB \leftrightarrow cC + dD$**

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

**only for species that are aqueous or gaseous**

### Example Exercises:

Write an equilibrium constant expression for each of these systems:

1.  $3\text{Fe}(s) + 3\text{H}_2\text{O}(g) \leftrightarrow \text{Fe}_3\text{O}_4(s) + 3\text{H}_2(g)$   $K=12.3$  at 800K
2.  $\text{C}(s) + \text{H}_2\text{O}(g) \leftrightarrow \text{H}_2(g) + \text{CO}(g)$   $K= 10.0$  at 1100K
3.  $\text{C}_2\text{H}_5\text{OH}(aq) + \text{CH}_3\text{COOH}(aq) \leftrightarrow \text{CH}_3\text{COOC}_2\text{H}_5(aq) + \text{H}_2\text{O}(l)$   
 $K= 0.11$  at 343K
4.  $\text{CO}(g) + 2\text{H}_2(g) \leftrightarrow \text{CH}_3\text{OH}(g)$   $K= 14.5$  at 500K

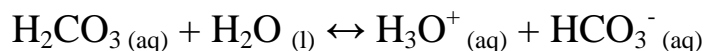
### Hints:

- arrange the species so that the concentrations of the product(s) are on top and the concentrations of the reactants are on bottom
- put in the coefficients from the balanced equation

There are a number of different types of problems that use the equilibrium constant expression (K)

**1. Calculate K given all equilibrium concentrations**

Example: What is the K value for the following system at equilibrium at 25°C?



$$[\text{H}_2\text{CO}_3] = 3.3 \times 10^{-2} \text{ M}$$

$$[\text{H}_3\text{O}^+] = 1.19 \times 10^{-4} \text{ M}$$

$$[\text{HCO}_3^-] = 1.19 \times 10^{-4} \text{ M}$$

$$\begin{aligned} K &= \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \\ &= \frac{(1.19 \times 10^{-4})(1.19 \times 10^{-4})}{(3.3 \times 10^{-2})} \\ &= 4.3 \times 10^{-7} \end{aligned}$$

(Note that we don't use units for K)

**THE MAGNITUDE OF K ENABLES US TO PREDICT WHETHER REACTANTS OR PRODUCTS ARE FAVOURED AT EQUILIBRIUM. USE THE FOLLOWING CRITERIA:**

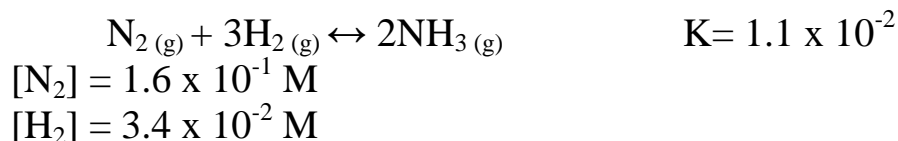
**K > 1, PRODUCTS ARE FAVOURED**

**K < 1, REACTANTS ARE FAVOURED**

**K = 1, NEITHER IS FAVOURED**

**2. Given K and almost all of the equilibrium concentrations, calculate the missing equilibrium concentration by rearranging the formula.**

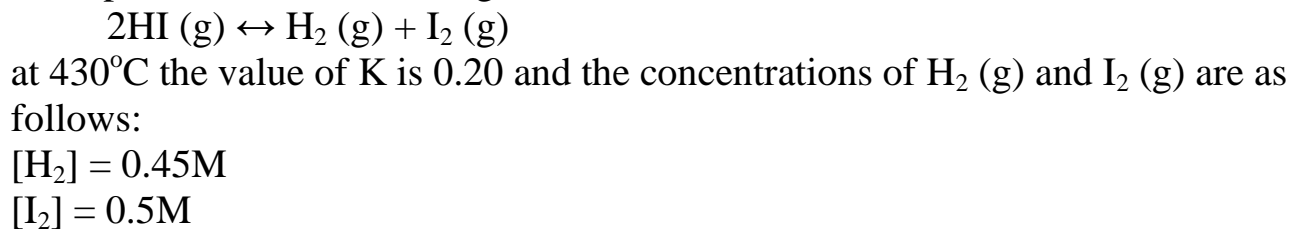
Example: Given the following system and observed measurements, calculate the equilibrium concentration of ammonia at 25°C



$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$K \times [\text{N}_2][\text{H}_2]^3 = [\text{NH}_3]^2$$
$$[(1.1 \times 10^{-2})(1.6 \times 10^{-6})(3.4 \times 10^{-2})^3] = [\text{NH}_3]^2$$
$$\sqrt{(1.1 \times 10^{-2})(1.6 \times 10^{-6})(3.4 \times 10^{-2})^3} = [\text{NH}_3]$$
$$2.6 \times 10^{-4} = [\text{NH}_3]$$

Example: Given the following reaction:



What is [HI] at equilibrium?

**3. Calculate equilibrium concentrations when initial concentrations of reactants and one equilibrium concentration are known.**

This type of problem can be solved mathematically by using an ICE table. (♫ ICE ICE table insert Vanilla Ice song Ice Ice Baby just to drive you crazy!))

**I** for initial concentration

**C** for change in concentration

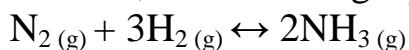
**E** for equilibrium

Values are placed in the table as you work through the problem using

stoichiometry and subtraction. You use either mol/L in your ICE table, because that is what we use for K. In many exercises the reactions take place in a 1L vessel to avoid confusion. Sometimes you may need to calculate concentration first, if the vessel is greater than 1 L.

Example: Given the following system and information determine whether reactants or products are favoured. (In other words, calculate K and analyze your answer)

In a 1L vessel, the following equilibrium is established:



initial  $[\text{N}_2] = 1.444 \text{ M}$

initial  $[\text{H}_2] = 3.576 \text{ M}$

equilibrium  $[\text{NH}_3] = 1.45 \text{ M}$

Plan your strategy:

A. You need to set up an ICE table and fill in the given data.

	$\text{N}_2$	$3\text{H}_2$	$2\text{NH}_3$
I	1.444	3.576	0
C			
E			1.45

B. Using the given data and your stoichiometric skills, find the **change** in concentration for each species. This will involve finding the change for one species from initial concentration to equilibrium concentration.

In our reaction the  $[\text{NH}_3]$  went from 0 to 1.45, a gain of 1.45 mol/L. This means the reactants must have decreased in concentration. How much they decreased can be determined using **mole ratios** - multiply  $\frac{3}{2}$  times the gain of  $[\text{NH}_3]$  to get the  $[\text{H}_2]$  and multiply  $\frac{1}{2}$  times the gain of  $[\text{NH}_3]$  to get the loss of  $[\text{N}_2]$

$$1.45 \times \frac{3}{2} = [\text{H}_2]$$

$$-2.175 = [\text{H}_2]$$

$$1.45 \times \frac{1}{2} = [\text{N}_2]$$

$$-0.725 = [\text{N}_2]$$

(these are negatives because they must have lost concentration in order for ammonia to gain)

Put these numbers in your ICE table:

	$\text{N}_2$	$3\text{H}_2$	$2\text{NH}_3$
I	1.444	3.576	0
C	<b>-0.725</b>	<b>-2.175</b>	<b>1.45</b>
E			1.45

C. Calculate the equilibrium concentrations by subtracting from the initial concentrations.

	$\text{N}_2$	$3\text{H}_2$	$2\text{NH}_3$
I	1.444	3.576	0
C	-0.725	-2.175	1.45
E	<b>0.719</b>	<b>1.401</b>	1.45

D. Now we have all values to calculate K

$$K = \frac{[\text{NH}_3]^2}{[0.719][1.401]^3}$$

$$K = 1.06$$

Since  $K > 1$ , the products are favoured but only slightly.

More examples:

An equilibrium was established after 1.00 mol of hydrogen gas and 0.100 mol of iodine gas were added to an empty 1.00 L reaction vessel and heated to 700K. The colour intensity of the mixture changed from deep purple to a lighter purple colour. At equilibrium, the concentration of iodine was 0.0213 mol/L. Calculate the equilibrium concentrations of the other species.

$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2 \text{HI}(\text{g})$$
  
initial  $[\text{H}_2] = 0.100 \text{ mol/L}$   
initial  $[\text{I}_2] = 0.100 \text{ mol/L}$   
initial  $[\text{HI}] = 0$   
at equilibrium  $[\text{I}_2] = 0.0213 \text{ mol/L}$

	$\text{H}_2$	$\text{I}_2$	2 HI
I	0.100	0.100	0.000
C	<b>-0.0787</b>	<b>-0.0787</b>	<b>0.1574</b>
E	0.0213	0.0213	0.1574

The equilibrium concentration of hydrogen is 0.0213 mol/L and the equilibrium concentration of hydrogen iodide is 0.1574 mol/L.

**4. Calculate equilibrium concentrations or K when initial reactant concentration is known and percent reaction is given.**

Example: Initially 0.886 mol/L of SO<sub>3</sub> (g) was placed in a vessel and allowed to reach equilibrium according to the system below.



Are the reactants or products favoured if the percent reaction of the SO<sub>3</sub> was 31.6%?

In order to answer the question we need to find the value of K and in order to do that we need equilibrium concentrations for all species, so ICE table:



	2SO <sub>3</sub> (g)	2SO <sub>2</sub> (g)	O <sub>2</sub> (g)
I	0.886	0	0
C	<b>(0.886 x .316)* - 0.280</b>	<b>(x <sup>2</sup>/<sub>2</sub> ratio) 0.280</b>	<b>(x <sub>1</sub>/<sub>2</sub> ratio) 0.140</b>
E	0.606	0.280	0.140

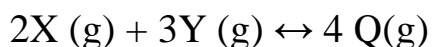
\* To find out how much changed (reacted) multiply the decimal version of 31.6% by the initial concentration of SO<sub>3</sub>

$$K = \frac{[0.280]^2 [0.140]}{[0.606]^2}$$

$$= 2.99 \times 10^{-2}$$

Therefore, reactants are favoured.

Example: Given the following system:



The following observations were made at equilibrium at 300K : [X] = 0.445 mol/L

$$[\text{Y}] = 0.864 \text{ mol/L}$$

$$[\text{Q}] = 1.05 \text{ mol/L}$$

The temperature was then raised by 100K and a new equilibrium was

established. The percent reaction of the Q was 48.3%. Find the new equilibrium concentration of X.

$$2X(g) + 3Y(g) \leftrightarrow 4Q(g)$$

I	<b>0.445</b>	<b>0.864</b>	<b>1.05</b>
C	(x <sup>2/4</sup> ) +0.254	(x <sup>3/4</sup> ) +0.380	(48.3% reacts) -0.507
E	0.699	1.24	0.543

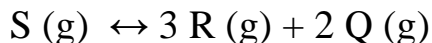
New [X] = 0.699 mol/L

**5. Concentrations are not given, only amounts, in moles, and the size of the reaction vessel**

ALL OF THE PREVIOUS EXAMPLES/PROBLEMS INVOLVED MOLAR CONCENTRATIONS. IT WAS ALSO ASSUMED THAT THE VESSEL WAS 1.0L. THIS IS NOT ALWAYS THE CASE!

IF THE VESSEL IS NOT 1.0 L AND AMOUNTS GIVEN ARE IN MOLES YOU MUST FIRST DETERMINE THE MOLAR CONCENTRATIONS USING  $C = n/v$

example: 2.6 mol of Q, 3.1 mol of R and 1.8 mol of S were placed in a 2.0L reaction vessel at 350K and allowed to reach equilibrium. At equilibrium, 3.2 mol of R were found. Calculate the value of K at equilibrium of the system:



Find all concentrations you can:

$$\text{Initial [Q]} = 2.6 \text{ mol}/2.0\text{L} = 1.30 \text{ mol/L}$$

$$\text{Initial [R]} = 3.1 \text{ mol}/2.0\text{L} = 1.55 \text{ mol/L}$$

$$\text{Initial [S]} = 1.8 \text{ mol}/2.0\text{L} = 0.90 \text{ mol/L}$$

$$\text{Equilibrium [R]} = 3.2 \text{ mol}/2.0\text{L} = 1.60 \text{ mol/L}$$

Do your ICE table:

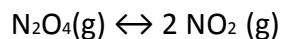
	S (g)	↔	3 R (g)	+ 2 Q (g)
I	<b>0.90</b>		<b>1.55</b>	<b>1.30</b>
C	(x $\frac{1}{3}$ ) - 0.0167		+0.05	(x $\frac{2}{3}$ ) +0.033
E	0.8833		<b>1.60</b>	1.267

Calculate K:

$$K = \frac{[R]^3 [Q]^2}{[S]} = \frac{[1.60]^3 \times [1.267]^2}{[0.8833]} = 7.4$$

Now, you try these:

1. Calculate  $K_{eq}$  if 1.0 mol of  $N_2O_4$  is initially placed into a 1.0 L vessel, and at equilibrium 0.75 mol of  $N_2O_4$  remains in the vessel.



2. 4.00 mol of  $H_2S(g)$  is placed in a 2.00 L flask at 1400 EC. When the equilibrium below is reached, 6.00 % of the  $H_2S(g)$  has reacted. Calculate the value of the equilibrium constant.

