CHEMICAL EQUILIBRIUM

6.3 Le Chatelier's Principle

At the end of the lesson, students should be able to:

a) State Le Chatelier's principle

b) Explain the effect of the following factors on a system at equilibrium by using Le Chatelier's principle:

   i. Concentration of reacting species

   ii. Pressure and volume (include the addition of inert gas at constant pressure and at constant volume)

   iii. Temperature

   iv. catalyst

LESSON DURATION: 1 hour

LE CHÂTELIER'S PRINCIPLE

When a chemical system is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance.

Three common disturbances:

- **Change in concentration**
- **Change in pressure**
  (caused by change in volume)
- **Change in temperature**

"net reaction" = shift in the equilibrium position of the system to either right or left

Henry Louis Le Châtelier (1850 – 1936). French chemist.

LE CHÂTELIER'S PRINCIPLE

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

Add NH_3

Original equilibrium: $Q = K$

Disturbance:

- ☞ Add NH_3
- ☞ $[NH_3]$ increase
- ☞ $Q \neq K$

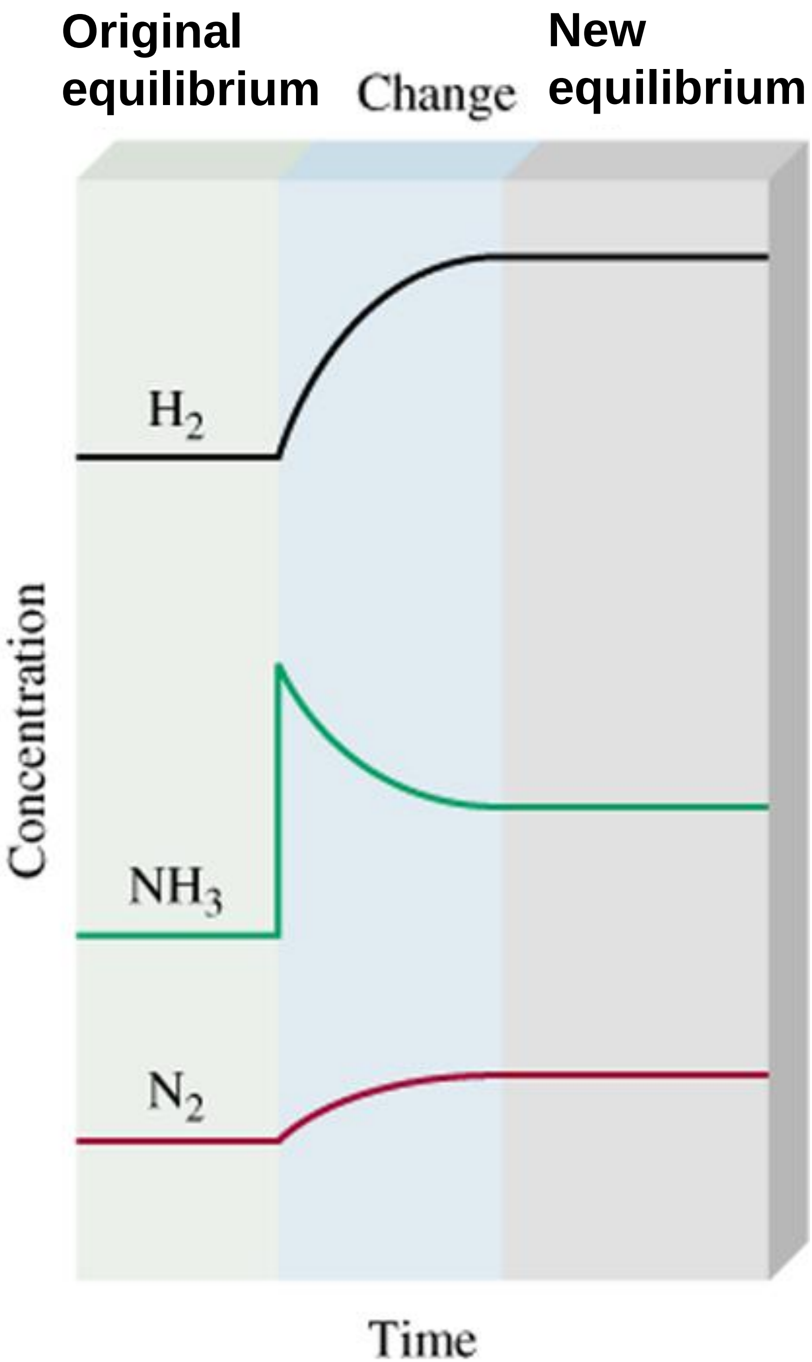
Reduce Disturbance:

- ☞ reduce increase of $[NH_3]$
- ☞ net reaction proceeds to the left

New equilibrium: $Q = K$

Keep in mind!

The disturbance (addition of NH_3) is reduced but not eliminated.



The Effect of Added Cl_2 on PCl_3–Cl_2–PCl_5 System

Concentration (*M*)	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
Original equilibrium	0.200		0.125		0.600
Disturbance			+0.075		
New initial	0.200		0.200		0.600
Change	$-x$		$-x$		$+x$
New equilibrium	$0.200 - x$		$0.200 - x$		$0.600 + x$
	0.163		**0.163**		**0.637** *

*Experimentally determined value.

	Original equilibrium	New initial (just after Cl_2 added)	New equilibrium
$[PCl_5]$	0.600 *M*	0.600 *M*	0.637 *M*
$[Cl_2]$	0.125 *M*	0.200 *M*	0.163 *M*
$[PCl_3]$	0.200 *M*	0.200 *M*	0.163 *M*

CHANGES IN CONCENTRATION

If the concentration increases, the system reacts to consume some of it.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

add Cl_2

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

$Q_c < K_C$ **(not at equilibrium)**

System will reduce the disturbance (increase of $[Cl_2]$) by:

- **proceeding to the right**
- **Consuming some additional Cl_2**
- **$[PCl_5]$ increase**
- **$[PCl_3]$ decrease**

	Original equilibrium	New initial (just after Cl_2 added)	New equilibrium
$[PCl_5]$	0.600 *M*	0.600 *M*	0.637 *M*
$[Cl_2]$	0.125 *M*	0.200 *M*	0.163 *M*
$[PCl_3]$	0.200 *M*	0.200 *M*	0.163 *M*

At the new equilibrium: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

- $[PCl_5]$ is higher than its original concentration.
- $[Cl_2]$ is higher than its original concentration but lower than the concentration just after the Cl_2 added (disturbance is reduced but not eliminated).
- $[PCl_3]$ is lower than its original concentration because some reacted with the added Cl_2.

	Original equilibrium	New initial (just after Cl_2 added)	New equilibrium
$[PCl_5]$	0.600 *M*	0.600 *M*	0.637 *M*
$[Cl_2]$	0.125 *M*	0.200 *M*	0.163 *M*
$[PCl_3]$	0.200 *M*	0.200 *M*	0.163 *M*

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

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

At the original equilibrium:

$$K_C = \frac{0.600}{(0.200)(0.125)} = 24.0$$

At the new equilibrium:

$$K_C = \frac{0.637}{(0.163)(0.163)} = 24.0$$

At a given temperature, K_C does not change with a change in concentration.

CHANGES IN CONCENTRATION

If the concentration decreases, the system reacts to produce some of it.

remove PCl_3

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

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

$Q_c > K_C$ (not at equilibrium)

System will reduce the disturbance (decrease of $[PCl_3]$):

- ☞ proceeding to the left
- ☞ $[PCl_3]$ and $[Cl_2]$ increase
- ☞ $[PCl_5]$ decrease

Remove Add   Remove Add

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

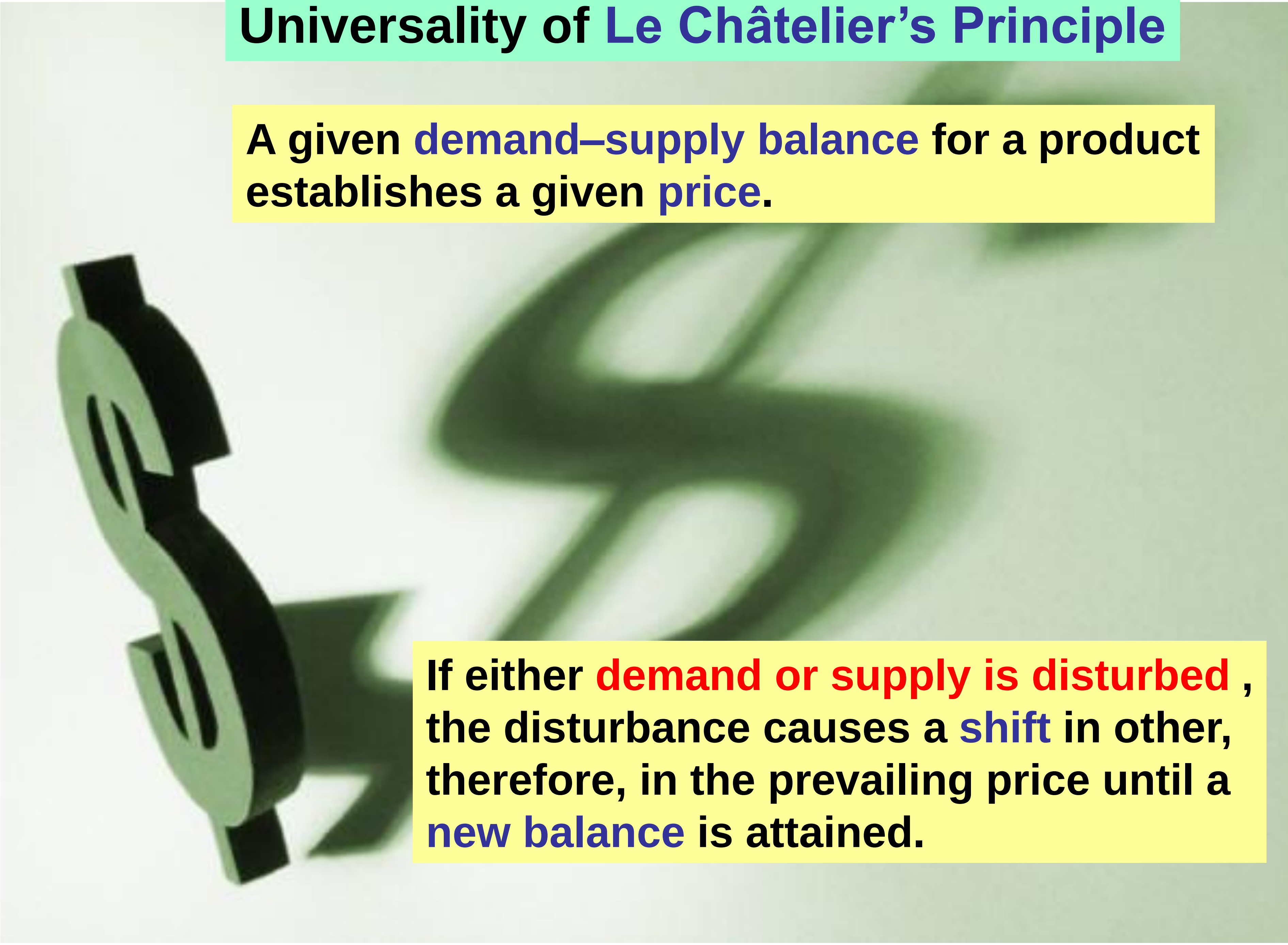
Change	Shifts in the Equilibrium
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

Universality of Le Châtelier's Principle

On the African savannah, the number of herbivores (antelope, wildebeast, zebra) and carnivores (lion, cheetah) are in delicate balance.

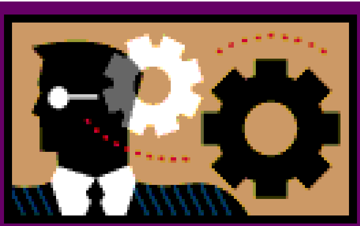
Any disturbance (drought, disease) causes shifts in the relative numbers until they attain new balance.

Universality of Le Châtelier's Principle



A given demand–supply balance for a product establishes a given price.

If either demand or supply is disturbed , the disturbance causes a shift in other, therefore, in the prevailing price until a new balance is attained.



EXERCISE - 53

To improve air quality and obtain a useful product, sulphur is often removed from coal and natural gas by treating the fuel contaminant hydrogen sulphide with O_2:

$$2H_2S(g) + O_2(g) \rightleftharpoons 2S(s) + H_2O(g)$$

What happen to

a) $[H_2O]$ if O_2 is added?
b) $[H_2S]$ if O_2 is added?
c) $[O_2]$ if H_2S is removed?
d) $[H_2S]$ if sulfur is added?

CHANGES IN PRESSURE (VOLUME)

- Only involve systems with **gaseous components.**
- Liquids and **solids** are **nearly incompressible.**

Pressure changes can occur in 3 ways:

- Changing **concentration** of a **gaseous component**.
- Adding **inert gas.**
- Changing the **volume of the reaction vessel**.

a cylinder–piston assembly

CHANGES IN PRESSURE (VOLUME)

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas　　　　1 mol gas

Disturbance: volume decrease

☞ **gas pressure immediately increases.**

☞ **$Q_c \neq K_C$ (not at equilibrium)**

System will reduce the disturbance

- ☞ **Reduce number of gas molecules**
- ☞ **proceeding to the right**
- ☞ **$[PCl_3]$ and $[Cl_2]$ decrease**
- ☞ **$[PCl_5]$ increase**

CHANGES IN PRESSURE (VOLUME)

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas | **1 mol gas**

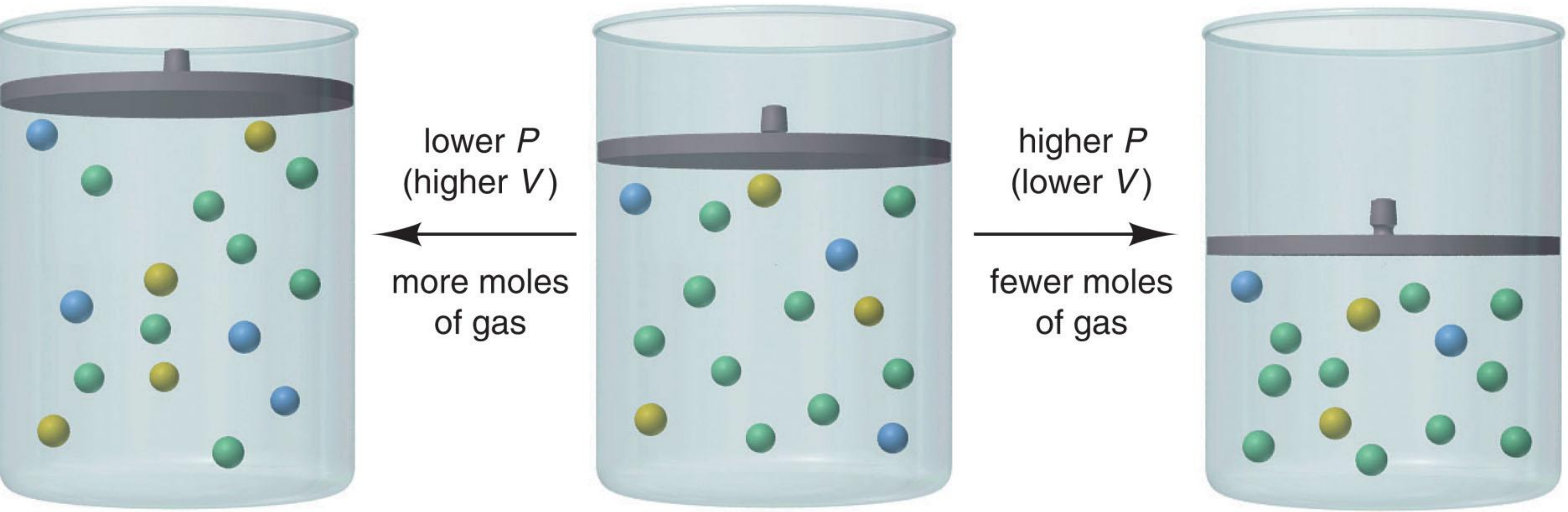
Disturbance: volume increase

☞ **gas pressure immediately decreases.**

☞ **$Q_c \neq K_C$ (not at equilibrium)**

System will reduce the disturbance

- ☞ **Increase number of gas molecules**
- ☞ **proceeding to the left**
- ☞ **$[PCl_3]$ and $[Cl_2]$ increase**
- ☞ **$[PCl_5]$ decrease**



lower P
(higher V)
more moles
of gas
higher P
(lower V)
fewer moles
of gas

KEEP IN MIND!

Changes	Shifts in the Equilibrium
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

EXERCISE - 54

What effect does an increase in pressure have on each of the following systems at equilibrium? The temperature is kept constant and in each case, the reactants are in a cylinder fitted with a movable piston.

a) $A(s) \rightleftharpoons 2B(s)$
b) $2A(l) \rightleftharpoons B(l)$
c) $A(s) \rightleftharpoons B(g)$
d) $A(g) \rightleftharpoons B(g)$
e) $A(g) \rightleftharpoons 2B(g)$

EXERCISE - 55

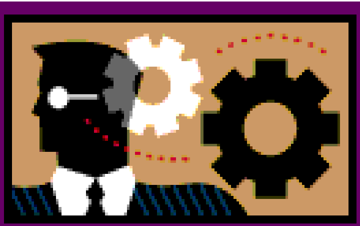
Predict the effect of increasing the container volume on the amounts of each reactant and product in the following:

a) $F_2(g) \rightleftharpoons 2F(g)$

b) $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

c) $CH_3OH(l) \rightleftharpoons CH_3OH(g)$

d) $CH_4(g) + NH_3(g) \rightleftharpoons HCN(g) + 3H_2(g)$



EXERCISE - 56

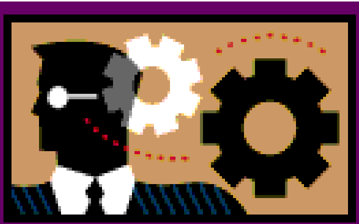
Predict the effect of decreasing the container volume on the amounts of each reactant and product in the following:

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

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

c) $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(l)$

d) $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$



EXERCISE - 57

Consider the following equilibrium systems:

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

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

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

d) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

Predict the direction of the net reaction in each case as a result of increasing the pressure (decreasing volume) on the system at constant temperature.

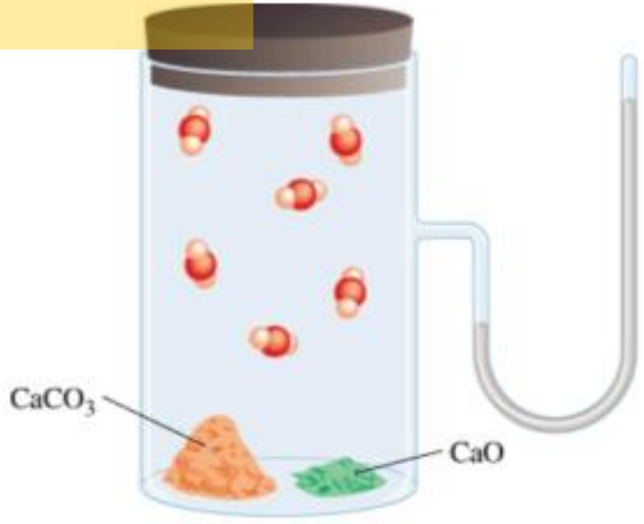
EXERCISE - 58

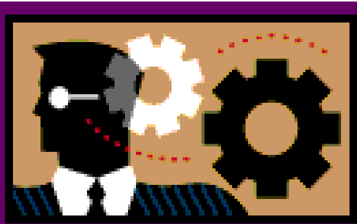
How would you change the volume of each of the following reaction to increase the yield of the products?

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

b) $S(s) + 3F_2(g) \rightleftharpoons SF_6(g)$

c) $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl(g)$





EXERCISE - 59

How would you change the pressure (via a volume change) the following reaction to decrease the yield of the products?

a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3g)$

b) $4NH_3(g) + 3O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

c) $CaC_2O_4(g) \rightleftharpoons CaCO_3(s) + CO(g)$

EXERCISE - 60

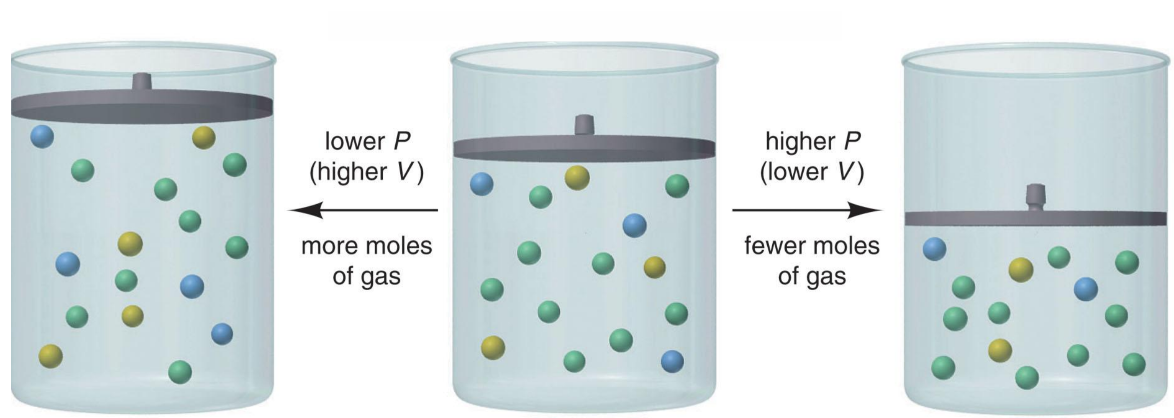
How would you adjust the volume of the reaction vessel in order to maximize product yield in the following reactions?

a) $Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)$

b) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

c) $Na_2O_2(s) \rightleftharpoons 2Na(l) + O_2(g)$

d) $C_2H_2(g) + 2H_2(g) \rightleftharpoons C_2H_6(g)$



ADDITION OF INERT GAS

- **The total pressure of an equilibrium system can be changed without changing its volume by adding an inert gas.**
- **However, adding an inert gas has no effect on the equilibrium position**
- **The effect of the addition of an inert gas to the equilibrium system can be studied based on these two conditions:**

    I. **At constant pressure**

    II. **At constant volume**

THE EFFECT OF THE ADDITION OF INERT GAS ON EQUILIBRIUM

- **At constant pressure:**

* **The partial pressures for the gases in the system are lowered**

* **The net effect is as though the gases at equilibrium are subjected to a lower total pressure**

* **According to Le Chatelier’s principle, addition of a noble gas favours the direction that increases the number of moles of gas**

ADDITION OF INERT GAS AT CONSTANT PRESSURE

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 mol gas

Add noble gas

1 mol gas

Disturbance: addition of inert gas

☞ **Total gas pressure decreases.**

System will reduce the disturbance

☞ **By increasing the number of gas molecules**

☞ **proceeding to the left (less products will be produced)**

☞ **[PCl_3] and [Cl_2] increase**

☞ **[PCl_5] decrease**

☞ **Equilibrium favours the reactants**

ADDITION OF INERT GAS AT CONSTANT PRESSURE

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

2 mol gas | Add noble gas | 3 mol gas

Disturbance: addition of inert gas

☞ **Total gas pressure decreases.**

System will reduce the disturbance

☞ **By increasing the number of gas molecules**

☞ **proceeding to the right (more products produced)**

☞ **$[H_2]$ and $[O_2]$ increase**

☞ **$[H_2O]$ decrease**

☞ **Equilibrium favours the products**

ADDITION OF INERT GAS AT CONSTANT PRESSURE

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

2 mol gas

Add noble gas

2 mol gas

Disturbance: addition of inert gas

- ☞ **The equilibrium position is not affected**
- ☞ **Number of moles of reactants and products are the same**

THE EFFECT OF A NOBLE GAS ON EQUILIBRIUM

At constant volume:

- **The total number of gaseous molecules increases**
- **The total pressure of the equilibrium system increases**
- **However, the partial pressures of each of the gases in the equilibrium system remains unchanged**

KEEP IN MIND!!!

- From Dalton's law:

$$\boxed{P_A = n_A\,(RT/V)}$$

P_A = partial pressure of any gas, A

- Adding inert gas at constant volume does not change any of the quantities on the right side of the above equation
- So, P_A remains constant
- Therefore, addition of inert gas at constant volume has no effect on the equilibrium position and the composition of the equilibrium mixture

CHANGES IN TEMPERATURE

☞ **Only temperature changes can alter *K*.**

$$\mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \rightleftharpoons \mathrm{PCl_5}(g) \qquad \Delta H = -111\ \mathrm{kJ}$$

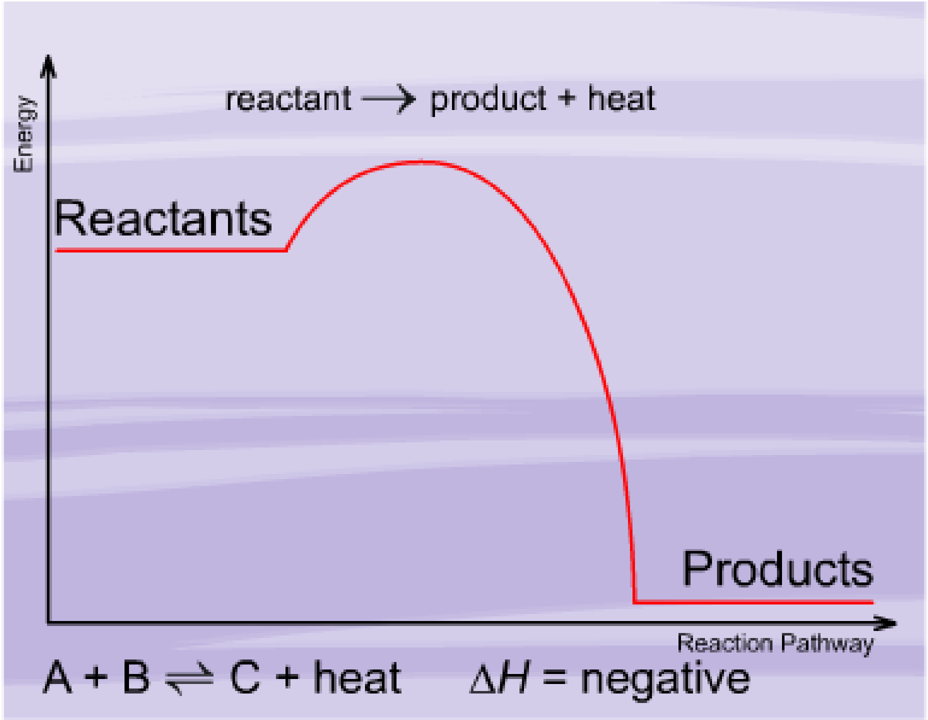
forward reaction is exothermic (heat released)

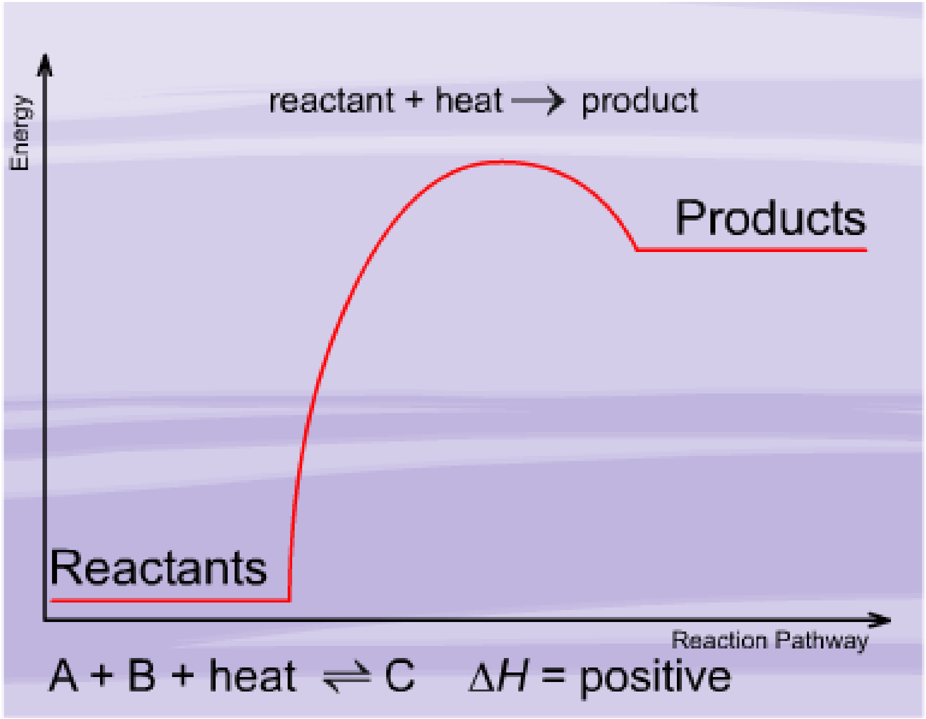
$$\mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{PCl_5}(g) + \text{heat} \qquad \Delta H = -111\ \mathrm{kJ}$$

Exothermic ☞ heat released

$$\mathrm{PCl_5}(g) + \text{heat} \longrightarrow \mathrm{PCl_3}(g) + \mathrm{Cl_2}(g) \qquad \Delta H = +111\ \mathrm{kJ}$$

Endothermic ☞ heat absorbed


Energy
reactant ⟶ product + heat
Reactants
Products
Reaction Pathway
A + B ⇌ C + heat
ΔH = negative


Energy
reactant + heat ⟶ product
Products
Reactants
Reaction Pathway
A + B + heat ⇌ C
ΔH = positive

CHANGES IN TEMPERATURE

Exothermic ☞ heat released

heat released

$$PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g) + \text{heat} \qquad \Delta H = -111 \text{ kJ}$$

Disturbance:

- ☞ **rise in temperature**
- ☞ **"adds" heat to the system**
- ☞ **exothermic reaction is not favorable**

Disturbance:

- ☞ **drop in temperature**
- ☞ **"removes" heat from the system**
- ☞ **exothermic reaction is favorable**

CHANGES IN TEMPERATURE

Endothermic ☞ heat absorbed

$$PCl_5(g) + \text{heat} \longrightarrow PCl_3(g) + Cl_2(g) \qquad \Delta H = +111\ \text{kJ}$$

absorbed heat

Disturbance:

- ☞ **rise in temperature**
- ☞ **"adds" heat to the system**
- ☞ **endothermic reaction is favorable**

Disturbance:

- ☞ **drop in temperature**
- ☞ **"removes" heat from the system**
- ☞ **exothermic reaction is not favorable**

CHANGES IN TEMPERATURE

(exothermic)

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H = -111\ \text{kJ}$$

(endothermic)

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

Changes	Net reaction	Exothermic
Increase temperature	Left	K decreases
Decrease temperature	Right	K increases

Temperature decrease favors an exothermic reaction.

CHANGES IN TEMPERATURE

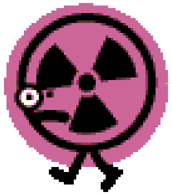
(endothermic) →

$$SO_2(g) \rightleftharpoons S(s) + O_2(g) \quad \Delta H = 178\ \text{kJ}$$

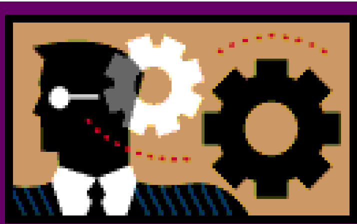
← (exothermic)

$$K_c = \frac{[O_2]}{[SO_2]}$$

Changes	Net reaction	Endothermic
Increase temperature	Right	K increases
Decrease temperature	Left	K decreases



Temperature increase favors an endothermic reaction.



EXERCISE - 61

How does an increase in temperature affect the equilibrium concentration of the underlined substance and the value of *K*:

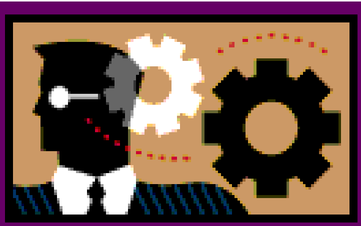
a) $CaO(s) + H_2O(l) \rightleftharpoons Ca(OH)_2(g)$ $\Delta H = -82$ kJ

b) $CaCO_3(g) \rightleftharpoons CaO(s) + CO_2(g)$ $\Delta H = 178$ kJ

c) $C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$ $\Delta H = -75$ kJ

d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = 181$ kJ

e) $P_4(s) + 10Cl_2(g) \rightleftharpoons 4PCl_5(g)$ $\Delta \mathrm{H} -1528$ KJ



EXERCISE - 62

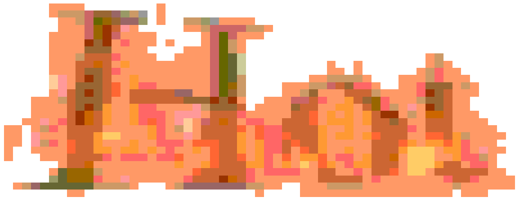
Predict the effect of increasing the temperature on the amounts of products in the following reactions:

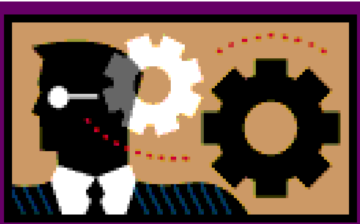
a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90.7\ kJ$

b) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad \Delta H = 131\ kJ$

c) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ (endothermic)

d) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ (exothermic)





EXERCISE - 63

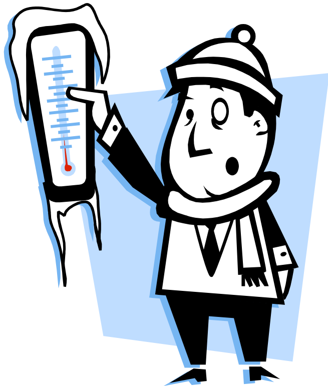
Predict the effect of decreasing the temperature on the amounts of products in the following reactions:

a) $C_2H_2(g) + H_2O(g) \rightleftharpoons CH_3CHO(g) \quad \Delta H = -151\ \text{kJ}$

b) $CH_3CH_2OH(l) + O_2(g) \rightleftharpoons CH_3CO_2H(l) + H_2O(g) \quad \Delta H = -451\ \text{kJ}$

a) $2C_2H_4(g) + O_2(g) \rightleftharpoons 2CH_3CHO(g)$ (exothermic)

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



EFFECT OF CATALYST

Catalyst **speeds up** a reaction.

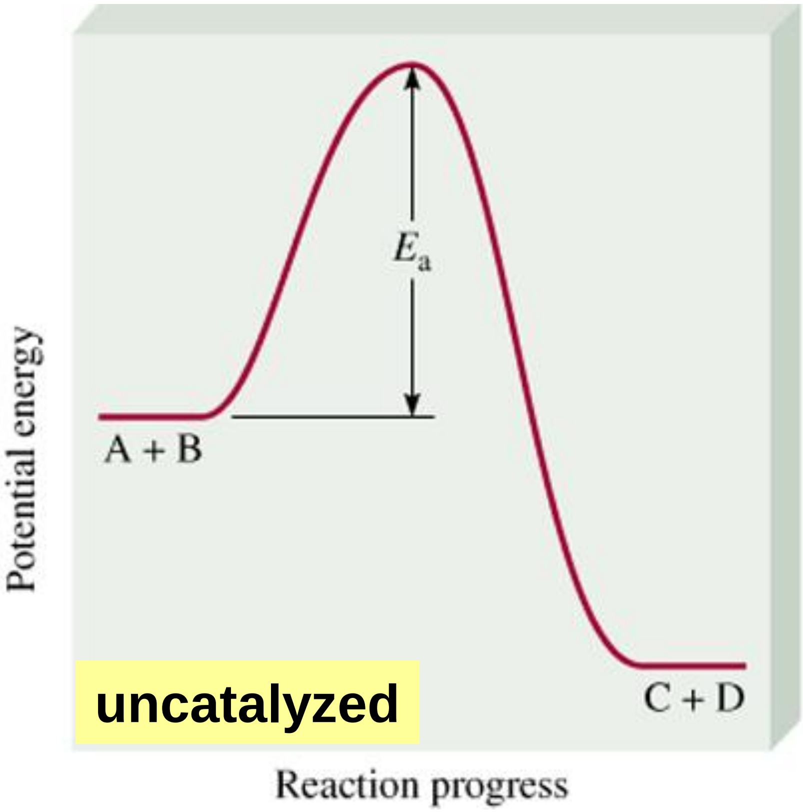
☞ by providing **alternative mechanism** with **lower activation energy**.

☞ **Increasing forward** and **reverse rates** to the **same extent**.

☞ **Shorten** the **time** taken to **reach equilibrium**.

BUT, REMEMBER…

Catalyst has **no effect on the equilibrium position** and **value of K_C**.



Catalyst lowers activation energy, E_a
for both forward and reverse reactions.

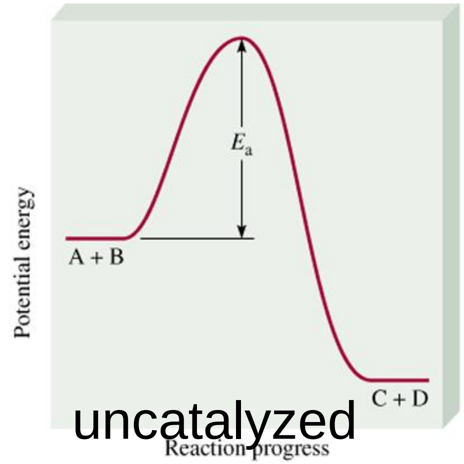
EXERCISE - 64

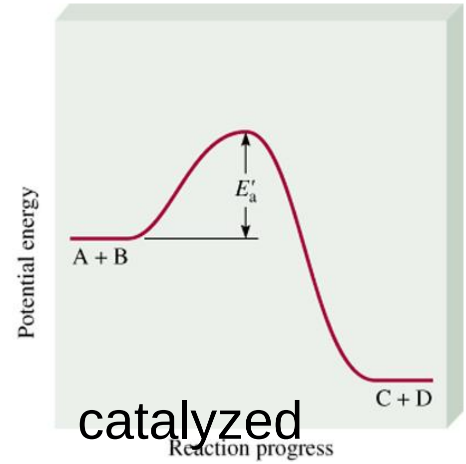
5.1

In the uncatalyzed reaction

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

the pressure of the of the gases at equilibrium are $P_{N_2O_4}$= 0.377 atm and P_{NO_2}= 1.5 atm at 100°C. What would happen to these pressures if a catalyst to the mixture ?





Keep in MIND

Changes	Shift Equilibrium	Change Equilibrium Constant (value of *K*)
Concentration	**yes**	**no**
Pressure	**yes**	**no**
Volume	**yes**	**no**
Temperature	**yes**	**yes**
Catalyst	**no**	**no**

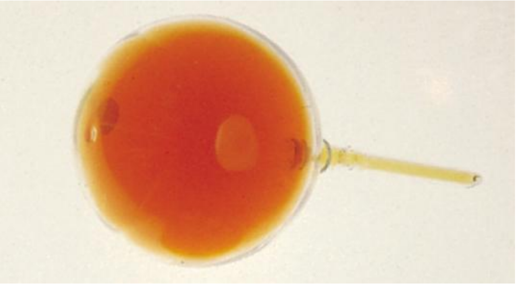
EXERCISE - 65

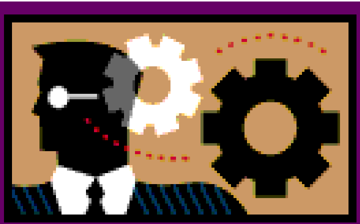
Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \quad \Delta H = 38.5 \text{ kJ}$$

Predict the changes in equilibrium if

a) the reaction mixture is heated
b) NF_2 gas is removed
c) the pressure decrease
d) inert gas, such as He, is added





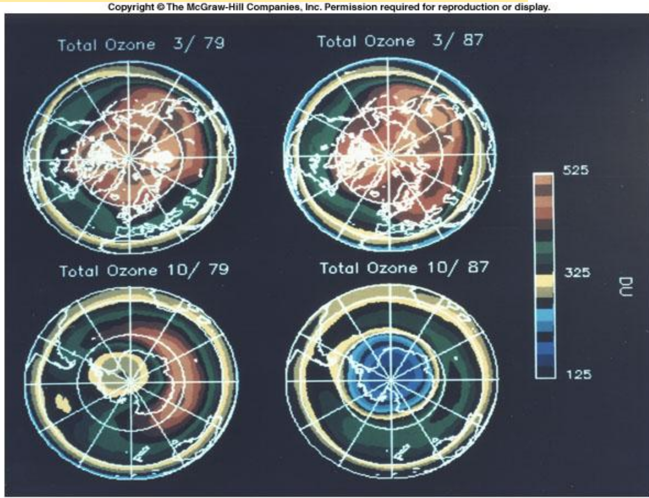
EXERCISE - 66

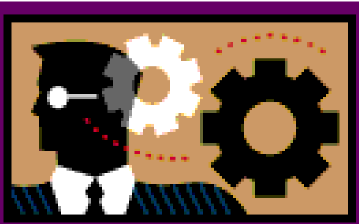
Consider the equilibrium between molecular oxygen and ozone

$$3O_2(g) \rightleftharpoons 2O_3(g) \quad \Delta H = 284\text{kJ}$$

What would be the effect of

a) increasing pressure by decreasing volume
b) increasing pressure by adding O_2
c) decreasing the temperature
d) adding a catalyst





EXERCISE - 67

Heating solid sodium bicarbonate in a closed vessel establishes the following equilibrium:

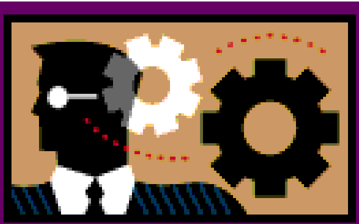
$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

What would happen to the equilibrium position if

a) some of the CO_2 were removed

b) some solid Na_2CO_3 were removed

c) some solid $NaHCO_3$ were removed



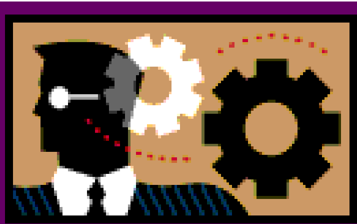
EXERCISE - 68

Consider the following equilibrium process:

$$PCl_5(g) \rightleftharpoons PCl_3(s) + Cl_2(g) \quad \Delta H = 92.5\ \text{kJ}$$

Predict the direction of the shift in equilibrium when

a) the temperature is raised
b) more chlorine gas is added
c) some PCl_3 is removed
d) pressure on the gases is increased
e) a catalyst is added to the reaction mixture



EXERCISE - 69

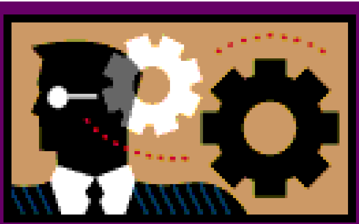
Consider the following equilibrium reaction in a closed container:

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

What happen if

a) the volume is increased
b) some CaO is added
c) some CO_2 is added
d) a few drops of a NaOH solution are added
e) a few drops of a HCl solution is added
f) temperature is increased

Note: Decomposition reactions are endothermic.



EXERCISE – 70

Consider this equilibrium system

$$CO(g) + Fe_3O_4(s) \rightleftharpoons CO_2(g) + 3FeO(s)$$

How does the equilibrium position shift if:

a) CO is added
b) Solid NaOH is added
c) Fe_3O_4 is added
d) Dry ice is added at constant temperature

DRY ICE ($CO_2(s)$)

EXERCISE - 71

Sodium bicarbonate undergoes thermal decomposition according to the reaction

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

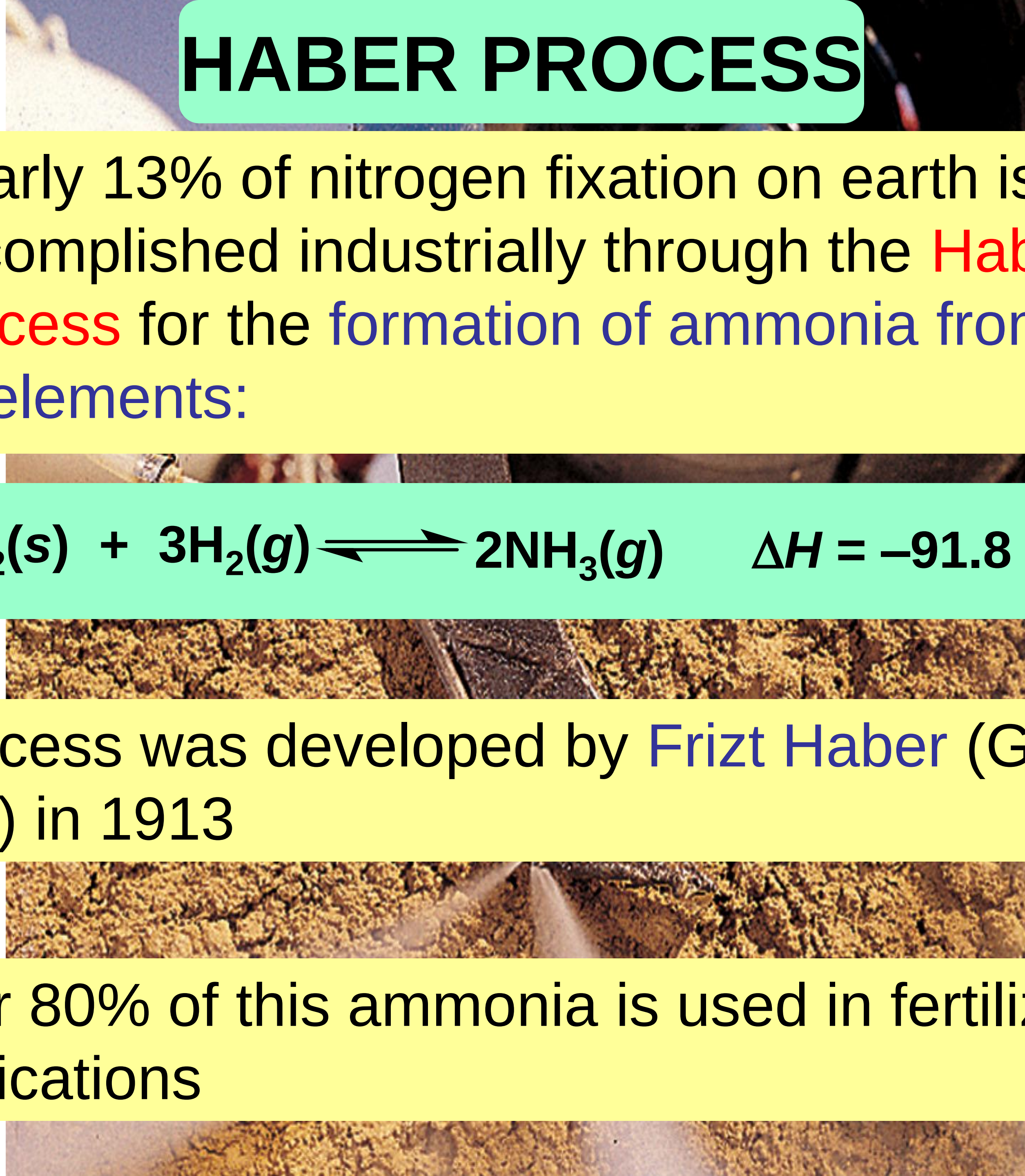
How does the equilibrium position shift as a results of each of the following disturbances:

a) **0.20 atm of argon gas is added**
b) **$NaHCO_3(s)$ is added**
c) **$Mg(ClO_4)$ is added as a drying agent to remove water**
d) **Dry ice is added at constant temperature**

SYNTHESIS OF AMMONIA: HABER PROCESS

- Nitrogen can be found in many essential natural and synthetic compounds
- Richest source of nitrogen: atmosphere (4 of every 5 molecules are N_2)
- However, due to the low reactivity of N_2, the supply of usable nitrogen has become limited
- Nitrogen atom is very difficult to “fix” (combine with other atoms) due to the strong triple bond that holds the two N atoms together

HABER PROCESS



- Nearly 13% of nitrogen fixation on earth is accomplished industrially through the Haber process for the formation of ammonia from its elements:

$$\mathbf{N_2(\mathit{s}) + 3H_2(\mathit{g}) \rightleftharpoons 2NH_3(\mathit{g}) \qquad \Delta \mathit{H} = -91.8\ kJ}$$

The process was developed by Frizt Haber (German chemist) in 1913

Over 80% of this ammonia is used in fertilizer applications

APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS

- **To make an industrial process economically worthwhile**

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

Three ways to maximize the yield of ammonia:

✓ **Decrease [NH_3]**

✓ **Decrease volume (increase pressure)**

✓ **Decrease temperature**

Application of Le Chatelier's principle

APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8\ \text{kJ}$$

Decrease [NH_3]

- Product: Ammonia
- By removing ammonia, the system will produce more in continual drive to reattain equilibrium
- The equilibrium will shift to the right

APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

4 mol of gas

2 mol of gas

Decrease volume (increase pressure)

- 4 mol of gas **reacts to form** 2 mol of gas
- Decreasing the volume will shift the equilibrium towards fewer moles of gas
- Produces more ammonia

APPLICATION OF EQUILIBRIUM PRINCIPLES IN THE HABER PROCESS

$$N_2(s) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

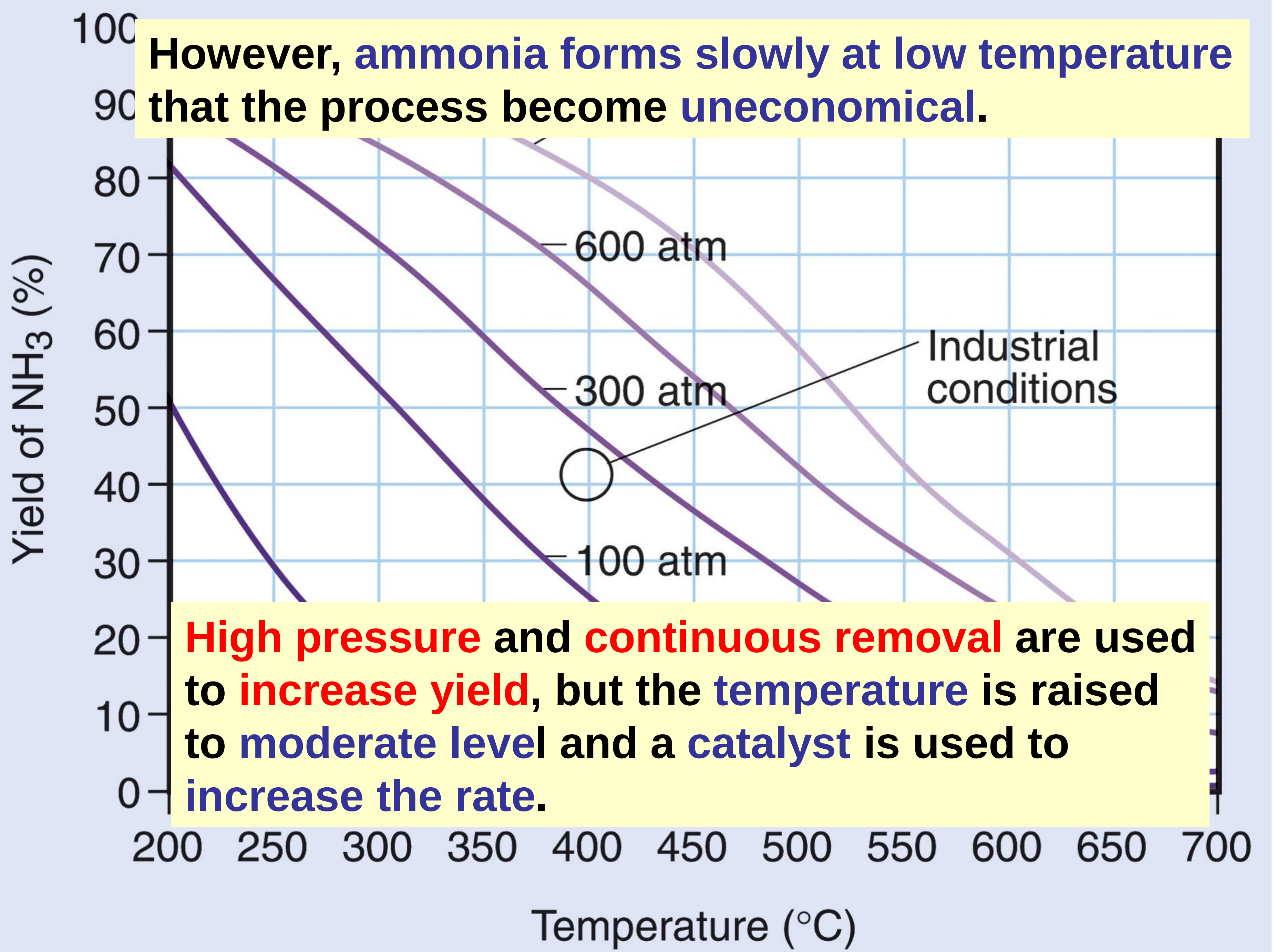
Decrease temperature

- **Formation of ammonia is exothermic**
- **Decreasing temperature (removing heat) will shift the equilibrium to the right**
- **K_C will increase**

Effect of Temperature on K_c for Ammonia Synthesis

T (K)	K_c
200.	7.17×10^{15}
300.	2.69×10^{8}
400.	3.94×10^{4}
500.	1.72×10^{2}
600.	4.53×10^{0}
700.	2.96×10^{-1}
800.	3.96×10^{-2}

However, **ammonia forms slowly at low temperature** that the process become **uneconomical**.



High pressure and **continuous removal** are used to **increase yield**, but the **temperature** is raised to **moderate level** and a **catalyst** is used to **increase the rate**.

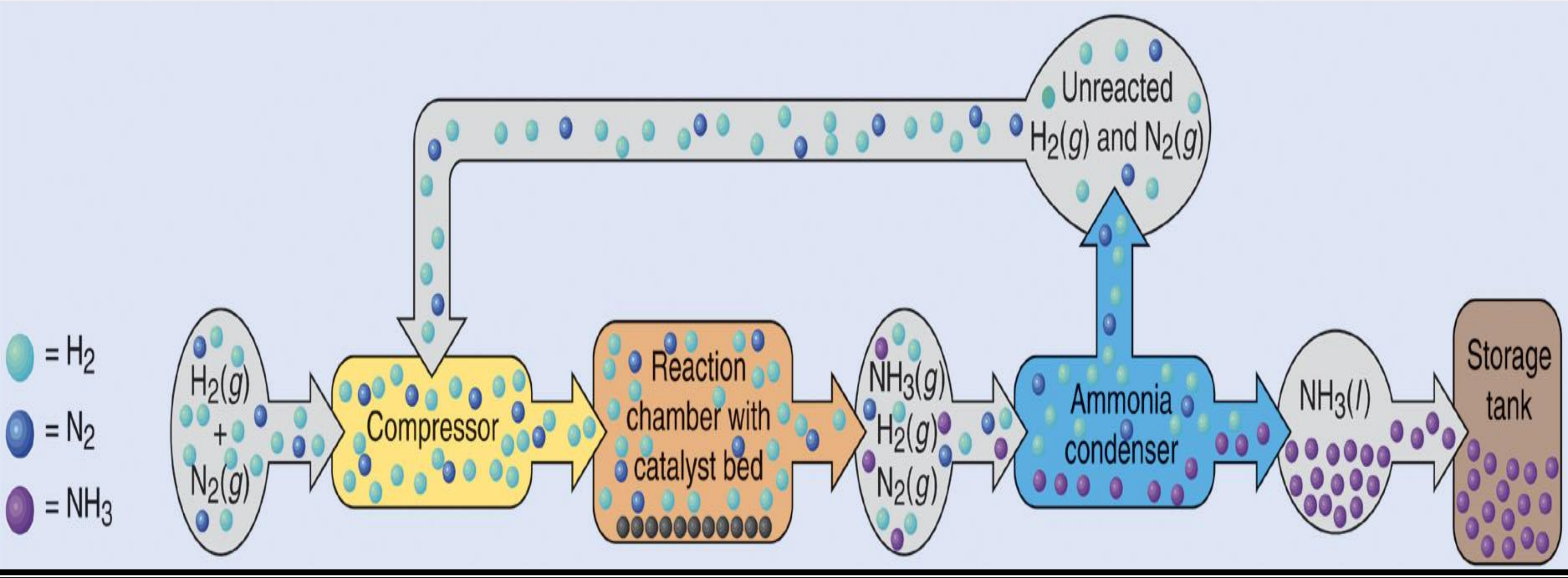
Keep In Mind!!!

- In Haber process, low temperature will increase the yield of ammonia, but the rate of reaction will be too slow

IDEAL CONDITIONS:

- **Temperature:** 450°C - 500°C (to **optimize yield and rate**)
- **Catalyst:** Iron (**to speed up the reaction**)
- **Promoter:** Aluminium oxide (**to increase catalyst's efficiency**)
- **Pressure:** Between 200 – 1000 atm (**to save cost**)

KEY STAGES IN THE HABER PROCESS FOR SYNTHESIZING AMMONIA

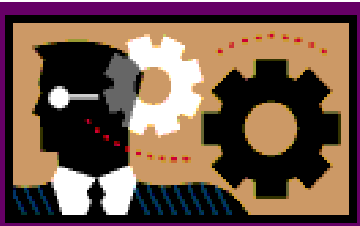


EXERCISE - 72

Lime (CaO) used primarily in the manufacture of steel, glass, and high–quality paper. It is produced in an endothermic reaction by thermal decomposition of limestone:

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

How would control reaction conditions to produce the maximum amount of lime?



EXERCISE - 73

The oxidation of SO_2 to SO_3 is an important industrial reactions because it is the key in sulfuric acid production:

$$SO_2(g) + \frac{1}{2}O_2 \rightleftharpoons SO_3(g) \quad \Delta H = -99.2\ \text{kJ}$$

a) **What qualitative combination of *T* and *P* maximizes SO_3 yield?**

b) **How does addition of O_2 affect *Q*? *K*?**

c) **Suggest a reason catalysis is used in the manufacture of H_2SO_4?**

END OF SLIDE SHOW