

Chapter 19b: Equilibrium

Notes: Part 1 – Introduction to Equilibrium

Chemical Equilibrium

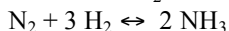
Chemical Equilibrium is a condition in which two opposing reactions are going on at equal rates producing no overall change in the concentrations of the substances involved. For example, if H_2 and N_2 are placed in a reaction chamber they react and join together according to the reaction $\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$ and, as the N_2 and H_2 get used up in the reaction, the reaction slows down. However, the N_2 and the H_2 are never completely used up because as soon as some of NH_3 is produced by the above reaction, the reverse reaction: $2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$ starts to take place and it speeds up as more and more NH_3 is produced. This “production of and using up of” NH_3 goes on until eventually the reverse reaction is using the NH_3 as quickly as the forward reaction is producing it. At this point, the concentrations of the NH_3 , N_2 , and H_2 remain constant. This is called the equilibrium point. During the time when the rates of the forward and reverse reactions are NOT equal, the system is said to be approaching equilibrium. If the forward reaction is faster than the reverse reaction, it is said to be proceeding to the right or that there is a net forward reaction.

How Equilibrium Reactions are Different from Other Reactions

If you were asked how many moles of water can be formed from 0.25 moles of H_2 when it burns according to the equation: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$, you could use the equation to say that 2 moles of hydrogen produce 2 moles of H_2O and so, 0.25 moles of H_2 would produce 0.25 moles of H_2O . These statements are true because all of the 0.25 moles of H_2 are used up since there is no reverse reaction. However, if there is a reverse reaction and the equations involve an equilibrium system, the situation is different because not all of the reactants are used up.

For example, if you were asked the following question:

How many moles of NH_3 could be formed from 0.25 moles of H_2 where the reaction is as follows:



(Note: the double arrows indicate an equilibrium system where there is a forward and a reverse reaction.)

You could not say “3 moles of H_2 produce 2 moles of NH_3 and so, 0.25 moles of H_2 would produce $0.25 \text{ mol H}_2 \times 2 \text{ mol NH}_3 / 3 \text{ mol H}_2 = 0.17$ moles of NH_3 because not all of the 0.25 moles of H_2 would be used up. HOWEVER, THE EQUATION DOES TELL THE RELATION BETWEEN THE NUMBERS OF MOLES THAT ARE USED UP OR PRODUCED.

Using the above situation, for example, if you know that, at equilibrium, there was still 0.10 moles of H_2 remaining, this would tell you that $0.25 \text{ mol starting total} - 0.10 \text{ mol remaining} = 0.15$ moles used up. Then you would be able to calculate that $0.15 \text{ moles H}_2 \text{ used} \times 2 \text{ mol NH}_3 / 3 \text{ mol H}_2 = 0.10$ moles of NH_3 produced.

Example: If 0.50 moles of H_2 and 1.50 moles of I_2 are placed in a container and react according to the equation: $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$, and if, at equilibrium, there is still 1.25 moles I_2 remaining, how many moles of H_2 and HI are in the equilibrium mixture?

Answer:

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Assignment: Part 1 – Introduction to Equilibrium

Answer the following questions showing all work, set-ups, units, etc.

1. If 1.7 mole SO_2 and 1.9 mole O_2 are placed in a reaction chamber, and if, at equilibrium, there is still 1.0 mol SO_2 remaining, how many moles of O_2 and SO_3 are in the equilibrium mixture?
The equation is: $2 \text{SO}_2 + \text{O}_2 \leftrightarrow 2 \text{SO}_3$
2. 2.6 mol P_4 and 3.6 mol H_2 are reacted until the following equilibrium is established: $\text{P}_4 + 6 \text{H}_2 \leftrightarrow 4 \text{PH}_3$. If, at equilibrium, 1.6 mol PH_3 are formed, how many moles of P_4 and H_2 are in the equilibrium mixture?
3. 1.0 mol of NH_3 , 1.0 mol of O_2 , 1.0 mol of NO , and 1.0 mol of H_2O are mixed and the following equilibrium is reached: $4 \text{NH}_3 + 5 \text{O}_2 \leftrightarrow 4 \text{NO} + 6 \text{H}_2\text{O}$. How many moles of (a) O_2 (b) NO and (c) H_2O remain, if, at equilibrium, there is still 0.80 moles of NH_3 remaining?
4. 1.5 mol N_2 and 1.5 mol O_2 are mixed. The equation is $\text{N}_2 + \text{O}_2 \leftrightarrow 2 \text{NO}$. If the number of moles of NO at equilibrium is 'x', how many moles of N_2 are left (in terms of 'x')?
5. 1.5 moles of CO and 1.5 moles of O_2 are placed together and the following equilibrium is reached: $2 \text{CO} + \text{O}_2 \leftrightarrow 2 \text{CO}_2$. If the number of moles of O_2 is reduced by 'x' moles at equilibrium, how many moles of CO and CO_2 remain once the system has reached equilibrium?
6. 2.2 mol N_2 , 3.3 mol H_2 , and 1.0 mol NH_3 are approaching equilibrium as shown by the equation: $\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3$. If, at equilibrium, the number of moles of NH_3 has increased by 'x' moles, what is the number of moles of N_2 and the number of moles of H_2 in the equilibrium mixture?
7. 1.2 mol HI is placed in a vessel and the following equilibrium is attained: $\text{H}_2 + \text{I}_2 \leftrightarrow 2 \text{HI}$. If, at equilibrium, the number of moles of HI has been reduced by 'x' moles, what is the number of moles of H_2 and the number of I_2 in the equilibrium mixture?

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Notes: Part 2 – Equilibrium Expressions

Mass Action Expression:

For the general balanced equation, $n A + m B \dots \leftrightarrow p C + q D \dots$

the Mass Action Expression is
$$\frac{[C]^p [D]^q}{[A]^n [B]^m}$$

where square brackets mean the concentration of the substance in MOLARITY.

(Note: it's the product of the product side concentrations over the product of the reactant side concentrations.)

Example 1: Write the mass action expression for $N_2 + 3 H_2 \leftrightarrow 2 NH_3$.

Example 2: If 1.5 moles of N_2 , 2.5 moles of H_2 and 0.50 moles of NH_3 are approaching equilibrium, according to the above equation, in a 500. mL container. What is the value of the mass action expression? (Remember that the concentration must be MOLARITY.)

The Law of Chemical Equilibrium

In a system at chemical equilibrium, the concentrations of the materials involved must be such that the mass action expression equals a certain constant called the equilibrium constant.

Equilibrium Condition refers to the expression
$$\frac{[C]^p [D]^q}{[A]^n [B]^m} = K_{eq}$$

where K_{eq} is called the equilibrium constant.

To Derive or Prove the Equilibrium Constant

- Consider the general equation as a 1 step reaction: $n A + m B \leftrightarrow p C + q D$
- The rate law for the forward reaction is: $rate = k_1 [A]^n [B]^m$
- The rate law for the reverse reaction is: $rate = k_2 [C]^p [D]^q$
- Since at equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction:
$$k_1 [A]^n [B]^m = k_2 [C]^p [D]^q$$
- When we solve for a single constant:
$$\frac{k_1}{k_2} = \frac{[C]^p [D]^q}{[A]^n [B]^m}$$
- So, letting $k_1/k_2 = K_{eq}$, we get the equilibrium condition of the above.

Significance of the Size of the Equilibrium Constant

A large value for K_{eq} (i.e. 10^n) means that at equilibrium nearly all reactants have been used up and there are mainly products remaining. The reaction is said to go almost to completion.

A small value for K_{eq} (i.e. 10^{-n}) means that at equilibrium there is very little of the products and most of the reactants are left, i.e. it doesn't proceed very far to the right.

Evaluating K_{eq}

For the reaction, $n A + m B \leftrightarrow p C + q D$, the usual equilibrium condition is
$$\frac{[C]^p [D]^q}{[A]^n [B]^m}$$

However, since the concentration of any solid (and in some cases, liquids) is fairly constant, it is left out of the mass action expression for the equilibrium constant and thereby it is included in the value of K_{eq} .

For example, the equilibrium condition for the following reaction: $C_{(s)} + O_{2(g)} \leftrightarrow CO_{2(g)}$
is: $[CO_2]/[O_2]$

To determine the value of K_{eq} , you substitute the concentrations that are known to exist at equilibrium.

Example: It is known that at a certain high temperature, there exists in equilibrium, 2.5 mol CO_2 , 1.5 mol O_2 , and 2.5 mol C in a 2.5 L container. What is the value for K_{eq} ?

We use the equilibrium expression from above and plug in the concentrations.

(Remember, the concentrations are in MOLARITY – which is moles/L.)

Answer:

(Note: the carbon is omitted because it is solid and its concentration does not change.)

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Assignment: Part 2 – Equilibrium Expressions

Answer the following questions **on a separate sheet of paper**, showing all work, set-ups, units, etc.

- Write the mass action expression for the following equilibrium systems:
 - $2 SO_2 + O_2 \leftrightarrow 2 SO_3$
 - $COCl_2 \leftrightarrow CO + Cl_2$
 - $P_4 + 6 H_2 \leftrightarrow 4 PH_3$
 - $4 NH_3 + 5 O_2 \leftrightarrow 4 NO + 6 H_2O$
- What is the value of the mass action expression for the equation in question 1(a) when 2.50 mol SO_2 and 1.00 mol O_2 are placed in a 500. mL container?
 - What is the value of the expression after 0.500 mol of SO_2 have been used up?
 - What is the value at equilibrium if, at equilibrium, there are still 1.50 mol of SO_2 remaining?
- What is the value of the mass action expression for the equation in question 1(d) when, in a 2.50 L container, there are 7.50 mol NH_3 , 5.00 mol O_2 , 25.0 mol NO , and 2.50 mol H_2O ?
 - What is the value of mass action expression if, at equilibrium, the concentration of the NO has increased to 11M?
- Find the value of K_{eq} if, at equilibrium, there are 10.0 moles of P_4 , 25.0 moles of H_2 , and 5.00 moles PH_3 in a 5.00 L container. The equation is: $P_{4(g)} + 6 H_{2(g)} \leftrightarrow 4 PH_{3(g)}$.
- Find the value of K_{eq} for the equilibrium system, $ZnO_{(s)} + CO_{(g)} \leftrightarrow CO_{2(g)} + Zn_{(g)}$ if, at equilibrium, there are 3.00 moles of CO , 4.00 moles Zn , 4.00 moles CO_2 in a 500. mL container.
- Find K_{eq} for $H_{2(g)} + S_{(l)} \leftrightarrow H_2S_{(g)}$ if, at equilibrium, the concentration of H_2 and H_2S are 1.5 M and 2.5 M, respectively.
- For the system $P_{4(s)} + 5 O_{2(g)} \leftrightarrow P_4O_{10(s)}$, find the value of K_{eq} if initially there was 12.8 g P_4 and 1.00 mol O_2 in a 1.00 L container and if, at equilibrium, 0.400 g P_4 remained.
- Initially the concentrations of N_2 and O_2 are 1.80 M and 1.80 M, respectively, and there is no NO . If, at equilibrium, the concentration of NO is 1.80 M, find K_{eq} . The reaction $N_{2(g)} + O_{2(g)} \leftrightarrow 2 NO_{(g)}$
- For the system $4 H_{2(g)} + Fe_3O_{4(s)} \leftrightarrow 3 Fe_{(s)} + 4 H_2O_{(g)}$, find K_{eq} if, initially, there is only 1.60 M H_2 and 100. g Fe_3O_4 and if, at equilibrium, the concentration of H_2 is 1.00 M.
- Find K_{eq} for the equilibrium system $2CO_{(g)} + O_{2(g)} \leftrightarrow 2 CO_{2(g)}$ if, initially, there are 5.00 moles of CO , 10.0 moles of O_2 , and 1.00 mole of CO_2 in a 2.00 L container and if, at equilibrium, there is a CO_2 concentration of 2.50 M.

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Notes: Part 3 – More Equilibrium Expressions

Determining Equilibrium Concentrations from Equilibrium Constants

Example: How many moles of CO_2 would exist in equilibrium with 1.0 mole H_2 , 2.0 moles CO , and 3.0 moles H_2O if $K_{\text{eq}} = 1.60$ for the system $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \leftrightarrow \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ at 986°C in a 500. mL container?

Answer:

Determining Equilibrium Concentrations from Initial Concentrations

Steps:

- Select the substance in the equation with the lowest coefficient in front of it and
 - o if it is on the left side of the equation, make it into a statement, “Let ‘x’ M of it be used up”.
 - or
 - o if it is on the right side of the equation, make it into the statement, “Let ‘x’ M of it be produced”.
- Write down the concentrations used up or produced of all the other substances, using the coefficients in the balanced equation.

For example: If the equation is $4 \text{HCl} + \text{O}_2 \leftrightarrow 2 \text{Cl}_2 + 2 \text{H}_2\text{O}$, you would “Let x M of O_2 be used up” and also “4x M of HCl would also be used up.” You would then say “Let 2x M of Cl_2 and 2x M of H_2O are then produced.”

- In order to write the reaction equilibrium concentrations in terms of ‘x’, you either
 - o (i) subtract the concentration used up from the initial concentrations given
 - or
 - o (ii) add the concentration produced to the initial concentration given (if any).
- Substitute the above equilibrium concentrations and the given value for K_{eq} into the equilibrium condition expression and solve for ‘x’.
- To determine the final answer for the equilibrium concentrations go back to the third step and put in the value for ‘x’.

Example: At a certain temperature, $K_{\text{eq}} = 49.0$ for the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \leftrightarrow 2\text{C}(\text{g})$. If, initially, 5.00 mol A and 5.00 mol B are placed in a 5.00 L container, what will be the equilibrium concentration of C? How many moles of A will be left?

Answer:

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Assignment – Part 3 – More Equilibrium Expressions

Answer the following on a separate sheet of paper, showing all work ,set-ups, units, etc.

1. If $K_{\text{eq}} = 46.0$ for $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2 \text{HI}(\text{g})$, what concentration of I_2 would be in equilibrium with 0.500 M HI and 0.100 M H_2 ?
2. For the reaction $\text{A}(\text{s}) + 2 \text{B}(\text{g}) \leftrightarrow 2 \text{C}(\text{g})$, $K_{\text{eq}} = 2.00$ at 325 K. Find the equilibrium concentration of C if, at equilibrium, there are 3.00 moles of B and 1.00 moles of A in a 250. mL container.
3. At equilibrium in a 5.00 L container there are 5.00 mol HCl, 10.0 mol O_2 , 15.0 mol Cl_2 , and 20.0 mol H_2O . Find K_{eq} for $4 \text{HCl}(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{Cl}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$. How many moles of O_2 could exist in this container with 0.500 moles of each HCl, Cl_2 , and H_2O ?
4. At a certain temperature there exists in equilibrium 10.0 M SO_2 , 10.0 M O_2 and 3.50 M SO_3 . The equation is $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{SO}_3(\text{g})$. At the same temperature, how many moles of SO_3 would be in equilibrium in a 2.50 L container with 25.0 mol O_2 and 5.00 mol SO_2 ?
5. $K_{\text{eq}} = 81.0$ at a certain temperature for the reaction $4 \text{A}(\text{g}) + \text{B}(\text{s}) \leftrightarrow 2 \text{C}(\text{g}) + 2 \text{D}(\text{g})$. If, initially, there were 7.00 moles of A and 7.00 moles of B in a 500.0 mL container, what would be the equilibrium concentration of C?
6. If $K_{\text{eq}} = 1.00 \times 10^{-4}$ for the system $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{NO}(\text{g})$, find the number of moles of NO in a 10.0 L container if the initial concentrations of N_2 and O_2 are each 1.00 M.
7. $K_{\text{eq}} = 25.0$ for the reaction $\text{C}(\text{s}) + \text{O}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{g})$. Find the equilibrium concentration of CO_2 if, initially, there are 100. moles of C, 50.0 moles of O_2 , and 2.00 moles of CO_2 in a 2.00 L container.
8. If, for the system, $\text{NH}_4\text{Cl}(\text{s}) \leftrightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$, $K_{\text{eq}} = 1.00 \times 10^{-4}$. Find the moles of NH_3 in a 100.0 L container, if, initially, there were 10.0 mol NH_3 added to 10.0 mol HCl

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Notes: Part 4 – Concentrations at Equilibrium

Predicting if Certain Concentrations will be at Equilibrium

Basic Idea: If you substitute the values for K_{eq} and the equilibrium concentrations into the equilibrium condition, the left and right sides MUST be EQUAL if there is equilibrium. If they are not equal, i.e. if K_{eq} does not equal the mass action expression, there are two possibilities:

(1) The mass action expression may be less than K_{eq} . In this case (a) the system is not at equilibrium, (b) there is a NET FORWARD REACTION, (c) the forward reaction is faster than the reverse and this causes an (d) increase in the concentration of products (on the right side) and this makes the mass action expression larger until it equals K_{eq} and there is equilibrium.

(2) The mass action expression may be greater than K_{eq} . In this case (a) the system is not at equilibrium, (b) there is a NET REVERSE REACTION, (c) the reverse reaction is faster than the forward one and this causes (d) an increase in the concentration of the reactants (on the left side) and this makes the mass action expression smaller until it equals K_{eq} and there is equilibrium.

Example: If $K_{eq} = 0.90$ for $N_2 + 3 H_2 \leftrightarrow 2 NH_3$ (all gases), will the following be at equilibrium: 0.50 M of NH_3 , 0.10 M of N_2 , and 0.10 M of H_2 ?

Answer:

Since the mass action expression has a value of 2500 which is greater than the $K_{eq} = 0.9$, the system is not in equilibrium. There would be a net reverse reaction that would increase the concentration of N_2 and H_2 and decrease the concentration of NH_3 and so thereby make the value of the mass action expression smaller.

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Assignment: Part 4 – More Equilibrium Expressions

For each the following problems, answer each the following questions:

- (A) Is there equilibrium?
- (B) Which reaction is faster, the forward or the reverse?
- (C) Which concentrations are increasing? Which concentrations are decreasing?

1. $K_{eq} = 25.0$ for the system $A(s) + 2 B(g) \leftrightarrow C(g)$. At a certain temperature, $[B] = 2.00 M$ and $[C] = 50.0 M$.

2. At a certain temperature, in a 2.00 L container, there exists in equilibrium 5.00 mol CO_2 , 5.00 mol CO , and 0.200 mol O_2 . Find K_{eq} . Would there be equilibrium at the same temperature if the concentrations were $[\text{CO}_2] = 15.8 \text{ M}$, $[\text{CO}] = 10.0 \text{ M}$, and $[\text{O}_2] = 0.250 \text{ M}$? The equation is $2 \text{CO}_{(\text{g})} + \text{O}_{2(\text{g})} \leftrightarrow 2 \text{CO}_{2(\text{g})}$.
3. $K_{\text{eq}} = 16.0$ for the system $2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})} \leftrightarrow 2 \text{SO}_{3(\text{g})}$. Initially, the concentrations are $[\text{SO}_2] = 5.00 \text{ M}$, $[\text{O}_2] = 10.0 \text{ M}$, and $[\text{SO}_3] = 0.0 \text{ M}$. After 2 hours, the O_2 concentration has dropped to 7.90 M.
4. At a certain temperature, the following concentrations are at equilibrium: 0.100 M H_2O , 2.00 M O_2 , 0.500 M NH_3 , and 0.200 M NO . The equation is $4 \text{NH}_{3(\text{g})} + 5 \text{O}_{2(\text{g})} \leftrightarrow 4 \text{NO}_{(\text{g})} + 6 \text{H}_2\text{O}_{(\text{g})}$. Answer the questions based on the following mixture: 0.750 mol H_2O , 12.0 mol NO , 30.0 mol O_2 , and 0.300 mol NH_3 in a 3.00 L container.
5. $K_{\text{eq}} = 46.0$ for $\text{H}_{2(\text{g})} + \text{I}_{2(\text{g})} \leftrightarrow 2 \text{HI}_{(\text{g})}$. Initially, there are 69.0 mol H_2 and 24.0 mol I_2 in a 10.0 L container. After 5 hours, there is still 1.00 mol I_2 left.
6. At a certain temperature, there exists an equilibrium when $[\text{A}] = 1.00 \text{ M}$, $[\text{B}] = 2.50 \text{ M}$, and $[\text{C}] = 3.00 \text{ M}$. The equation is $\text{A}(\text{g}) + 2 \text{B}(\text{g}) \leftrightarrow 3 \text{C}(\text{g})$. Answer the question based on the following mixture: Initially, the concentrations of $\text{C} = 18.0 \text{ M}$ and $\text{B} = 6.00 \text{ M}$ and $[\text{A}] = 0.0 \text{ M}$ and after some time 2.00 M of A has been produced.

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Notes: Part 5 – Solubility Product Constant

What is K_{sp} and How Do I Find It?

Soluble is a relative term. Most insoluble ionic solids are actually soluble in water to a limited extent. These solids dissociate slightly in water. The compound silver chloride dissociates slightly in water to silver ions (Ag^+) and chloride ions (Cl^-). An equilibrium is established in the saturated solution between the solid and the ions in solution. The equation for this equilibrium is:
 $\text{AgCl}_{(s)} \leftrightarrow \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$.

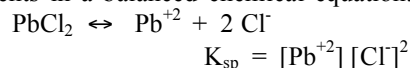
The above equation can be represented mathematically by a constant, K_{eq} , called the equilibrium constant. By definition, this constant is equal to the molar concentration of the products divided by the molar concentration of the reactants. The concentration of each ion is raised to a power equal to the coefficient of the ion in the balanced equation. This constant can be expressed as follows:

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The concentration of a pure solid, such as AgCl , is a constant. Since both terms, AgCl and K_{eq} , are constants, they may be multiplied together to form a new constant, which is known as the solubility product constant, or the K_{sp} .

$$[\text{Ag}^+][\text{Cl}^-] = K_{eq} [\text{AgCl}] = K_{sp}$$

The solubility product constant, K_{sp} , is the product of the concentration of the ions in a saturated solution raised to the power of the coefficients in a balanced chemical equation. For example, the expression of the solubility product constant for PbCl_2 would be:



Using the equation for K_{sp} it is possible to calculate the solubility of a salt if its K_{sp} is known, or to calculate the K_{sp} from the solubility. The K_{sp} is an experimental value and depends upon the temperature, as does K_{eq} . The solubility of a salt must be expressed as the molar solubility of the salt, the Molarity, M.

Example 1: A 1.00 L saturated solution of AgCl is evaporated to dryness and the residue is equivalent to 1.34×10^{-5} mole of AgCl . What is the experimental K_{sp} of the silver chloride?

Example 2: At a specified temperature, the K_{sp} of AgCl is 1.56×10^{-10} . Determine the solubility of the AgCl in grams per Liter.

Using K_{sp} Values

A useful application of K_{sp} is to determine if precipitation will occur when a salt and a solution or when two solutions are mixed. Precipitation takes place when the ion product EXCEEDS the K_{sp} value.

Ion product < K_{sp}	no precipitation will occur, unsaturated solution
Ion product = K_{sp}	no precipitation will occur, saturated solution
Ion product > K_{sp}	precipitation will occur, saturated with excess

Remember that if the final solution is formed by mixing two solutions it is necessary to consider the dilution. Each solute is diluted when the other solution is added. In other words, when a 1.00 mole sample that was dissolved to make 1.00 L of solution is mixed with another solution that also has a volume of 1.00 L, then the new volume is 2.00 L. So the molarity of the salt then needs to be calculated using the 2.00 L volume.

Example 3: Will precipitation occur when 50.0 mL of a 3.00×10^{-2} M $\text{Pb}(\text{NO}_3)_2$ solution is mixed with 50.0 mL of a 2.00×10^{-3} M KCl ? The K_{sp} of PbCl_2 is 1.62×10^{-5} .

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Assignment: Part 5 – Solubility Product Constant

Answer the following problems **on a separate sheet of paper**, showing all work, set-ups, units, etc.

- From the given solubilities, determine the experimental values of the K_{sp} for the following compounds:
 - BaCO_3 solubility = 7.00×10^{-5} M
 - $\text{Pb}(\text{OH})_2$ solubility = 4.20×10^{-6} M
 - CaF_2 solubility = 0.0170 grams / L
- Given the K_{sp} values, calculate the solubility, in Molarity, of the following compounds:
 - CuS $K_{\text{sp}} = 6.31 \times 10^{-36}$
 - $\text{Al}(\text{OH})_3$ $K_{\text{sp}} = 1.26 \times 10^{-33}$
 - SrC_2O_4 $K_{\text{sp}} = 1.58 \times 10^{-7}$
- Determine if precipitation would occur in the following cases.
 - 25.0 mL of a 6.00×10^{-6} M $\text{Sr}(\text{NO}_3)_2$ solution is mixed with 25.0 mL of a 4.00×10^{-7} M H_3PO_4 solution. The K_{sp} of $\text{Sr}_3(\text{PO}_4)_2$ is 4.07×10^{-28} . Will precipitation occur?
 - 100.0 mL of 5.00×10^{-3} M $\text{Ba}(\text{NO}_3)_2$ is mixed with 100.0 mL of 2.00×10^{-2} M NaF . The K_{sp} of BaF_2 is 1.05×10^{-6} . Will precipitation occur?
 - 50.0 mL of 6.00×10^{-4} M AgNO_3 is mixed with 25.0 mL of 5.00×10^{-4} M K_2CrO_4 . The K_{sp} of silver chromate is 9.00×10^{-12} . Will precipitation occur?

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Notes: Part 6 - Predicting the Effects of Disturbing a System in Equilibrium

Introduction:

In predicting the effects of disturbing a system in equilibrium, there are three principles that you should be able to use: Le Chatelier's Principle, the principles of reaction kinetics, and the Principle of the Equilibrium Constant.

Le Chatelier's Principle:

Le Chatelier's Principle is not really an explanation of why an equilibrium system behaves as it does, but it is a handy, easy-to-use rule for predicting the effects of "stresses" on a system in equilibrium.

Le Chatelier's Principle states that when a stress is applied to a system in equilibrium, the system proceeds either forward or backward so as to offset the stress. The stresses and the action that would offset them are listed below in the following table.

	<i>Stress</i>	<i>Action that would offset the stress</i>
1	Increasing the concentration of a substance. (Another way of saying this is "the partial pressure of a gaseous substance is increased.")	Using up that substance (in either forward or reverse reaction) will offset the stress.
2	Decreasing the concentration of a substance. Remember, a solid reactant cannot increase or decrease in concentration.)	Producing more of that substance in a forward or reverse reaction (since this will reduce pressure).
3	Decreasing the enclosing volume of a gaseous mixture. This is the same as increasing the pressure of the gaseous mixture as a whole.	Producing fewer gas molecules in a forward or reverse reaction (since this will reduce pressure).
4	Increasing temperature	Using up heat in a forward or reverse reaction.
5	Decreasing temperature	Producing heat in a forward or reverse reaction.

Note: A catalyst is NOT considered a stress because it speeds up both reactions, the forward and the reverse, at equal rates.

Example 1 If the following system is in equilibrium: $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \leftrightarrow 2\text{HI}(\text{g})$, and then some more H_2 is added to a container of constant volume, what is the effect on equilibrium?

Answer: The stress:

Offset by:

Reaction:

[] Change:

Example 2: The following system is in equilibrium: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g}) + 22 \text{ kcal}$

Then (a) the temperature is raised, and
(b) the total volume is compressed.

What is the effect on the equilibrium of each of these stresses?

Answer (a): The stress:

Offset by:

Reaction:

[] Change:

Answer (b): The stress:

Offset by:

Reaction:

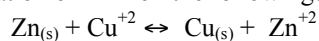
[] Change:

Chapter 19b: Reaction Equilibrium

Assignment: Part 6 – Predicting the Effects of Disturbing a System in Equilibrium

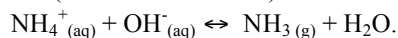
Answer the following. For each of the following, state (a) the stress, (b) how the stress is offset, (c) which reaction is favored, and (d) the concentration changes.

1. What is the effect of reducing the concentration of Zn^{+2} on the following:



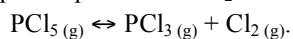
- a. _____
b. _____
c. _____
d. _____

2. Explain in detail the effect of adding NaOH (forms Na^+ and OH^-) to the following system in equilibrium:



- a. _____
b. _____
c. _____
d. _____

3. Explain in detail the effect of increasing the partial pressure of Cl_2 in the following equilibrium system:



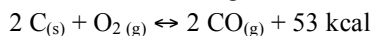
- a. _____
b. _____
c. _____
d. _____

4. Explain the effect of raising the temperature on the following:



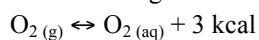
- a. _____
b. _____
c. _____
d. _____

5. Explain the effect of reducing the temperature on the following:



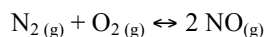
- a. _____
b. _____
c. _____
d. _____

6. Explain the effect of raising the temperature on the following:



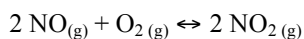
- a. _____
b. _____
c. _____
d. _____

7. Explain the effect of decreasing the enclosing volume of:



- a. _____
b. _____
c. _____
d. _____

8. Explain the effect of compressing the equilibrium mixture of the following:



- a. _____
b. _____
c. _____
d. _____

Chapter 19b: Reaction Equilibrium

Notes: Part 7 – More Stresses on a System in Equilibrium

Reaction Kinetics

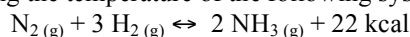
You should also be able to use the principles of reaction kinetics in order to predict and explain the effects of disturbing a system in equilibrium. The important points of reaction kinetics are:

- Concentration of Reactants – The rate law for a one step reaction, $nA + mB \rightarrow \text{products}$ is: $\text{rate} = k [A]^n [B]^m$.
- Temperature – All reactions, exothermic and endothermic, are faster at higher temperatures. Although all reactions are speeded up by a rise in temperature, endothermic reactions are speeded up **MORE** than exothermic ones, and they are also slowed down more by a decrease in temperature.
- Catalysis – catalysts increase the rate by decreasing the activation energy barrier and thereby allowing a greater fraction of molecules to have the necessary energy to cause chemical change when they collide

Example 1: Explain by the principles of reaction kinetics the effect of removing some H_2 from the following system in equilibrium: $H_{2(g)} + I_{2(g)} \leftrightarrow 2 HI_{(g)}$.

Answer: Reaction:
Net reaction:
[] Change:

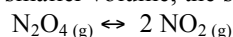
Example 2: What is the effect of decreasing the temperature of the following system:



Answer: Reaction:
Net reaction:
[] Change:

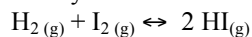
Recall: With regard to decreasing the volume of a reaction of a mixture of gases in equilibrium, although the concentration of all substances in the equilibrium increase with a decrease in volume and, although this tends to increase both forward and reverse reactions, if the *number of molecules* of reactants for the *forward reaction* is greater than that for the *reverse reaction*, the *forward reaction is speeded up more than the reverse*.

Example 3: What is the effect of compressing to a smaller volume, the system:



Answer: Reaction:
Net reaction:
[] Changes:

Example 4: What is the effect of adding a catalyst to the following system in equilibrium:



Answer: Reaction:
Net reaction:
[] Change:

Principle of the Equilibrium Constant

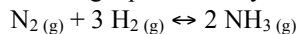
The basic idea of the equilibrium constant is that (a) when a system is at equilibrium there is an equality between K_{eq} and the Mass Action Expression and (b) if the equality is upset by (1) changing the value of K_{eq} by raising or lowering the temperature or (2) changing the concentrations of the substances in the Mass Action Expression, the system will proceed to restore equality between K_{eq} and the Mass Action Expression.

Example 5: What is the effect of removing some I_2 from the system: $H_2 + I_2 \leftrightarrow 2 HI$.

Answer: K_{eq} or MAE:

Restore equality:

Example 6: Explain the effect of compressing the following equilibrium system:



Answer:

Recall:

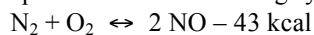
A **RISE** in temperature causes K_{eq} to

- (i) **DECREASE** if the forward reaction is exothermic
- (ii) **INCREASE** if the forward reaction is endothermic

A **DROP** in temperature causes K_{eq} to

- (i) **INCREASE** if the forward reaction is exothermic
- (ii) **DECREASE** if the forward reaction is endothermic

Example 7: What is the effect of raising the temperature of the following system:



Answer:

Chapter 19b: Reaction Equilibrium

Assignment: Part 7 – More Stresses on a System in Equilibrium

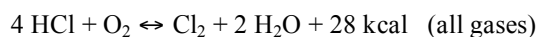
Answer the following on a separate sheet of paper. Show all parts, including which reaction is favored to offset the given stress.

1. Explain in terms of kinetics the effect of each of the following stresses on the system in equilibrium:



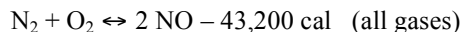
- (a) more Cl_2 is added
- (b) the enclosing volume is decreased
- (c) a catalyst is added

2. Explain the effect of the following stresses on the system:



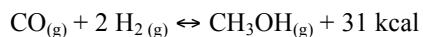
- (a) the concentration of H_2O is decreased
- (b) the temperature is raised

3. Explain the effect of the stresses on the system:



- (a) decreasing the enclosing volume
- (b) lowering the temperature

4. Explain in terms of the equilibrium constant the effect of the following changes on the equilibrium of the system:



- (a) adding more CO
- (b) compression to a smaller volume
- (c) raising the temperature

5. Explain the effect on the equilibrium of the system by the following changes:



- (a) compression to a smaller volume
- (b) a rise in temperature