Unit 9: Chemical Kinetics & Equilibrium

LT 9 I can provide an explanation about the factors impacting reaction rate and refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.

9.1 I can explain the factors that affect the rate of chemical reactions.

Reaction Rates

Chemical Kinetics:

Chemical reactions occur at different rates

The basis for the study of the rate of chemical reactions is …

- ____ of reaction rate and mechanism

Collision Theory

- Explains why different reactions occur at different rates, and suggests ways to change the rate of a reaction.
- States that for a chemical reaction to occur, the reacting particles must ____________________ with one another.
  - The rate of the reaction depends on the ____
  - The theory also tells us that reacting particles often ____
- For collisions to be successful, reacting particles must collide
  - with ______________________________________ (has to be hard enough to react)
  - with_______________________________________ (like a puzzle!)

Questions related to kinetics . . .

- How quickly can a medicine work?
- Is ozone forming at the same rate it is depleting?
- What determines how quickly food spoils?
- How would you design a fast-setting material for dental fillings?
- What controls the rate at which fuel burns in your car's engine?

Factors Affecting Reaction Rates

Four factors control the rate of reaction

1.
2.
3.
4.

Concentration

Summary of Observations

Molecular level drawing

Conclusions drawn

Surface Area

Summary of Observations

Molecular level drawing

Conclusions drawn

Temperature

Summary of Observations

Molecular level drawing

Conclusions drawn

Catalysis

Summary of Observations

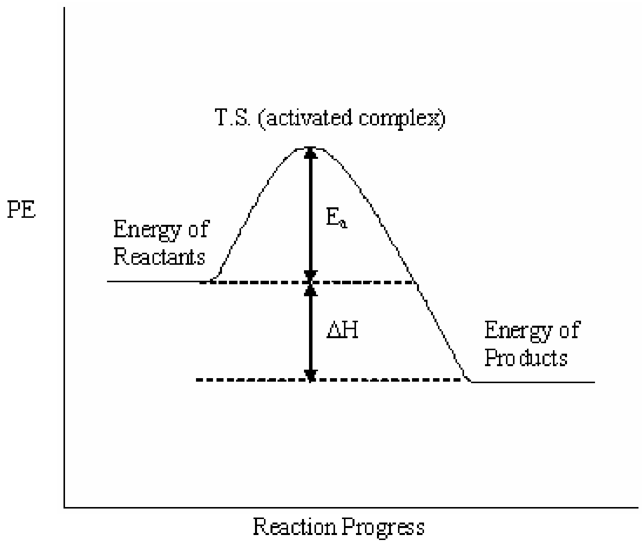
Molecular level drawing

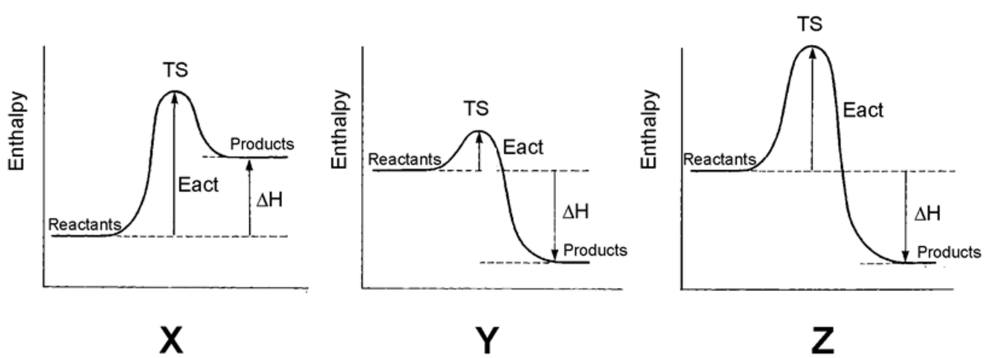
Conclusions drawn

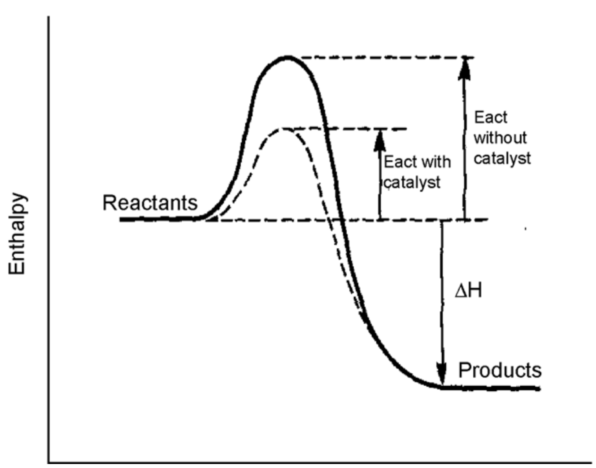
Potential Energy Diagrams

Show potential energy changes as a reaction progresses

- Exothermic Reaction
  - Net loss of energy:
- Endothermic reaction
  - Net gain of energy:







LT 9 I can provide an explanation about the factors impacting reaction rate and refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.

9.2 I can describe the dynamic nature of equilibrium systems

Chemical Reactions

Chemical reactions occur to . . .

Reactions "end" when a reactant is used up, or when the system reaches a state of maximum stability as a result of opposing forces (reactions) balancing out

Knowing how to predict and control the final composition of a reaction system is the study of …

Very important to industrial chemical processes. Why?

Irreversible Reactions

- reactants are . . .
- products are . . .
- Examples
  - o
  - o

Reversible Reactions

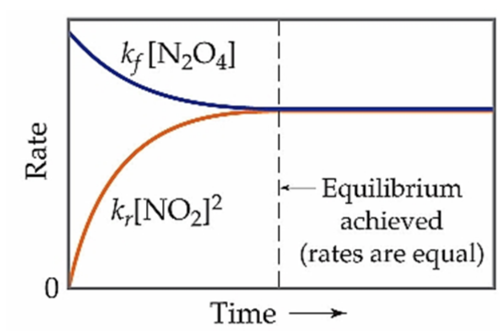
Reaction in which the **____**.

The reaction can go both ways:

Initially, __________________ reaction dominates due to relative concentration of reactants and products

As products increase and reactants decrease, reverse reaction ___________ and forward reaction _________

What happens when the rate of the forward reaction becomes equal to the rate of the reverse reaction?



Equilibrium

A chemical reaction is in equilibrium when there is no net change in the amount of reactants and products

Rate of forward and reverse reactions are equal.

equilibrium is a *dynamic process* in which ***microscopic change*** (the forward and reverse reactions) continues to occur, but ***macroscopic change*** (changes in the quantities of substances) is absent.

For $H_2 + I_2 \rightleftharpoons 2HI$

At equilibrium, HI breaks down as fast as it forms

LT 9 I can provide an explanation about the factors impacting reaction rate and refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.

9.3 I can derive reaction quotients (Q) and equilibrium constants (K) for both homogeneous and heterogeneous reactions in concentration and pressure, and use them to predict properties of an equilibrium mixture.

Reaction Quotient, Q

The status of a reversible reaction can be determined by looking at its reaction quotient, Q. This is a comparison between the relative amounts of____

____

Q_C = reaction quotient expressed in terms of ___________________________

Suitable for___________________________________

Q_P = reaction quotient expressed in terms of ___________________________

Only for __________________

*m*A + *n*B ↔ *x*C + *y*D

Q_c =

Q_p =

Practice: Writing Q_c expressions

Write the reactant quotient expression (Q_C) for the following reactions

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

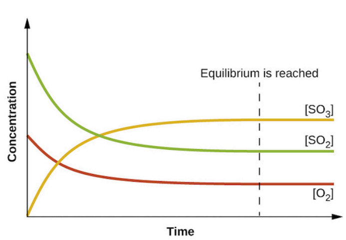
$Cd^{2+}_{(aq)} + 4Br^-_{(aq)} \rightleftharpoons CdBr^{2-}_{(aq)}$

$2O_{3(g)} \rightleftharpoons 3O_{2(g)}$

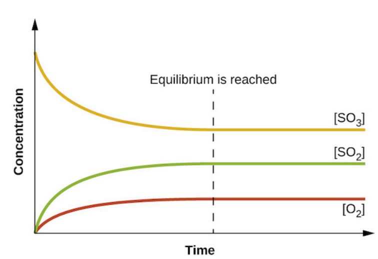
$2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl_{(g)}$

$Cd^{2+}_{(aq)} + 4Br^-_{(aq)} \rightleftharpoons CdBr^{2-}_{(aq)}$

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$



All product no reactant,



All reactant no product,

Reaction proceeds ___________ to reach equilibrium

Reaction proceeds ____________ to reach equilibrium

We're at Equilibrium...now what???

The reaction will move forward or reverse to reach ________________________

Once at equilibrium, Q becomes _____________________

This is referred to as the ____

Law of Mass Action

Expresses the relationship between product and reactant ________________________________

In a reaction *m*A + *n*B ↔ *x*C + *y*D,

Depends only on ...

Temperature ...

Practice: Haber Process

Write the equilibrium constant expression (K_c and K_p for the Haber process: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Heterogeneous Equilibria

Reaction system in which more than one phase is present

Examples

- $CaCO_3(s) \Leftrightarrow CO_2(g) + CaO(s)$
- $CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(l)$
- $I_2(s) \Leftrightarrow I_2(g)$

Position of equilibrium does not depend on ________________________________ as long as some is present

Terms for _______________________________ need not appear in expression for K

Example: Heterogeneous Reactions

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

K_c=

K_p=

Practice: Heterogeneous Reactions

Write K_c and K_p expressions for the following:

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

$H_2O(l) + CO_3^{2-}(aq) \leftrightarrow OH^-(aq) + HCO_3^-(aq)$

$Cr(s) + 3Ag^+(aq) \leftrightarrow Cr^{3+}(aq) + 3Ag(s)$

$Zn(s) + 2H^+(aq) \leftrightarrow Zn^{2+}(aq) + H_2(g)$

$I_2(s) \leftrightarrow I_2(g)$

Summary of Equilibrium Constant Expression Rules

Equilibrium systems may involve . . .

For the reaction quotient (Q) and equilibrium constant expression (K):

- Gases enter as their partial pressures in atm
- Pure liquids or solids do not appear; neither does solvent for a reaction in dilute solution
- Species (ions or molecules) in water solution enter as their molar concentrations

Equilibrium Constant and Extent of Reaction

Interpretation of size of K

- equilibrium constants within range of roughly…
- chemically significant amount of all components of the reaction system will be present in an equilibrium mixture
- reaction will be **…**

As equilibrium constant approaches zero

-

As equilibrium constant approaches infinity

-

K depends only on…

Example: Interpreting Magnitude

For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, K_p=794 at 298 K and K_p=54 at 700 K. Is the formation of HI favored more at high temperatures or low temperatures? Why?

\Comparison of Q to K

- Q < K
  - Too much ________________ compared to ______________
  - Reaction proceeds in …
- Q = K
  - System at ________________
  - Forward and reverse reactions …
- Q > K
  - Too much ________________ compared to ______________
  - Reaction proceeds in …

Example: Direction of Reaction

Consider the following reaction system at 100.°C

$N_2O_4(g) \Leftrightarrow 2NO_2(g)$ $K_p = 11$

Predict the direction in which the reaction will occur to reach equilibrium starting with 0.20 mole of N_2O_4 and 0.20 mole of NO_2 in a 4.0 L container.

Practice: Direction of Reaction

At 448 ˚C: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ K_c=50.5

Predict in which direction the reaction will proceed to reach equilibrium at 448 ˚C if we start with $2.0\text{x}10^{-2}$ mol of HI, $1.0\text{x}10^{-2}$ mol of H_2, and $3.0\text{x}10^{-2}$ mol of I_2 in a 2.00-L container.

Practice: Direction of Reaction

At 1000 K, $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ K_p=0.338

Calculate Q_p and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are P_{SO_3}=0.16 atm, P_{SO_2}=0.41 atm and P_{O_2}=2.5 atm

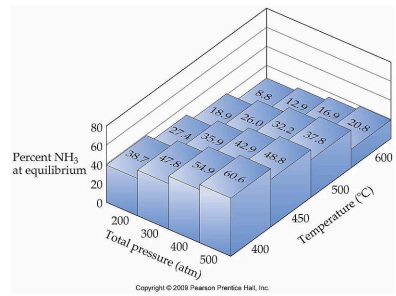
LT 9 I can provide an explanation about the factors impacting reaction rate and refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.

9.4 I can define Le Chatelier's principle and apply it to predict the shift in a reaction when conditions (concentration, pressure, temperature) are changed.

Haber Process in Practice

Haber experimented with all kinds of circumstances to figure out how to best produce NH_3

He was looking for the highest % of product at equilibrium



Effect of Changes in Conditions Upon an Equilibrium System

Le Chatelier's Principle: If a system at equilibrium is disturbed (placed under stress) by a change in concentration, pressure, or temperature, the system will, …

Deficit stress-

- Causes the reaction to …

Excess stress-

- Causes the reaction to …

Adding or Removing Gaseous Species

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

Add $N_2O_4(g)$-

- Forward reaction …
- Some of the added $N_2O_4(g)$ is …
- System shifts to the …

Remove $N_2O_4(g)$-

- Forward reaction …
- Reverse reaction …
- System shifts to the…

Predict the effects of

- Adding $NO_2(g)$

- Removing $NO_2(g)$

Compression or Expansion

Reaction: $N_2O_4(g) \Leftrightarrow 2NO_2(g)$

Compression

-
- Reaction takes place …

Expansion

-
- Reaction takes place …
-

Effect of Pressure upon the Position of Gaseous Equilibria			
System	Δn_{gas}	P_{tot} Increases	P_{tot} Decreases
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	+1	←	→
$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$	-½	→	←
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	-2	→	←
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2$	+1	←	→
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	0	0	0

Practice: Effect of Total Pressure on Equilibrium

The pressure of each of the following systems is decreased from 5 atm to 1 atm. Which way does the equilibrium shift?

- $2CO_2(g) \Leftrightarrow 2CO(g) + O_2(g)$
- $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$
- $H_2(g) + I_2(s) \Leftrightarrow 2HI(g)$

Changing Temperature

Treat heat term in a thermochemical equation as …

Endothermic-

Exothermic-

Increase T-"excess shift"

Decrease T-"deficit stress"

$N_2O_4(g) \Leftrightarrow 2NO_2(g)$ $\Delta H° = +57.2$ kJ or $N_2O_4(g) + 57.2\text{ kJ} \Leftrightarrow 2NO_2(g)$

Increase heat-

Decrease heat-

Example: Temperatures Effect on K

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H° = -92.2$ kJ

Determine how the equilibrium constant for this reaction should change with temperature.

Practice: Temperatures Effect on K

Using thermodynamic data, determine the enthalpy change for the reaction

$2POCl_{3(g)} \rightleftharpoons 2PCl_{3(g)} + O_{2(g)}$ $\Delta H° = +545.6$ kJ

Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Example: Le Châtelier's Principle

Consider the equilibrium: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H° = +57.2$ kJ

In which direction will the equilibrium shift when

- N_2O_4 is added
- NO_2 is removed
- the total pressure is increased by addition of $N_{2(g)}$
- the volume is increased
- the temperature is decreased

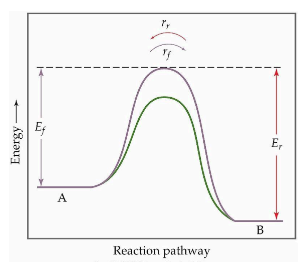
Practice: Le Châtelier's Principle

For the reaction $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $\Delta H° = +87.9$ kJ

In which direction will the equilibrium shift when

- $Cl_{2(g)}$ is removed
- the temperature is decreased
- the volume of the reaction system is increased
- $PCl_{3(g)}$ is added

Effect of Catalyst on Equilibrium



Catalysts do not affect the position of the equilibrium, …

Forward and reverse reaction rates are …

LT 9 I can provide an explanation about the factors impacting reaction rate and refine the design of a chemical system by specifying a change in conditions that would produce increased amounts of products at equilibrium.

9.5 I can calculate equilibrium concentrations using the value of the equilibrium constant, Keq.

Determination of K

There are a variety of calculations that can be done involving K:

- All equilibrium values are given

- A mix of initial and equilibrium values are given
- All initial values are given

Example: All Equilibrium concentrations are known

Ammonium chloride is sometimes used as a flux in soldering because it decomposes upon heating:

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

The HCl formed removes oxide films from metals to be soldered. In a certain equilibrium system at 400°C, 12.0 g of NH_4Cl is present; the partial pressures of NH_3 and HCl are 3.0 atm and 5.0 atm respectively. Calculate K_p at 400°C.

Example: All Equilibrium concentrations are known

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 ˚C. The equilibrium mixture of gasses was analyzed and found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction.

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Practice: All Equilibrium values are known

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 ˚C: $[HC_2H_3O_2]$=1.65x 10^{-2} *M*; $[H^+]$= 5.44x10^{-4} *M;* and $[C_2H_3O_2^-]$ = 5.44x10^{-4} *M*. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 ˚C.

$HC_2H_3O_{2(aq)} \rightleftharpoons H^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$

Relative Changes in Amount

Equation	Direction?
$2SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)}$	
$C_4H_{8(g)} + \rightleftharpoons 2C_2H_{4(g)}$	
$4NH_{3(g)} + 7O_{2(g)} \rightleftharpoons 4NO_{2(g)} + 6H_2O_{(g)}$	

ICE Tables

Example: Initial and Equilibrium values are known

Consider the equilibrium system:

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

Originally, there is only HI at a pressure of 1.00 atm at 520°C. The equilibrium partial pressure of H_2 is found to be 0.10 atm. Calculate P_{I_2} and P_{HI} at equilibrium, and K_p

Example: Initial and Equilibrium concentrations are known

A closed system initially containing 1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2 at 448 ˚C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} *M*. Calculate K_c at 448 ˚C for the reaction taking place, which is $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Practice: Initial and Equilibrium concentrations are known

Sulfur trioxide decomposes at high temperature in a sealed container:

$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

Initially, the vessel is charged at 1000 K with SO_3 at a partial pressure of 0.500 atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

Extent of Reaction; Equilibrium Partial Pressures

Steps for Problem Solving

1. Write expression for K using balanced equation
2. Express equilibrium partial pressures (or concentrations) in terms of “x” using stoichiometry
3. Substitute equilibrium terms into expression for K and solve for “x” (you may need to use the quadratic equation!)
4. Substitute “x” back into equilibrium expressions to find equilibrium partial pressures or concentrations.

Relative Changes in Amount

Equation	Direction?
$C_2H_{2(g)} + 2Br_{2(g)} \rightleftharpoons C_2H_2Br_{4(g)}$	
$I_{2(aq)} + I^-_{(aq)} \rightleftharpoons I_3^-{}_{(aq)}$	
$C_3H_{8(g)} + 5O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$	

Example: Calculating P from K

For the Haber process, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ with K_p=1.45x10^{-5} at 500˚C. In a equilibrium mixture of these three gases at 500˚C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 at equilibrium?

Practice: Calculating P from K

At 500 K, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ K_p = 0.497
In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Example: Calculating Equilibrium from Initial Amounts

A 1.000-L flask is filled with 1.000 mol of H_2 and 2.000 mol of I_2 at 448 ˚C. The value of the equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 448 ˚C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI?

Example: Calculating Equilibrium from Initial Amounts

For the system at 900K :

$CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g)$ $K_p=0.64$

Originally, only CO_2 and H_2 are present, each at a partial pressure of 1.00 atm. What are the equilibrium partial pressures of all species?

Practice: Calculating Equilibrium from Initial Amounts

Phosgene ($COCl_2$) is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant K_p = 0.0041 at 600K. Find the equilibrium composition of the system after 0.124 atm of $COCl_2$ is allowed to reach equilibrium at this temperature.

Practice: Calculating Equilibrium from Initial Amounts

Consider the following reaction system at 100°C, $N_2O_4(g) \Leftrightarrow 2NO_2(g)$ K_p = 11

Starting with pure N_2O_4 at a pressure of 2.00 atm, what will be the equilibrium partial pressures of NO_2 and N_2O_4?

Practice: Calculating Equilibrium from Initial Amounts

At equilibrium at 500 K, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ K_p=0.497

A gas cylinder at 500 K is charged with $PCl_{5(g)}$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of $PCl_{5(g)}$, $PCl_{3(g)}$, and $Cl_{2(g)}$ at this temperature?

Putting it all Together

At temperatures near 800 ˚C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2: **$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$**

The mixture of gases that results is an important industrial fuel called *water gas*.

At 800 ˚C the equilibrium constant for this reaction is K_p = 14.1.

- What are the equilibrium partial pressures of H_2O, CO, and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00-L vessel?
- What is the minimum amount of carbon required to achieve equilibrium under these conditions?
- What is the total pressure in the vessel at equilibrium?
- At 25 ˚C the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic?
- To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?