# Equilibrium

# Collision

$$A + B \rightarrow C$$
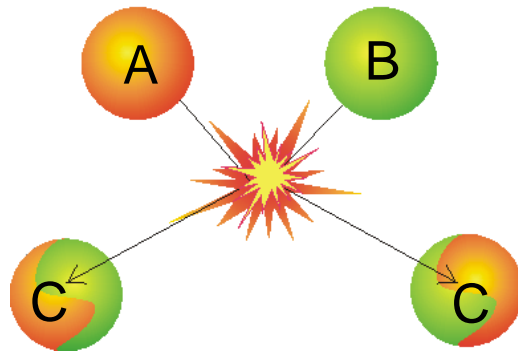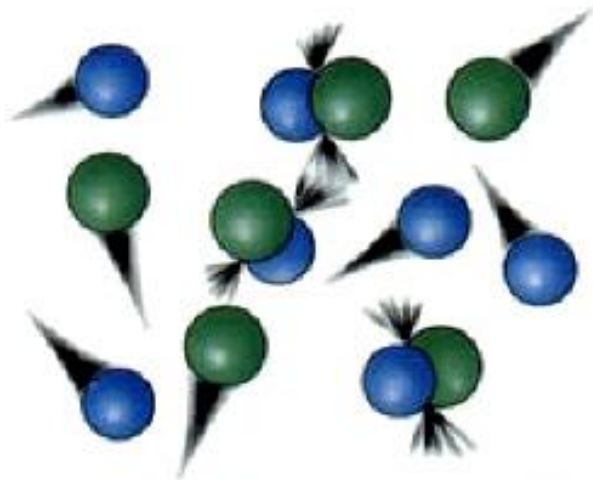
Effective collision: a collision that results in a chemical reaction.
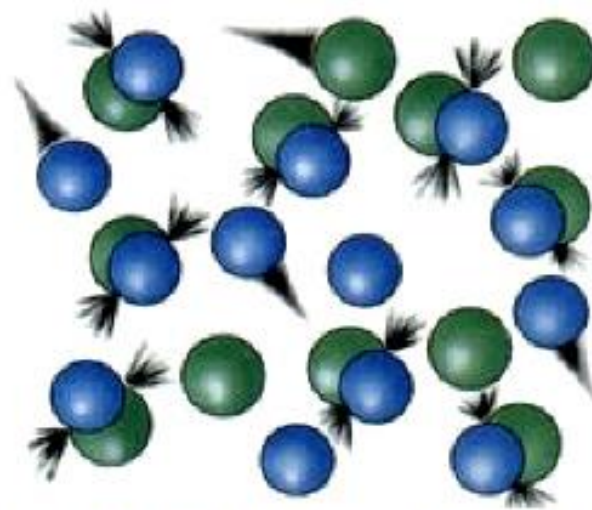
# Effective Collision

## 1. Concentration:



Low concentration = Few collisions

High concentration = More collisions

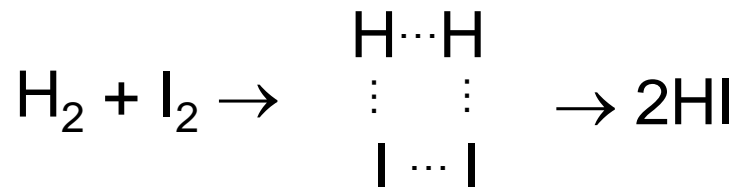Rate of chemical reaction increases with increasing concentration of the reactants.

# Effective Collision

## 2. Energy & Temperature:

Activation Energy ($E_a$): the minimum energy necessary to start a reaction.



**before collision**    **collision**    **after collision**

transition state

$$H_2 + I_2 \rightarrow \begin{matrix} H \cdots H \\ \vdots \quad \vdots \\ I \cdots I \end{matrix} \rightarrow 2HI$$
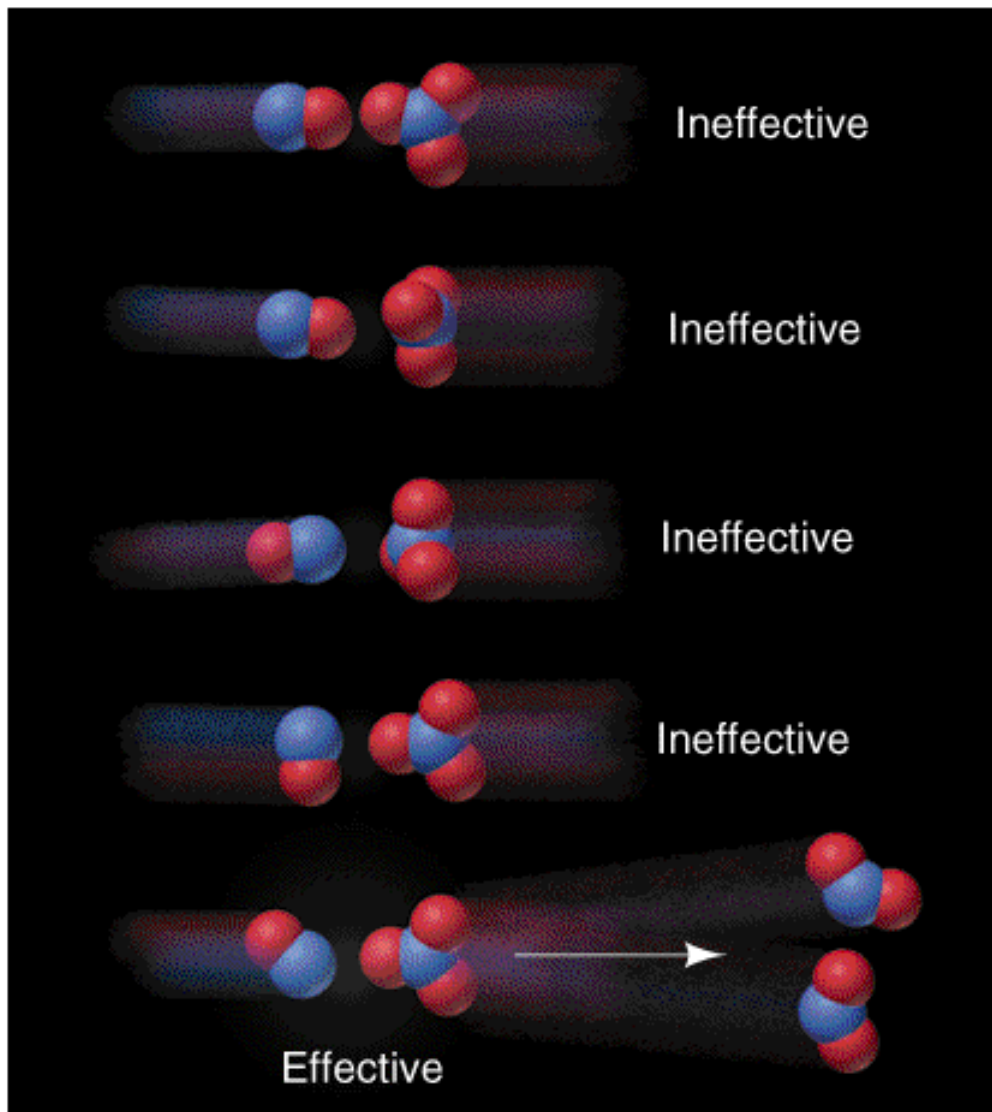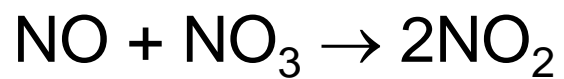
Rate of chemical reaction increases with increasing temperature.

# Effective Collision

## 3. Angle & Orientation:

$$NO + NO_3 \rightarrow 2NO_2$$

# Catalyst

- A catalyst speeds up a reaction (it increases the rate of a reaction).

- But, they are not changed (used up) at the end of the reaction.

- Lower the activation energy for the reaction.

$$H_2 + I_2 \rightarrow \quad \begin{matrix} H \cdots H \\ \vdots \quad \vdots \\ I \cdots I \end{matrix} \quad \rightarrow 2HI$$



Uncatalyzed

$E_{act}$

Catalyzed

$E_{act}$

Reactants

Products

Energy

Progress of reaction
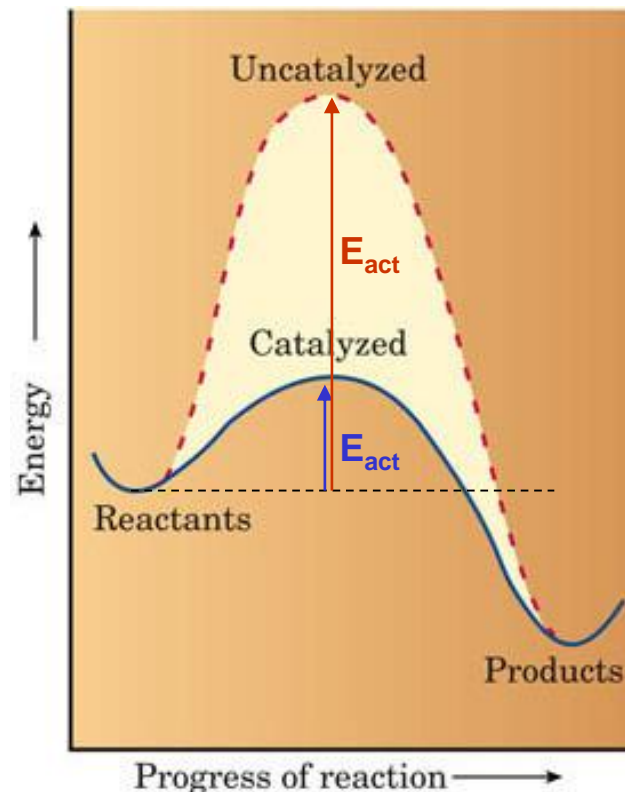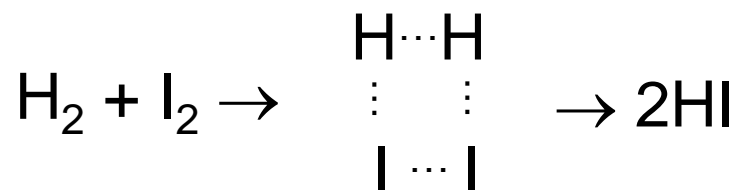
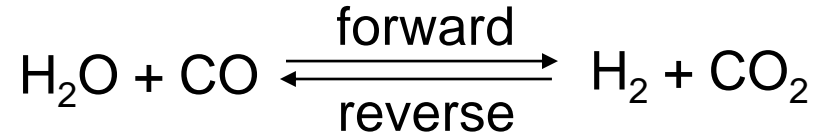- Less energy is required to convert reactants to products.

# 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

$$\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$$

The concentration of all reactants and products remain constant.
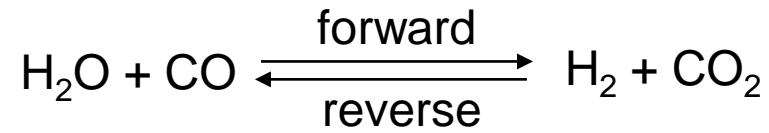
Has reaction stopped???

# Equilibrium

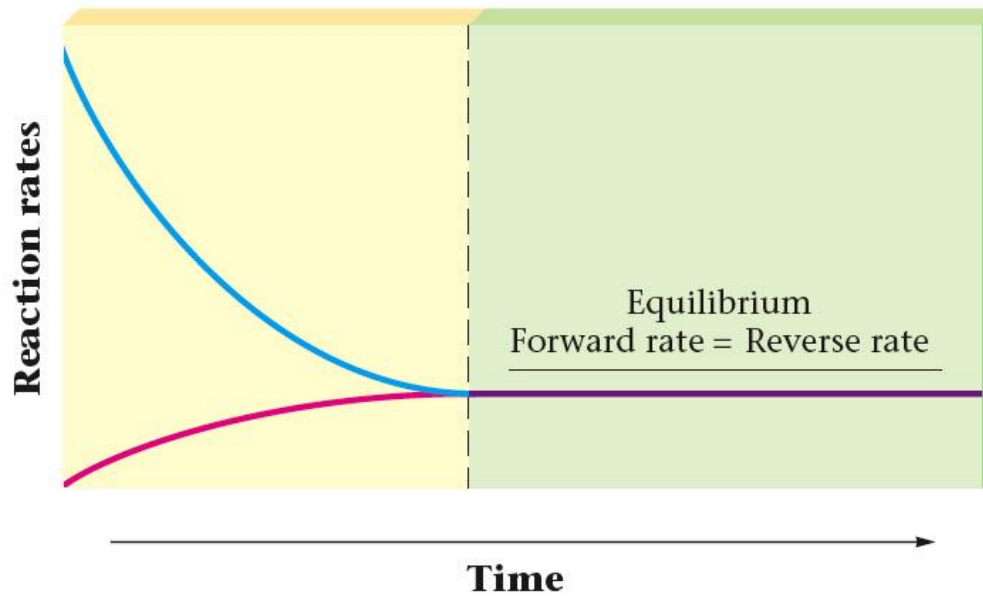At equilibrium, the reaction has not stopped and the system is dynamic.



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

# Equilibrium

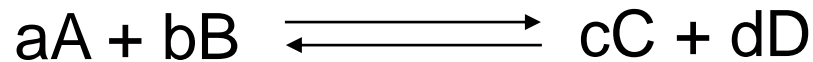$$H_2O + CO \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftharpoons}} H_2 + CO_2$$



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

# Law of Chemical Equilibrium

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

Equilibrium expression

$$K = \frac{[Product(s)]}{[Reactant(s)]}$$

[ ]: M or mol/L

K: Equilibrium constant

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

K > 1 $\Longrightarrow$ [product(s)] ↑     It lies to the right.

K < 1 $\Longrightarrow$ [reactant(s)] ↑     It lies to the left.

# Law of Chemical Equilibrium

Practice:

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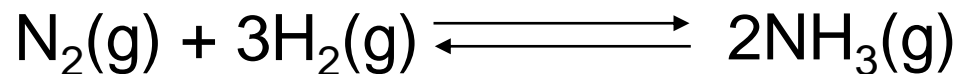
$[N_2] = 0.921$ M, $[H_2] = 0.763$ M, and $[NH_3] = 0.157$ M

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

→ Product (coefficient of 2 becomes power of 2)

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

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

# Law of Chemical Equilibrium
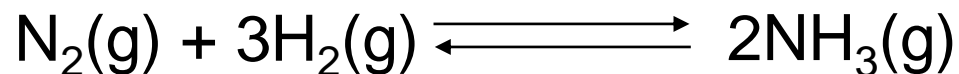
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

**Table 17.1** Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 °C

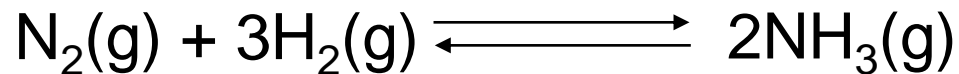| | Initial Concentrations | | | Equilibrium Concentrations | | | $\dfrac{[NH_3]^2}{[N_2][H_2]^3} = K^*$ |
|---|---|---|---|---|---|---|---|
| Experiment | $[N_2]_0$ | $[H_2]_0$ | $[NH_3]_0$ | $[N_2]$ | $[H_2]$ | $[NH_3]$ | |
| I | 1.000 M | 1.000 M | 0 | 0.921 M | 0.763 M | 0.157 M | $\dfrac{(0.157)^2}{(0.921)(0.763)^3} = 0.0602$ |
| 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).
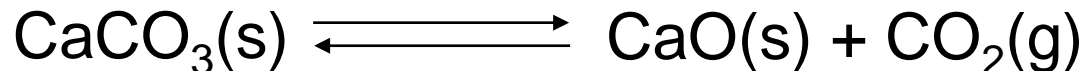
K remains the same even with the different equilibrium concentrations.

# 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.

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

The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.
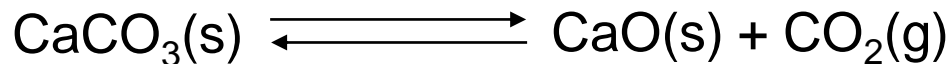
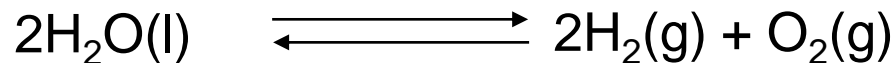$$K' = \frac{[CaO]\,[CO_2]}{[CaCO_3]} \qquad\qquad K' = \frac{C_1\,[CO_2]}{C_2}$$

$$\frac{C_2\,K'}{C_1} = K = [CO_2]$$
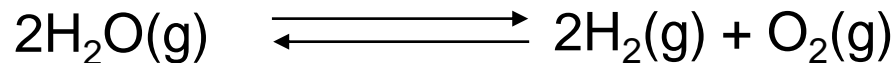
The concentrations of pure solids or pure liquids are not included in equilibrium expression.

# Heterogeneous Equilibria

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

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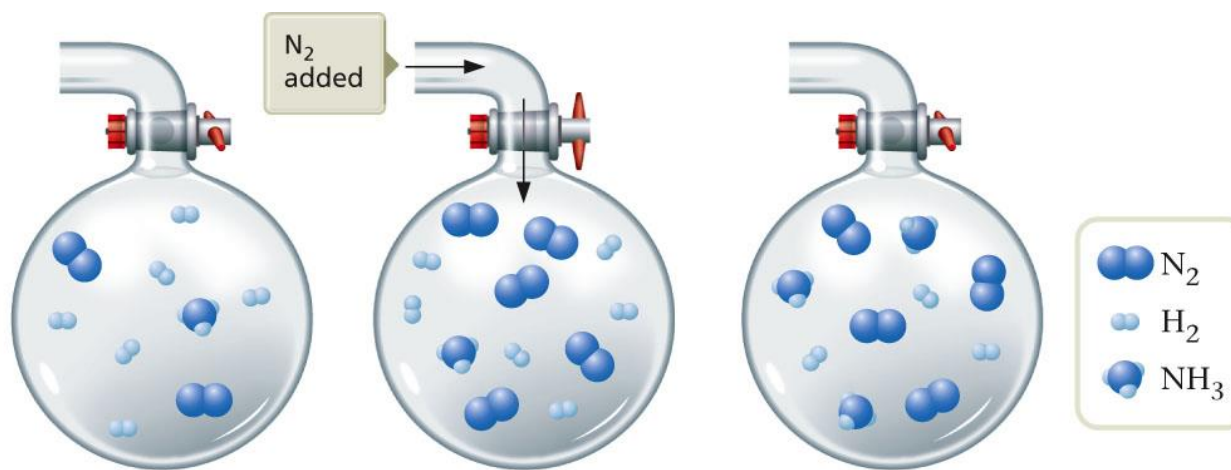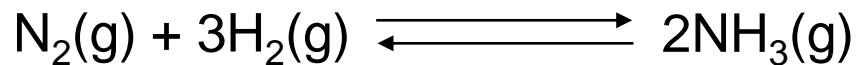
$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

# Le Châtelier's Principle

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 $N_2$ $\Longrightarrow$ $[NH_3] \uparrow$ and $[H_2] \downarrow$

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

# 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 $NH_3$ $\implies$ $[N_2]$ ↑ and $[H_2]$ ↑

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

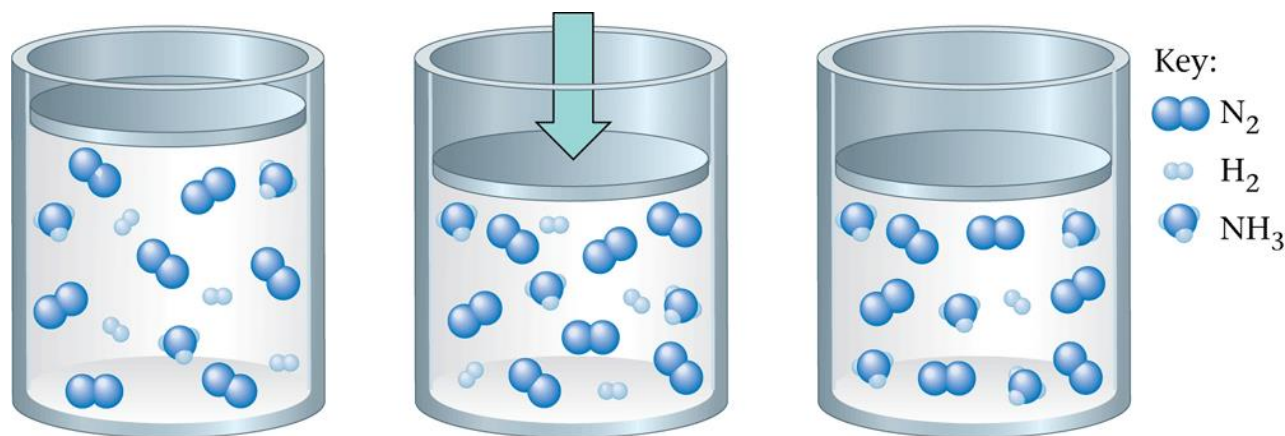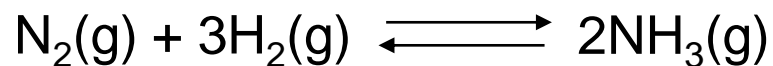Remove $NH_3$ $\implies$ $[N_2]$ ↓ and $[H_2]$ ↓

# Le Châtelier's Principle

1. Effect of a change in concentration:

K (equilibrium constant) does not change.

It remains constant.

# Le Châtelier's Principle

## 2. Effect of a change in volume:
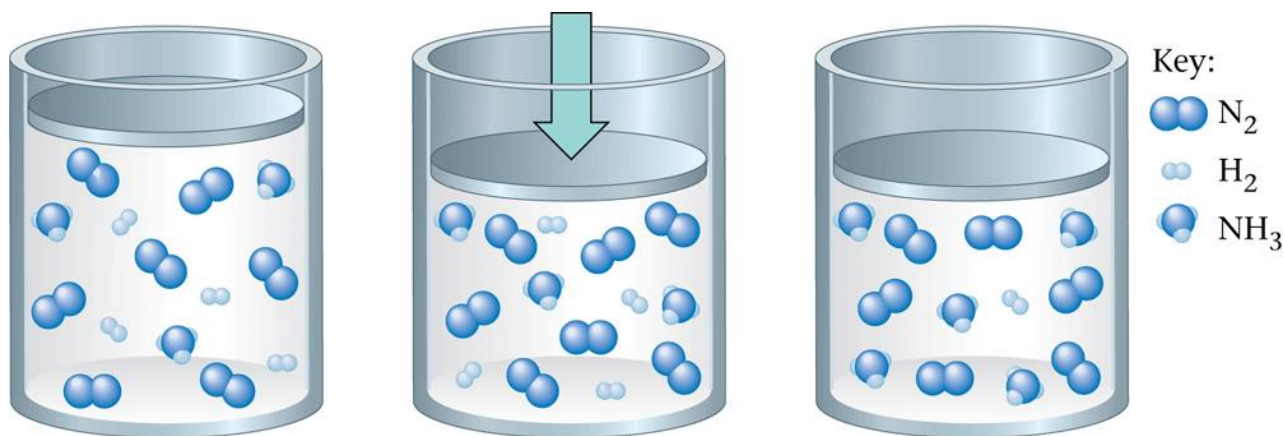
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$



Key:
- $N_2$
- $H_2$
- $NH_3$
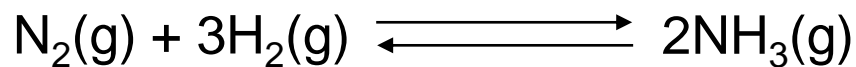
V is decreased → Molecules hit the wall more often → P is increased

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

# Le Châtelier's Principle

## 2. Effect of a change in volume:

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



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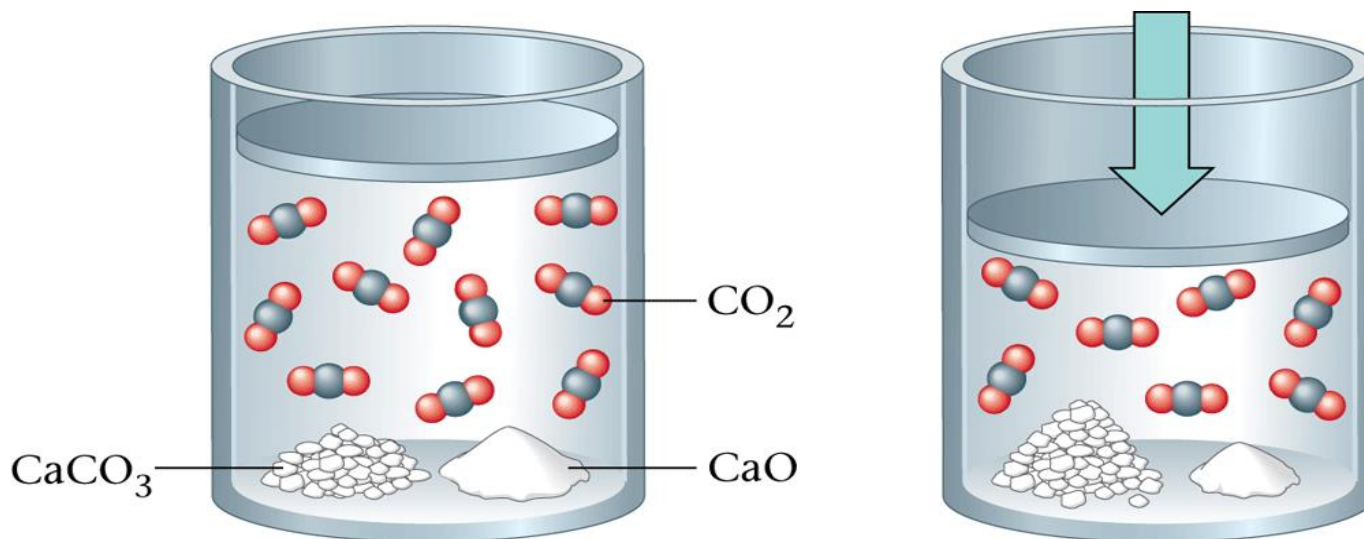
V↑ or P↓  ➡  Shifts toward the greater # of gas molecules.

It works if there is a gas molecule.

No gas molecule → No change in equilibrium

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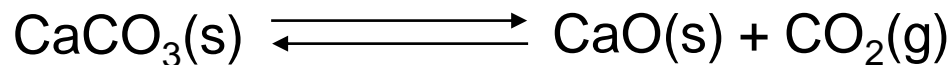
## 2. Effect of a change in volume:

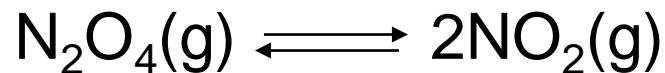$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



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:

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

$V\downarrow$ or $P\uparrow$ $\implies$ to the left $\implies$ $[N_2O_4] \uparrow$ and $[NO_2] \downarrow$

$V\uparrow$ or $P\downarrow$ $\implies$ to the right $\implies$ $[N_2O_4] \downarrow$ and $[NO_2] \uparrow$

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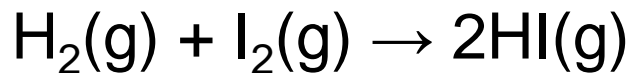
The same # of gas molecules $\implies$ The change of V (or P) dose not affect.

# 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 $N_2O_4(g)$.

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

$T \uparrow \implies$ to the left $\implies [NO_2] \uparrow$      <span style="color:red">It shifts to consume energy.</span>

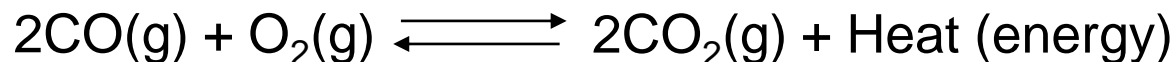$T \downarrow \implies$ to the right $\implies [N_2O_4] \uparrow$      <span style="color:red">It shifts to produce energy.</span>

# Le Châtelier's Principle

Example:

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

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 $[CO_2]$
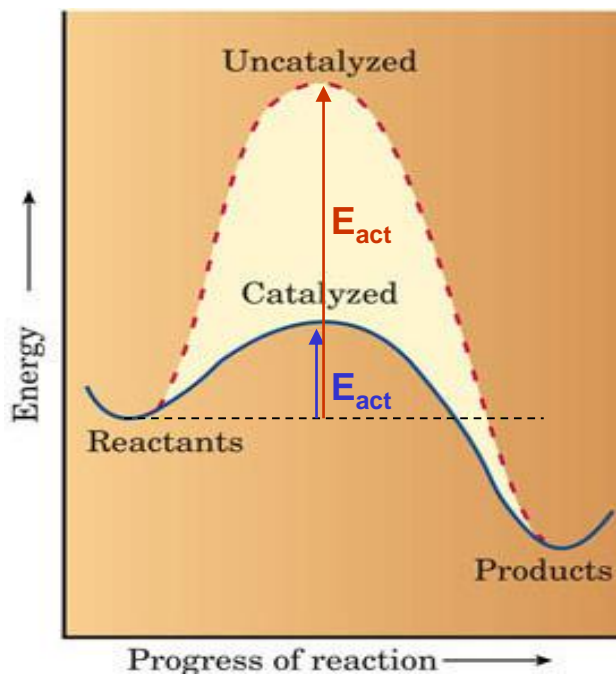
Add $[CO]$ or Add $[O_2]$

$\downarrow$ V (or $\uparrow$ P)

$\downarrow$ T

# 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.

# Solubility Equilibria

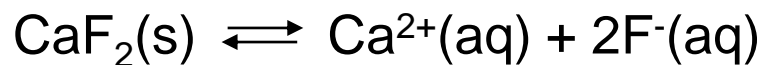A saturated solution is an equilibrium system.

# of solute dissolved = # of solute precipitated

Solubility is an equilibrium position.

Ions will collide in a solution and re-form the solid.

# Solubility Equilibria

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

At equilibrium:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

Solubility Product Constant (Solubility Product)

$CaF_2$ is a pure solid and it is not included.

Amount of excess solid present does not affect the position of the solubility equilibrium.

# Solubility Equilibria

**Practice:** $K_{sp}$ of solid AgI(s) is $1.5 \times 10^{-16}$ at 25°C. Calculate the solubility of AgI(s) in water at 25°C.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

$$K_{sp} = [Ag^+][I^-]$$

x mol/L  AgI(s) $\rightleftharpoons$ x mol/L  $Ag^+(aq)$ + x mol/L  $I^-(aq)$

$[Ag^+]$ = x mol/L

$[I^-]$ = x mol/L

$K_{sp} = 1.5 \times 10^{-16} = (x)(x) = x^2$

$x = \sqrt{1.5 \times 10^{-16}} = 1.2 \times 10^{-8}$ mol/L          Solubility of AgI