Chapter 17

Warm Up (rates and equilibrium)

- Consider the forward reaction:

$$CaO_{(s)} + CO_{2\,(g)} \rightarrow CaCO_{3\,(s)}$$

Write the equilibrium equation for the forward and reverse reaction.

If the rate of formation of $CaCO_3$ = 0.1 M/s, what is the rate of decay of CaO and CO_2?

Warm Up continued

(Only 1 piece of graph paper/person!)

Given the concentrations at t = 0 seconds:

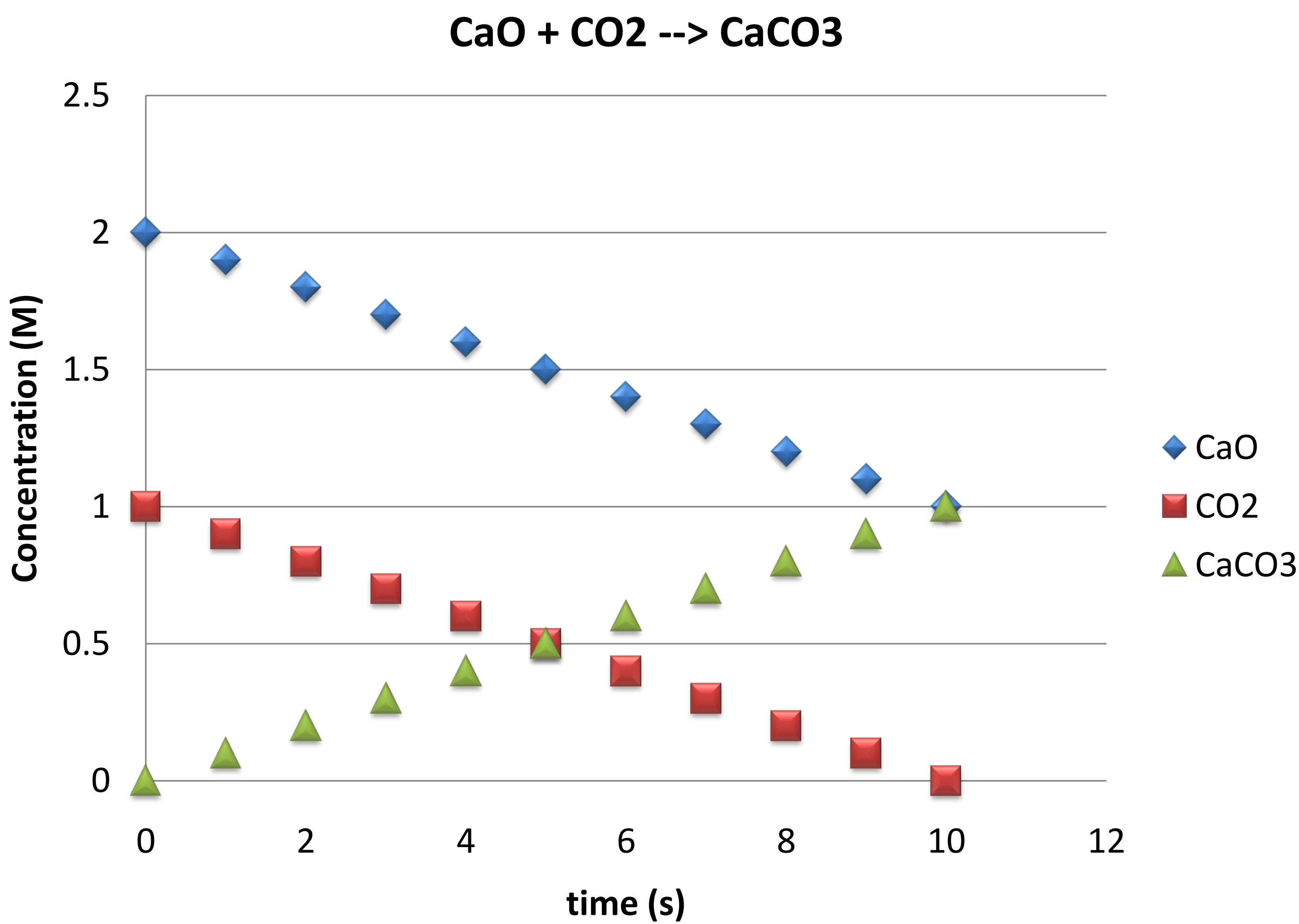
$$[CaO] = 2\ M$$

$$[CO_2] = 1\ M$$

$$[CaCO_3] = 0\ M$$

and the rate of 0.1 M/s…

Graph concentration vs. time for each reactant.


CaO + CO2 --> CaCO3
2.5
2
1.5
1
0.5
0
0
2
4
6
8
10
12
Concentration (M)
time (s)
CaO
CO2
CaCO3

Turn graph paper over

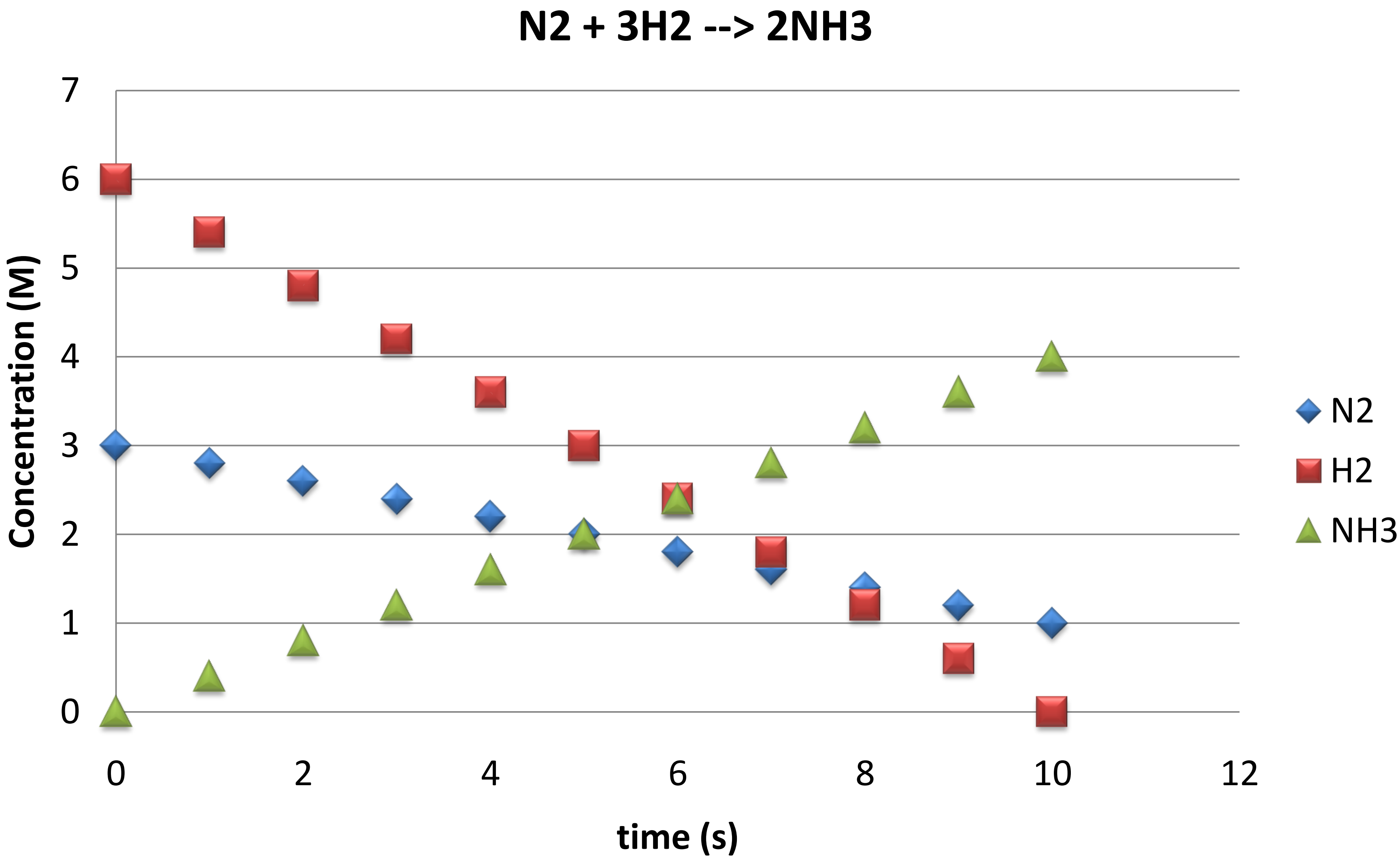
- Consider the forward reaction and assume it reacts COMPLETELY:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

If the decay rate of N_2 is -0.2 M/s, what is the decay rate of H_2 and the formation rate of NH_3? (HINT: Stoichiometry is important)

If $[N_2]$ = 3M, $[H_2]$ = 6 M, and $[NH_3]$ = 0 at t = 0 sec,

graph concentration vs. time for the reaction above.


N2 + 3H2 --> 2NH3
Concentration (M)
0
1
2
3
4
5
6
7
0
2
4
6
8
10
12
time (s)
N2
H2
NH3

Today's Agenda

- QOTD: What is chemical equilibrium and how can we write an equilibrium expression?

- Concentration vs time graphs
- Equilibrium conditions
- Writing an equilibrium expression

- Homework: Ch 17 34-62 evens Due Friday
- Quiz: rates and equilibrium on Friday

Equilibrium

- After a certain time, t, the **reactants** no longer form **products** even though there is still some present to react! Most reactions do not **go to completion**.
- **Reversible reactions** – a chemical reaction that can occur both in the forward and reverse directions.

Equilibrium

- Forward: $N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$
- Reverse: $N_{2\,(g)} + 3H_{2\,(g)} \leftarrow 2NH_{3\,(g)}$
- Equilibrium: $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$

- Why does this occur? Remember from kinetics that concentration affects rate. The **more** of a substance present, the **faster** the reaction.

Equilibrium

- At t_0 there are **zero products** so the **forward** reaction is fast.

- As NH_3 is produced, its concentration increases while less and less N_2 and H_2 are present, so the **forward** reaction decreases in rate and the **reverse** reaction becomes faster.

Equilibrium

- This is how **chemical equilibria** work. Equilibrium is the state in which the forward reaction and reverse reactions take place at **equal rates**.

- BUT….this does **NOT** mean that the concentrations are **equal** on either side!!! Look at the plot above, the concentrations are different at equilibrium, but the **RATES** are **equal**.

Equilibrium

- The substances continue to undergo the forward and reverse reaction, so the reactions **do not STOP** reacting. It is a balance between reactants forming products, and products decomposing into reactants. Equilibrium is **DYNAMIC**.

Equilibrium Constant Expression

- At a given temperature, a chemical system may reach a state in which a **ratio of reactant and product** concentrations has a constant value. This constant is $\mathbf{K_{eq}}$.

- For the generic reaction: $\mathbf{aA + bB \rightleftharpoons cC + dD}$
- The equilibrium constant expression is:

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

(remember products OVER reactants!)

Equilibrium Constant Expression

- If K_{eq} **>** 1 , the **products** are favored (meaning products are in higher concentration)
- If K_{eq} **<** 1 , the **reactants** are favored

Favor Products or Reactants?

- $N_{2(g)} + O_{2(g)} \rightarrow 2\ NO_{(g)}$ $K_{eq} = 5 \times 10^{-31}$ at 25°C

  $K < 1$ reactants favored!

- $3\ H_{2(g)} + N_{2(g)} \rightarrow 2\ NH_{3(g)}$ $K_{eq} = 7 \times 10^{5}$ at 25°C

  $K > 1$ products favored!

- $H_{2(g)} \rightarrow 2\ H_{(g)}$ $K_{eq} = 1 \text{ x } 10^{-36}$ at 25°C

  $K < 1$ reactants favored!

- $H_2O_{(g)} \rightarrow H_{2(g)} + ½\ O_{2(g)}$ $K_{eq} = 8 \times 10^{-41}$ at 25°C

  $K < 1$ reactants favored!

- $C_2H_4O_{2(l)} \rightarrow 2\ H_2O_{(l)} + 2\ C_{(s)}$ $K_{eq} = 1 \text{ x } 10^{13}$ at 25°C

  $K > 1$ products favored!

Warm Up

- Write the balanced chemical equation for the equilibrium reaction of hydrogen and oxygen

Today’s Agenda

K_{eq}

- Notice the problems above have used only gases. If there is a **heterogeneous** mixture of states, like a gas and a solid or a gas and a liquid, you only include **GASES** and **AQUEOUS** solutions in an equilibrium expression! NO PURE **SOLIDS** OR **LIQUIDS**.

Practice

- Write K_{eq} expressions for the following equations:

1. $Sn_{(s)} + 4H^{+1}_{(aq)} + 4NO_3{}^{-1}_{(aq)} \Leftrightarrow SnO_{2(s)} + 4NO_{2(g)} + 2H_2O_{(l)}$

2. $4NO_{(g)} + 6H_2O_{(l)} \Leftrightarrow 4NH_{3(aq)} + 5O_{2(g)}$

3. $Pb_{(s)} + PbO_{2(s)} + 2H^{+1}_{(aq)} + 2HSO_4{}^{-1}_{(aq)} \Leftrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

4. $2C_6H_5NO_{(l)} + 28O_{2(g)} \Leftrightarrow 12CO_{2(g)} + 5H_2O_{(l)} + N_{2(g)}$

Calculating K_{eq}

- If the concentrations at **equilibrium** are known, we can calculate $\mathbf{K_{eq}}$.

- K_{eq} does **not** require units! **NO UNITS!**

Find K_{eq}

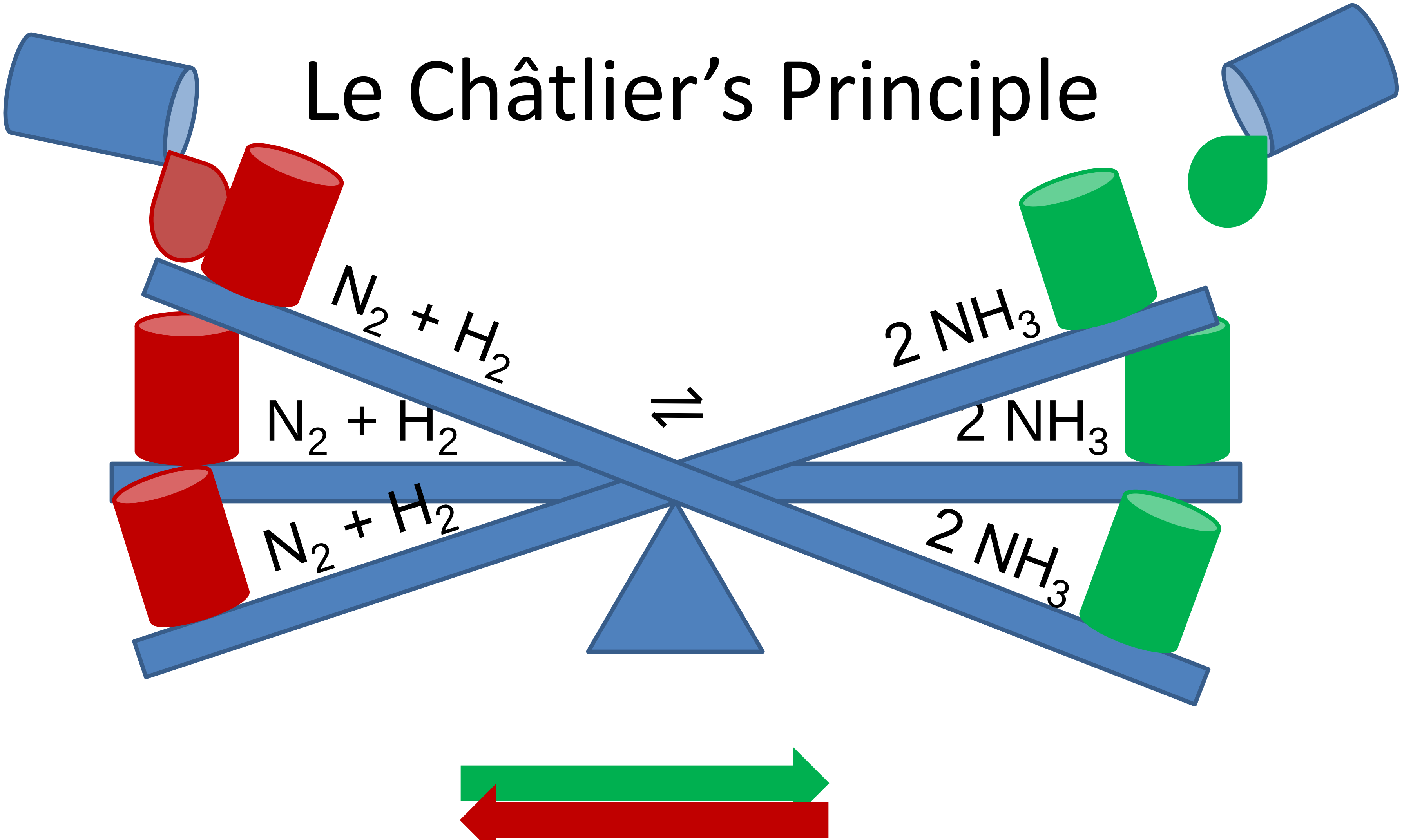
1. For $H_2O(l) \Leftrightarrow H^{+1}(aq) + OH^{-1}(aq)$, at eq. the $[H^+] = 1 \times 10^{-8}$ M $[OH^-] = 1 \times 10^{-6}$ M. What is the K_{eq}?
2. For $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$, at eq. the $[SO_2] = 0.025$ M, $[O_2] = 0.15$ M, and $[SO_3] = 0.16$ M. What is the K_{eq}?
3. The system $2H_2S(g) \Leftrightarrow 2H_2(g) + S_2(g)$ reaches equilibrium in a 2.6 liter container. At a certain temperature the container holds 1.82 mol H_2S, 0.62 mol H_2, and 0.36 mol S_2. Calculate the equilibrium constant.

Le Châtlier's Principle

- If **stress** is applied to a system at equilibrium, the system **shifts** in the direction that **relieves** the stress.

- By changing something about the **reaction conditions**, one can **shift the equilibrium**! Important to note that $\mathbf{K_{eq}}$ does **NOT** change, only concentrations.

Le Châtlier's Principle



MORE PRODUCTS form to BALANCE out Equilibrium!
MORE REACTANTS form to BALANCE out Equilibrium!

Concentration Changes

- **Increased** reactant concentration - shifts the equilibrium to the **right** to form more **products** and balance out stress!
- **Decreased** product concentration – shifts the equilibrium to the right to form more products! **Same result** as adding more reactants.
- Increased **product** concentration – shifts the equilibrium to the **left** to form more **reactants** and balance out stress!

Volume/pressure changes

- **Decreased volume/increased pressure** - shifts the equilibrium to the **right** to form more products only if the **moles of gaseous products differs from the moles of gaseous reactants!** If the moles are the **same**, volume and pressure changes will have **no effect**.

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)}$$

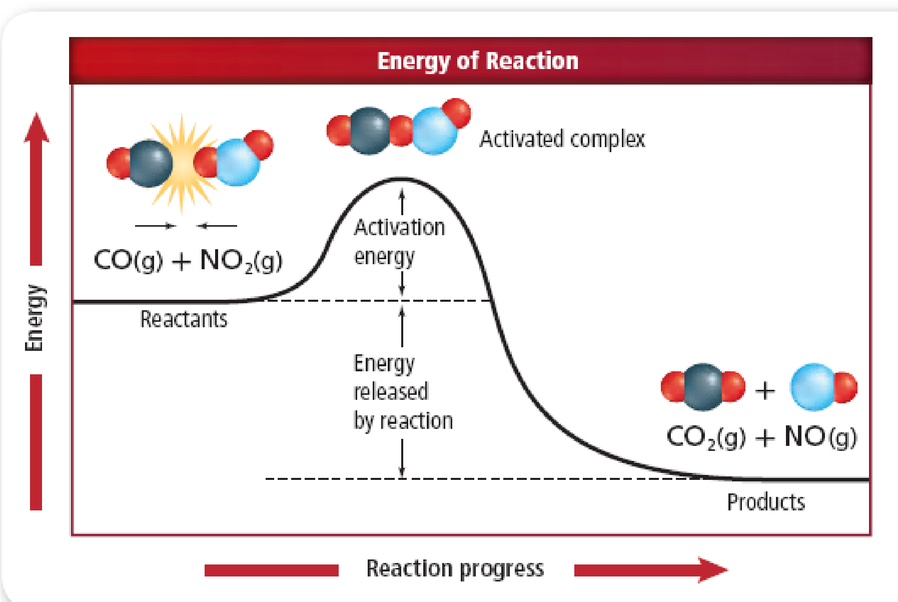
- How many moles of gas do you have on the reactant side?

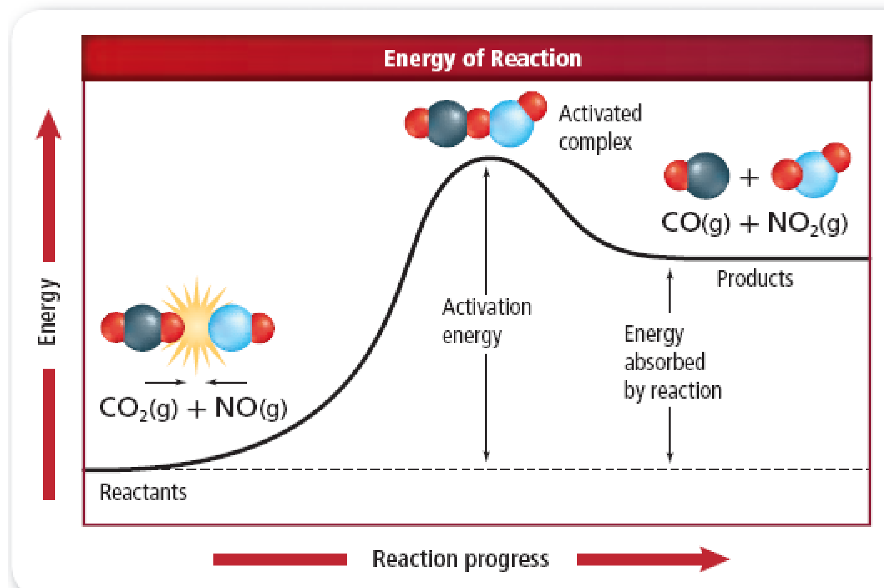
- How many moles of gas are on the product side?

- An increase in pressure will shift the equilibrium....

Temperature

- The effect of increasing or decreasing **temperature** on equilibrium **depends** on whether the reaction is **endothermic or exothermic**.

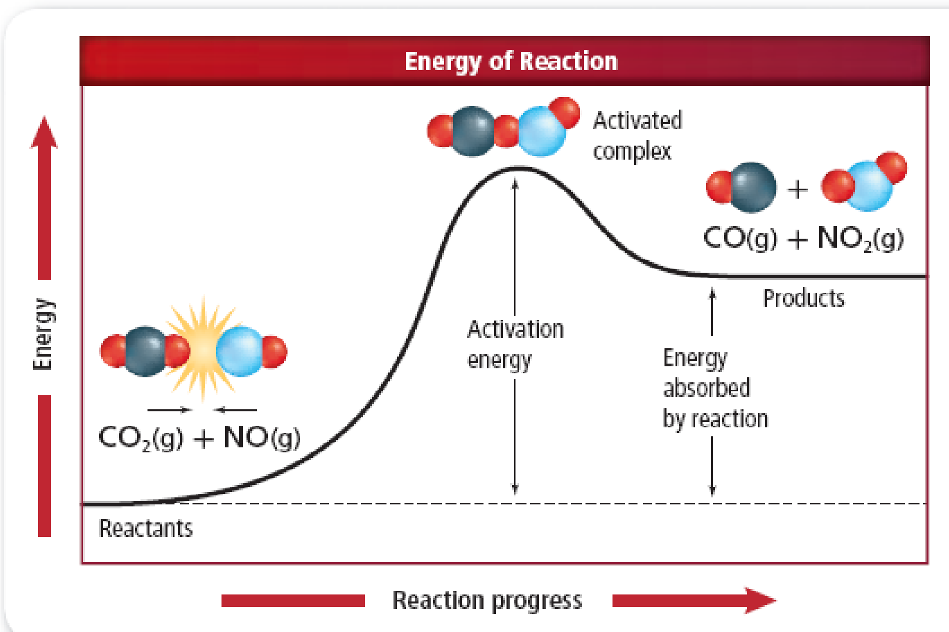




Temp and Endothermic Rxns

- In an endothermic reaction heat acts as a **reactant**, so increasing heat shifts the equilibrium to the **right** to form more **products**. Decreasing heat will have the **opposite** effect here.

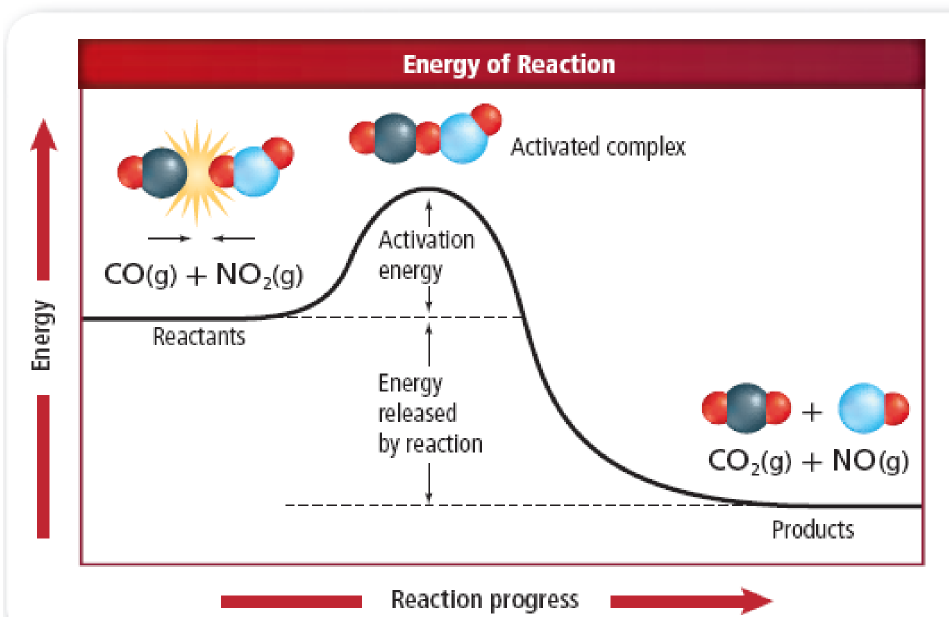
$$CO_2\ (g) + NO\ (g) + \text{heat} \rightleftharpoons CO\ (g) + NO_2\ (g)$$



Temp and Endothermic Rxns

- In an exothermic reaction, heat acts as a **product**, so increasing heat shifts the equilibrium to the **left** to form more **reactants**. Decreasing heat has the **opposite** effect here.

$$CO\,(g) + NO_2\,(g) \rightleftharpoons CO\,(g) + NO_2\,(g) + \text{heat}$$



Warm Up

- At 298 K the $K_{eq} = 0.0211$ for the equilibrium $PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$

Write the equilibrium expression.

What is $[Cl_2]$ at equilibrium if $[PCl_5] = 0.865$ M, and $[PCl_3] = 0.135$ M at equilibrium?

What is $[PCl_5]$ at equilibrium if $[PCl_3] = 0.1$ M, and $[Cl_2] = 0.2$ M at equilibrium?

Today's Agenda

- QOTD: How do you use an equilibrium expression to find initial and equilibrium concentrations of substances?

- Using equilibrium to solve problems
- R.I.C.E. tables
- Solubility product constant