Lecture 9

Spring 2022

General Chemistry II

Chem 102

Chemical Equilibrium

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Meaning of equilibrium

- Reactions proceed either to completion or to equilibrium.

$$\mathbf{2NO_2(g)} \quad \leftrightarrow \quad \mathbf{N_2O_4(g)}$$

Dark brown colorless

- When NO_2 is placed in an evacuated, sealed glass vessel at 25ºC, 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 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.

Equilibrium Position

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

$$2H_2(g) + O_2(g) \leftrightarrow 2H_2O\,(g)$$

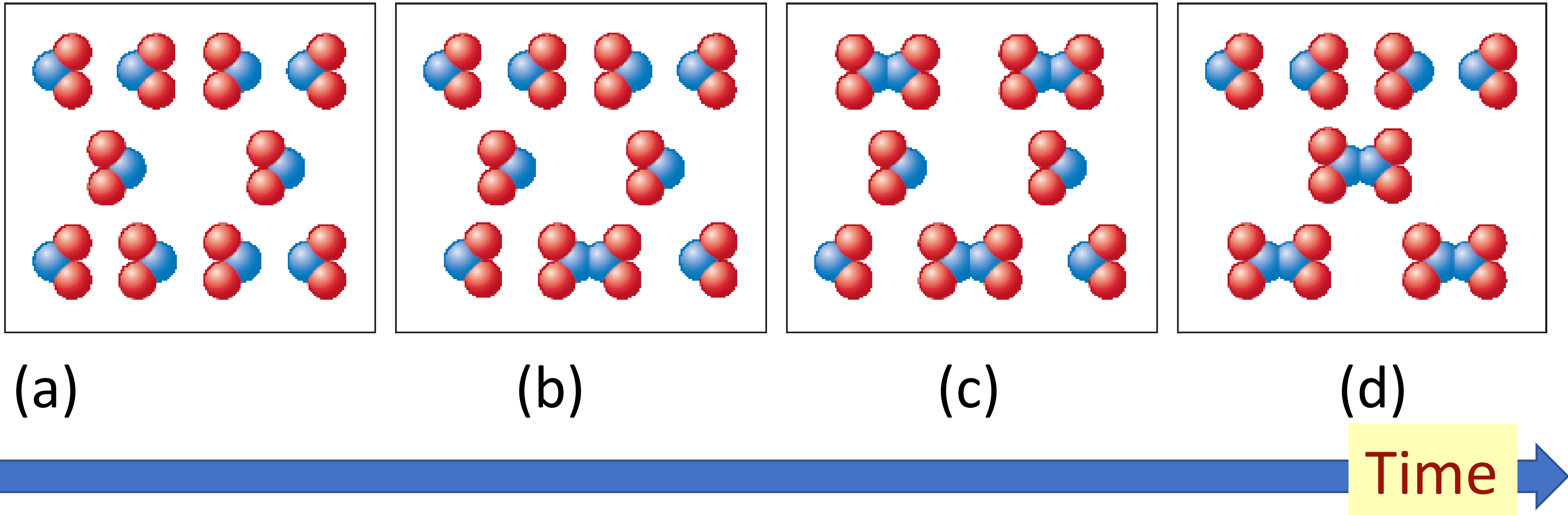
  - ✓ The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible.

- Lies far to the **left** (in the direction of the reactants)

$$2CaO(s) \xleftrightarrow{25^{o}C} 2Ca\,(s) + O_2(g)$$

  - ✓ These reactions occur only to a slight extent.
  - ✓ Decomposition to Ca (s) and O_2 (g) is virtually undetectable.

Dynamic not Static equilibrium



$2NO_2(g)$ ↔ $N_2O_4(g)$

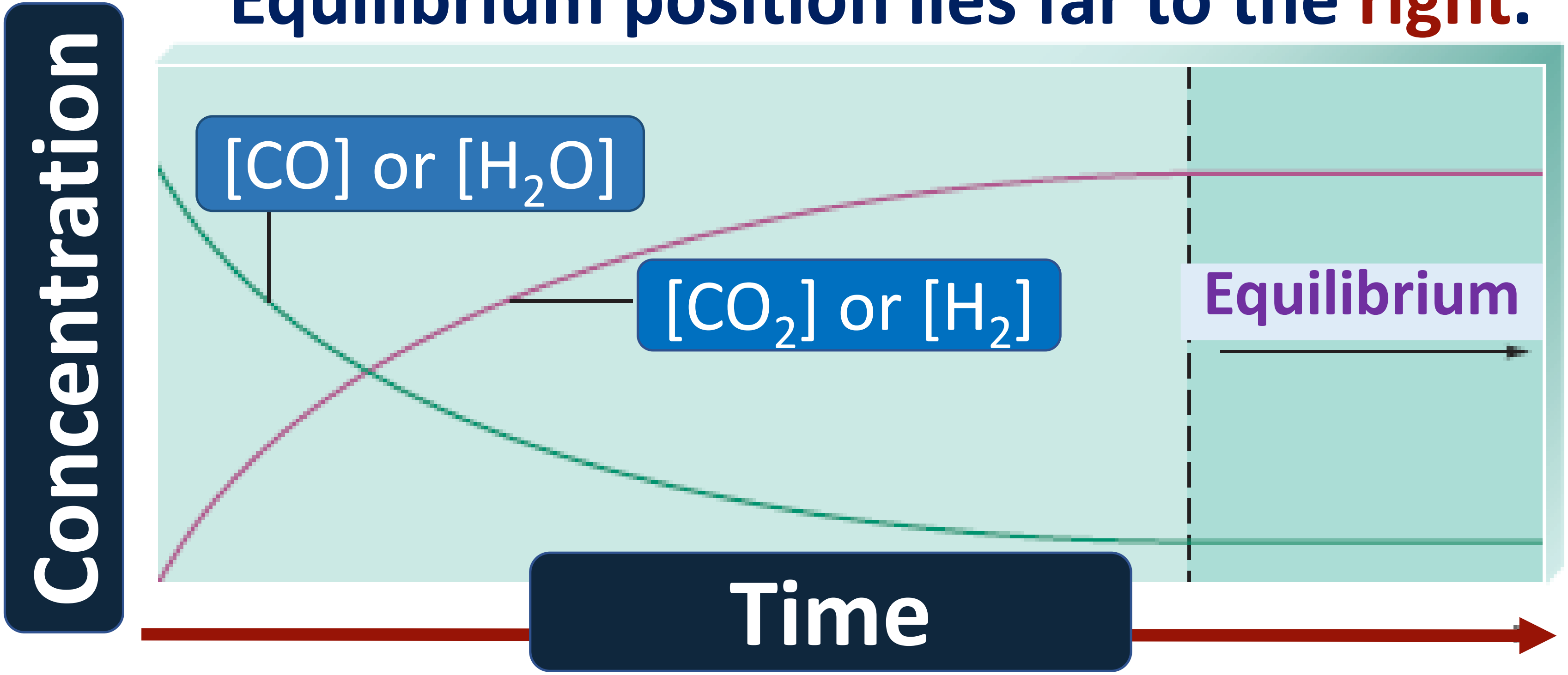
Dark brown colorless

- Numbers of **NO_2** and **N_2O_4** in the container become **constant** (c and d) after sufficient time has passed.

Concentration Profiles

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

Equilibrium position lies far to the right.



- Same number of moles of CO and H_2O are mixed.
- **[CO]** and **[H_2O]** are always equal. **Stoichiometry**
- **[H_2]** and **[CO_2]** are always equal.

Why equilibrium?

- 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

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

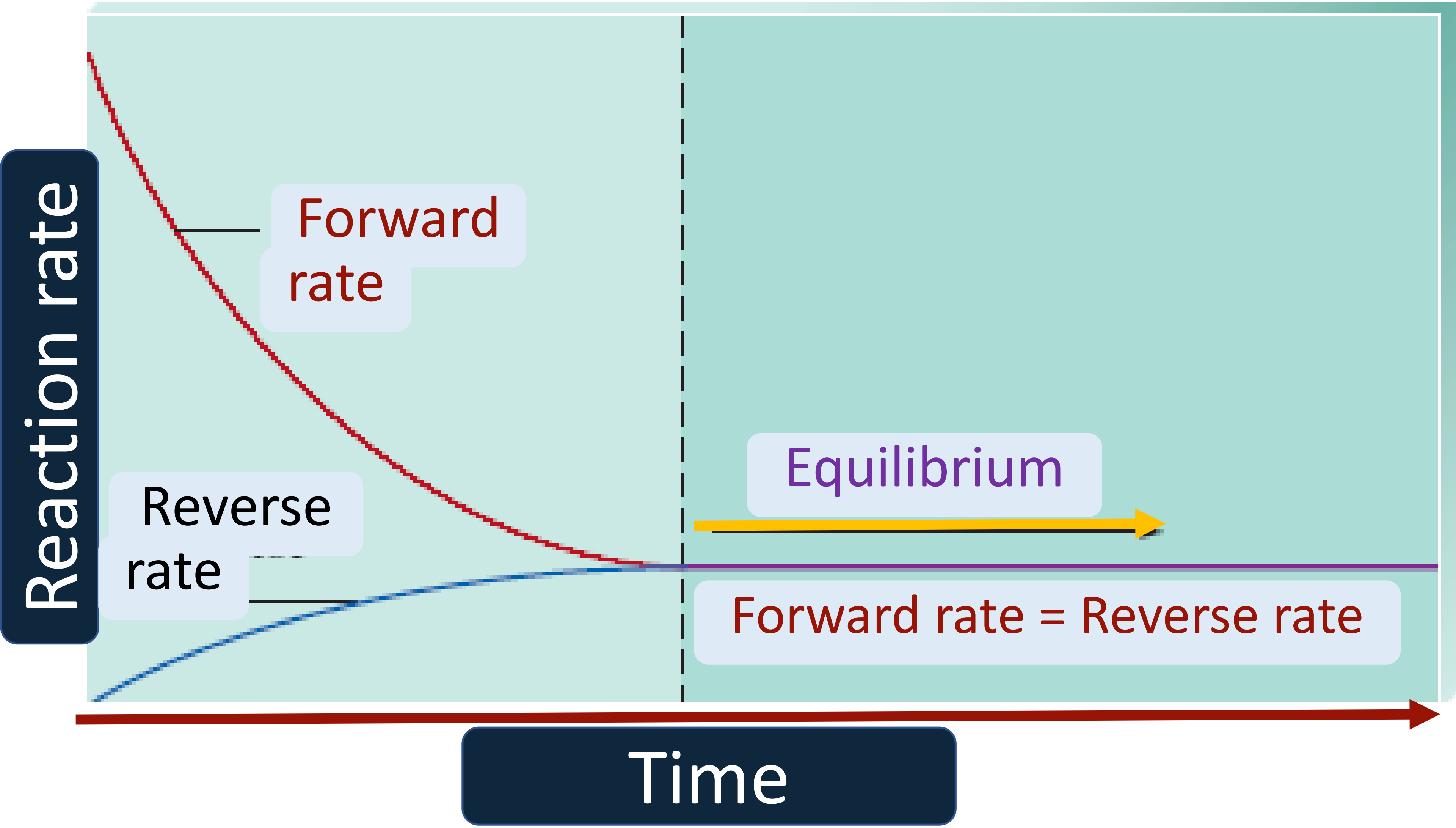
- Initially, there was neither H_2 nor CO_2; the rate of the reverse reaction was zero. As the forward reaction proceeds, the $[H_2]$ and $[CO_2]$ build up, and the rate of the reverse reaction increases.

$$H_2O\ (g) + CO(g) \quad \leftarrow \quad H_2(g) + \ CO_2(g)$$

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

Rate Profile

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



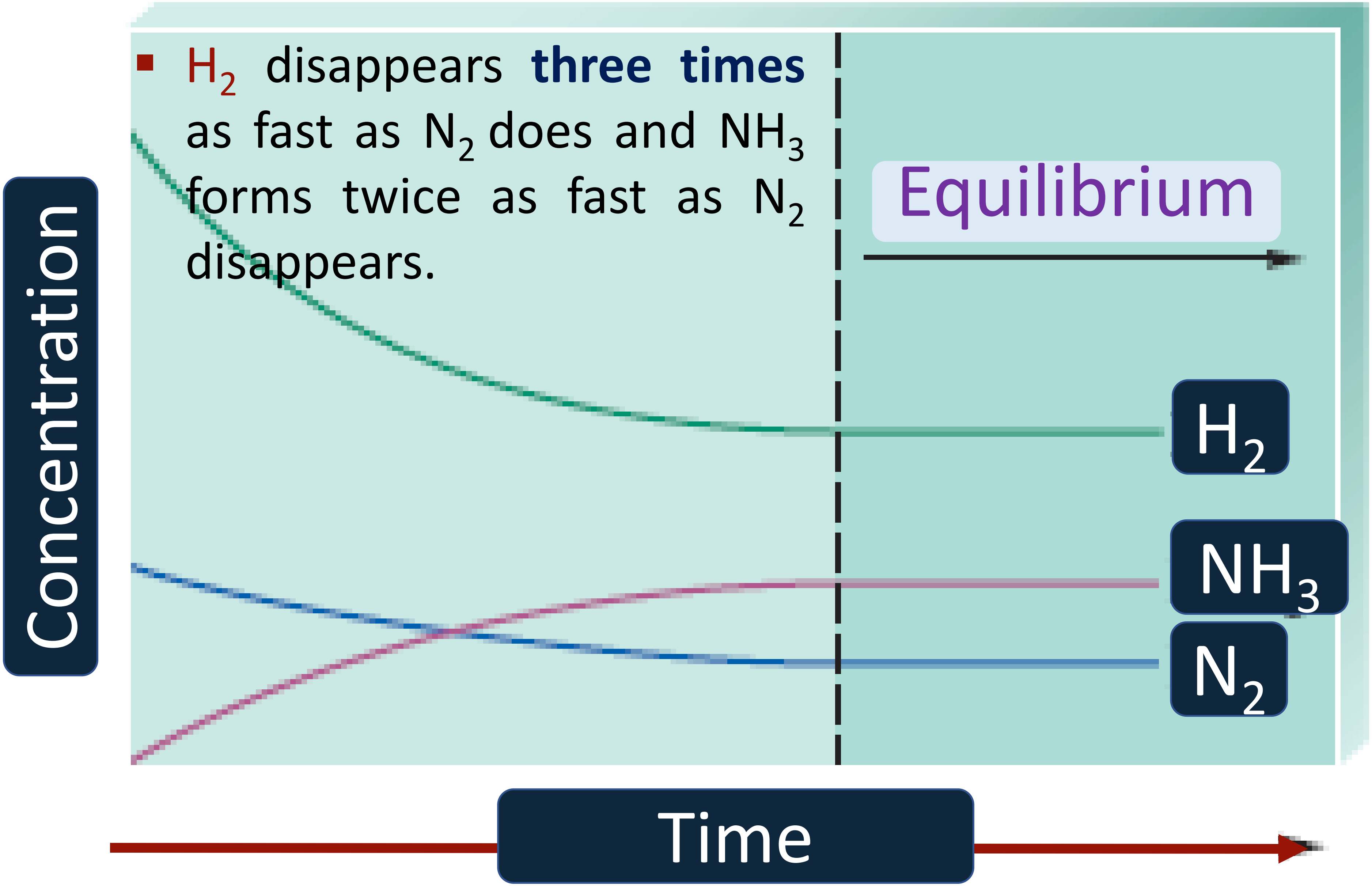
Equilibrium Position

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.

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



- H_2 disappears **three times** as fast as N_2 does and NH_3 forms twice as fast as N_2 disappears.

N_2 (g) + $3H_2$(g) ↔ NH_3(g)

- When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25^0C, 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 this general equation at equilibrium:

$$jA + kB \leftrightarrow lC + mD$$

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

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.

Exercise

- Write the equilibrium expression for the following reaction:

$$4NH_3\ (g) + 7O_2(g) \leftrightarrow 4NO_2(g) + 6H_2O(g)$$

Solution

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

Exercise

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?

$$2NH_3\,(g) \leftrightarrow N_2(g) + 3H_2(g)$$

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

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \leftrightarrow NH_3\,(g)$$

Solution

a.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3\,(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(3.1\times10^{-2}\right)^2}{(8.5\times10^{-1})(3.1\times10^{-3})^3} = 3.8 \times 10^4\ mol^{-2}\ L^2$$

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

$$2NH_3\,(g) \leftrightarrow N_2(g) + 3H_2(g)$$

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}\ mol^2\ L^{-2}$$

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

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \leftrightarrow NH_3\,(g)$$

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^{1/2}$$

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

$$= 1.9 \times 10^2$$

Generally,

For a reaction $\mathrm{jA + kB \leftrightarrow lC + mD}$

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

For a reverse reaction $\mathrm{lC + mD \leftrightarrow jA + kB}$

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

Multiplying in a factor $\mathrm{nlC + nmD \leftrightarrow njA + nkB}$

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

Equilibrium Position

For a Rx at 500 ^{0}C $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3\ (g)$

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

- Whenever N_2, H_2, and NH_3 are mixed together at 500 ^{0}C, system will reach an equilibrium position such that K = 6.0 × 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	6.02×10^{-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	6.02×10^{-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	6.02×10^{-2}
	$[H_2]_0$=1.000	$[H_2]$=2.77	
	$[NH_3]_0$=3.000	$[NH_3]$=1.82	

Note

- 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_Pressure

For gases reactions

C: mol/L

$$\mathrm{PV = nRT}$$ ➡

$$\mathrm{P = \frac{n}{V}RT}$$ ➡ $$\mathrm{P = CRT}$$

Ammonia Synthesis

$$\mathrm{N_2(g) + 3H_2(g) \leftrightarrow 2NH_3\,(g)}$$

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

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

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

Generally, for the following gaseous reaction

$$\mathrm{jA + kB \leftrightarrow lC + mD}$$

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

Or

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

where

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

Gaseous reactants and products are only involved

Exercise

- Using the value of $K_p = 1.9 \times 10^3$, calculate the value of K at 25°C for the reaction

$$2NO\,(g) + Cl_2(g) \leftrightarrow 2NOCl(g)$$

Solution

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

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

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

Unit???

Heterogeneous Equilibria

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

- 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.

$$K = [CO_2]$$

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

$$K = [H_2]^2[O_2] \qquad K_P = \left(P_{H_2}{}^2\right)\left(P_{O_2}\right)$$

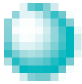
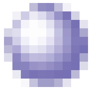
$$2H_2O(g) \leftrightarrow 2H_2(g) + O_2(g)$$

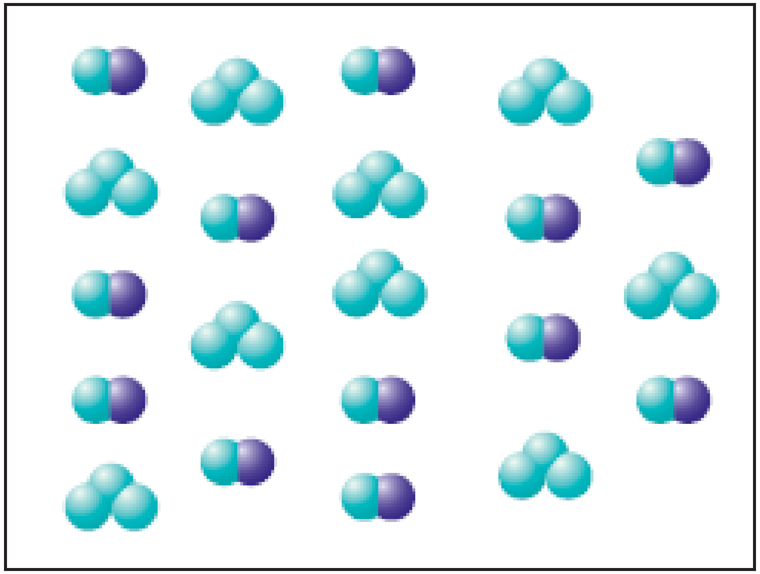
$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2} \qquad K_P = \frac{\left(P_{H_2}{}^2\right)\left(P_{O_2}\right)}{\left(P_{H_2O}{}^2\right)}$$

Consider

A + B → C + D

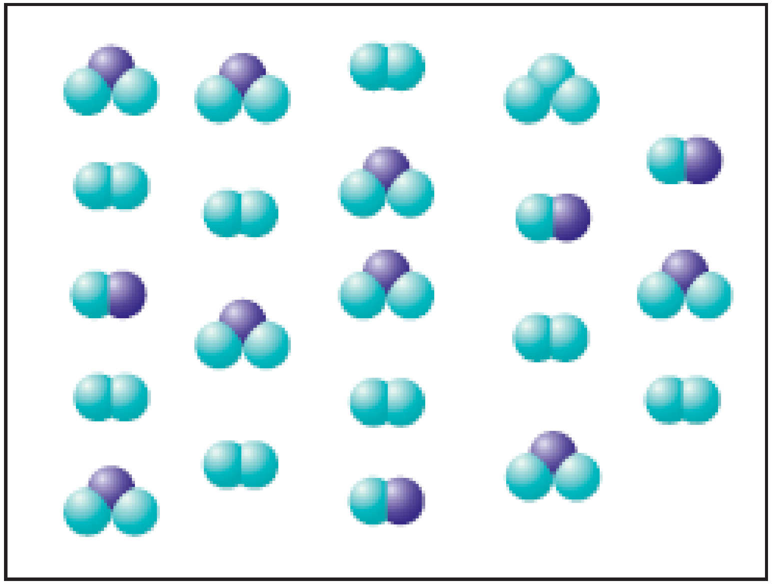
K = 16

where  and  represent two different types of atoms.



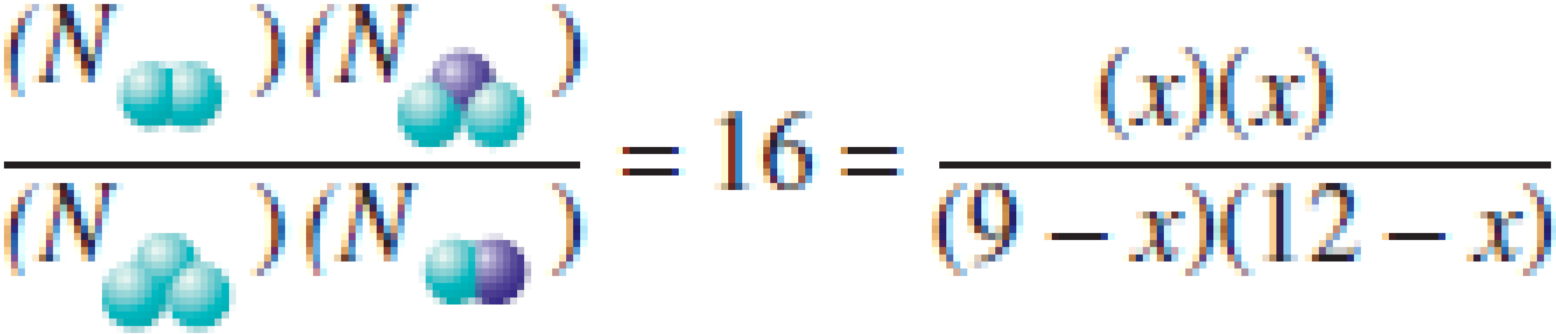
A=9, B=12, C=D=0

Initially

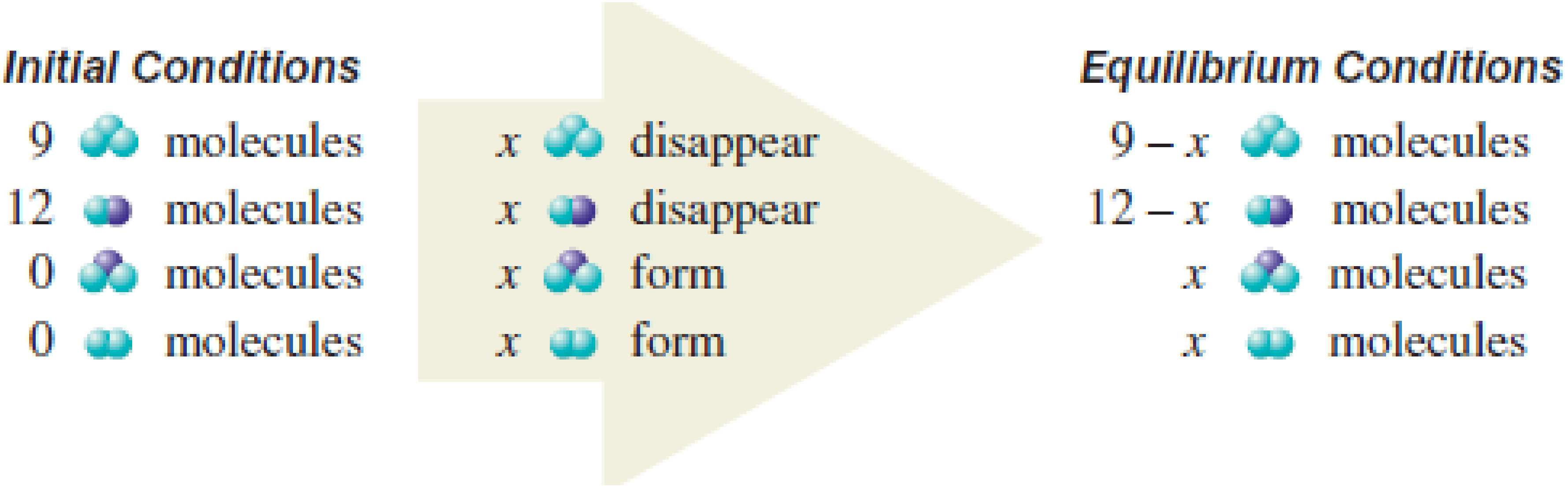


A=1, B=4, C=D=8

Equilibrium



$$\frac{(N\ )(N\ )}{(N\ )(N\ )} = 16 = \frac{(x)(x)}{(9-x)(12-x)}$$



Initial Conditions

9 molecules

12 molecules

0 molecules

0 molecules

x disappear

x disappear

x form

x form

Equilibrium Conditions

$9-x$ molecules

$12-x$ molecules

x molecules

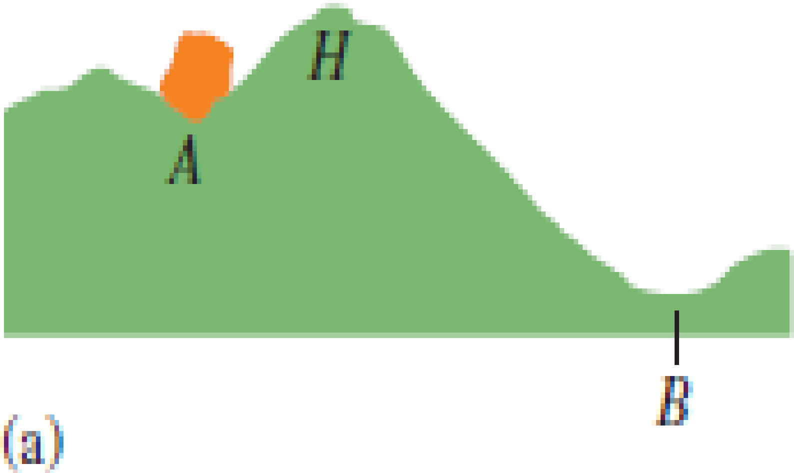
x molecules

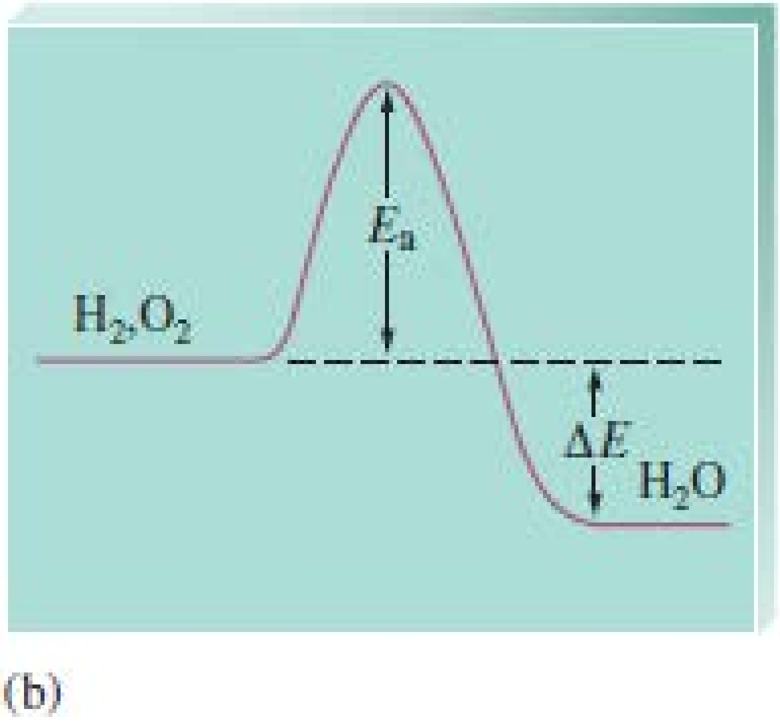
$x = 8$

Equilibrium: thermodynamics & Kinetics

- The size of K (**thermodynamics parameter**) and the time (**Kinetic parameter** depending on activation energy) required to reach equilibrium **are no**t 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.

Reaction Extent





- 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°C.
- In other words, the magnitude of K for the reaction depends on ΔE, but the reaction rate depends on E_a.

Reaction Quotient, Q

- It applies the law of mass action for initial concentrations

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

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

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.

Exercise

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

a

$[N_2]_0 = 1.0 \times 10^{-5}$ M
$[H_2]_0 = 2.0 \times 10^{-3}$ M
$[NH_3]_0 = 1.0 \times 10^{-3}$ M

b

$[N_2]_0 = 1.5 \times 10^{-5}$ M
$[H_2]_0 = 3.54 \times 10^{-1}$ M
$[NH_3]_0 = 2.0 \times 10^{-4}$ M

c

$[N_2]_0 = 5$ M
$[H_2]_0 = 1.0 \times 10^{-2}$ M
$[NH_3]_0 = 1.0 \times 10^{-4}$ M

Solution

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3\,(g)$$

$$N_2(g) + 3H_2(g) \leftarrow \; 2NH_3\,(g)$$

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

System shifts to left

$$\frac{\left(1.0\times 10^{-3}\right)^2 \square}{\left(1.0\times 10^{-5}\right)\left(2.0\times 10^{-3}\right)^3} = 1.3\times 10^{7} >> K$$

$$N_2(g) + 3H_2(g) \leftrightarrow \; 2NH_3\,(g)$$

$$Q =$$

System at equilibrium

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

$$\mathrm{N_2(g) + 3H_2(g) \rightarrow 2NH_3\,(g)}$$

$$\boldsymbol{Q = \frac{\left(1.0\times10^{-4}\right)^2 \square}{\left(5\right)\left(1.0\times10^{-2}\right)^3} = 2.0\times10^{-3} \ll K}$$

System shifts to right

Exercise

- 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.

Solution

$$\mathrm{CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g)}$$

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

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

$$Q = \frac{[CO_2]_0[H_2]_0}{[CO]_0[H_2O]_0} = \frac{(1.0\text{mol/L})(1.0\text{mol/L})}{(1.0\text{mol/L})(1.0\text{mol/L})} = 1.0$$

$Q << K$ Rx shifts to right

Initial Conc. (mol/L)	Change (mol/L)	Eq. Conc. (mol/L)
$[CO]_0 = 1.0$	– x	1.0 – x
$[H_2O]_0 = 1.0$	– x	1.0 – x
$[CO_2]_0 = 1.0$	+ x	1.0 + x
$[H_2]_0 = 1.0$	+ x	1.0 + x

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

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

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

Eq. Conc.

➡

$$[CO] = [H_2O] = (1.0 - x) = 0.613M$$
$$[CO_2] = [H_2] = (1.0 + x) = 1.387M$$

Exercise

- Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 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?

Solution

Solving a quadratic equation

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

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

Exercise

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

Solution

$$\mathrm{H_2(g) + I_2(g) \leftrightarrow \quad 2HI(g)}$$

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

$$\mathrm{P_{HI}^0} = 5.0 \times 10^{-1}\mathrm{atm}, \qquad \mathrm{P_{H_2}^0} = 1.0 \times 10^{-2}\mathrm{atm}$$

$$, \qquad \mathrm{P_{I_2}^0} = 5.0 \times 10^{-3}\mathrm{atm}$$

$$Q_p = \frac{\left(P^0_{HI}\right)^2}{\left(P^0_{H_2}\right)\left(P^0_{I_2}\right)} = \frac{(5.0 \times 10^{-1}\mathrm{atm})^2}{(1.0 \times 10^{-2}\mathrm{atm})(5.0 \times 10^{-3}\mathrm{atm})} = 5.0 \times 10^3$$

$Q >> K$

System shifts to left

	$H_2(g)$	$+$	$I_2(g)$	$\leftrightarrow$	$2HI(g)$
Initial	1.0×10^{-2}		5.0×10^{-3}		5.0×10^{-1}
Change	$+x$		$+x$		$-2x$
Eqm.	$\left(1.0 \times 10^{-2}\right) + x$		$\left(5.0 \times 10^{-3}\right) + x$		$\left(5.0 \times 10^{-1}\right) - 2x$

$$K_p = \frac{\left(P_{HI}^2\right)}{\left(P_{H_2}\right)\left(P_{I_2}\right)} =$$

$$\frac{(5.0 \times 10^{-1} - 2x)^2}{(1.0 \times 10^{-2} + x)(5.0 \times 10^{-3} + x)} = 1.0 \times 10^2$$

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

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

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

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".

Exercise

$$As_4O_6(s) + 6C(s) \leftrightarrow As_4(g) + 6CO(g)$$

Predict the direction the Rx should shift to attain an equilibrium position in case of:

a. Addition of carbon monoxide (Left)

b. Addition or removal of carbon or tetraarsenic hexoxide (As_4O_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.

c. Removal of gaseous arsenic (As_4) (Right)

Effect of Changing Pressure

There are three ways to change the pressure of a reaction system involving gaseous components:

1) Add or remove a gaseous reactant or product. (previously considered)

2) 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.

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. $\boxed{V\ \alpha\ n}$
- ✓ 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,

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3\ (g) + 92\text{kJ}$$

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

For endothermic Rx,

$$CaCO_3(s) + 556\ \text{kJ} \leftrightarrow CaO\ (s) + CO_2(g)$$

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