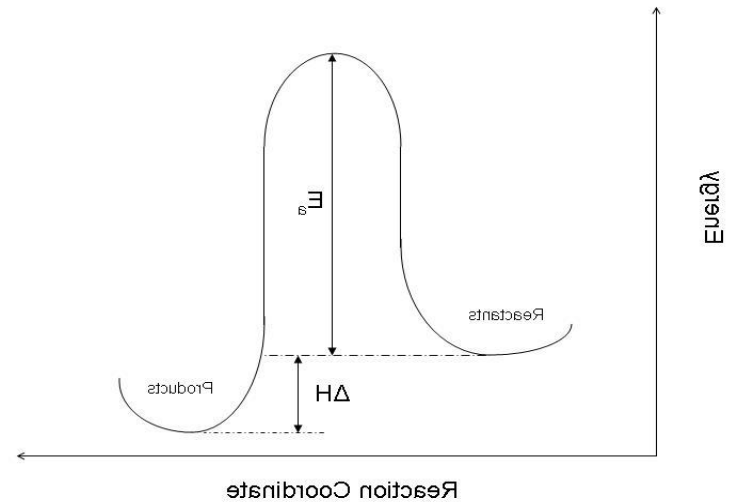
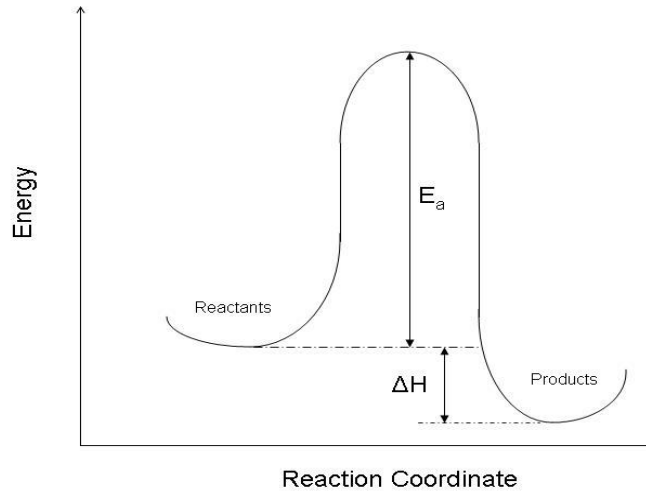


Review of Basic Equilibrium

Forward to the Past!

Everything is simply reversed:
The E_a is different, the ΔH is inverted



Reactions can go both ways

- The hill is just higher going one way than the other.
- If it is exothermic going one way, it is endothermic going the other way.
- The world is reversible! (Well, except for time 😊)

Implications for Chemical Reactions

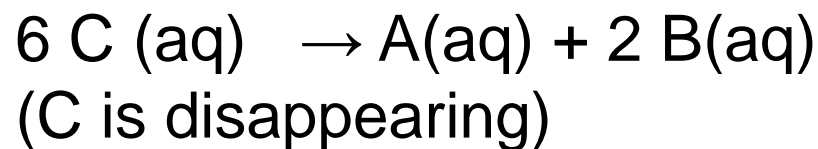
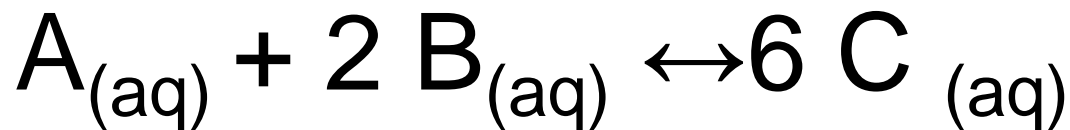
The reversibility of chemical reactions means that rather than proceed from reactants to products, most reactions reach a state where there is no further change.

THIS DOES NOT MEAN NOTHING IS HAPPENING!

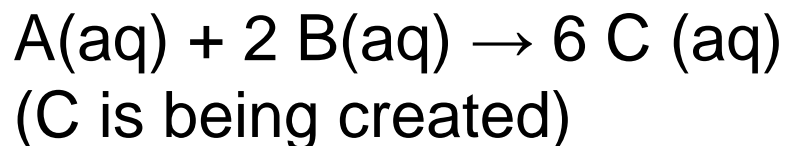
DYNAMIC EQUILIBRIUM

Chemical Equilibrium is a **Dynamic Equilibrium**.

It is not that there is no reaction occurring, it is that the forward reaction and the reverse reaction are occurring at equal rates.



$$Rate = -\frac{1}{6} \frac{\Delta[C]}{\Delta t}$$



$$Rate = +\frac{1}{6} \frac{\Delta[C]}{\Delta t}$$

Both reactions occur simultaneously with:
Rate of destruction = rate of creation

Equilibrium is Balance

- The forward and reverse reactions are balanced
- The concentrations of all species (reactants and products) become stable
- The equilibrium position is not the same for all reactions – it depends specifically on the reaction and the temperature.

All equilibrium problems have...

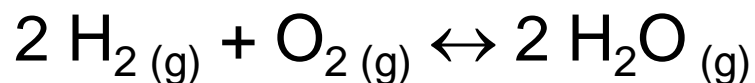
- A. 1 part
- B. 2 parts
- C. 3 parts
- D. 4 parts
- E. I need to see the problem.

3 Magic Parts

1. Balanced equation – it's CHEMISTRY!
2. Equilibrium Constant Expression (K) – this defines (or confines) the concentrations of everything at equilibrium.
3. ICE ICE, BABY, ICE ICE!!!

Clicker Question

What is the Equilibrium Constant Expression for the following reaction?



A. $K = \frac{[\text{H}_2\text{O}]}{[\text{H}_2][\text{O}_2]}$

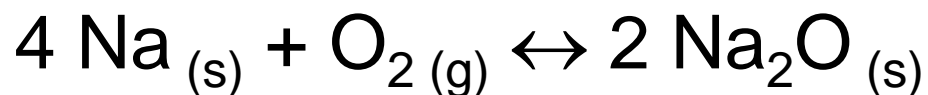
B. $K = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2}$

C. $K = \frac{[\text{H}_2][\text{O}_2]}{[\text{H}_2\text{O}]}$

D. $K = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$

Clicker Question

What is the Equilibrium Constant Expression for the following reaction?



A. $K = \frac{[\text{Na}_2\text{O}]^2}{[\text{O}_2]}$

B. $K = \frac{[\text{Na}_2\text{O}]}{[\text{Na}][\text{O}_2]}$

C. $K = \frac{[\text{Na}_2\text{O}]^2}{[\text{Na}]^4 [\text{O}_2]}$

D. $K = \frac{1}{[\text{O}_2]}$

K_c vs K_p

- When a reaction occurs in the gas phase, you can use the **partial pressure** of the gas instead of the concentration.
- To separate the 2 different expressions, they are written differently:
 - K_c = equilibrium constant with concentrations of species
 - K_p = equilibrium constant with partial pressures of the species

$$PV = nRT$$

$$P = \frac{n}{V} RT$$

The only difference between P and $[\text{conc}]$ is “ RT ”.

Net Result

$$K_C = K_p (1/RT)^{\Delta n}$$

Δn = total moles of product gas – total moles of reactant gas

This is the general relationship between K_p and K_c for all gas phase reactions.

Or, equivalently,

$$K_p = K_c (RT)^{\Delta n}$$

More subscripts...

The next two chapters are all about K with different subscripts...

K IS K IS K IS k

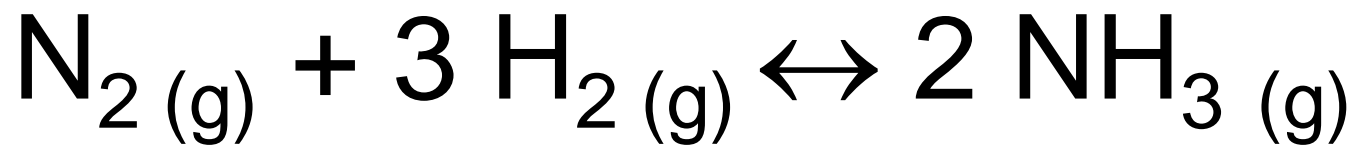
3 Parts

1. Balanced equation – it's CHEMISTRY!
2. Equilibrium Constant Expression (K) – this defines (or confines) the concentrations of everything at equilibrium.
3. ICE ICE, BABY, ICE ICE!!!

A little test...

Ammonia gas (NH_3) can be made from nitrogen and hydrogen gas. Into a 2 L flask at 400 K, I put 1.0 g of nitrogen and 1.0 g of hydrogen. At equilibrium, the pressure in the flask is 8.5 atm. What is the equilibrium constant (K_p) for the reaction at 400 K?

- A. 1.2×10^{-2}
- B. 2.3×10^{-4}
- C. 3.4×10^{-2}
- D. 2.6×10^{-3}
- E. 4.2×10^{-4}



$$1.0 \text{ g N}_2 * \frac{1 \text{ mol N}_2}{28.02 \text{ g}} = 0.0357 \text{ mol N}_2$$

$$1.0 \text{ g H}_2 * \frac{1 \text{ mol H}_2}{2.016 \text{ g}} = 0.496 \text{ mol H}_2$$

Moles is good, atm is better – at least if K_p is what you care about!

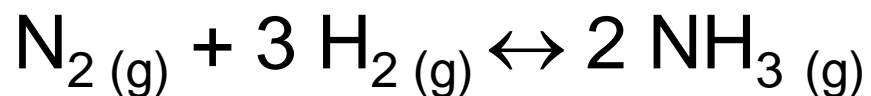
$$P = nRT/V$$

$$P_{N_2} = \frac{0.0357 \text{ mol } N_2 \times 0.082056 \frac{L \cdot \text{atm}}{\text{mol} \cdot K} \times 400 K}{2L}$$

$$P_{N_2} = 0.586 \text{ atm}$$

$$P_{H_2} = \frac{0.496 \text{ mol } H_2 \times 0.082056 \frac{L \cdot \text{atm}}{\text{mol} \cdot K} \times 400 K}{2L}$$

$$P_{H_2} = 8.14 \text{ atm}$$



I 0.586 atm 8.14 atm 0 atm

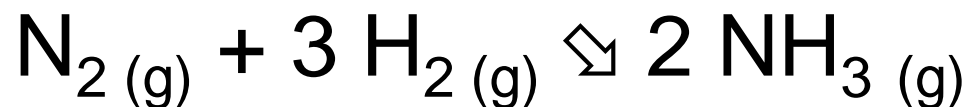
C -x -3x +2x

E 0.586 - x 8.14 - 3x 0 + 2x

$$K_p = \frac{(2x)^2}{(0.586 - x)(8.14 - 3x)^3}$$

I need x, but I know one more thing

$$P_{\text{final}} = 8.5 \text{ atm}$$



$$\text{I} \quad 0.586 \text{ atm} \quad 8.14 \text{ atm} \quad 0 \text{ atm}$$

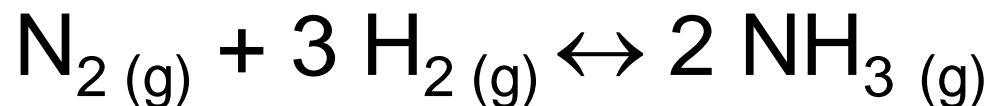
$$\text{C} \quad -x \quad -3x \quad +2x$$

$$\text{E} \quad 0.586 - x \quad 8.14 - 3x \quad 0 + 2x$$

$$P_{\text{final}} = 8.5 \text{ atm} = 2x + (8.14 - 3x) + (0.586 - x)$$

$$8.5 = -2x + 8.726$$

$$x = 0.113$$



I	0.586 atm	8.14 atm	0 atm
C	-0.113	-3(0.113)	+2(0.113)
E	0.473	7.801	0.226

$$K_p = \frac{(0.226)^2}{(0.473) (7.801)^3}$$

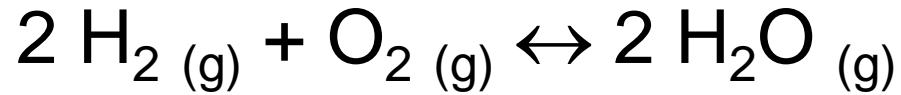
$$K_p = 2.27 \times 10^{-4}$$

A little equilibrium problem

Hydrogen and oxygen gas will react to form steam (gaseous water). 4.36 g of hydrogen and 28.6 g of oxygen were mixed in a 2 L flask at 250 C. After equilibrium was established, it was determined that there was 6.6 g of water. What is the equilibrium constant for this reaction at 250 C?

A series of simple calculations

1st you need a balanced equation:



This allows us to immediately write the equilibrium constant expression:

$$K_{\text{eq}} = K_{\text{c}} = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$$

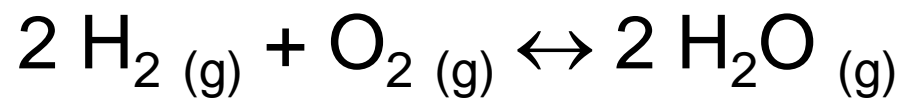
The question is: what are the equilibrium concentrations of all of the species?

Determining the concentrations

ICE - ICE - BABY - ICE – ICE

The easiest way to solve this problem is by using an I-C-E chart (“ice chart”) where I = initial concentration, C= change in concentration, and E = the equilibrium concentration.

An ICE Chart



Initial

Change

Equilibrium

What do you know?

$$4.36 \text{ g hydrogen} * \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 2.16 \text{ mol H}_2$$

(this is the INITIAL amount)

$$28.6 \text{ g oxygen} * \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = 0.894 \text{ mol O}_2$$

(this is the INITIAL amount)

$$6.6 \text{ g H}_2\text{O} * \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 0.366 \text{ mol H}_2\text{O}$$

(this is the EQUILIBRIUM AMOUNT)

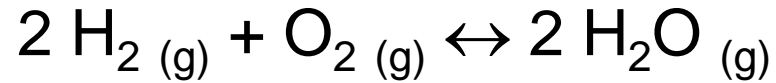
UNITS! UNITS! UNITS!

An ICE chart can use EITHER moles or concentration (molarity) or even pressure (atm), but you must use only one of these in any single ICE chart.

K_c uses molarity, so it is usually easiest to use concentration

I will do the problem both ways!

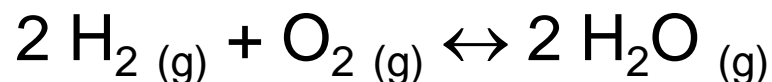
An ICE Chart



Initial	2.16 mol	0.894 mol	0 mol
Change	?????	?????	???????
Equilibrium	????	?????	0.366 mol

What is the change in quantities?

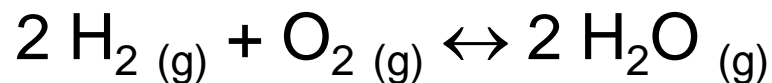
The “change” is all about stoichiometry!



Initial	2.16 mol	0.894 mol	0 mol
Change	- 2 x	-x	+ 2 x
Equilibrium	????	?????	0.366 mol

Now it is easy to finish filling in the ICE chart!

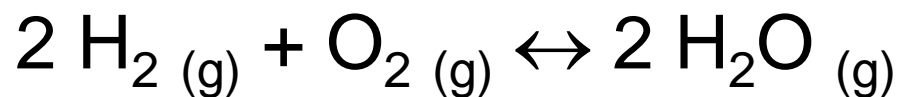
An ICE chart is really just “accounting for moles”



Initial	2.16 mol	0.894 mol	0 mol
Change	- 2 x	-x	+ 2 x
Equilibrium	2.16 - 2 x	0.894 - x	2 x = 0.366 mol

It is often helpful to use an ICE chart for other types of problems, it is a great way to keep track of what is going on.

Determining x allows me to fill in the rest of the chart



Initial

2.16 mol	0.894 mol	0 mol
- 2 x	-x	+ 2 x
2.16 - 2 x	0.894 - x	2 x = 0.366 mol

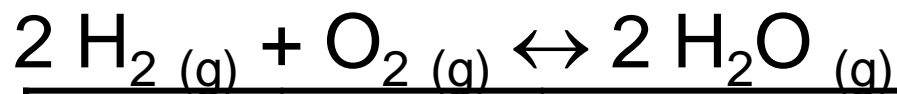
Change

Equilibrium

$$2 x = 0.366 \text{ mol}$$

$$x = 0.183 \text{ mol}$$

Determining x allows me to fill in the rest of the chart



Initial

2.16 mol	0.894 mol	0 mol
- 2 (0.183 mol)	-0.183 mol	+ 2 (0.183 mol)
2.16 - 2 (0.183) 1.794 mol	0.894 - 0.183 0.711 mol	0.366 mol

Change

Equilibrium

Now we need to calculate the concentrations and put them into K_c

$$[\text{H}_2] = 1.794 \text{ mol}/2\text{L} = 0.897 \text{ M}$$

$$[\text{O}_2] = 0.711 \text{ mol}/2\text{L} = 0.356 \text{ M}$$

$$[\text{H}_2\text{O}] = 0.366 \text{ mol}/2\text{L} = 0.183 \text{ M}$$

$$K_{\text{eq}} = K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$$

$$K_{\text{eq}} = K_c = \frac{[0.183]^2}{[0.897]^2[0.356]}$$

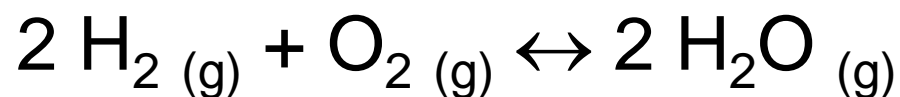
$$K_c = 0.117$$

Another Simple Problem

The K_c value for the formation of water from hydrogen and oxygen at 850 C is 4×10^{-6} .
If I mix 5.0 grams of hydrogen and 5.0 grams of oxygen in a 3 L flask at 850 C, what is the equilibrium concentration of the water?

Another simple solution

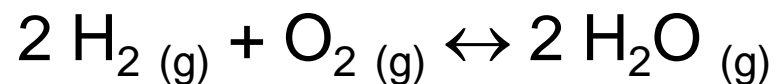
1st you need a balanced equation:



This allows us to immediately write the equilibrium constant expression:

$$K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]} = 4 \times 10^{-6}$$

Again, the Power of ICE



Initial			
Change	-2x	-x	+ 2 x
Equilibrium			

The “Change” line is always just stoichiometry

We already know a couple of things

$$5.0 \text{ g hydrogen} * \frac{1 \text{ mol H}_2}{2.016 \text{ g H}_2} = 2.48 \text{ mol H}_2$$

$$\frac{2.48 \text{ mol H}_2}{3 \text{ L}} = 0.827 \text{ M}$$

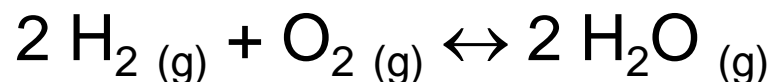
3 L

$$5.0 \text{ g oxygen} * \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = 0.156 \text{ mol O}_2$$

$$\frac{0.156 \text{ mol O}_2}{3 \text{ L}} = 0.0533 \text{ M}$$

3 L

Again, the Power of ICE



Initial	0.827 M	0.0533 M	0 M
Change	-2x	-x	+ 2 x
Equilibrium	$0.827 - 2 x$	$0.0533 - x$	2 x

Now, we know everything – well, sort of.

We have all of the equilibrium concentrations in terms of x ...

...we can use K_c to solve for x

$$K_c = \frac{[\underline{\text{H}_2\text{O}}]^2}{[\text{H}_2]^2[\text{O}_2]} = 4 \times 10^{-6}$$

$$0.000004 = \frac{(2x)^2}{(0.827 - 2x)^2(0.0533 - x)}$$

It looks like a mess...

...and it sort of is (although your calculator can probably solve it)

BUT you can simplify it with a helpful assumption:

ASSUME $x \ll 0.0533$

If we assume x is small

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = 4 \times 10^{-6}$$

$$4 \times 10^{-6} = \frac{(2x)^2}{(0.827 - 2x)^2(0.0533 - x)}$$

$$.0533 - x \approx 0.0533$$

$$0.827 - 2x \approx 0.827$$

A very simple problem remains

$$4 \times 10^{-6} = \frac{(2x)^2}{(0.827 - 2x)^2(0.0533 - x)}$$

$$4 \times 10^{-6} = \frac{(2x)^2}{(0.827)^2(0.0533)}$$

$$4 \times 10^{-6} = \frac{4x^2}{0.03645}$$

$$1.458 \times 10^{-7} = 4x^2$$

$$3.645 \times 10^{-8} = x^2$$

$$x = 1.91 \times 10^{-4}$$

Was the assumption good?

We started by assuming $x \ll 0.0533$

We now “know” that, with this assumption, x
is 1.91×10^{-4}

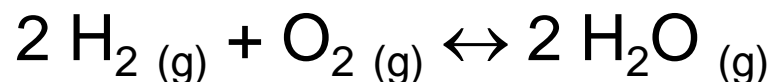
Is $1.91 \times 10^{-4} \ll 0.0533$?

Critical Judgment

How small is small depends on how accurate an answer you need: If you need 1 sig fig, than any number that is a factor of 10-20 smaller is insignificant. If you need 2 sig figs, then it must be about 100 times smaller. If you need 3 sig figs it must be about 1000 times smaller.

A good general rule for our purposes is that if a number is $<5\%$ of another number, it is significantly smaller. This maintains 2 sig figs in all the concentrations – usually enough.

We put x back into the ICE chart



Initial	0.827 M	0.0533 M	0 M
Change	-2 (1.91x10 ⁻⁴)	- 1.91x10 ⁻⁴	+ 2 (1.91x10 ⁻⁴)
Equilibrium	0.827 - 2 (1.91x10 ⁻⁴) = 0.827	0.0533 - 1.91x10 ⁻⁴ = 0.053	3.8x10 ⁻⁴

And we have our answer.

Clickers!

The K_c value for the formation of H_2O from H_2 and O_2 at 500 C is 3.2×10^{-4} . I put 5.0 mol of H_2 and 5.0 mol of O_2 in a 2 L flask at 500 C, what is the $[\text{H}_2\text{O}]$ at equilibrium?

A. 0.035 M

B. 0.050 M

C. 0.001 M

D. 0.070 M

E. 0.100 M