

## Lecture 8

# Chemical Equilibrium

### Meaning of equilibrium

✚ Reactions proceed either to **completion** or to **equilibrium**.



✚ When  $\text{NO}_2$  is placed in an evacuated, sealed glass vessel at  $25^\circ\text{C}$ , the **intensity** of the **dark brown color decreases** with time but **does not become colorless**.

✚ **Eventually**, the intensity of the brown color becomes constant, which means that the concentration of  $\text{NO}_2$  is no longer changing.

✚ The system has reached **chemical equilibrium**, the state where the concentrations of all reactants and products remain constant with time.

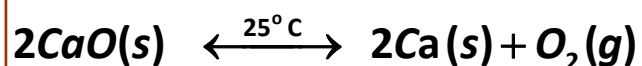
## Positions of equilibrium

✚ Lies far to the right (in the products direction)



✓ The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible.

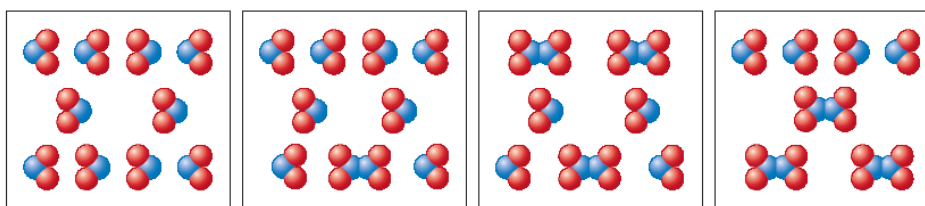
✚ Lies far to the left (in the direction of the reactants)



✓ These reactions occur only to a slight extent.

✓ Decomposition to Ca (s) and O<sub>2</sub> (g) is virtually undetectable.

## Equilibrium is not static but is a highly dynamic situation



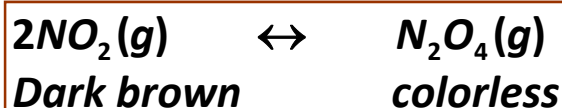
(a)

(b)

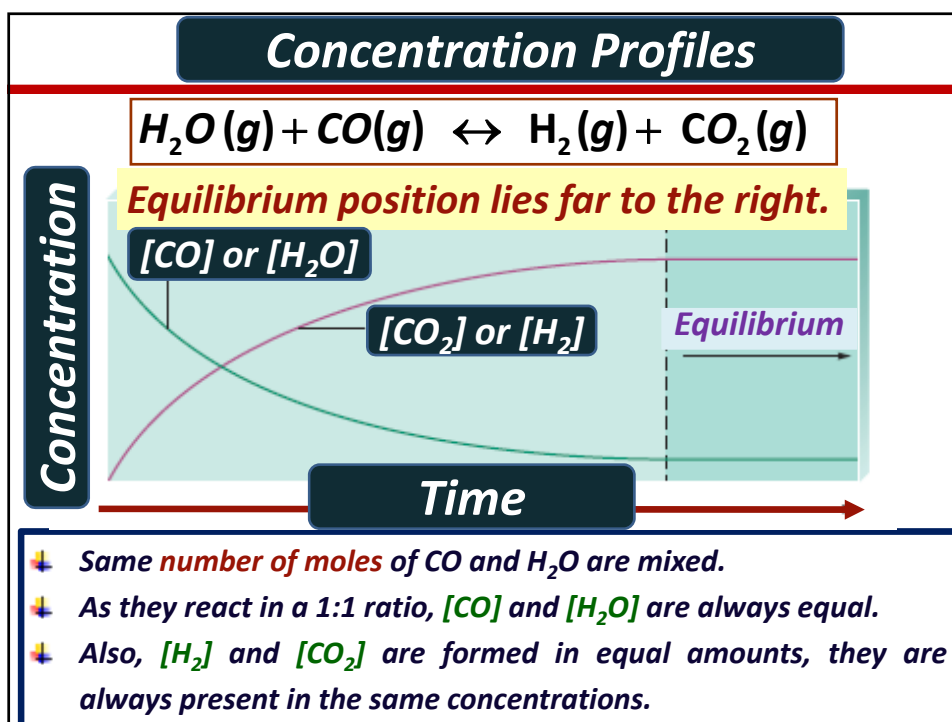
(c)

(d)

Time →



✚ **Note:** the numbers of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> in the container become constant (c and d) after sufficient time has passed.



### Why does equilibrium occur?

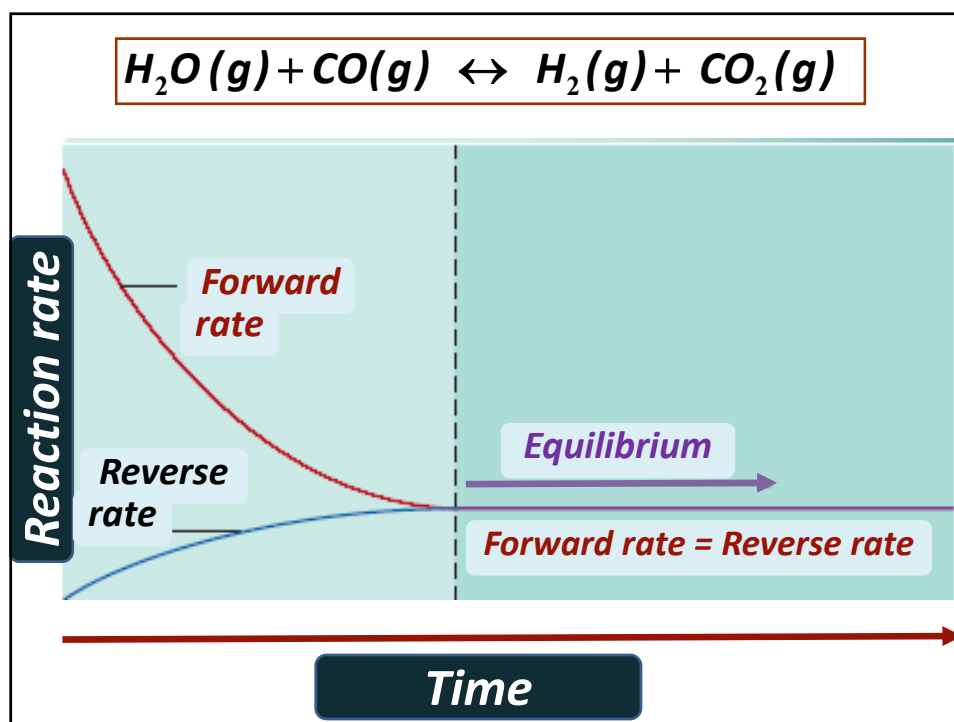
- ✚ Molecules react upon **collision** (**Higher concentrations** lead to **more collisions and faster reactions**).
- ✚ As the reaction proceeds, the reactants' concentration decreases and the rate of forward reaction decreases

$$\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$$

- ✚ Initially, there was neither H<sub>2</sub> nor CO<sub>2</sub>; the rate of the reverse reaction was **zero**. As the **forward reaction proceeds**, the [H<sub>2</sub>] and [CO<sub>2</sub>] build up, and the rate of the reverse reaction increases.

$$\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \leftarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g})$$

- Eventually, the concentrations reach levels where the rates of forward and reverse reactions become equal. **The system has reached equilibrium.**

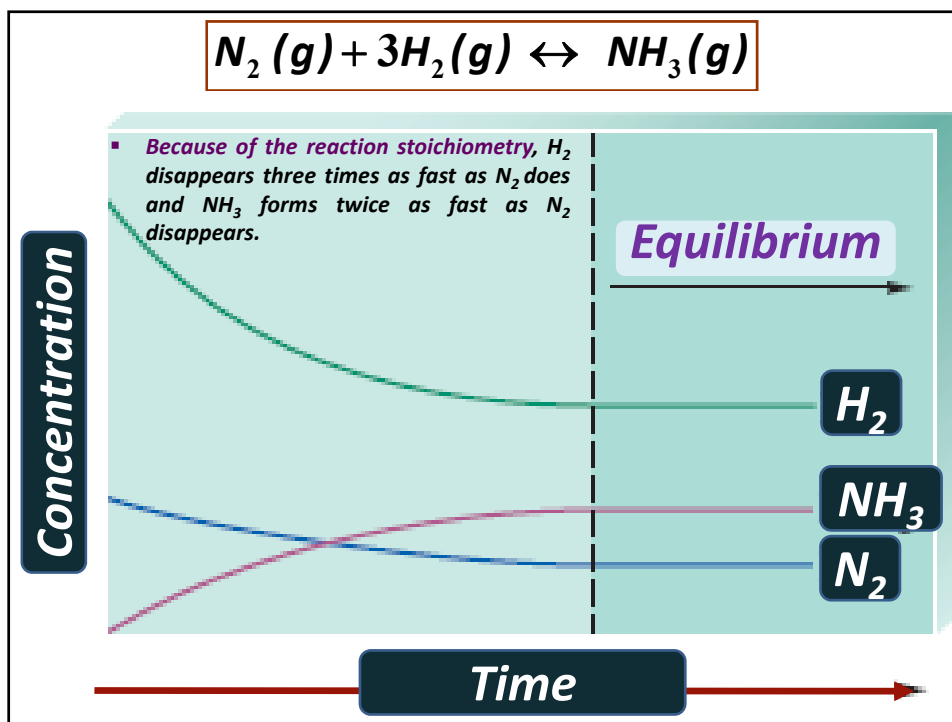


### Equilibrium position

*The equilibrium position of a reaction—left, right, or somewhere in between—is determined by many factors:*

- ✚ The initial concentrations,
- ✚ the relative *energies* of the reactants and products, and
- ✚ the relative degree of “*ordering*” of the reactants and products.

▪ *Reactions move in the direction achieving the minimum energy and maximum disorder.*



$N_2(g) + 3H_2(g) \leftrightarrow NH_3(g)$

When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25°C, no apparent change in the concentrations occurs over time, regardless of the original amounts of the gases. Why?

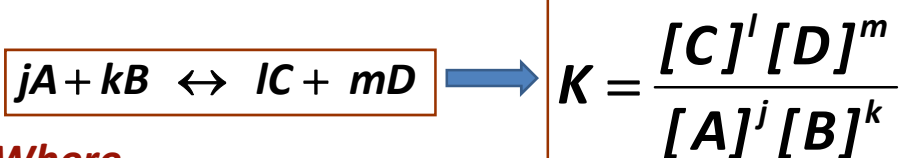
Possibly

- 1) The system is at **chemical equilibrium**.
- 2) The forward and reverse reactions are so **slow** that the system moves toward equilibrium at a rate that cannot be detected.

*The second reason applies because of the **very strong bonds** in  $N_2$  and  $H_2$*

## Equilibrium constant

✚ The **law of mass action** proposes for this general equation at equilibrium:

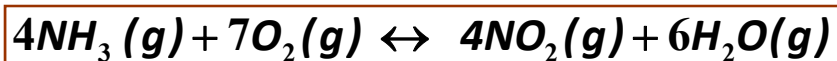


**Where**

- ✚ A, B, C and D represent chemical species.
- ✚ j, k, l and m are their coefficients in the balanced equation.
- ✚ The square brackets indicate the concentrations (mol/L) of the chemical species at equilibrium.
- ✚ K is the **equilibrium constant**.

## Example

✚ Write the equilibrium expression for the following reaction:



**Solution**

$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$

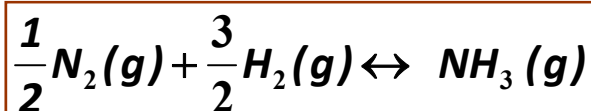
## Haber Process

✚ The following equilibrium concentrations (mol/L) were observed for the Haber process for synthesis of ammonia at 127°C:  $[NH_3] = 3.1 \times 10^{-2}$ ,  $[N_2] = 8.5 \times 10^{-1}$ ,  $[H_2] = 3.1 \times 10^{-3}$ .

- a. Calculate the value of  $K$  at 127°C for this reaction?
- b. Calculate the value of the equilibrium constant at 127°C for the reaction?



- c. Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation?



### Solution

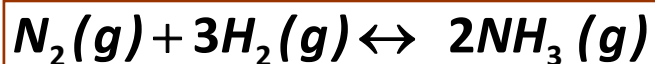


$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

**b.** Rx is written in reverse order



**Recall that**

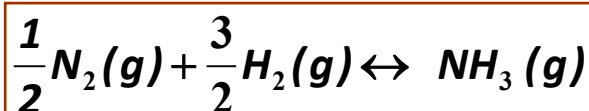


$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 3.8 \times 10^4$$

**For the reverse Rx**

$$K' = \frac{1}{K} = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}$$

**c.** Rx is multiplied by a factor



**Recall that**



**For the reverse Rx**

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 3.8 \times 10^4$$

$$K'' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \left( \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2} =$$

$$K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$



## Important information

For a reaction



$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

✚ If Rx is reversed



$$K' = \frac{1}{K} = \frac{[A]^j [B]^k}{[C]^l [D]^m}$$

✚ If Rx is multiplied by a factor n

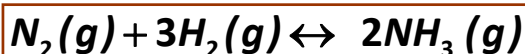


$$K'' = K^n = \frac{[C]^{nl} [D]^{nm}}{[A]^{nj} [B]^{nk}} = \left( \frac{[C]^l [D]^m}{[A]^j [B]^k} \right)^n$$

## Equilibrium position

For this reaction at  
500 °C

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$$



✚ Whenever  $N_2$ ,  $H_2$ , and  $NH_3$  are mixed together at 500 °C, system will reach an equilibrium position such that  $K = 6.0 \times 10^{-2}$ , **regardless** of the amounts of the gases that are mixed together initially.

✚ The **equilibrium concentrations** will not always be the same but influenced by the initial concentrations mixed.

✚ Each set of equilibrium concentrations is called an **equilibrium position**.

$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$			$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$
Exp.	Initial Conc./M	Eq. Conc./M	K
1	$[N_2]_0 = 1.000$	$[N_2] = 0.921$	$6.02 \times 10^{-2}$
	$[H_2]_0 = 1.000$	$[H_2] = 1.763$	
	$[NH_3]_0 = 0$	$[NH_3] = 0.157$	
2	$[N_2]_0 = 0$	$[N_2] = 0.399$	$6.02 \times 10^{-2}$
	$[H_2]_0 = 0$	$[H_2] = 0.203$	
	$[NH_3]_0 = 1.000$	$[NH_3] = 0.157$	
3	$[N_2]_0 = 2.000$	$[N_2] = 2.59$	$6.02 \times 10^{-2}$
	$[H_2]_0 = 1.000$	$[H_2] = 2.77$	
	$[NH_3]_0 = 3.000$	$[NH_3] = 1.82$	

### Important information

- There is only **one** equilibrium constant for a particular system at a **particular temperature**, but there are an **infinite** number of equilibrium positions.
- The specific **equilibrium position** adopted by a system **depends** on the **initial concentrations**, but the **equilibrium constant** does not.

## Equilibrium Expressions Involving Pressures

For gases reactions

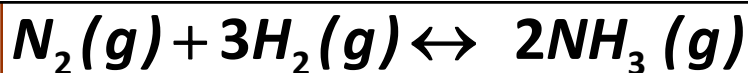
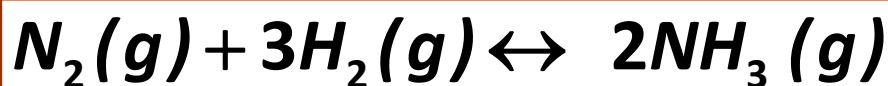
C: mol/L

$$PV = nRT \quad \rightarrow$$

$$P = \frac{n}{V}RT$$

$$P = CRT$$

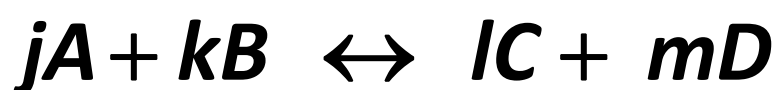
Ammonia Synthesis



$$K = \frac{C_{NH_3}^2}{C_{N_2} C_{H_2}^3} = \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right) \left(\frac{P_{H_2}}{RT}\right)^3}$$

$$= \left(\frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3}\right) (RT)^2 = K_p (RT)^2$$

Generally, for the following gaseous reaction



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

Or

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

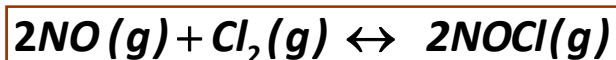
where

$$\Delta n = (l + m) - (j + k)$$

Gaseous reactants and products are only involved

### Example

Using the value of  $K_p = 1.9 \times 10^3$ , calculate the value of  $K$  at  $25^\circ\text{C}$  for the reaction



**Solution**

$$\Delta n = (2) - (2 + 1) = -1$$

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

$$(1.9 \times 10^3) (0.08206 \times 298) = 4.6 \times 10^4$$

## Heterogeneous Equilibria



✚ **Experimental** results show that the position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids (changed a little).

✚ If pure solids or liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression for the reaction.

$$K = [\text{CO}_2]$$



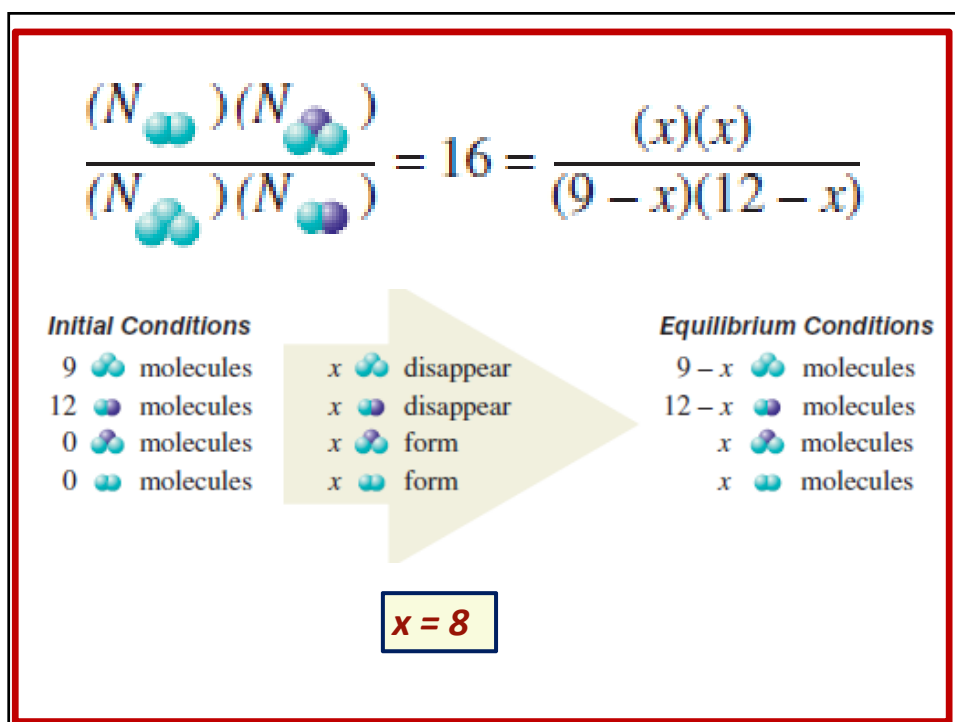
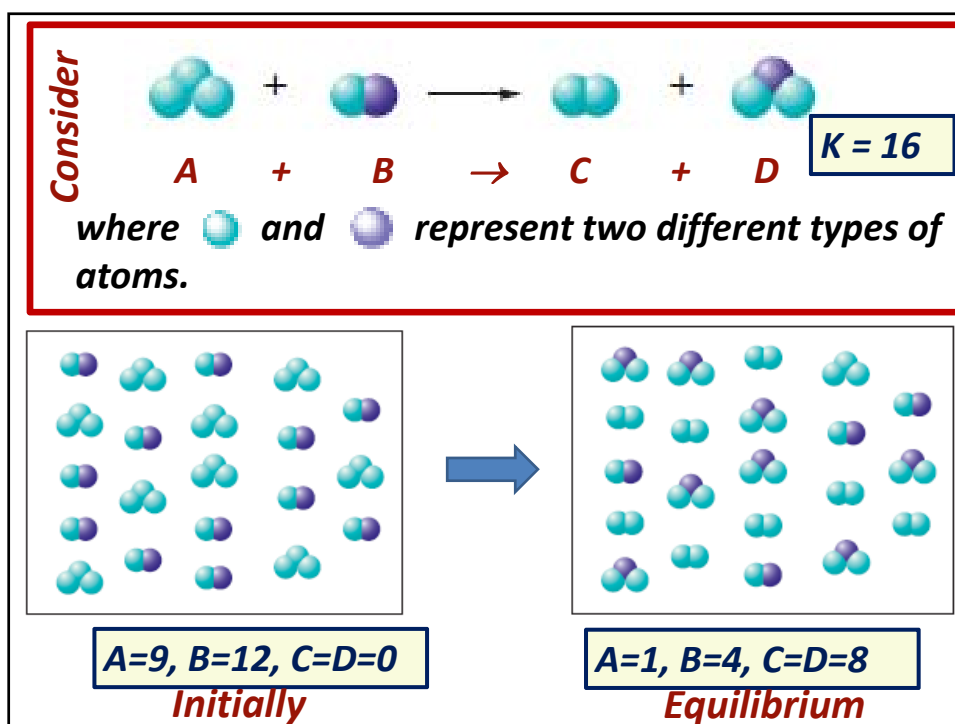
$$K = [\text{H}_2]^2 [\text{O}_2]$$

$$K_P = (P_{\text{H}_2})^2 (P_{\text{O}_2})$$



$$K = \frac{[\text{H}_2]^2 [\text{O}_2]}{[\text{H}_2\text{O}]^2}$$

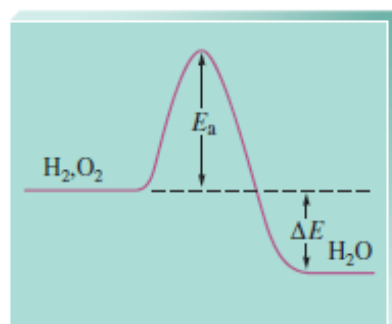
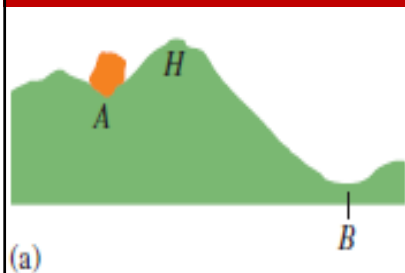
$$K_P = \frac{(P_{\text{H}_2})^2 (P_{\text{O}_2})}{(P_{\text{H}_2\text{O}})^2}$$



## Equilibrium: Thermodynamics and kinetics

- ✚ The size of  $K$  (*thermodynamics parameter*) and the time (*Kinetic parameter* depending on *activation energy*) required to reach equilibrium are not directly related.
- ✚ The *size of  $K$*  is determined by thermodynamic factors such as the difference in energy between products and reactants.
- ✚ Reactions having  $K$  much larger than 1 will have their equilibria *lying to the right* — the reaction system will consist mostly of products. The extreme of these reactions is to go almost to completion.
- ✚ Reactions having very small  $K$  values will have their equilibria *lying to the left* — the reaction system will consist mostly of reactants.

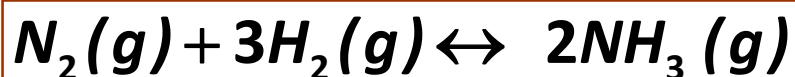
## The Extent of a Reaction



- The reactants  $H_2$  and  $O_2$  have a strong tendency to form  $H_2O$ .
- That is,  $H_2O$  has lower energy than  $H_2$  and  $O_2$ .
- However, the *large activation energy  $E_a$*  prevents the reaction at  $25^\circ\text{C}$ .
- In other words, the *magnitude of  $K$*  for the reaction depends on  $\Delta E$ , but the reaction rate depends on  $E_a$ .

## Reaction Quotient, Q

✚ It applies the law of mass action for initial concentrations



$$Q = \frac{[NH_3]_0^2}{[N_2]_0 [H_2]_0^3}$$

## Q/K

- 1) *Q is equal to K. The system is at equilibrium; no shift will occur.*
- 2) *Q is greater than K. To reach equilibrium, a net change of products to reactants must occur. The system shifts to the left, consuming products and forming reactants, until equilibrium is achieved.*
- 3) *Q is less than K. The system must shift to the right, consuming reactants and forming products, to attain equilibrium.*



## Example

✚ For the synthesis of ammonia at 500°C,  $K = 6.0 \times 10^{-2}$ . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

**a**

$$[N_2]_0 = 1.0 \times 10^{-5} \text{ M}$$

$$[H_2]_0 = 2.0 \times 10^{-3} \text{ M}$$

$$[NH_3]_0 = 1.0 \times 10^{-3} \text{ M}$$

**b**

$$[N_2]_0 = 1.5 \times 10^{-5} \text{ M}$$

$$[H_2]_0 = 3.54 \times 10^{-1} \text{ M}$$

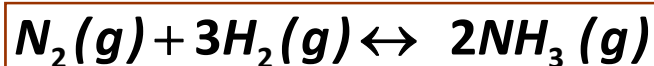
$$[NH_3]_0 = 2.0 \times 10^{-4} \text{ M}$$

**c**

$$[N_2]_0 = 5 \text{ M}$$

$$[H_2]_0 = 1.0 \times 10^{-2} \text{ M}$$

$$[NH_3]_0 = 1.0 \times 10^{-4} \text{ M}$$



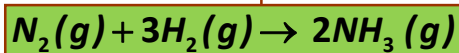
$$Q = \frac{[NH_3]_0^2}{[N_2]_0 [H_2]_0^3} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} = 1.3 \times 10^7 \gg K$$

*System shifts to left*

$$Q = \frac{(2.0 \times 10^{-4})^2}{(1.5 \times 10^{-5})(3.54 \times 10^{-1})^3} = 6.01 \times 10^{-2} = K$$

*System at equilibrium*

$$Q = \frac{(1.0 \times 10^{-4})^2}{(5)(1.0 \times 10^{-2})^3} = 2.0 \times 10^{-3} \ll K$$



*System shifts to right*

### Example

🚩 Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mole of each component is mixed in a 1.000-L flask.



$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.10$$

$$[CO]_0 = [H_2O]_0 = [CO_2]_0 = [H_2]_0 = \frac{1.0 \text{ mol}}{1.0 \text{ L}} = 1.0 \text{ M}$$

$$Q = \frac{[\text{CO}_2]_0[\text{H}_2]_0}{[\text{CO}]_0[\text{H}_2\text{O}]_0} = \frac{(1.0 \text{ mol/L})(1.0 \text{ mol/L})}{(1.0 \text{ mol/L})(1.0 \text{ mol/L})} = 1.0$$

$$Q \ll K$$

*Rx shifts to right*

Initial Conc. (mol/L)	Change (mol/L)	Eq. Conc. (mol/L)
$[\text{CO}]_0 = 1.0$	$-x$	$1.0 - x$
$[\text{H}_2\text{O}]_0 = 1.0$	$-x$	$1.0 - x$
$[\text{CO}_2]_0 = 1.0$	$+x$	$1.0 + x$
$[\text{H}_2]_0 = 1.0$	$+x$	$1.0 + x$

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 5.10$$

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

$$\sqrt{5.10} = \frac{(1.0 + x)}{(1.0 - x)} \quad x = 0.387 \text{ mol/L}$$

**Eq. Conc.**  $\rightarrow$

$$[\text{CO}] = [\text{H}_2\text{O}] = (1.0 - x) = 0.613 \text{ M}$$

$$[\text{CO}_2] = [\text{H}_2] = (1.0 + x) = 1.387 \text{ M}$$

## Homework

✚ Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of  $1.15 \times 10^2$  at a certain temperature. In a particular experiment, 3.000 moles of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species?

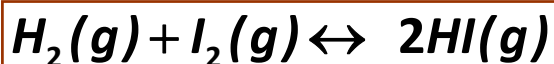
Solving a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

## Example

✚ Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is  $1.00 \times 10^2$ . Suppose HI at  $5.000 \times 10^{-1}$  atm,  $H_2$  at  $1.000 \times 10^{-2}$  atm, and  $I_2$  at  $5.000 \times 10^{-3}$  atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.



$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = 1.0 \times 10^2$$

$$P_{HI}^0 = 5.0 \times 10^{-1} \text{ atm}, P_{H_2}^0 = 1.0 \times 10^{-2} \text{ atm}, P_{I_2}^0 = 5.0 \times 10^{-3} \text{ atm}$$

$$Q_p = \frac{(P^0)^2}{(P_{H_2}^0)(P_{I_2}^0)} = \frac{(5.0 \times 10^{-1} \text{ atm})^2}{(1.0 \times 10^{-2} \text{ atm})(5.0 \times 10^{-3} \text{ atm})} = 5.0 \times 10^3$$

$Q \gg K$

*System shifts to left*

	$H_2(g)$	+	$I_2(g)$	$\leftrightarrow$	$2HI(g)$
<i>Initial</i>	$1.0 \times 10^{-2}$		$5.0 \times 10^{-3}$		$5.0 \times 10^{-1}$
<i>Change</i>	+x		+x		-2x
<i>Eqm.</i>	$(1.0 \times 10^{-2}) + x$		$(5.0 \times 10^{-3}) + x$		$(5.0 \times 10^{-1}) - 2x$

$$K_p = \frac{(P^2)_{HI}}{(P_{H_2})(P_{I_2})} = \frac{(5.0 \times 10^{-1} - 2x)^2}{(1.0 \times 10^{-2} + x)(5.0 \times 10^{-3} + x)} = 1.0 \times 10^2$$

$$9.6 \times 10^1 x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

$$x = 3.55 \times 10^{-2}$$

	$H_2(g)$	+	$I_2(g)$	$\leftrightarrow$	$2HI(g)$
<i>Eqm. P</i>	$(4.55 \times 10^{-2})$		$(4.05 \times 10^{-2})$		$(4.29 \times 10^{-1})$

## Le Châtelier's principle

*"if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change".*

**Example**



Predict the direction the Rx should shift to attain an equilibrium position if:

- Addition of carbon monoxide **(Left)**
- Addition or removal of carbon or tetraarsenic hexoxide ( $\text{As}_4\text{O}_6$ )  
*Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon or tetraarsenic hexoxide will have no effect.*
- Removal of gaseous arsenic ( $\text{As}_4$ ) **(Right)**

## Effect of Changing Pressure

- There are three ways to change the pressure of a reaction system involving gaseous components:
  - Add or remove a gaseous reactant or product. *(previously considered)*
  - Add an inert gas (one not involved in the reaction). *That will increase the total pressure but has no effect on the concentrations or partial pressures of the reactants or products. The added molecules do not participate in the reaction in any way and thus cannot affect the equilibrium in any way. Thus the system remains at the original equilibrium position.*

## Effect of Changing Pressure

### 3) Change the volume of the container.

When the volume of the container is changed, the concentrations (and thus the partial pressures) of both reactants and products are changed. We could calculate  $Q$  and predict the direction of the shift.

**For systems involving gaseous components**, We focus on the vessel volume ( $V$ ).

- ✓ If  $V$  is reduced, the system responds by reducing its own volume. This is done by **decreasing the total number of gaseous molecules in the system**.  $V \propto n$
- ✓ When the container volume is increased, the system will shift so as to increase its volume.

## Changing Reaction Volume

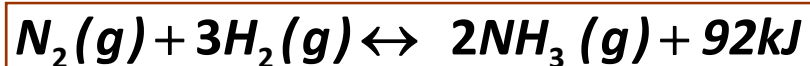
**For this Rx,**  $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

- If we suddenly reduce the volume, the reaction system can reduce its volume by reducing the number of molecules present. This means that the reaction will shift to the right.

## Effect of Changing Temperature

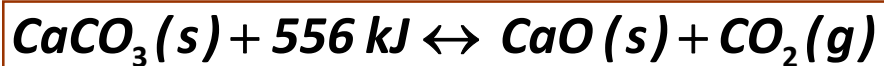
Changing the temperature affects both the *equilibrium position* and *equilibrium constants*.

For exothermic Rx,



- Increasing *T* shifts the Rx to *left*, *K* decreases
- Decreasing *T* shifts the Rx to *right*, *K* increases

For endothermic Rx,



- Increasing *T* shifts the Rx to *right*, *K* increases
- Decreasing *T* shifts the Rx to *left*, *K* decreases