# Chemical Equilibrium

Reactions at Equilibrium

One examples of equilibrium are people's optimal weight; we are constantly gaining and loosing to be at a desirable weight.

Thermal equilibrium is maintaining a constant temperature.

When we open a freezer, the freezer gets warmer. A cycle to cool it back to it's original temperature begins all over again once the door is closed.
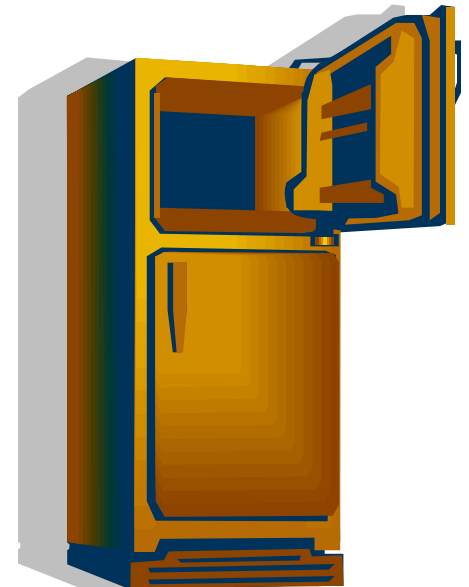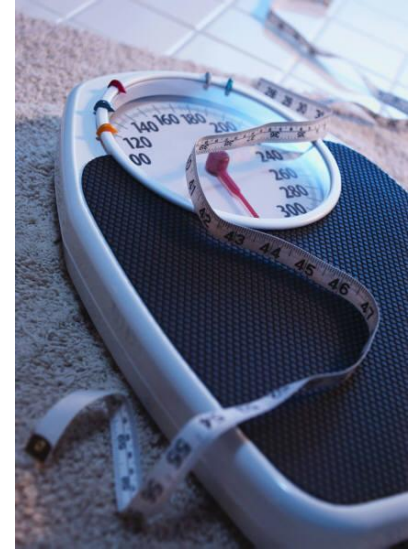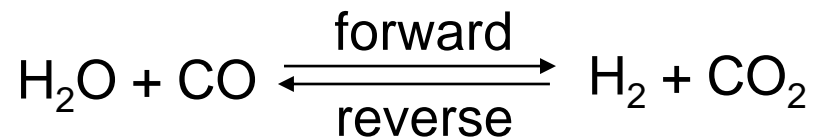
Equilibrium

The exact balancing of two processes, one of which is the opposite if the other.

Equilibrium

Rate of evaporation = Rate of condensation

Equilibrium

$$H_2O + CO \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftarrows}} H_2 + CO_2$$

Equilibrium: rate of the forward reaction = rate of reverse reaction

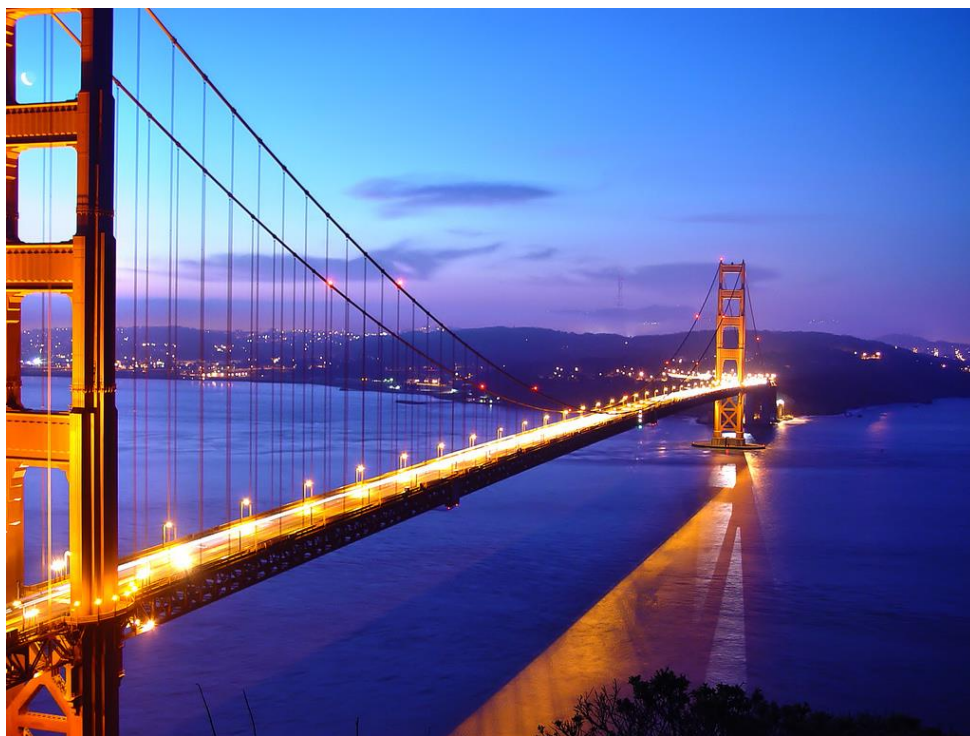$$Rate_{forward} = Rate_{reverse}$$

The concentration of all reactants and products remain constant.

No net change in speed
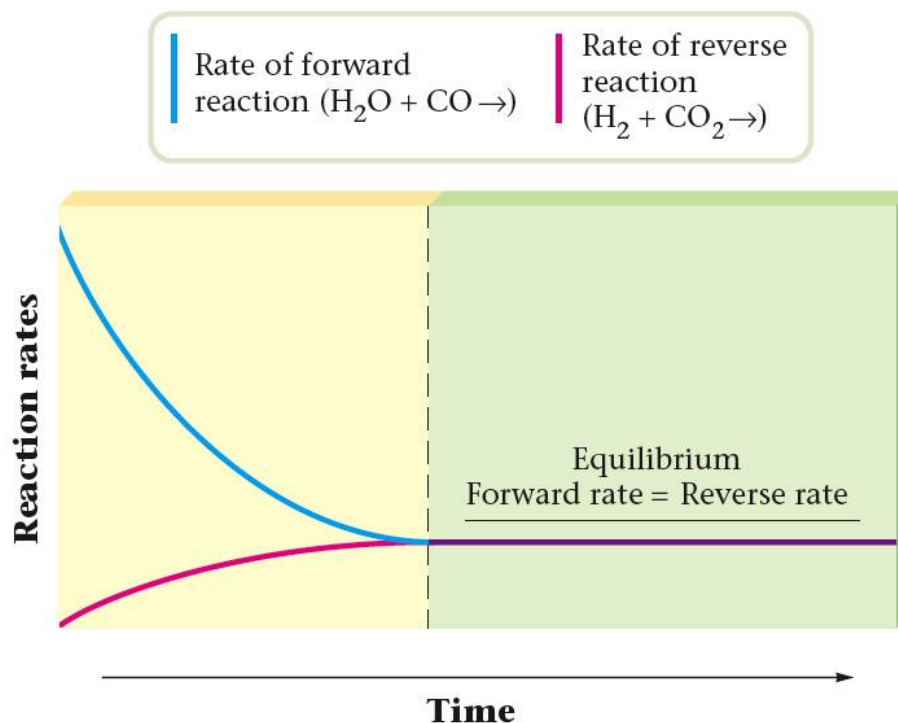
Has reaction stopped???

Equilibrium

At equilibrium, the reaction has not stopped and the system is dynamic.

There is motion on the bridge, but the number of cars is constant.

Equilibrium

$$H_2O + CO \xrightleftharpoons[\text{reverse}]{\text{forward}} H_2 + CO_2$$

| Rate of forward reaction ($H_2O + CO \rightarrow$) | Rate of reverse reaction ($H_2 + CO_2 \rightarrow$) |

Reaction rates

Equilibrium
Forward rate = Reverse rate

Time
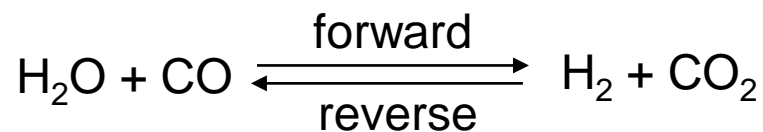
Note, it's **<u>impossible</u>** <u>to make more product</u> when at equilibrium. The reaction just **appears to have stopped moving**.

Reactions **not** at Equilibrium

Burning methane, CH_4, in oxygen is a one-way reaction,

$$CH_4(g) \; + \; 2O_2(g) \; \rightarrow \; CO_2(g) \; + 2H_2O(g) + Energy$$
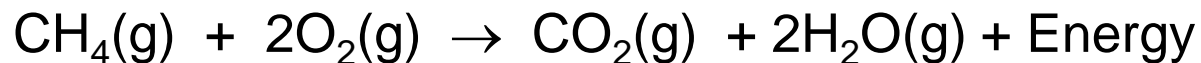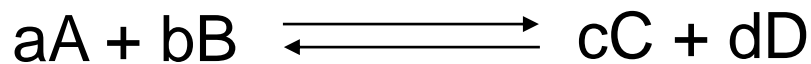
- here we only make products.

Energy released from eating food.

Time only moves in one direction (as we experience it).

Law of Chemical Equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

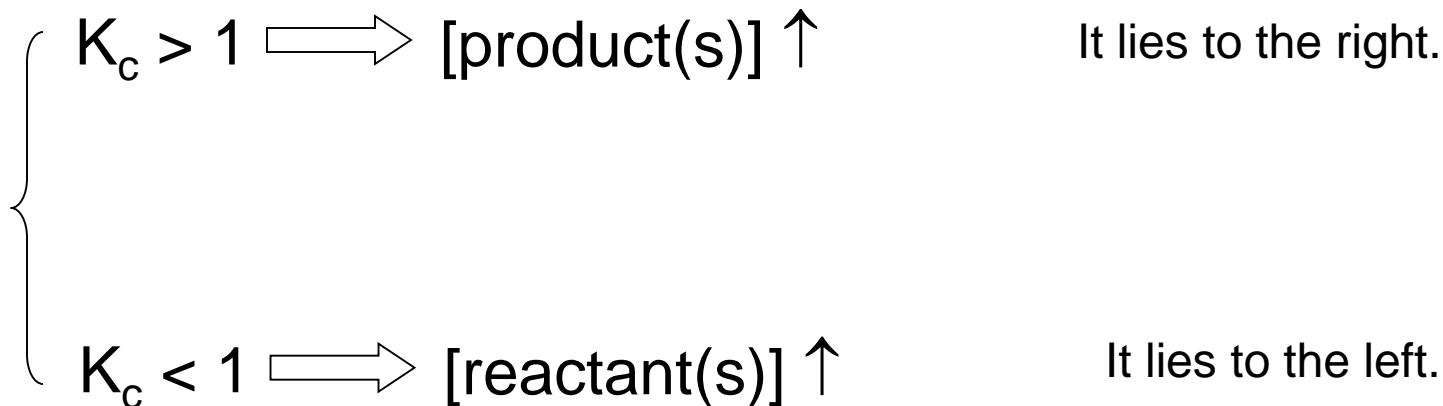Equilibrium expression $\qquad K_c = \dfrac{[Product(s)]}{[Reactant(s)]} \qquad$ [ ]: M or mol/L

K_c: Equilibrium constant

$$K_c = \dfrac{[C]^c \, [D]^d}{[A]^a \, [B]^b}$$

$K_c > 1 \implies$ [product(s)] ↑ $\qquad$ It lies to the right.

$K_c < 1 \implies$ [reactant(s)] ↑ $\qquad$ It lies to the left.

Practice 1:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
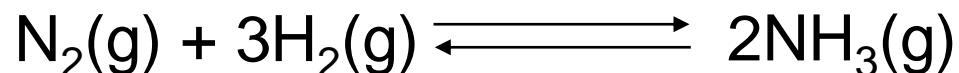
$[N_2] = 0.921$ M, $[H_2] = 0.763$ M, and $[NH_3] = 0.157$ M

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

→ Product (coefficient of 2 becomes power of 2)

→ Reactants
(coefficients of 1 & 3 become powers of 1 & 3)

$$K_c = \frac{(0.157)^2}{(0.921)(0.763)^3} = 0.0602$$

Law of Chemical Equilibrium

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Table 17.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 °C
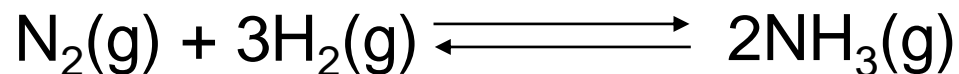
	Initial Concentrations			Equilibrium Concentrations			$\dfrac{[NH_3]^2}{[N_2][H_2]^3} = K^*$
Experiment	$[N_2]_0$	$[H_2]_0$	$[NH_3]_0$	$[N_2]$	$[H_2]$	$[NH_3]$	
I	1.000 M	1.000 M	0	0.921 M	0.763 M	0.157 M	$\dfrac{(0.157)^2}{(0.921)(0.763)^3} = 0.0602$
II	0	0	1.000 M	0.399 M	1.197 M	0.203 M	$\dfrac{(0.203)^2}{(0.399)(1.197)^3} = 0.0602$
III	2.00 M	1.00 M	3.00 M	2.59 M	2.77 M	1.82 M	$\dfrac{(1.82)^2}{(2.59)(2.77)^3} = 0.0602$

*The units for K are customarily omitted.

Each set of equilibrium concentration is called an equilibrium position and it depends on the initial concentrations (there are an infinite # of equilibrium positions but only one equilibrium constant).

K remains the same even with the different equilibrium concentrations.

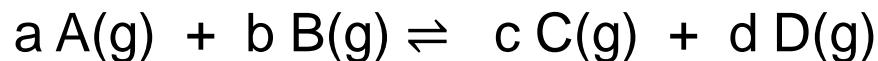# Equilibrium and the Law of Mass Action

For gases:

Equilibrium expression

$$K_p = \frac{\text{Partial pressure of product}}{\text{Partial pressure of reactants}}$$

K_p: Equilibrium constant

$$a\,A(g)\ +\ b\,B(g) \rightleftharpoons\ c\,C(g)\ +\ d\,D(g)$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

here $\underline{P}$ means partial pressure

$K_p \neq K_c$, something we'll look at shortly.

Practice 2: Write the expression for the equilibrium constant for:

$2 H_2S(g) + 3 O_2(g) \rightleftharpoons 2 SO_2(g) + 2 H_2O(g)$.
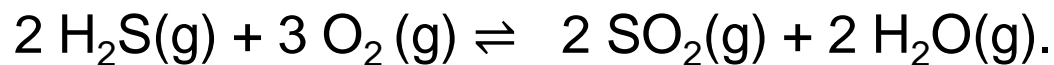
Using $K_p = \dfrac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$

$K_p = \dfrac{(P_{SO2})^2(P_{H2O})^2}{(P_{H2S})^2(P_{O2})^3}$

Reminder this is the same as $K_p = \dfrac{(P_{SO2})^2 \times (P_{H2O})^2}{(P_{H2S})^2 \times (P_{O2})^3}$

Homogeneous & Heterogeneous Equilibriums

Homogeneous Equilibria: when all substances are in the same state.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
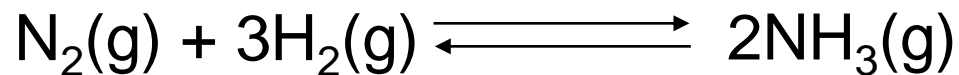
Heterogeneous Equilibria: when more than one state are involved.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
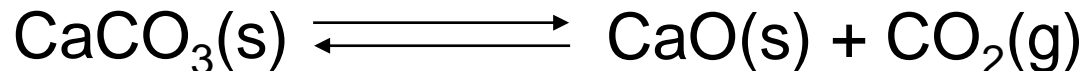
Heterogeneous Equilibria

The concentration of "pure" **solids** and **liquids** cannot change and they are constants.

$\Downarrow$

The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
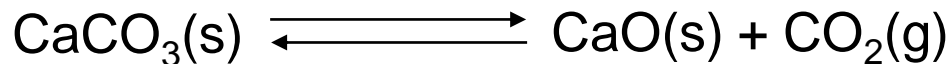
$$K' = \frac{[CaO]\,[CO_2]}{[CaCO_3]} \qquad K' = \frac{C_1\,[CO_2]}{C_2}$$

$$\frac{C_2\,K'}{C_1} = K = [CO_2]$$

The concentrations of pure **solids** or pure **liquids** are not included in equilibrium expression.

Heterogeneous Equilibria

Practice 3:

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$
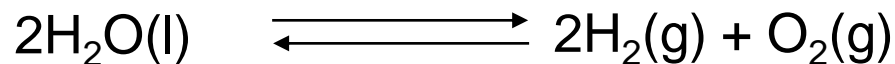
Water is not included because is a pure liquid.

$$K = [H_2]^2[O_2]$$

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$
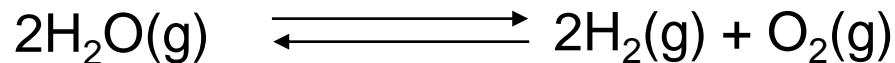
Water is included because is a vapor (gas).

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

Temperature & K

Each reaction has its own characteristic equilibrium constant, at it's own temperature.

The *extraordinary empirical result*, is that, regardless of the initial composition, the *reaction adjusts* so the activities give **the same characteristic value of K** for each reaction at that temperature.

	T(K)	K
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	4.0×10^{31}
	500	4.0×10^{18}
	1000	5.1×10^{8}
$I_2(g) \rightleftharpoons 2I^-(g)$	800	2.1×10^{-3}
	1000	0.26
	1200	6.8

Different ways to relate K_p and K_c

Being able to express equilibrium constants in terms of pressure and concentration are critical to industry.

The important relationship between K_p and K_c is,

$$K_p = (RT)^{\Delta n} K_c$$ (has the form of P=cRT, and c is mol·L^{-1})

K_p = equilibrium constants in terms of pressure
K_c = equilibrium constants in terms of concentration
Δn, n is moles, and Δn is $n_{products} - n_{reactants}$

Note: your textbook writes K as the standard form, and written here as K_p to help differentiate the two.

Practice 3: At 400.°C, the equilibrium constant K_p for
$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ is 3.1×10^4. What is the value of K_c at this temperature?

$K_p = (RT)^{\Delta n}\ K_c$, R is the universal gas constant, $0.08206\ atm \cdot L \cdot mol^{-1} \cdot K^{-1}$

$\Delta n,\ n_{products} - n_{reactants},\ \ 2 - (2 + 1) = -1$

$K_c = \dfrac{K_p}{(RT)^{\Delta n}}$, $\dfrac{3.1 \times 104}{[(.08206)(400.°C + 273)K]-1} = 1.7 \times 10^6$

An alternative method, using bar, $K_p = \left(\dfrac{c°RT}{P°}\right)^{\Delta n} K_c$ where

$\dfrac{c°R}{P°} = \dfrac{1\ bar}{(8.3145 \times 10^{-2} L \cdot bar \cdot K^{-1} \cdot mol^{-1})(1\ mol \cdot L^{-1})} = 12.03$ K, and

substituting this we end up with: $K_p = \left(\dfrac{T}{12.03K}\right)^{\Delta n} K_c$
Both methods are equivalent.

Alternative Forms of the Equilibrium Constant

The following algebraic manipulations are helpful for deriving different forms of equilibrium constant expressions.

$$H_2(g) \; + \; I_2(g) \; \rightleftharpoons \; 2\,HI(g) \;, \quad K = \frac{[HI]^2}{[H_2][I_2]} \; = \; 54 \;\; \text{at 700.°C}$$
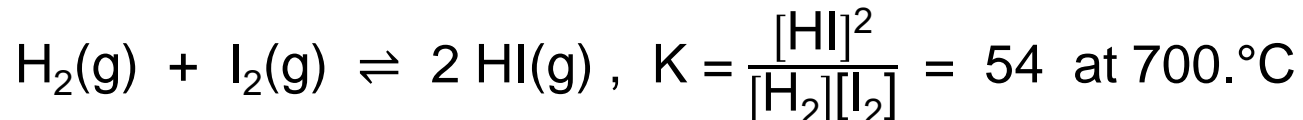
1

Multiply the equation by 2, $2\,H_2(g) \; + \; 2\,I_2(g) \; \rightleftharpoons \; 4\,HI(g),$

$$K = \frac{[HI]^4}{[H_2]^2[I_2]^2} \; = \; 54^2 = 2900$$

2

Reversing the equation, $2\,HI(g) \rightleftharpoons \; H_2(g) \; + \; I_2(g),$

$$K = \frac{[H_2][I_2]}{[HI]^2} \; = \; \frac{1}{54} = 0.019$$

Alternative Forms of the Equilibrium Constant

Combining multiply equations and multiply K's to find <u>Overall equilibrium constant</u>.

For example if K's are known for Equations 1 and 2 but not 3 we can manipulate 1 & 2 to get 3's K.

Eq. 1 $2 P(g) + 3 Cl_2(g) \rightleftharpoons 2 PCl_3(g)$
Eq. 2 $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
Eq. 3 $2 P(g) + 5 Cl_2(g) \rightleftharpoons 2 PCl_5(g)$
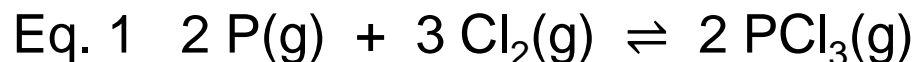
Eq. 1 can remain unchanged.

$$K_1 = \frac{P_{PCl3}{}^2}{P_P{}^2 P_{Cl2}{}^3}$$

Eq. 2 is multiplied by 2, $2 PCl_3(g) + 2 Cl_2(g) \rightleftharpoons 2 PCl_5(g)$

$$K_2{}^2 = \frac{P_{PCl5}{}^2}{P_{PCl3}{}^2 P_{Cl2}{}^2}$$

Alternative Forms of the Equilibrium Constant

Next combine Eq. 1 and Eq. 2 and cancel like species.

Combine K_1 and K_2 (K_2 is now square, K_2^2)

Eq. 1 $2\,P(g) + 3\,Cl_2(g) \rightleftharpoons 2\,PCl_3(g)$

Eq. 2 $2\,PCl_3(g) + 2\,Cl_2(g) \rightleftharpoons 2\,PCl_5(g)$

Eq. 3 $2\,P(g) + 5\,Cl_2(g) \rightleftharpoons 2\,PCl_5(g)$
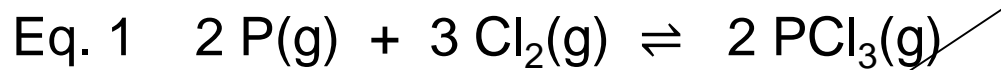
$$K_1 = \frac{P_{PCl3}^{\,2}}{P_P^{\,2}\,P_{Cl2}^{\,3}}$$

$$K_2^{\,2} = \frac{P_{PCl5}^{\,2}}{P_{PCl3}^{\,2}\,P_{Cl2}^{\,2}}$$

When you add two equation, you should multiply the K values.

$$K_1(K_2)^2 = K_3 = \frac{P_{PCl5}^{\,2}}{P_P^{\,2}\,P_{Cl2}^{\,5}}$$

Using equilibrium constants

Equilibrium constants are "**constants**" and are therefore, **powerful predicting tools**! Next we look at:

1. Calculating K's from knowing equilibrium concentrations;

2. Calculating equilibrium concentrations from knowing K's.

	P_{SO2} (bar)	P_{O2} (bar)	P_{SO3} (bar)	K
Exp 1	0.660	0.390	.0840	0.0415
Exp 2	0.110	.0110	.00750	0.0423
Exp 3	1.44	1.98	0.410	0.0409

Regardless of the initial compositions, the final K is always the same.

Using equilibrium constants

Equilibrium reactions like $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, have **initial**, **changing**, and **final** conditions in units of either pressures (P) or concentrations (mol·L⁻¹).

The **most universally adopted method** to solve changing condition problems is to set up an **equilibrium table**.
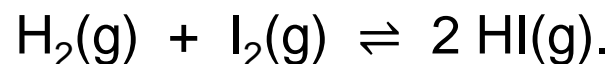
$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g).$$

	H_2	I_2	HI
initial			
change			
equil. (final)			

Values going into the matrix are either pressure or mol·L⁻¹ .

Practice 4: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, starting with 1 bar each of H_2 and I_2, the equilibrium pressure of HI was found to be 0.8 bar. What are the final pressures of H_2 and I_2? Calculate K_p.

- We start by building an equilibrium table, and plugging in the given data;
- **Initially** 1 bar each of H_2 and I_2 and no HI;
- **final** or at equilibrium was 0.8 bar of HI;

This is enough information to solve the rest of the table.

	H_2	I_2	HI
initial	1	1	0
change			
equil. (final)			0.8

$$H_2(g) + I_2(g) \rightleftharpoons 2\, HI(g)$$
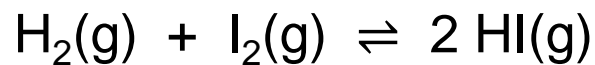
	H_2	I_2	HI
initial	1	1	0
change	- ½ 0.8 = - 0.4	- ½ 0.8 = - 0.4	+ 0.8
equil.	1 - 0.4 = 0.6	1 - 0.4 = 0.6	0.8

To go from 0 to 0.8, it must have **changed** by 0.8; notice it is "+" because it was created;

The **changes** are all related by **stoichiometry**; note the "-" because it is consumed;

The **final** H_2 and I_2 are found by combining the **initial** and **changes**;

Practice 4: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, starting with 1 bar each of H_2 and I_2, the equilibrium pressure of HI was found to be 0.8 bar. What are the final pressures of H_2 and I_2? Calculate K_p.

A cleaned-up table.

	H_2	I_2	HI
initial	1	1	0
change	- 0.4	- 0.4	+ 0.8
equil.	0.6	0.6	0.8

At equilibrium $P_{H2} = P_{I2} = 0.6$ bar, and $P_{HI} = 0.8$ bar;

we can calculate K_p:

$$K_p = \frac{(0.8\ bar)^2}{(0.6\ bar)(0.6\ bar)} = 2$$

Practice 5: $3 H_2(g) + N_2(g) \rightleftharpoons 2 NH_3(g)$, starting with 0.5 bar each of H_2 and N_2, it was found at equilibrium that the pressure of NH_3 was 0.02 bar. What are the final pressures of H_2 and N_2? Calculate K_p.

- Make an equilibrium table with starting values;
- Calculate the one <u>change</u> we know, here NH_3;
- Using stoichiometry, calculate the changes in H_2 and N_2;
- Combine the initial and change to find the final;

Important to remember "-" means consumed (going away) and "+" means being produced (making it).

	H_2	N_2	NH_3
initial	0.50	0.50	0
change	- (3/2) 0.02 = - 0.03	- (½) 0.02 = - 0.01	+ 0.02
equil.	0.50 - 0.03 = 0.47	0.50 - 0.01 = 0.49	0.02

Practice 5: $3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$, starting with 0.5 bar each of H_2 and N_2, it was found at equilibrium that the pressure of NH_3 was 0.02 bar. What are the final pressures of H_2 and N_2? Calculate K_p.

	H_2	N_2	NH_3
initial	0.50	0.50	0
change	- 0.03	- 0.01	+ 0.02
equil.	0.47	0.49	0.02

At equilibrium $P_{H2} = 0.47$ bar, $P_{N2} = 0.49$ bar, and $P_{NH3} = 0.02$ bar;

We have the information to calculate K_p,

$$K_p = \frac{(P_{NH3})^2}{(P_{H2})^3 P_{N2}} \cong \frac{(0.02)^2}{(0.47)^3(0.49)} = 7.9 \times 10^{-3}$$

Another way to use equilibrium expressions

1. The previous 2 examples <u>found K (or K_p)</u> from pressures (or concentrations).

Method 1; Exp 3: $\dfrac{(0.00750)^2}{(0.110)^2(0.110)} = 0.0423$

If we know these

We can find this

2. Now we'll <u>find the final pressures (or concentrations)</u> from K (or K_p).

We can find these

If we know this

Method 2; Exp 1: $\dfrac{(P_{so3})^2}{(P_{so2})^2(P_{o2})}, \dfrac{(0.0840)^2}{(0.660)^2(0.390)} = 0.0415$

Practice 6: Suppose that a mixture of 0.482 mol N_2 and 0.933 mol O_2 is transferred to a reaction vessel of volume 10.0 L and allowed to form N_2O at 800. K; at this temp. $K_p = 3.2 \times 10^{-28}$ for the reaction
$2 N_2(g) + O_2(g) \rightleftharpoons 2 N_2O(g)$. Calculate the partial pressures of the gases in the equilibrium mixture.

First we find the pressure for each gas using PV = nRT

$$P_{N2} = \frac{(0.482 \text{ mol})(8.3145 \times 10^{-2} \text{ L·bar·K}^{-1}\text{·mol}^{-1})(800.K)}{10.0 \text{ L}} = 3.21 \text{ bar}$$
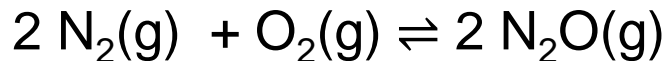
$$P_{O2} = \frac{(0.933 \text{ mol})(8.3145 \times 10^{-2} \text{ L·bar·K}^{-1}\text{·mol}^{-1})(800.K)}{10.0 \text{ L}} = 6.21 \text{ bar}$$

$P_{N2O} = 0$ (initially)

We make our equilibrium table from known values.

Here we use "x" to denote the change in concentration which is based on stoichiometry; remembering that "+" means producing and "-" means going away.

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	$-2x$	$-x$	$+2x$
equil.	$3.21 - 2x$	$6.21 - x$	$+2x$

$$2 N_2(g) + O_2(g) \rightleftharpoons 2 N_2O(g)$$

Form an equilibrium expression,

$$K_p = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

Practice 6: Suppose that a mixture of 0.482 mol N_2 and 0.933 mol O_2 is transferred to a reaction vessel of volume 10.0 L and allowed to form N_2O at 800. K; at this temp. $K_p = 3.2 \times 10^{-28}$ for the reaction
$2 N_2(g) + O_2(g) \rightleftharpoons 2 N_2O(g)$. Calculate the partial pressures of the gases in the equilibrium mixture.

Our equilibrium expression,

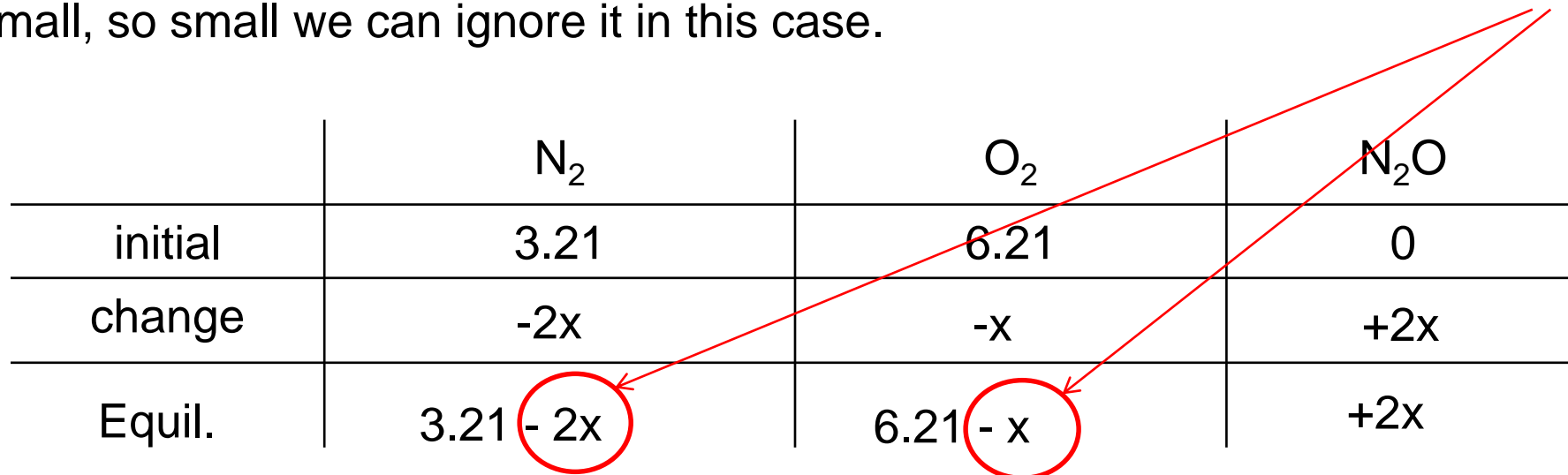$$K_p = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

This would be very difficult to solve *quickly* without using Newton's method or software.

Next we look at a method often called an **approximation** that can greatly reduce the time we spend solving complex problems.

Previously we found K_p is 3.2×10^{-28}, which is in fact very very small.

This means this is a "reactant-favored" reaction but more importantly, it tells us that K_p is so small that the amount of disassociation -that is **x**- is very very small, so small we can ignore it in this case.

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21 - 2x	6.21 - x	+2x

In reality, the disassociation is small because of K_p, that 3.21 and 6.21 are much LARGER, so that our table actually looks like this.

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21	6.21	+2x

This approximation greatly simplifies our K expression from

$$K_p = \frac{(2x)^2}{(3.21 - 2x)^2(6.21 - x)} = 3.2 \times 10^{-28}$$

to, $$3.2 \times 10^{-28} = \frac{(2x)^2}{(3.21)^2(6.21)} =$$

$$x = \sqrt{\frac{3.2 \times 10^{-28}(3.21)2(6.21)}{2}}$$

$$x = 7.2 \times 10^{-14}$$

Now we can solve for our final concentrations.

Substituting our **x** back into our table to find our final concentrations.

$$x = 7.2 \times 10^{-14}$$

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21 - 2x	6.21 - x	+2x

N_2:   3.21 - 2x , $3.21 - 2(7.2 \times 10^{-14}) = 3.21$ bar N_2

O_2:   6.21 − x , $6.21 - (7.2 \times 10^{-14}) = 6.21$ bar O_2

N_2O: 2x , $2(7.2 \times 10^{-14}) = 1.4 \times 10^{-13}$ bar N_2O

When K (or K_p) is small, and the starting concentrations are large, we assume disassociation, "x", is negligible.

$$K_p = 3.2 \times 10^{-28}$$

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21 - 2x	6.21 - x	+2x

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21	6.21	+2x

< 5% rule

The 5% rule says we can **ignore "x"** when there is **less than 5% decomposition or ionization change** (the definition of a weak acid). Previously: $x = 7.2 \times 10^{-14}$, our initial concentration 3.21 M.

% ionization $= \dfrac{7.2 \times 10^{-14}}{3.21} \times 100 = 2.2 \times 10^{-12}$ which <<< 5%.

	N_2	O_2	N_2O
initial	3.21	6.21	0
change	-2x	-x	+2x
Equil.	3.21 - 2x	6.21 - x	+2x

A note of good practice is, once solving for x, always plug x back into the original equilibrium table to make sure you're below 5% **-and-** to get your final values.

Practice 7: Hydrogen chloride gas at 0.012 bar is added to a reaction vessel containing solid iodine. At the temperature of the experiment, $K_p = 3.5 \times 10^{-32}$ for $2\,HCl(g) + I_2(s) \rightleftharpoons 2HI(g) + Cl_2(g)$. Assume that some I_2 remains at equilibrium. What are the equilibrium partial pressures of each gaseous substance in the reaction mixture?

	HCl	I_2	HI	Cl_2
initial	0.012		0	0
change	-2x		+2x	+x
equil.	0.012 - 2x		2x	x

Since K_p is very small, we'll make the assumption that the 2x in 0.012 – 2x is negligible; that HCl will not dissociate much.

We solve for x, $K = \dfrac{(2x)^2 x}{(0.012)^2} = 3.5 \times 10^{-32}$,

This simplifies to $3.5 \times 10^{-32} = \dfrac{4x^3}{(0.012)^2}$,

$x = 1.1 \times 10^{-12}$, test first for <5%

$$\% \text{ change} = \frac{1.1 \times 10{-12}}{0.012} \times 100 = 9.2 \times 10^{-9}$$ 👍

plugging x back into our original equation to find the final concentrations,

$HCl = 0.012 - x$, $\quad 0.012 - 1.1 \times 10^{-12} = 0.012$ bar

some I_2 remains

$HI = 2x$, $2(1.1 \times 10^{-12}) = 2.2 \times 10^{-12}$ bar

$Cl_2 = x$, $\quad = 1.1 \times 10^{-12}$ bar

Practice 8: Suppose that we place 3.12 g of PCl_5 in a reaction vessel of volume 500. mL and reach equilibrium at 250.°C, when K_p = 78.3 for the reaction

PCl_5 (g) $\rightleftharpoons$ PCl_3(g) + Cl_2(g). All three substances are gases at 250°C. Find the composition of the equilibrium mixture in bar.

Since we're given K_p, we have enough information to find the pressure of PCl_5. Using PV = nRT, we need mole first.

Mole PCl_5, $\dfrac{3.12\ g}{208.24\ g \cdot mol^{-1}}$

$P = \dfrac{nRT}{V}$, $\dfrac{\dfrac{3.12\ g}{208.24\ g \cdot mol^{-1}}\left(8.3145 \times 10^{-2} L \cdot bar \cdot K^{-1} \cdot mol^{-1}\right)523K}{0.500L} = 1.30$ bar

$K_p = 78.3$ for $PCl_5 (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

	PCl_5	PCl_3	Cl_2
initial	1.30	0	0
change	-x	+x	+x
equil.	1.30 - x	x	x

$K_p = \dfrac{x^2}{1.30 - x} = 78.3$ however, K_p is very large, which means "x" in 1.30-x will be *substantial*; **PCl₅** will **dissociate noticeably**.

We simplify to;

78.3 (1.30 - x) = x^2 ,   or x^2 + 78.3x - 102 the only way to solve this is with the quadratic equation.

K_p = 78.3 for the reaction $PCl_5\ (g) \rightleftharpoons PCl_3(g)\ + Cl_2(g)$.

$x^2\ +\ 78x\ -\ 102$, using $\dfrac{-b\pm\sqrt{b^2-4ac}}{2a}$

$\dfrac{-78\pm\sqrt{78^2-4(102)}}{2}$ we solve and find x = -79.6 and 1.28

Since a "-" means the opposite of "+" or perhaps anti-mass, which has no meaning in chemistry. Therefore, x = 1.28 bar

	PCl_5	PCl_3	Cl_2
initial	1.30	0	0
change	-x	+x	+x
final	1.30 - x	x	x

PCl_5 = 1.30 · Equil.   0 - 1.28   = 0.02 bar
PCl_3 = x   ,   = 1.28 bar
Cl_2 = x   ,   = 1.28 bar

% change = $\dfrac{1.28}{1.30} \times 100 = 98.5$ 👍

Le Châtelier's Principle

Because chemical equilibria are dynamic, they respond to changes or disturbances in concentrations, pressure and temperature.

Equilibrium shifts to counter a disturbance.

When a change is imposed on a system at equilibrium,
the position of the equilibrium shifts in a direction
that tends to reduce the effect of that change.

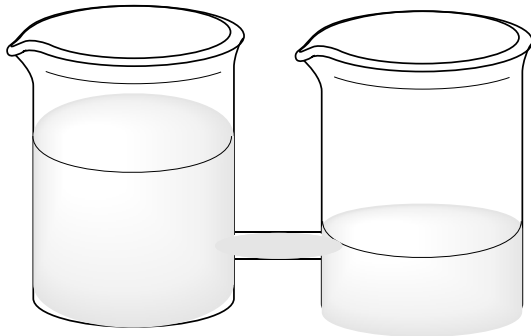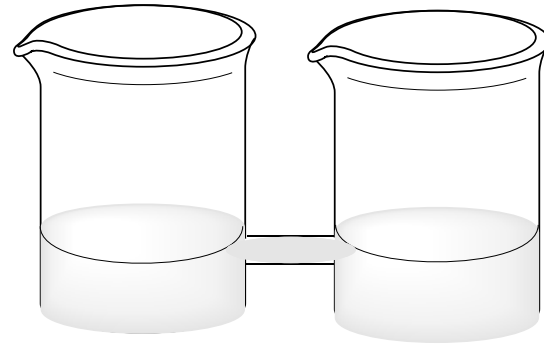# Le Châtelier's Principle

1. Effect of a change in concentration:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Add $N_2 \implies [NH_3] \uparrow$ and $[H_2] \downarrow$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
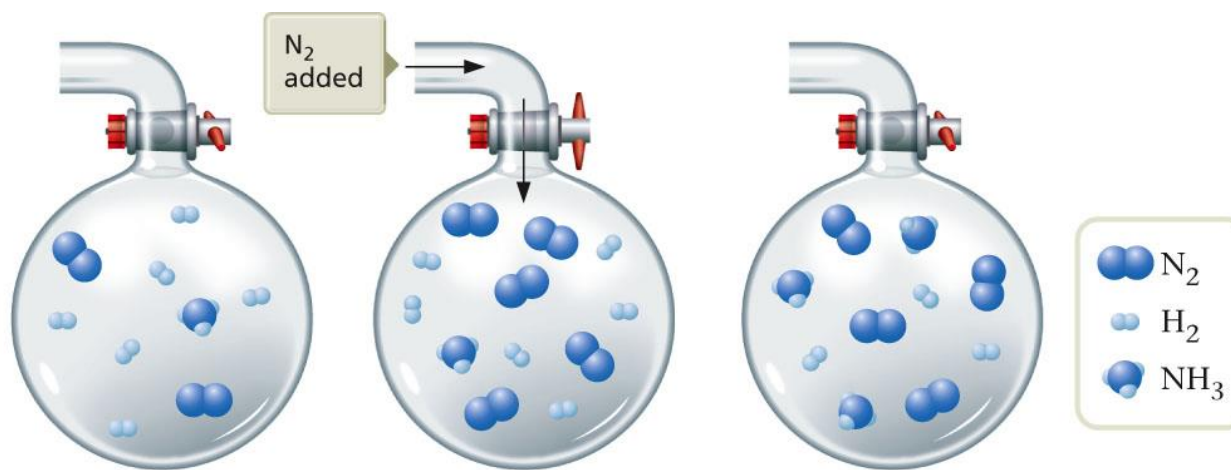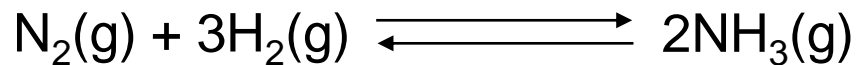
Le Châtelier's Principle

A more visual representation of an equilibria is what happens to the water level in two beakers joined, in such a way to allow water to freely move between the two beakers.

The water level is the same in each beaker, where the water level is representing an equilibrium in the two beakers.

Adding water to the left beaker will cause the water to flow to the right.
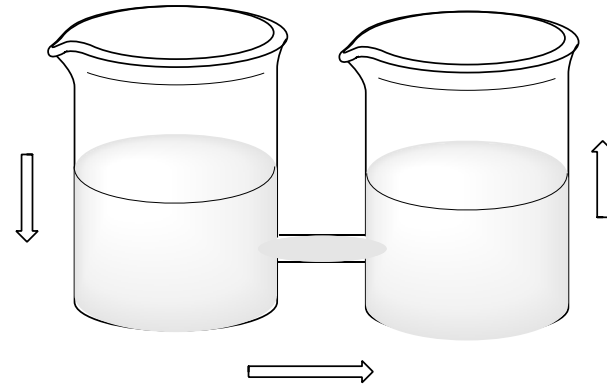
The water flows until a new equilibrium is reached.

Le Châtelier's Principle

1. Effect of a change in concentration:

- When a reactant or product is added the system shifts away from that added component.

- If a reactant or product is removed, the system shifts toward the removed component.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Add NH_3 $\Longrightarrow$ $[N_2]$ ↑ and $[H_2]$ ↑

Remove N_2 $\Longrightarrow$ $[NH_3]$ ↓ and $[H_2]$ ↑

Remove NH_3 $\Longrightarrow$ $[N_2]$ ↓ and $[H_2]$ ↓

Le Châtelier's Principle

1. Effect of a change in concentration:

K (equilibrium constant) does not change.

It remains constant.

Practice 9: Consider the equilibrium
$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$ Predict the effect on each equilibrium concentration of (a) the addition of N_2; (b) the removal of H_2O.

3. Over time **N_2** will ↓

(a) the addition of N_2, $4\ NH_3(g) + 3\ O_2(g) \rightleftharpoons 2\ N_2(g) + 6\ H_2O(g)$

3.↑   3.↑   1.↑   3.↓

⟵ 2.
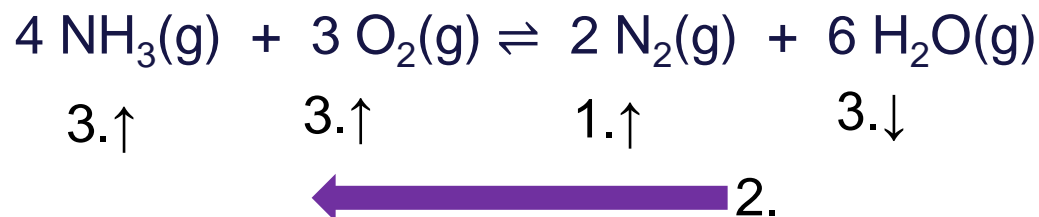
"1.↑" is an increase in concentration, and (1.) means it was the first event.

"2. ⟵ " means a shift in equilibrium to the left to get rid of excess N_2. Excess N_2 will react with H_2O producing more reactants (NH_3 and O_2).

All "3" arrows describe the changes in concentration to reach equilibrium.

Forcing products

Le Chatelier's principle suggests a good way to ensure that a reaction goes on generating a substance: simply *remove products as they are formed*.

(b) the **removal of H_2O**,

$$4\ NH_3(g)\ +\ 3\ O_2(g) \rightleftharpoons 2\ N_2(g)\ +\ 6\ H_2O(g)$$
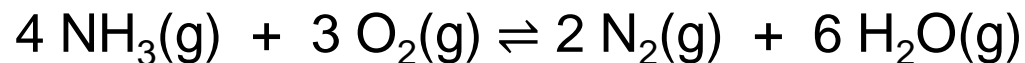
3.↓   3.↓   3.↑   1.↓

2. →

Practice 10: Using the final values from Practice 8 we <u>add 0.0100 mol $Cl_2(g)$</u> to the container (of volume 500. mL) (which is equal to 0.870 bar). Calculate the new composition of the equilibrium mixture,
$K = 78.3$ for the reaction PCl_5 (g) $\rightleftharpoons$ $PCl_3(g)$ + $Cl_2(g)$.

Practice 8:
PCl_5 = 0.02 bar
PCl_3 = 1.28 bar
Cl_2 = 1.28 bar

	PCl_5	PCl_3	Cl_2
initial	0.02	1.28	1.28 + 0.870
change	+x	-x	-x
final	0.02 + x	1.28 - x	2.15 - x

When we add to the product side, we expect to produce more reactant; Now the final.

Practice 10: Using the final values from Practice 8 we <u>add 0.0100 mol Cl_2(g)</u> to the container (of volume 500. mL) (which is equal to 0.870 bar). Calculate the new composition of the equilibrium mixture,
K = 78.3 for the reaction PCl_5 (g) $\rightleftharpoons$ PCl_3(g) + Cl_2(g).

Write the equilibrium expression

$$K = \frac{(1.28 - x)(2.15 - x)}{0.02 + x} = 78.3 \qquad \text{solved with software}$$
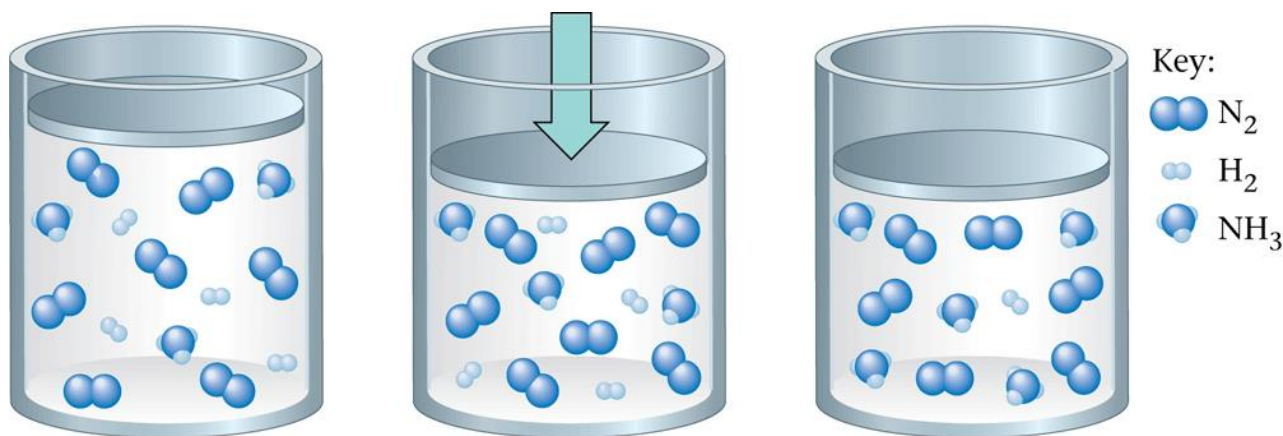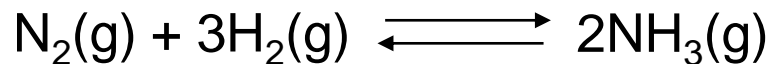
x = 81.7, 0.144 though only 0.144 makes sense.

PCl_5 = 0.02 + x, 0.02 + 0.144 = 0.03 bar
PCl_3 = 1.28 - x , 1.28 − 0.144 = 1.27 bar
Cl_2 = 2.15 - x , 2.15 − 0.144 = 2.14 bar

Le Châtelier's Principle

2. Effect of a change in volume:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
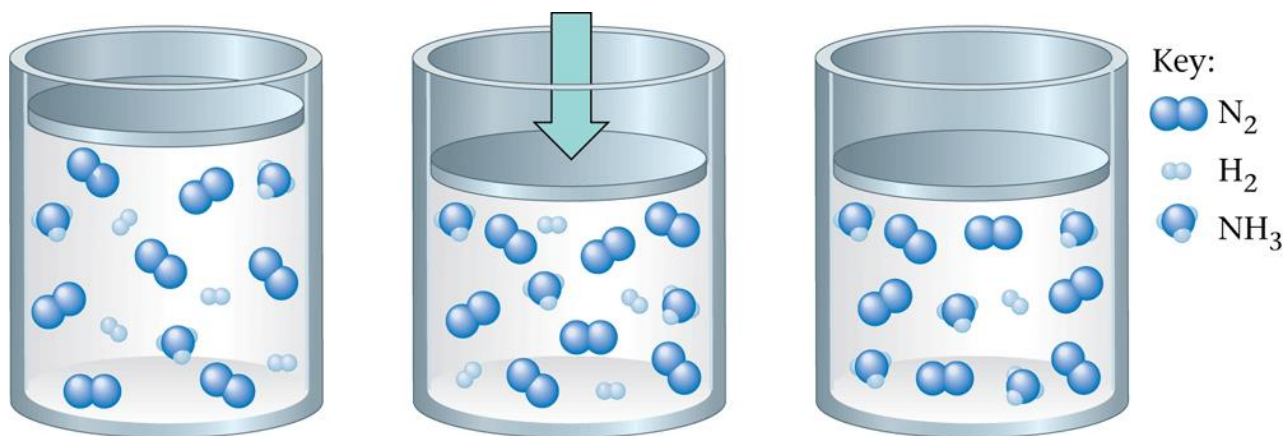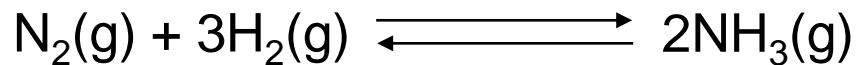

Key:
- N_2
- H_2
- NH_3

V is decreased → Molecules hit the wall more often → P is increased

Le Châtelier's Principle: System will shift in the direction that reduces P.

Le Châtelier's Principle

2. Effect of a change in volume:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Key:
- N_2
- H_2
- NH_3

System shifts in the direction that gives the smaller number of gas molecules.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Le Châtelier's Principle

2. Effect of a change in volume:

V↓ or P↑ ➡ Shifts toward the smaller # of gas molecules.
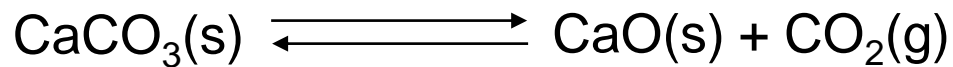
V↑ or P↓ ➡ Shifts toward the greater # of gas molecules.

It works if there is a gas molecule.

No gas molecule → No change in equilibrium

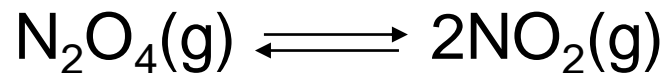# Le Châtelier's Principle
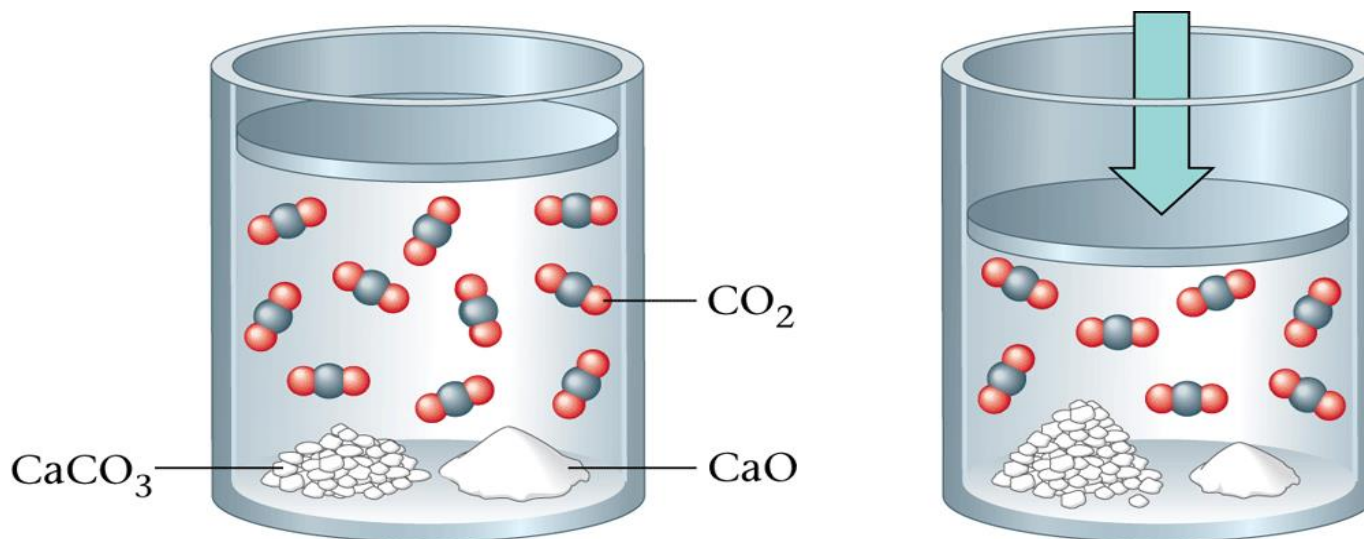
2. Effect of a change in volume:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

System shifts in the direction that gives the smaller number of gas molecules.

$$CaCO_3(s) \longleftarrow \longrightarrow CaO(s) + CO_2(g)$$

Le Châtelier's Principle

2. Effect of a change in volume:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

V↓ or P↑ $\Longrightarrow$ to the left $\Longrightarrow$ [N$_2$O$_4$] ↑ and [NO$_2$] ↓

V↑ or P↓ $\Longrightarrow$ to the right $\Longrightarrow$ [N$_2$O$_4$] ↓ and [NO$_2$] ↑

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$
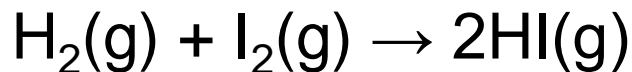
The same # of gas molecules $\Longrightarrow$ The change of V (or P) dose not affect.

Le Châtelier's Principle

2. Effect of a change in volume:

K (equilibrium constant) does not change.

It remains constant.

Le Châtelier's Principle

3. Effect of a change in temperature:

K (equilibrium constant) changes with T.

Exothermic reactions: $A + B \rightarrow C + D + energy\ (heat)$

Heat is a product.

Endothermic reactions: $A + B + energy\ (heat) \rightarrow C + D$

Heat is a reactant.

Le Châtelier's Principle

a At 100 °C the flask is definitely reddish-brown due to a large amount of NO_2 present.

b At 0 °C the equilibrium is shifted toward colorless $N_2O_4(g)$.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + Heat\ (energy)$$

$T \uparrow \implies$ to the left $\implies [NO_2] \uparrow$ It shifts to consume energy.

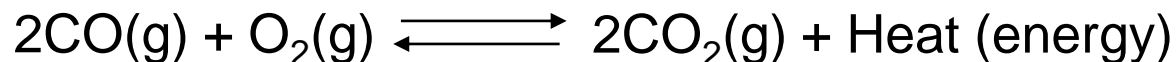$T \downarrow \implies$ to the right $\implies [N_2O_4] \uparrow$ It shifts to produce energy.

Le Châtelier's Principle

Practice 11:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H = -566 \text{ kJ}$$

If we would like to increase the amount of product, how can we change the concentrations, P (or V), and T?
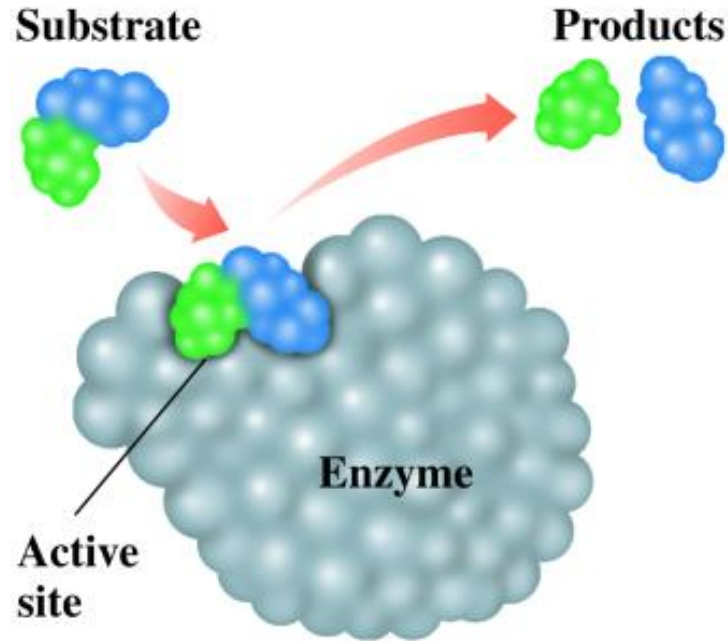
An exothermic reaction → Heat is a product.

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{Heat (energy)}$$

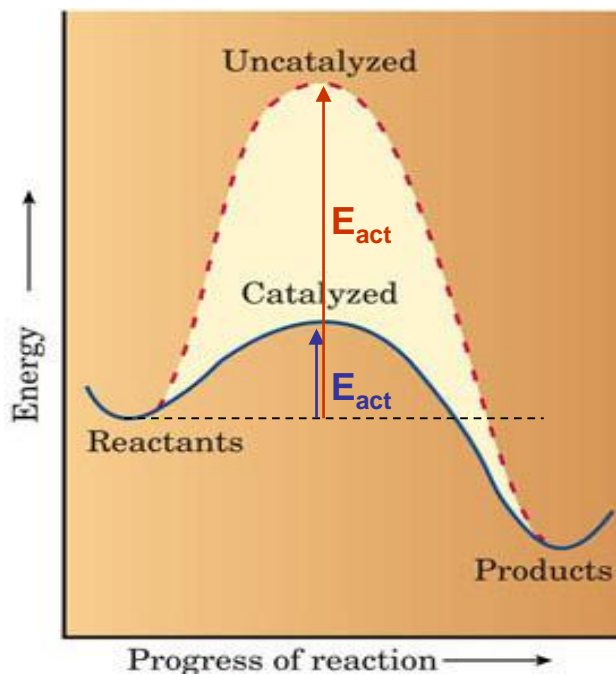Remove [CO$_2$]

Add [CO] or Add [O$_2$]

↓ V (or ↑ P)

↓ T

Catalyst & Le Châtelier's Principle

A catalyst increases the rate of a chemical reaction without being consumed itself.

Le Châtelier's Principle

A catalyst has no effect on the position of an equilibrium.

The rate of a reaction increases for the both directions at the same extent.