In the last unit, we handled chemical reactions from the perspective of stoichiometry and Limiting reactants; if a reaction happens, it will proceed until one reactant runs out. This is definitely NOT always the case. More commonly, reactions proceed until an equilibrium has been established.

Last lecture we noted that all reactions also occur in the reverse direction.

- When these reactions are physical (e.g. $l \to g$), it's really easy to visualize & accept this
- But, this statement is also true for chemical reactions!

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

The $\rightleftharpoons$ symbol indicates that both the forward and reverse reactions are occurring.

Anytime BOTH reactions are occurring, an equilibrium will be reached. This is when the rate of the forward reaction is exactly the same as the reverse. For this reason, concentrations don't change!

The "progress" of a reaction boils down to the ratio of [Products] to [Reactants] and can be described by an equilibrium constant (K)

$$aA + bB \rightleftharpoons cC + dD \qquad K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Solids & liquids Never show up in K

- The units can be [ ] or pressure
  ($[\,]$ → K_c; pressure → K_p)

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

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

1 mol gas → N_2O_4; 2 mol gas → $2NO_2$

$$\Delta n_{gas} = 2-1=1 \qquad K_p = K_c(RT)^1$$

- K is dependent on reaction direction + stoichiometry

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

- Reversing a reaction inverts the K

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_c' = \frac{[N_2O_4]}{[NO_2]^2}$$

$$K_c' = K_c^{-1}$$

Multiplying a reaction by a factor (2 in this case) K to the power of that factor

$$2N_2O_4 \rightleftharpoons 4NO_2 \qquad K_c'' = \frac{[NO_2]^4}{[N_2O_4]^2}$$

$$K_c'' = K_c^2$$

This is important: Equilibrium constants are CONSTANT @ a single Temp (yes, they change with temperature)

Sooo... It doesn't matter the amount of reactants that a reaction begins with. At equilibrium, the ratio will be K

For example: $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ $\quad K = \frac{[NO_2]^2}{[N_2O_4]}$

Initial Concentrations		Equilibrium concentration	
$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$
1.00 M	0 M	0.8 M	0.4 M
2.00 M	0 M	1.71 M	$\boxed{}$

What will this concentration be?

① determine K

② determine $[NO_2]$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.4\,M)^2}{0.8\,M} = 0.2\,M$$

$$0.2\,M = \frac{[NO_2]^2}{1.71\,M}$$

$$[NO_2]^2 = 0.342\,M^2$$

$$[NO_2] = 0.585\,M$$

EXAMPLE APPLICATIONS OF K

$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $\qquad K_p = 1.9\text{ atm} = \dfrac{P_{CO}^2}{P_{CO_2}}$

① AT 300 K, what is K_c?

$\Delta n_{gas} = 2 - 1 = 1$ $\qquad K_p = K_c(RT)^{\Delta n_{gas}}$

$1.9 = K_c\,(RT)^1$ $\qquad K_c = \dfrac{1.9\text{ atm}}{0.08206\,(300)} = 0.0772\text{ M}$

② At equilibrium $P_{TOT} = 4.00$ atm. What are the pressures of each gas?

$K_p = 1.9 = \dfrac{P_{CO}^2}{P_{CO_2}}$

We need to get rid of one of these variables in favor of something we know $\rightarrow P_{TOT}$

$P_{TOT} = P_{CO} + P_{CO_2}$ $\qquad P_{CO_2} = 4.00 - P_{CO}$ $\qquad 1.9 = \dfrac{P_{CO}^2}{4.00 - P_{CO}}$

$7.6 - 1.9P_{CO} = P_{CO}^2$

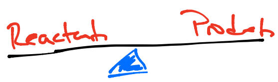
$0 = P_{CO}^2 + 1.9\,P_{CO} - 7.6$

$P_{CO} = 1.966$ or $\cancel{x = -2.03}$

$P_{CO_2} = 4.00 - 1.966 = 2.034\text{ atm}$

Check: $\dfrac{1.966^2}{2.034} = 1.9$ ✓

What would happen to this equilibrium if more CO_2 were added? Products will be formed



see below for a more thorough discussion

③ If 2.00 atm CO_2 is added to the chamber, calculate the equilibrium pressure of each gas

		C(s) +	CO_2 $\rightleftharpoons$	2 CO
Initial	= I		2.00	∅
Change	= C		$-x$	$+2x$
Equilibrium	= E		$2-x$	$2x$

$2x$ because 2 CO produced for every CO_2

$K_p = \dfrac{(2x)^2}{2-x} = 1.9$ $\qquad 3.8 - 1.9x = 4x^2$

$\underset{a}{4x^2} + \underset{b}{1.9x} \underbrace{-3.8}_{c}$

$x = \dfrac{-1.9 \pm \sqrt{1.9^2 - 4(4)(-3.8)}}{2(4)}$

At equilibrium:

$P_{CO_2} = 2 - x = 2 - 0.766 = 1.234 \text{ atm}$ $x = 0.766$ atm OR -1.21 atm

$P_{CO} = 2x = 2(0.766) = 1.531 \text{ atm}$

Always discard values that lead to impossible concentration / pressure values

Always go back and check your answers!

$$K_p = \frac{1.531^2}{1.234} = 1.9 \text{ atm} \checkmark$$

4) What is eq. pressure of CO_2 + CO if we start with 1.00 atm of each gas?

	C +	CO_2 ⇌	$2CO$
I		1.0	2.0
C		$-x$	$+2x$
E		$1.0-x$	$2.0+2x$

$$1.9 = \frac{(2+2x)^2}{1.0-x}$$

$1.9 - 1.9x = 4 + 8x + 4x^2$

$4x^2 + 9.9x + 2.1$

$x = -0.905$ atm OR -0.189 atm

* note that $x < 0$. This is ok, it just means that the reverse reaction will happen *

Both values of x end up with (+) pressures, so we need to calculate K to determine which is correct

$x = -0.905$ atm $P_{CO_2} = 1.905$ atm $P_{CO} = 0.189$ atm

$x = -0.234$ atm $P_{CO_2} = 1.234$ atm $P_{CO} = 1.531$ atm

$$K = \frac{0.189^2}{1.905} = 0.0188 \text{ atm}$$

$$K = \frac{1.531^2}{1.234} = 1.9 \text{ atm} \checkmark$$

Some Equilibrium Constants are very small - in some cases, these very small constants play a huge role in important chemical processes. In general, very small K lead to very small changes in concentrations

Note that when $K \ll 1$, reactants are largely favored. Alternately, $K \gg 1$ means that products are favored

reverse reaction is dominant

$$K = \frac{[Prod]}{[React]}$$

→ small $K \Rightarrow$ large [react]

large $K \Rightarrow$ small [React]

When K is really small, it is sometimes possible to make an assumption of the change. Really small K values lead to really small 'x' in the ICE table. When this happens, the 'x' in I−x may be insignificant and can be ignored.

$H_2 + Cl_2 \rightarrow 2HCl \qquad K_p = 9.1\times10^{-10}$

I	0.5	0.8	Ø
C	−x	−x	+2x
E	0.5−x	0.8−x	2x

$9.1\times10^{-10} = \frac{(2x)^2}{(0.5-x)(0.8-x)}$

① assume $x \ll 0.5$

$9.1\times10^{-10} = \frac{4x^2}{(0.5)(0.8)}$

$x^2 = 9.1\times10^{-11}$

$x = 9.54\times10^{-6}$

If "I" is 1000x larger than x, then this approximation is ok to use. Otherwise, use the quadratic.

TEST

$\frac{0.5}{9.54\times10^{-6}} = \boxed{52410}$

\# when > 1000, approx is acceptable

So... in this case, yes, we can simplify this expression

Predicting the direction of a reaction:

The reaction quotient (Q) is the ratio of [Prod]:[Reactants]. This does NOT need to be at equilibrium! Comparing Q & K will tell us which direction the reaction will shift.

$K < Q$ ← shifts to reactants

$K > Q$ → shifts to products

$K = Q$

@ equilibrium

the sign tells you the direction as long as K is written 1st

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_p = 0.012 = \frac{P_{NH_3}^2}{P_{N_2}\,P_{H_2}^3}$

$P_{N_2} = 26.40$ atm $\qquad P_{H_2} = 13.02$ atm $\qquad P_{NH_3} = 21.81$

$Q = \frac{21.81^2}{(26.4)(13.02)^3} = 8.16\times10^{-3}$ $\qquad K > Q$ → Products will form

$P_{N_2} = 25.54$ atm $\quad P_{H_2} = 10.42$ atm $\quad P_{NH_3} = 23.55$

$$Q = \frac{23.55^2}{(25.54)(10.42)^3} = 0.0192 \qquad K < Q$$

$\xleftarrow{}$ Reactants will form

If we are already at equilibrium ($Q=K$) and I add reactants, how will the concentration respond?

$\uparrow$ [react] $\Rightarrow$ Q gets smaller $\quad K > Q$, products form

- the opposite happens if products are added. Q increases $\quad K < Q$ & react. formed

This is known as LeChatelier's Principle: Adding reactants forces more products to be made. Adding products shifts the eq. to reactants

$H_2 + Cl_2 \rightleftharpoons 2HCl(g)$

If HCl is added, $\leftarrow$

If H_2 or Cl_2 is added, $\leftarrow$

If both are added, Time for an ICE table

Lastly, chemical equilibria expressions can be manipulated and combined:

① $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad K_{P,1} = 1.44$

② $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad K_{P,2} = 25.6\ atm^2$

Determine K_P for:

$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad K_{P,3} = ?$

$$K_{P,1} = 1.44 = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \qquad K_{P,2} = \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}} \qquad K_{P,3} = \frac{P_{CO_2} P_{H_2}^3}{P_{CH_4} P_{H_2O}}$$

③ = ① + ②

① $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

② $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$CO(g) + 2H_2O(g) + CH_4(g) \rightleftharpoons CO_2(g) + CO(g) + 4H_2(g)$

$2H_2O(g) + CH_4(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad K_{P,3}$

$$K_{P,1} * K_{P,2} = K_{P,3}$$

When equations are added, Ks are multiplied

$$\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} * \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}} = \boxed{\frac{P_{CO_2} P_{H_2}^4}{P_{CH_4} P_{H_2O}^2}} \longleftarrow K_{P,3}$$