Higher Technological Institute
Chemical Engineering Department

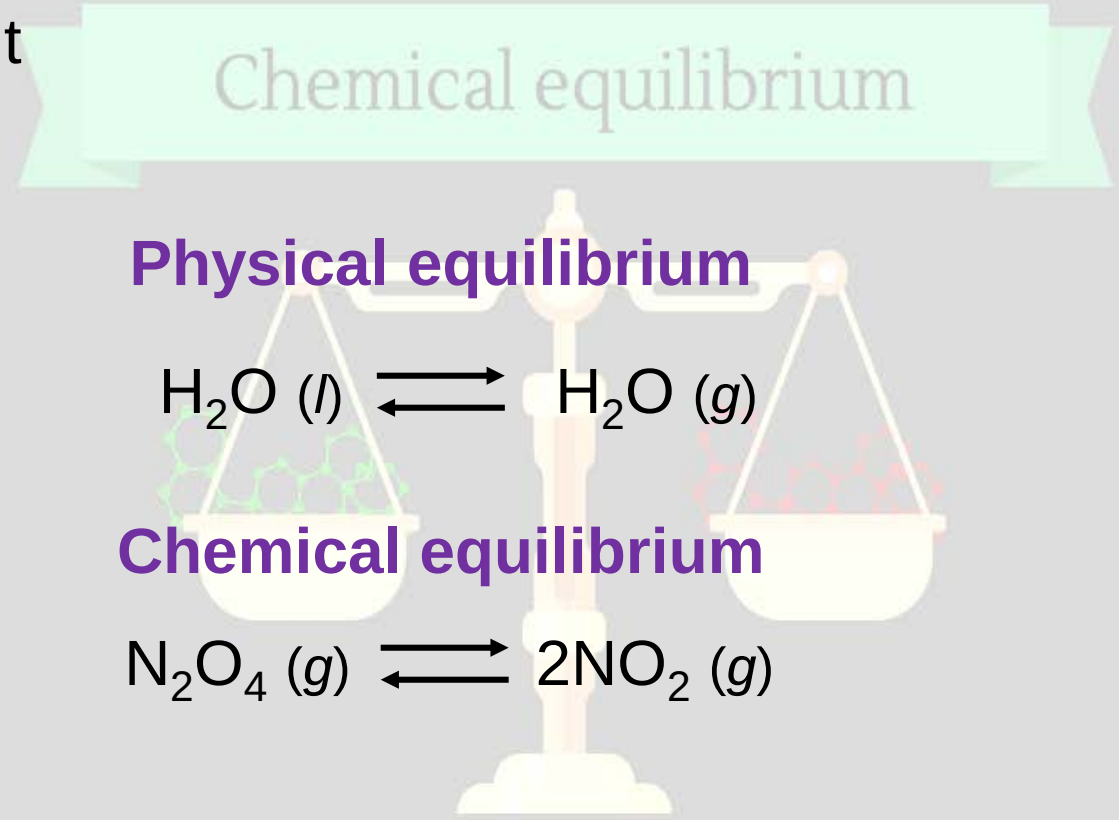
Chapter 3

Chemical Equilibrium

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant

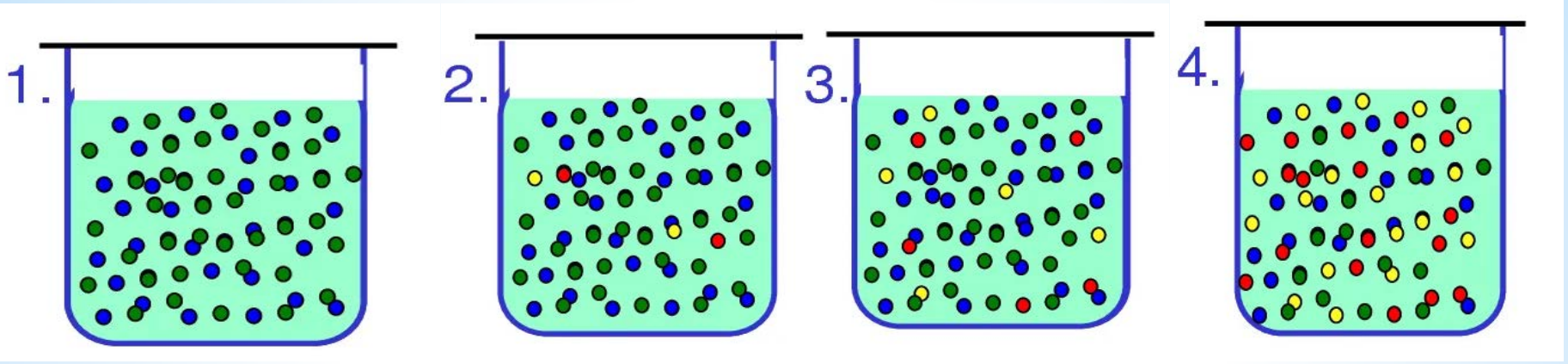


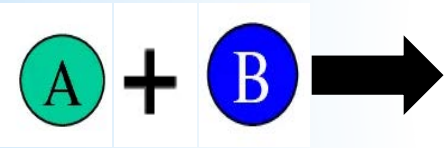
Physical equilibrium

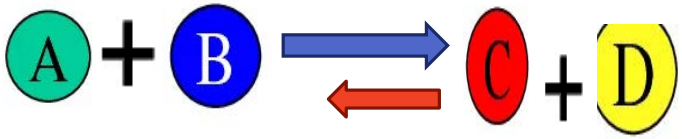
$H_2O\ (l) \rightleftharpoons H_2O\ (g)$

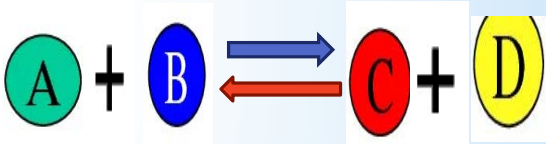
Chemical equilibrium

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









1.
- Reaction begins.
- No products yet formed.
- High rate of collisions between A & B.
- Rate of forward reaction HIGH.

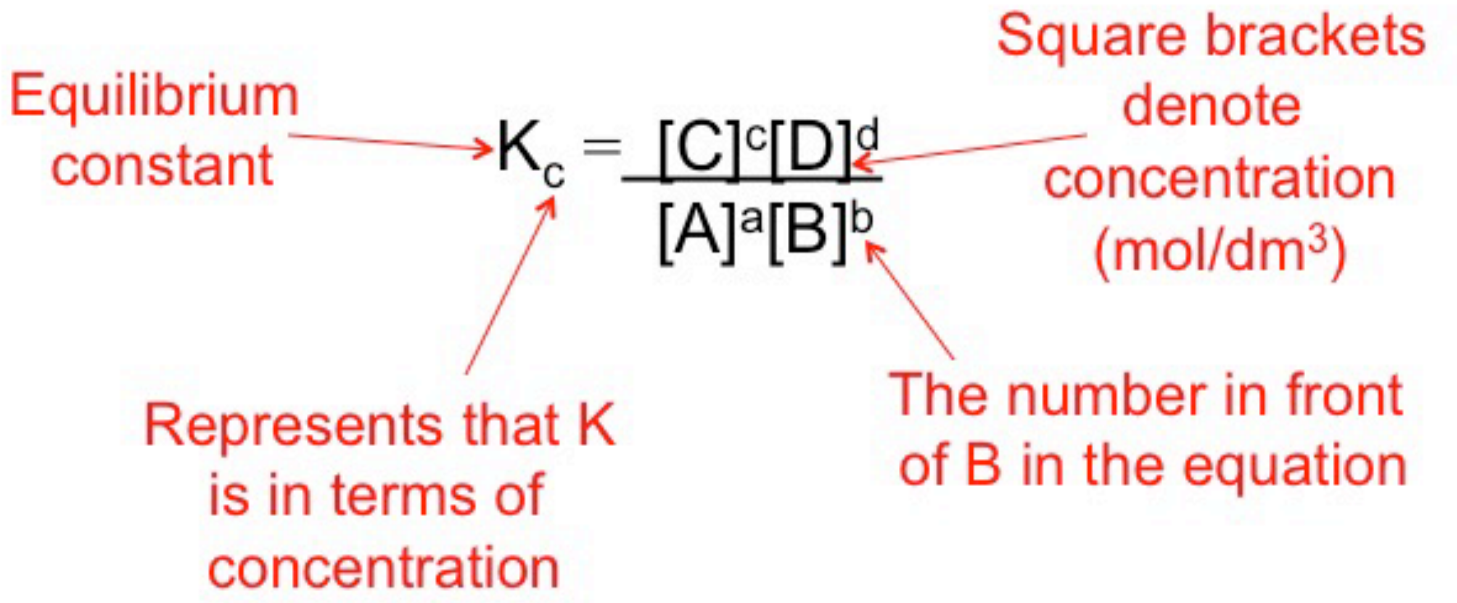
2 & 3
- Products formed
- Collisions between reactants decrease.
- Rate of forward reaction DECREASES
- Reverse reaction begins.

4.
- Rate of forward reaction EQUAL to rate of reverse reaction.
- **Dynamic equilibrium** established.
- Concentrations constant.

The Equilibrium Constant, K_c

Generally:

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



The Equilibrium Constant for Gases

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

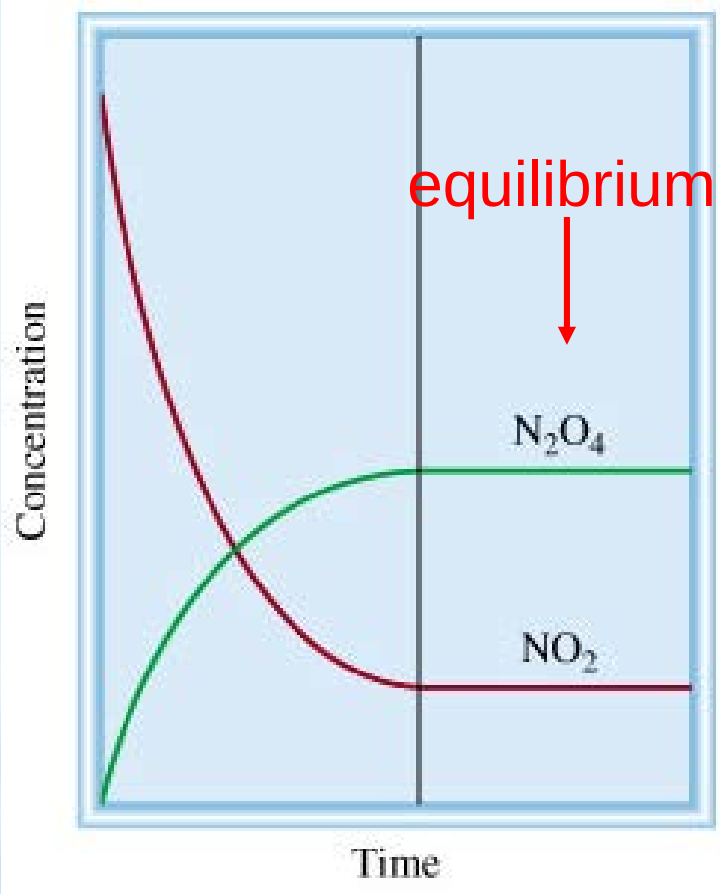
$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

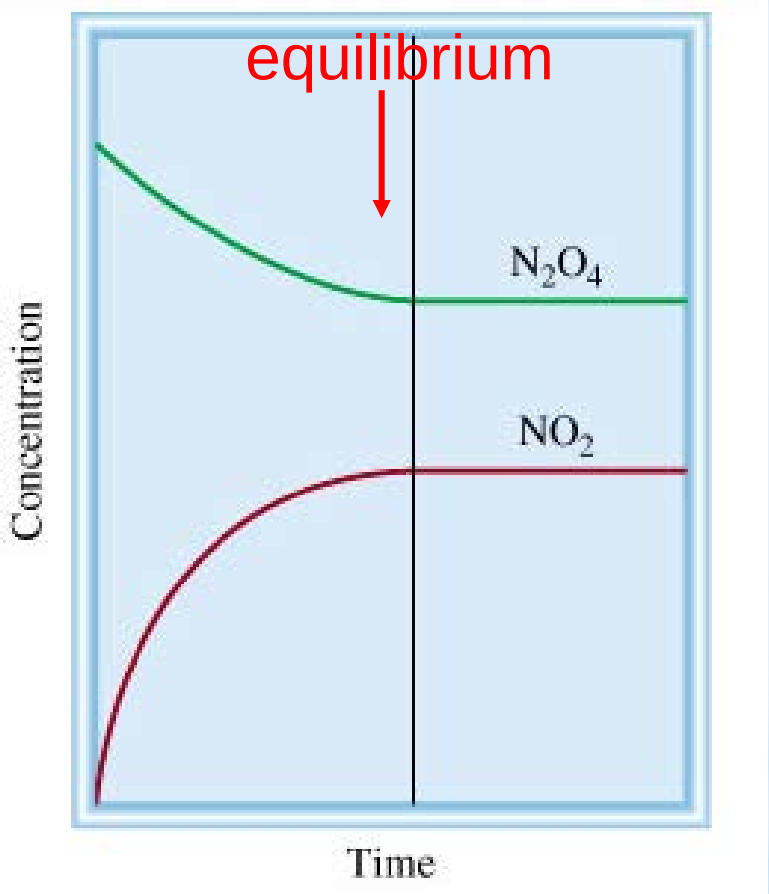
Because **pressure** is proportional to **concentration** for gases in a closed system, the equilibrium expression can also be written

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

where K_p = equilibrium constant for gases, and
P_x = partial pressure of each gas.

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





Start with NO_2

Start with N_2O_4

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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^{\ 2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\ (g) + bB\ (g) \rightleftharpoons cC\ (g) + dD\ (g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants

$$\Delta n = (c + d) - (a + b)$$

Homogeneous Equilibrium

has everything present in the same phase. The usual examples include reactions where everything is a gas, or everything is present in the same solution.

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$$

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH^-]}$$

$[H_2O]$ = constant

General practice not to include units for the equilibrium constant.

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (g) at 74^0C are [CO] = 0.012 M, $[Cl_2]$ = 0.054 M, and $[COCl_2]$ = 0.14 M. Calculate the equilibrium constants K_c and K_p.

$$CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$$

$$Kc = \frac{[COCl_2]}{[CO][Cl_2]} \qquad Kc = \frac{0.14}{0.012 \times 0.054} = 220$$

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

$\Delta n = 1 - 2 = -1$ R = 0.0821 $T = 273 + 74 = 347$ K

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

is 158 at 1000K. What is the equilibrium pressure of O_2 if the P_{NO2} = 0.400 atm and P_{NO} = 0.270 atm?

$$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_p \frac{P_{NO_2}^2}{P_{NO}^2}$$

$$P_{O_2} = 158 \times (0.400)^2/(0.270)^2 = 347 \text{ atm}$$

Heterogenous equilibrium

has things present in more than one phase. The usual examples include reactions involving solids and gases, or solids and liquids.

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

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2]$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction?

$$K_p = P_{NH_3} P_{H_2S} = 0.265 \times 0.265 = 0.0702$$

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

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

$$\Delta n = 2 - 0 = 2 \qquad T = 295\ K$$

$$K_c = 0.0702 \times (0.0821 \times 295)^{-2} = 1.20 \times 10^{-4}$$

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

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

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

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K}$$

When the equation for a **reversible reaction** is written in the **opposite direction**, the equilibrium constant becomes the **reciprocal of the original equilibrium constant**

So for a general

A ⟶ B $\qquad K_1$

n* (A ⟶ B) $\qquad K_2 = (K_1)^n$

n = -ve Or +ve

n = whole number Or fraction

Example

$$Cl_2(g) + PCl_3(g) \rightleftharpoons PCl_5(g) \qquad K_1 = 8.0\times10^{16}$$

$$K_1 = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

$$PCl_5(g) \rightleftharpoons Cl_2(g) + PCl_3(g) \qquad K_2 = ?$$

$$K_2 = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{1}{K_1} = \frac{1}{8.0\times10^{16}}$$

$$\frac{1}{2}PCl_5(g) \rightleftharpoons \frac{1}{2}Cl_2(g) + \frac{1}{2}PCl_3(g) \qquad K_3 = ?$$

$$K_3 = \frac{[PCl_5]^{\frac{1}{2}}}{[PCl_3]^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}} = \left(\frac{1}{K_1}\right)^{\frac{1}{2}} = \left(\frac{1}{8.0\times10^{16}}\right)^{\frac{1}{2}}$$

Notes

1. The concentrations of pure solids, pure liquid do not appear in the equilibrium constant expressions.

2. Solution concentration is by M, gase pressure by atm, Universal gas constant used by 0.082 atm.l/mole .K

3. The equilibrium constant is a dimensionless quantity.

Typical Problem: Mix 1.0 mol CO & 3.0 moles H_2 in a 1.0 L container. At equilibrium an analysis reveals that you have 0.40 mol H_2O. What is M of each at equilibrium? Let X = M of CO that reacts at equilibria.

	$1CO$ +	$3H_2$ ⇌	$1CH_4$ +	$1H_2O$
Starting M:	1.0	3.0	0.0	0.0
at Equilibria	1.0-X	3.0-3X	X	X

We know that X = 0.40; therefore, at equilibria:

M CO	= 1.0-X	= 1.0-0.4	=	0.6
M H_2	= 3.0-3X	= 3.0 - 1.2	=	1.8
M H_2O	= X	=		0.40
M CH_4	= X	=		0.40

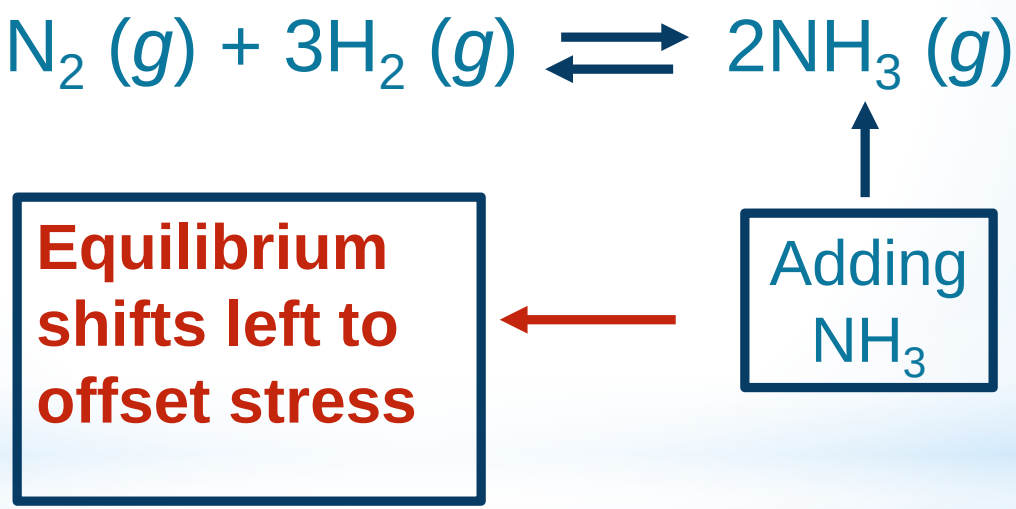
Le Châtelier's Principle

"The Equilibrium Law"

Whenever a system in equilibrium is disturbed the system will adjust itself in such a way that the effect of the change will be reduced or moderated.

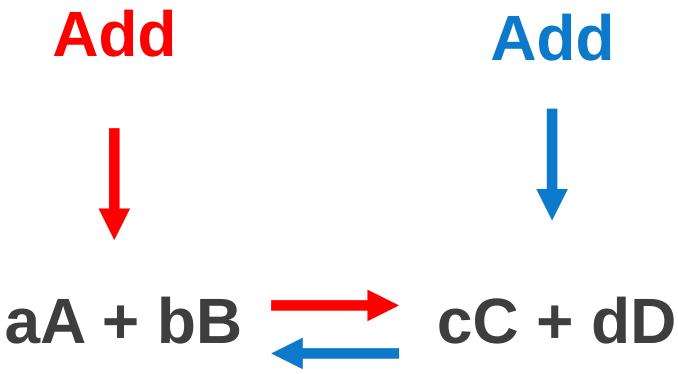
Le Châtelier's Principle

Changes in Concentration



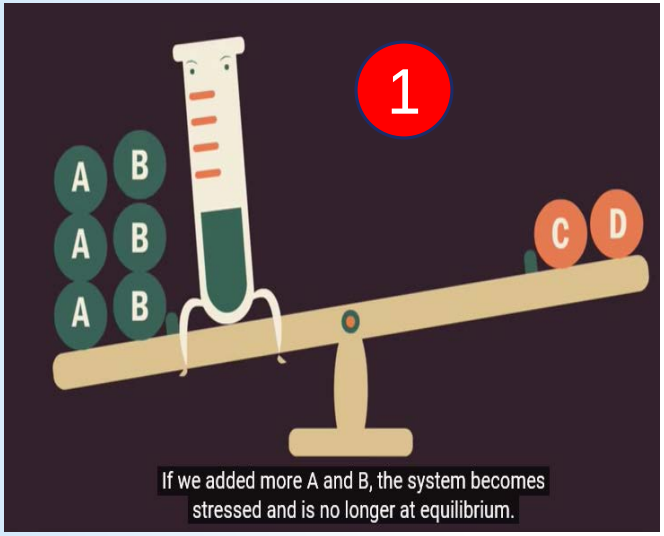
Le Châtelier's Principle

Changes in Concentration continued

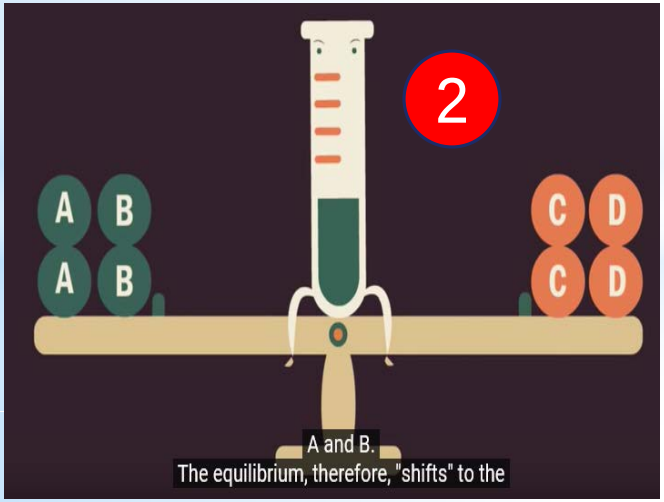


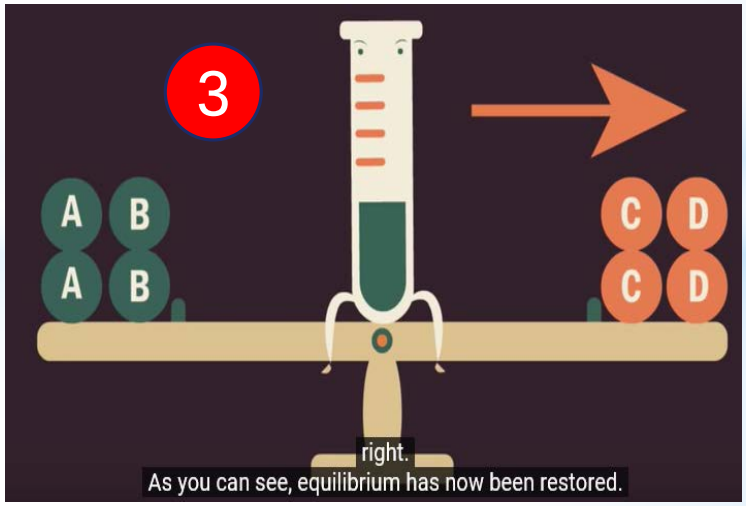
Change	Shifts the Equilibrium
Increase concentration of **product**(s)	**left** ←
Decrease concentration of **product**(s)	**right** →
Increase concentration of **reactant**(s)	**right** →
Decrease concentration of reactant(s)	**left** ←

Adding or removing a product or reactant

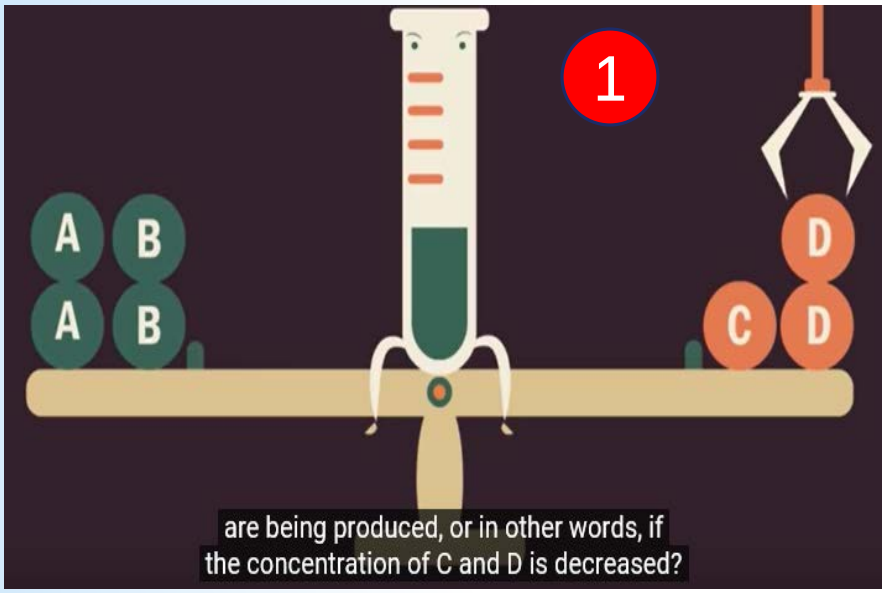


The equilibrium shifts to remove reactants or products that have been added

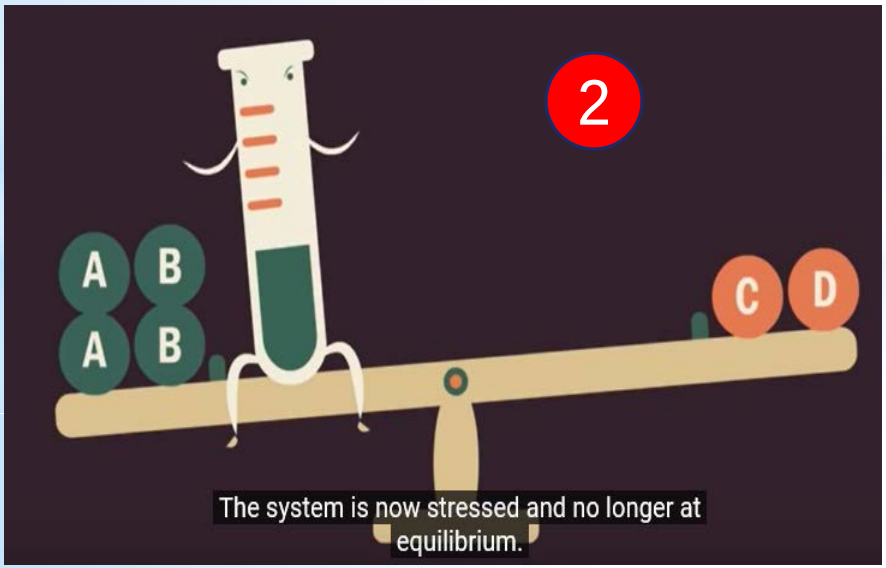


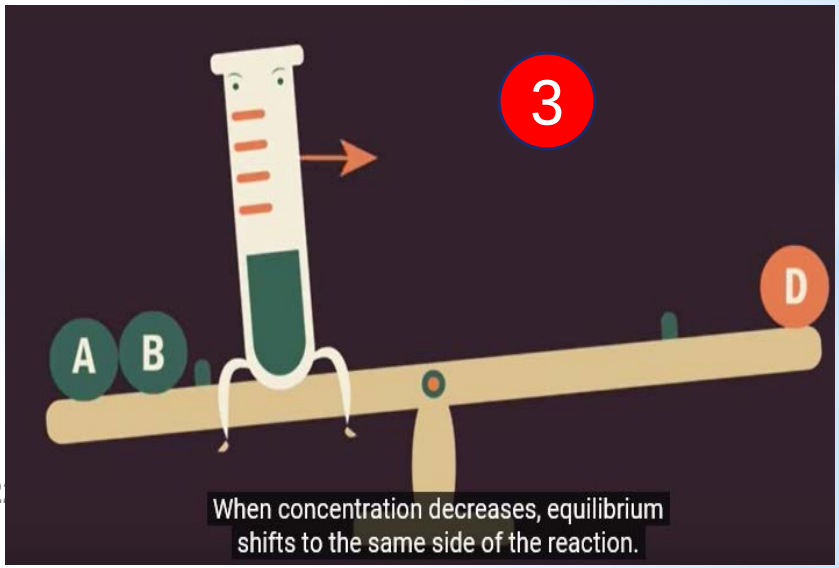


Adding or removing a product or reactant



The equilibrium shifts to replace reactants or products that have been removed

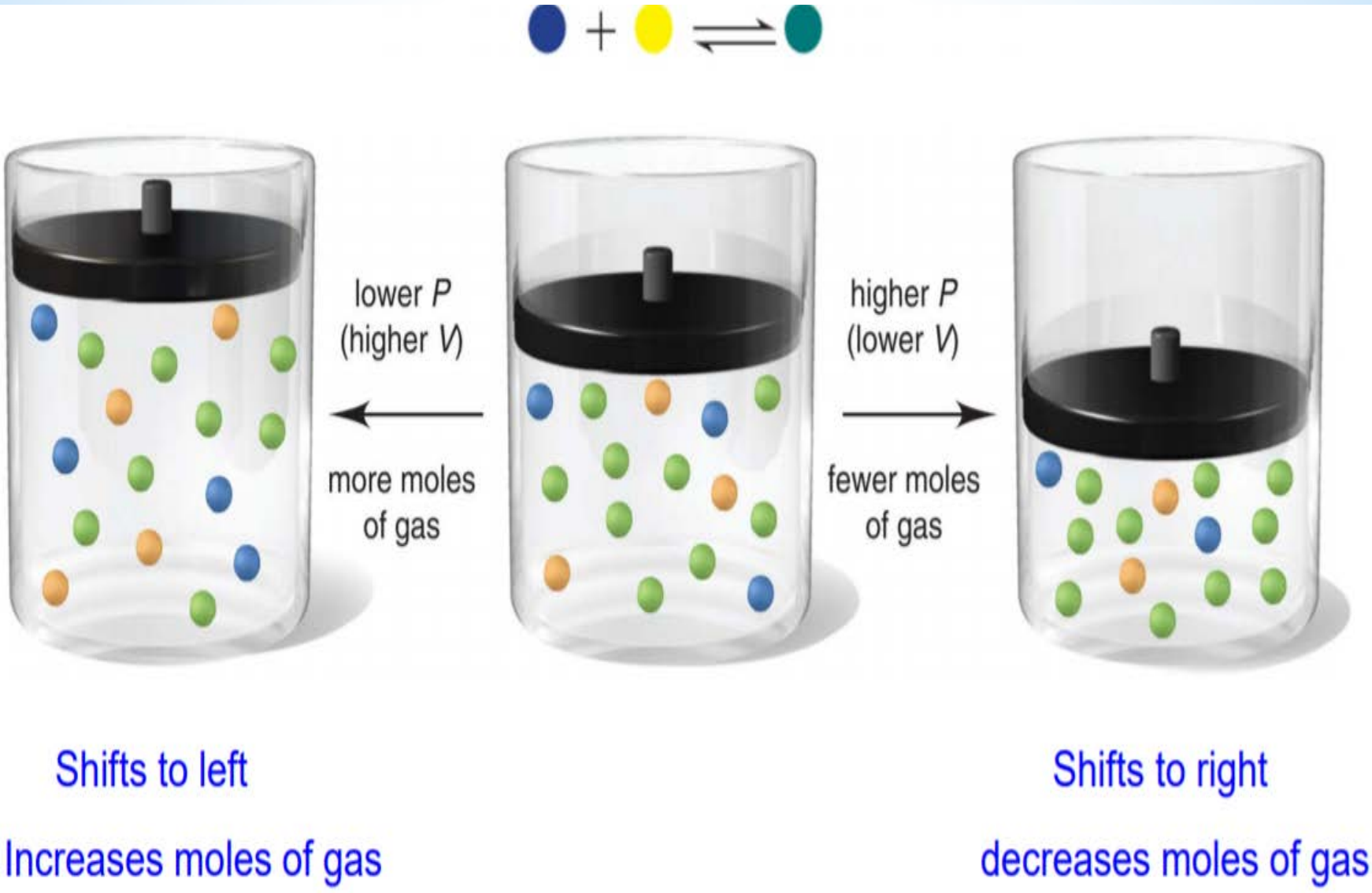




Changing the volume

Reducing the volume of a gaseous reaction causes the reaction to decreases the number of moles of gas

Moderate pressure changes have a negligible effect on reactions involving only liquids or solids


lower P
(higher V)
more moles
of gas
higher P
(lower V)
fewer moles
of gas
Shifts to left
Increases moles of gas
Shifts to right
decreases moles of gas

Le Châtelier's Principle

Changes in Volume and Pressure

Change	Shifts the Equilibrium
Increase pressure	Side with fewest moles of gas →
Decrease pressure	Side with most moles of gas ←

Example For each of the following equilibrium systems, predict the direction of net reaction in each case as a result of **increasing the pressure** on the system at constant temperature.

↑ pressure ::::: shift to the side of fewest (less) moles of gases moles

$$(a)\ \ 2PbS(s)+3O_2(g)\leftrightarrow 2PbO(s)+2SO_2(g)$$

Δn = 2 – 3 = -1 < 0 side of fewest gaseous moles is the product

THUS: the equilibrium will shift to the right

$$(b)\ \ PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$$

Δn = 2 – 1 = 1 > 0

side of fewest gaseous moles is the reactant

THUS: the equilibrium will shift to the left

$$(c)\ \ H_2(g) + CO_2(g) \leftrightarrow H_2O(g) + CO(g)$$

Δn = 2 – 2 = 0

THUS: the change in pressure has NO effect on the equilibrium

Changing the Temperature

- **Increasing the temperature shifts a reaction in a direction that produces an endothermic (heat-absorbing) change**

- **Decreasing the temperature shifts a reaction in a direction that produces an exothermic (heat-releasing) change**

Le Châtelier's Principle

Changes in Temperature

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.4\text{kJ}$$

Since ΔH is negative, the reaction to the right evolves heat

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92.4\text{kJ}$$

The forward reaction is *exothermic*

The reverse reaction is *endothermic*

If heat is added, the position of the equilibrium shifts to the left

Le Châtelier's Principle

Changes in Temperature

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

$\Delta H = +41 kJ$

$$CO_2(g) + H_2(g) + 41kJ \rightleftharpoons CO(g) + H_2O(g)$$

If heat is added the position of the equilibrium shifts to the right

The numerical value of the equilibrium constant changes when the temperature is changed

Example: If the reaction is endothermic and the temperature is raised, the amount of CO present will:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

a. increase.
b. decrease.
c. remain unchanged.
d. disappear.

C Addition of Catalyst

- does not affect the position and composition of the equilibrium of a reaction, because both the forward and backward reactions are sped up by the same factor

- also catalyst lowers Ea(activation energy) for both forward and reverse reactions

Example: If a catalyst is added to the equilibrium, the amount of CO present will:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

a. increase.
b. decrease.
c. remain unchanged.
d. disappear.

Le Châtelier's Principle

Change	Shift Equilibrium	Change Equilibrium Constant
Concentration	YES	NO
Pressure	YES	NO
Volume	YES	NO
Temperature	YES	YES
Catalyst	NO	NO

5. Le Chatelier's Principle: When a system at equilibrium is altered, then equilibrium will shift to relieve the alteration.

Examples:

1) HF is a weak acid. What will happen when one adds either a second source of H^+ from a strong acid like HCl or extra F^- from KF?

$$HF \rightleftharpoons H^+ + F^-$$

Extra H^+ or F^- will shift equilibria to left ←

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2) What will happen if one adds Ag^+ to HF equilibria? (AgF is insoluble). $HF \rightleftharpoons H^+ + F^-$

Will shift to right to replace F^- which is taken away through formation of $AgF_{(s)}$. →

3): $1CO_{g} + 3H_{2\,g} \rightleftharpoons 1CH_{4\,g} + 1H_2O_{g}$

How will equilibrium be shifted if one doubles the pressure?

Note: 4 moles gas $\rightleftharpoons$ 2 moles gas

- Equilibrium will shift to right to relieve (to lower) the pressure.

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4): Heat + $NH_4F \rightleftharpoons NH_4^+ + F^-$ (endothermic)

How will an increase in temperature influence the above reaction? Note: Treat heat as a reactant for endothermic rxn.

- The equilibrium will shift to remove the excess heat. It will force this reaction to the right.