



Equilibrium

A State of Balance

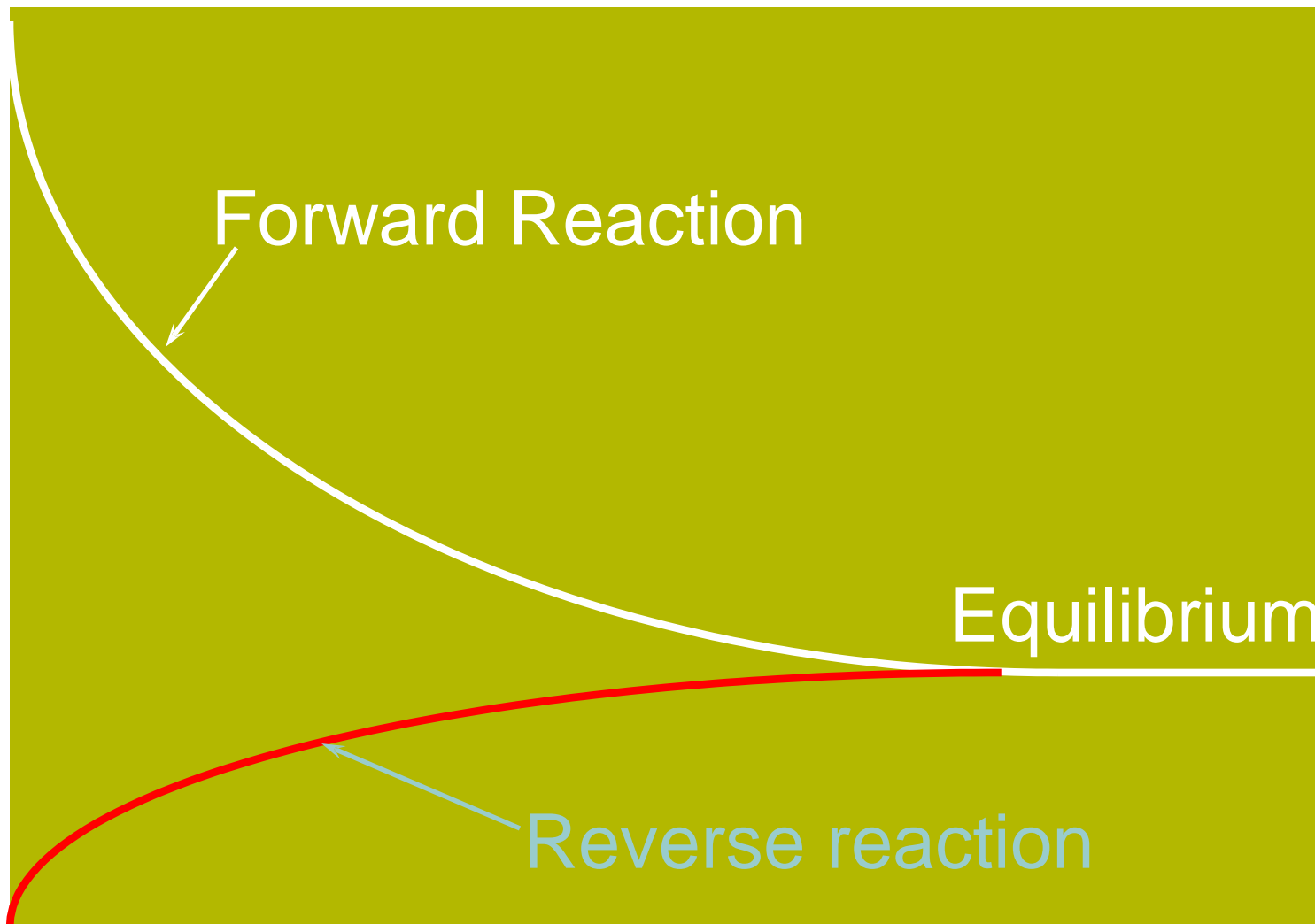
Chapter 15

Reactions are reversible

- $A + B \longrightarrow C + D$ (forward)
- $C + D \longrightarrow A + B$ (reverse)
- Initially there is only A and B so only the **forward** reaction is possible
- As C and D build up, the **reverse** reaction speeds up while the forward reaction slows down.
- Eventually the rates **are equal**



Reaction Rate



Forward Reaction

Equilibrium

Reverse reaction

Time



What is equal at Equilibrium?

- **Rates** are equal
- **Concentrations** are not.
- Rates are determined by concentrations and activation energy.
- The **net** concentrations do not change at equilibrium.

15.1 The Concept of Equilibrium

- An equilibrium mixture exists for the decomposition of N_2O_4 :
 - $\text{N}_2\text{O}_4 (\text{g}) \leftrightarrow 2\text{NO}_2 (\text{g})$
- Remembering kinetics, assume these are both elementary reactions:
 - **Rate Law** can be written from their chemical equations.

Equilibrium Rate Laws

- Forward Rx: $\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$
 - **Rate_f = $k_f [\text{N}_2\text{O}_4]$**
- Reverse Rx: $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$
 - **Rate_r = $k_r [\text{NO}_2]^2$**
- At equilibrium:
 - **$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$**

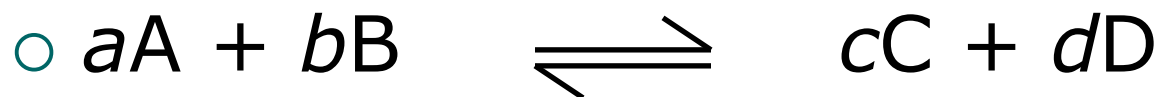
Rearrange...

○
$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant}$$

- This constant is called the **equilibrium constant**.
- Once equilibrium is reached, the concentrations of N_2O_4 and NO_2 no longer change. **NO NET CHANGE**.
- Reaction still occurs, it is in a state of **DYNAMIC EQUILIBRIUM**.

Law of Mass Action

- For any reaction



- $$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \frac{\text{PRODUCTS}^{\text{power}}}{\text{REACTANTS}^{\text{power}}}$$

- We call this relationship the equilibrium-constant expression.

Equilibrium constant

- K_c is the numerical value obtained when we substitute equilibrium concentrations into the equilibrium-constant expression.
- The subscript indicates that concentrations expressed in molarity are used to evaluate the constant.

Stoichiometry Dependant

- The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its **mechanism**.
- K_c at any given temperature does not depend on the initial amount of reactants and products.
- The value of the K_c depends only on the **particular reaction** and on the **temperature**.

Let's try some...

- Write the equilibrium expression for K_c for the following reactions:
 - $2 \text{O}_3 \leftrightarrow 3 \text{O}_2$
 - $2 \text{NO} + \text{Cl}_2 \leftrightarrow 2 \text{NOCl}$

The units for K

- Equilibrium constants are related not only to the kinetics of a reaction but also its thermodynamic measurements.
- Measured in *activities*, not concentration or pressure.
- Beyond the scope of our course...
- Are determined by the various powers and units of concentrations.
- They depend on the reaction.
- **IT IS ACCEPTED PRACTICE NOT TO INCLUDE UNITS ON EQUILIBRIUM CONSTANTS.**

K is CONSTANT

- At any temperature.
- Temperature affects rate.
- The equilibrium concentrations don't have to be the same only K.
- Equilibrium position is a set of concentrations at equilibrium.
- There are an unlimited number.

Experimental Data for $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$

Experiment	Initial $[\text{N}_2\text{O}_4]$	Initial $[\text{NO}_2]$	Equilibrium $[\text{N}_2\text{O}_4]$	Equilibrium $[\text{NO}_2]$	K_c
1	0.0	0.0200	0.0014	0.0172	?
2	0.0	0.0300	0.0028 0	0.0243	?
3	0.0	0.0400	0.00452	0.0310	?
4	0.200	0.0	0.00452	0.0310	?

Equilibrium constants in terms of pressure

- When the reactants and products are all gases, we can formulate the equilibrium constant expression in terms of partial pressures instead of molar concentrations.

- $$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

K_p and K_c

- For a given reaction, the numerical value of K_c is generally **different** from the numerical value of K_p.
- Be sure to indicate, via a subscript c or p, which of these equilibrium constants we are using.
- We can convert from one to the other.

Equilibrium and Pressure

- $PV = nRT$
- $P = (n/V)RT$
- For Substance A
 - $P_A = (n_A/V)RT = [A]RT$
- $K_p = K_c(RT)^{\Delta n}$
- The Δn is the change in the number of moles of gas in the chemical equation for the reaction.

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

Try One...

- In the synthesis of ammonia from its constituent elements, $K_c = 9.60$ at 300°C . Calculate K_p for this reaction at this temperature.

Another one...

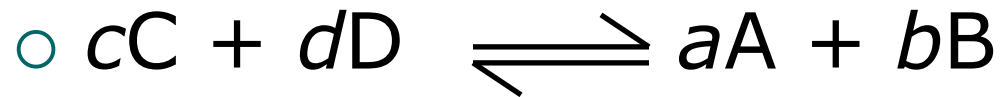
- For the equilibrium of sulfur trioxide gas decomposing into sulfur dioxide gas and oxygen gas, the K_c is 4.08×10^{-3} at 1000 Kelvin. Calculate the value for K_p .

15.3 Interpreting and Working with Equilibrium Constants

- The Magnitude of Equil. Constants
 - Range from very large to very small
- If $K \gg 1$: Equilibrium lies to the right; **products** are favored
- If $K \ll 1$: Equilibrium lies to the left; **reactants** are favored

The Direction of the Chemical Equation and K

○ If we write the reaction in reverse.



○ Then the new equilibrium constant is

○
$$Kc' = \frac{[A]^a[B]^b}{[C]^c[D]^d} = 1/Kc$$

Practice

- For the formation of ammonia from its constituent elements, $K_p = 4.34 \times 10^{-3}$ at 300C. What is the value of K_p for the reverse reaction?

Multiplying by a Number...

- If we multiply the equation by a constant
- $naA + nbB \rightleftharpoons ncC + ndD$
- Then the equilibrium constant is

$$\text{○ } K^c = \frac{[C]^{nc}[D]^{nd}}{[A]^{na}[B]^{nb}} = \frac{([C]^c[D]^d)^n}{([A]^a[B]^b)^n} = K_c^n$$

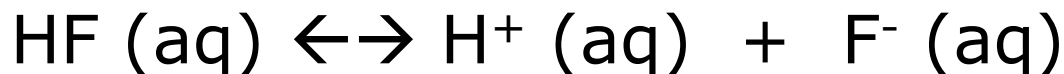
Give it some thought...

- How does the magnitude of the equilibrium constant K_p for the reaction $2\text{HI} \leftrightarrow \text{H}_2 + \text{I}_2$ change if the equilibrium is written $6 \text{HI} \leftrightarrow 3\text{H}_2 + 3\text{I}_2$?

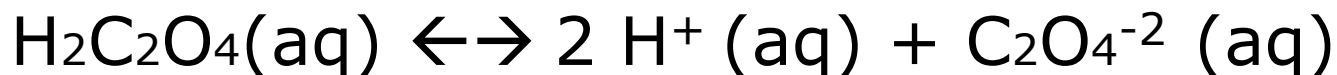
Hess' Law and K values

- $2 \text{NOBr} \leftrightarrow 2 \text{NO} + \text{Br}_2$ $K_c = 0.014$
- $\text{Br}_2 + \text{Cl}_2 \leftrightarrow 2 \text{BrCl}$ $K_c = 7.2$
- What is the value for K_c for the net sum of the equations above?
 - **$2\text{NOBr} + \text{Cl}_2 \leftrightarrow 2\text{NO} + 2\text{BrCl}$**
- The equilibrium constant for a net reaction made up of two or more steps is the PRODUCT of the equilibrium constants for the individual steps.

Try This One...

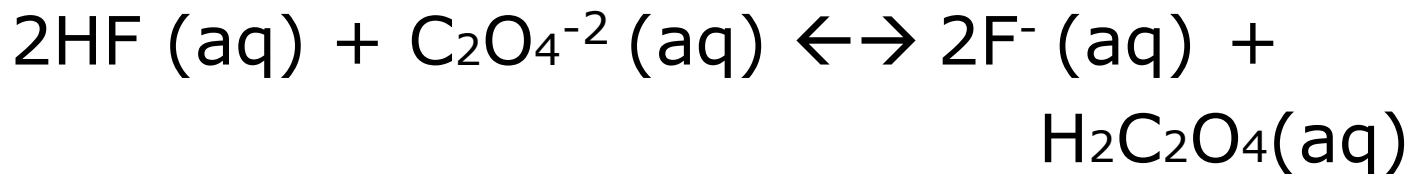


- $K_c = 6.8 \text{ E } -4$



- $K_c = 3.8 \text{ E } -6$

○ Determine the value of K_c for the reaction



How about this one...

- Given that, at 700 K, $K_p = 54.0$ for the reaction of hydrogen gas and iodine gas combining to form hydrogen iodide gas. Also, $K_p = 1.4 \times 10^{-4}$ for the reaction of hydrogen gas and nitrogen gas combining to form ammonia gas.
- Determine the K_p for this reaction:
Gaseous ammonia reacts with iodine gas to form gaseous hydrogen iodide and nitrogen gas at 700 K.

15.4 Homogeneous Equilibria

- So far every example dealt with reactants and products where all were in the **same phase.**
- We can use K in terms of either concentration or pressure.

Heterogeneous Equilibria

- If the substances in equilibrium are in **different** phases.
- $\text{PbCl}_2 (\text{s}) \leftrightarrow \text{Pb}^{+2} (\text{aq}) + 2 \text{Cl}^{-1} (\text{aq})$
- How do we express the concentration of a solid substance?
 - **We don't... leave it out**
 - $K_c = [\text{Pb}^{+2}][\text{Cl}^{-1}]^2$

Pure solids and Pure liquids

- **Excluded** from equilibrium constant expressions
- Write the equilibrium-constant expression for the evaporation of water in terms of partial pressures.
- Write the K_c and K_p for the decomposition of calcium carbonate



15.5 Calculating Equilibrium Constants

Calculating K when all Equilibrium Concentrations are known.

- A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain an equilibrium at 472 C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm hydrogen, 2.46 atm nitrogen, and 0.166 atm ammonia. Calculate the K_p .

Calculating K from Initial and Equilibrium Concentrations

- We often don't know the equilibrium concentrations of all chemical species in an equilibrium mixture.
- **Stoichiometry** helps us deduce the concentrations.

The following steps outline the procedure to do this

- 1. Tabulate all the known **initial** and **equilibrium** concentrations of the species that appear in the equilibrium-constant expression.
- 2. For those species for which both the initial and equilibrium concentrations are known, calculate the **change** in concentration that occurs as the system reaches equilibrium.

The following steps outline the procedure to do this

- 3. Use the **stoichiometry** of the reaction to calculate the changes in concentration for all the other species in the equilibrium.
- 4. From the initial concentrations and the changes in concentration, calculate the **equilibrium** concentrations.

Practice Together...

- A closed system initially containing $1.000 \times 10^{-3} \text{ M}$ Hydrogen gas and $2.000 \times 10^{-3} \text{ M}$ Iodine gas at 448 C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of the combination reaction product is $1.87 \times 10^{-3} \text{ M}$. Calculate K_c .

Try this one...

- Sulfur trioxide gas decomposes at high temperature in a sealed container producing gaseous sulfur dioxide and oxygen gas. 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 .200 atm. Calculate the value of K_p at 1000 K.

15.6 The Reaction Quotient

- Tells you the direction the reaction will go to reach equilibrium
- Calculated the same as the equilibrium constant, but for a system not at equilibrium
- $Q = \frac{[\text{Products}]^{\text{coefficient}}}{[\text{Reactants}]^{\text{coefficient}}}$
- Compare value to equilibrium constant

What Q tells us

- If $Q < K$
 - 📖 Not enough products
 - 📖 Shift to right
- If $Q > K$
 - 📖 Too many products
 - 📖 Shift to left
- If $Q = K$ system is at equilibrium

Example

- for the reaction
- $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$
- $K = 1.55 \times 10^{-5} \text{ M}$ at 35°C
- In an experiment 0.10 mol NOCl, 0.0010 mol NO(g) and 0.00010 mol Cl₂ are mixed in 2.0 L flask.
- Which direction will the reaction proceed to reach equilibrium?

Calculating Equilibrium Concentrations

- For the Haber Process, the production of ammonia at 500 C has a $K_p = 1.45 \times 10^{-5}$. In an equilibrium mixture of the three gases at 500 C, the partial pressure of hydrogen is 0.928 atm and that of nitrogen is 0.432 atm. What is the partial pressure of ammonia in this equilibrium mixture?

Calculating Equilibrium Concentrations from Initial Concentrations. (Quadratic Formula)

- A 1.000 Liter flask is filled with 1.000 mol of Hydrogen gas and 2.000 mol of Iodine gas at 448 C. The value of the equilibrium constant K_c for the combination reaction at 448 C is 50.5. What are the equilibrium concentrations for the reactants and product?

Another Try...

- If 200 atm nitrogen is mixed with 100 atm hydrogen at 250 C, find K_p at the same temperature if the final pressure of this system is 239 atm.
- Find K_c for this problem.

How about this one?

- Sodium bicarbonate can be decomposed with heat to what three products?
- If $K_p = 0.23$ for the reaction, find the total gas pressure at equilibrium.

15.7 Le Chatelier's Principle

- If a stress is applied to a system at equilibrium, the position of the equilibrium will shift to reduce the stress.
- 3 Types of stress

1. Change amounts of reactants and/or products

- Adding product makes $Q > K$ ←
- Removing reactant makes $Q > K$ ←
- Adding reactant makes $Q < K$ →
- Removing product makes $Q < K$ →
- Determine the effect on Q , will tell you the direction of shift

Give it some thought...

- What happens to the equilibrium
 - $2\text{NO (g)} + \text{O}_2 \text{(g)} \leftrightarrow 2\text{NO}_2 \text{(g)}$
if oxygen is added to the system?
 - If NO is removed?



2. Change Pressure

- By reducing the volume
- System will move in the direction that has the least moles of gas.
- Because partial pressures (and concentrations) change a new equilibrium must be reached.
- Opposite true, as well.



Change in Pressure

- By adding an inert gas
- Partial pressures of reactants and product are not changed
- No effect on equilibrium position

Give It Some Thought...

- What happens to the equilibrium
$$2\text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \leftrightarrow 2 \text{SO}_3 (\text{g})$$
 - if the volume of the system is increased?
 - If Argon is added to the reaction vessel causing an increase in pressure?

3. Change in Temperature

- Affects the rates of both the forward and reverse reactions.
- Doesn't just change the equilibrium position, changes the equilibrium constant.
- The direction of the shift depends on whether it is exo- or endothermic

Exothermic

- $\Delta H < 0$ (a negative value)
- Releases heat
- Think of heat as a product
- Raising temperature push toward reactants.
- Shifts to left.



Endothermic

- $\Delta H > 0$ (a positive value)
- Produces heat
- Think of heat as a reactant
- Raising temperature push toward products.
- Shifts to right.

Try This...

- $\text{N}_2\text{O}_4 (\text{g}) \leftrightarrow 2 \text{NO}_2 \quad \Delta H = 58.0 \text{ kJ}$
- In which direction will the equilibrium shift when
 - N_2O_4 is added?
 - NO_2 is removed?
 - Total pressure is increased by addition of $\text{N}_2 (\text{g})$?
 - The volume is increased?
 - The temperature is decreased?

A little review...

- Using the standard heat of formation data in appendix C, determine the standard enthalpy change for the reaction
 - $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \leftrightarrow 2 \text{NH}_3(\text{g})$
- Determine how the equilibrium constant for this reaction should change with temperature.

And this one...

- Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction



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

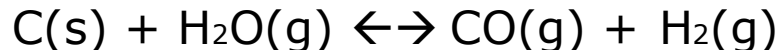


Catalysts

- Increases the rate at which equilibrium is achieved, but it does not change the composition of the equilibrium mixture.
- It will not affect the position of the equilibrium.

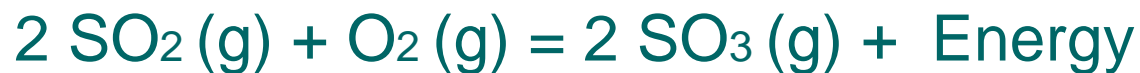
Putting Concepts Together

- At temperatures near 800 C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H₂:

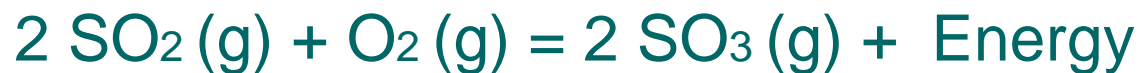


The mixture of gases that results is an important industrial fuel called water gas.

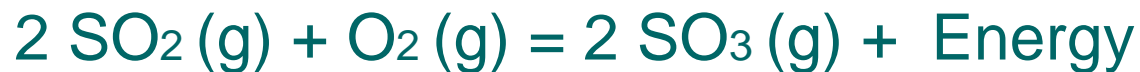
- At 800 C the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of water, carbon monoxide, and hydrogen in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of water in a 1.00 L vessel?
- What is the minimum amount 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 $K_p = 1.7 \times 10^{-21}$. Is this reaction exothermic or endothermic?
- To produce the maximum amount of Carbon monoxide and hydrogen gases at equilibrium, should the pressure of the system be increased or decreased?



- Predict the effect of each of the following changes on the value of the equilibrium constant
 - Decreasing the volume of the system
 - Adding oxygen to the equilibrium mixture
 - Raising the temperature of the system
 - Decreasing the pressure of the system
 - Adding a catalyst



- Predict the effect of each of the following changes on the number of moles of SO₃ present in the mixture at equilibrium
 - Decreasing the volume of the system
 - Adding oxygen to the equilibrium mixture
 - Raising the temperature of the system
 - Decreasing the pressure of the system
 - Adding a catalyst



- Predict the effect of each of the following changes on the rate of the forward reaction.
 - Decreasing the volume of the system
 - Adding oxygen to the equilibrium mixture
 - Raising the temperature of the system
 - Decreasing the pressure of the system
 - Adding a catalyst