5.1 - Reversible Reactions and Equilibrium kEY

5.1 Assignment KEY

1. Write reversible reactions for each of the following situations (be sure to balance your equations):

   a. Hydrogen iodide gas (HI) decomposes into its elements.

   $2HI_{(g)} \leftrightarrow I_{2(g)} + H_{2(g)}$

   b. Hydrogen and nitrogen gases combine to form ammonia gas, NH_3.

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

2. If the system represented by the following equation is found to be at equilibrium at a specific temperature, which of the following statements is true? Explain your answers.

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

   a. All species must be present in the same concentration.

   b. The rate of the forward reaction equals the rate of the reverse reaction. TRUE

   c. We can measure continual changes in the reactant concentrations.

3. Which of the following are equilibrium systems and which are steady state systems?

   a. A playing football team and a bench of reserve players. The number of players o the field is constant and the number of players on the bench is constant. (EQUILIBRIUM)

   b. A well fed tiger in a cage. The weight of the tiger is constant. (STEADY STATE)

   c. The Nipawin Dam and Codette Lake behind the dam. The water level is constant. (STEADY STATE)

   d. The liquid alcohol and alcohol vapor in a thermometer. The temperature is constant. (EQUILIBRIUM)

   e. A block of wood floating on water. (STEADY STATE)

4. Which of the following are chemical equilibria and which are physical equilibria systems?

   a. sublimation of dry ice (solid carbon dioxide) PHYSICAL

   b. a saturated magnesium chloride solution CHEMICAL

   c. the partial dissociation of 2 moles of HI molecules into 1 mole H_2 and 1 mole of I_2 molecules CHEMICAL

5.1 - Reversible Reactions and Equilibrium kEY

5.1 Assignment

5. Which of the following reactions are reversible?

   a. the evaporation of water (REVERSIBLE)

   b. the combustion of coal (IRREVERSIBLE)

   c. the magnetization of an iron bar (REVERSIBLE)

6. A chemist wished to prepare pure phosgene ($COCl_{2(g)}$) by reacting carbon monoxide and chlorine gas accoridng to the reaction:

$$CO_{(g)} + Cl2_{(g)} \rightleftharpoons COCl_{2(g)}$$

Why will this reaction NOT produce pure phosgene? If the chemist could somehow obtain a sample of pure $COCl_{2(g)}$, would it remain pure? Why?

-It will NOT produce pure phosgene because the product would being breaking down once it is produced as it is a reversible reaction. Even if they obtained a pure product, it would not remain pure because equilibria can be approached from the reactants or products.

7.

(a) The colour does not change, so $NO_2(g)$ is being made at the same rate that it is destroyed.

(b) Temperature CAN affect an equilibrium – the colour became lighter or darker when the temperature was changed, meaning more or less $NO_2(g)$ was present.

(c) The colour does not change while the tube full of gas remains at a constant 100°C. The colour would become very dark red–brown if the temperature were raised above 100°C.

(d) The reaction is endothermic as written: $N_2O_4(g) + \text{energy} \rightleftharpoons 2\ NO_2(g)$. As heat is added the forward reaction should occur to a greater extent and produce more of the red–brown $NO_2(g)$, which is exactly what occurred.

(e) $N_2O_4(g)$ predominated at low temperatures (colourless).
$NO_2(g)$ predominated at high temperatures (dark red–brown).
At room temperature the content of the tube was a mixture of $N_2O_4(g)$ and $NO_2(g)$.

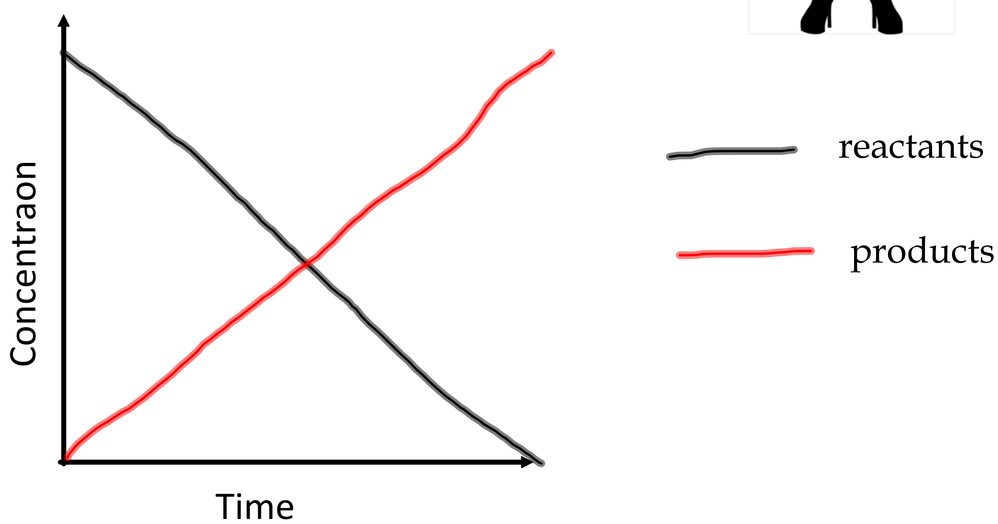
(f) The tubes should become the same colour. A tube containing mostly $N_2O_4(g)$ at low temperatures and another tube containing mostly $NO_2(g)$ at high temperatures eventually became the same colour at room temperature.

Unit 5 - Equilibrium

5.1 - Reversible Reactions and Equilibrium

pages 558-563 in Matter and Change

pages 514-520 in Health



Reversible Reactions

One misconception about chemical reactions is that they can only happen in one direction.

That is, in previous science courses one way we defined a chemical change is that they cannot be reversed. For example, frying an egg.

In this unit we will learn that reactions can be reversed under the right conditions. (note: almost all physical changes are reversible= **physical equilibria**)

For example, $2NO_2 \rightarrow N_2O_4$ and $N_2O_4 \rightarrow 2NO_2$.

In a situation like this, we can combine the two ideas by writing the equation using a double arrow ($\rightleftarrows$ or $\longleftrightarrow$):

$2NO_2 \rightleftarrows N_2O_4$

In this example, the cycle always continues. Once the $2NO_2$ forms the N_2O_4, the N_2O_4 will decompose back down to $2NO_2$ and the cycle repeats.

Regarding $2NO_2 \rightleftarrows N_2O_4$ we call the reaction where NO_2 is the reactant an N_2O_4 is the product the **forward** reaction.

Likewise, when N_2O_4 is the reactant and NO_2 is the product, we call this the **reverse** reaction.

Note that the forward reaction will always be read from left to right.

Equilibrium

If we add salt to a beaker of water, we will have the reversible reaction:

$NaCl_{(s)} \rightleftarrows NaCl_{(aq)}$

However, if we keep adding salt, we will reach a point where no more salt is able to dissolve and the excess sits at the bottom of the beaker.

One question we must ask is whether or not the dissolving process has stopped.

When a solution becomes saturated, it has reached the point of **equilibrium**. This means that the forward reaction:

$NaCl_{(s)} \rightarrow NaCl_{(aq)}$

and the reverse reaction:

$NaCl_{(aq)} \rightarrow NaCl_{(s)}$-

-happen at the same rate ($\text{Rate}_{\text{forward rxn}} = \text{Rate}_{\text{reverse rxn}}$)

This is why we think the dissolving process has stopped - we don't see any observable change in the amount of salt at the bottom of the solution. Only microscopic changes occur at equilibrium.

This may also be called **dynamic chemical equilibrium** , but we will just refer to it as equilibrium *(the concentration of products and reactions is not changing).*

Note that we are talking about equal **rates**, not equal concentrations of reactants and products.

Achieving equilibrium takes time-different amount of time for different reactions.

An analogy for equilibrium: subbing players into a sports game or juggling.

In order for equilibrium to be reached with a reversible reaction the system must be **closed**. Imagine if the product was removed as soon as it was formed, how could it be reversed into the reactants?

If you continuously add reactants to a system at the same rate you remove the products you create a **steady state system**.

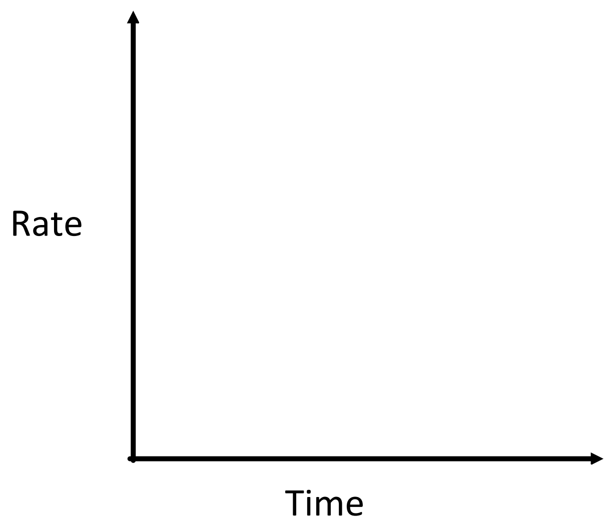
A factory with an assembly line is an example of a steady state system.

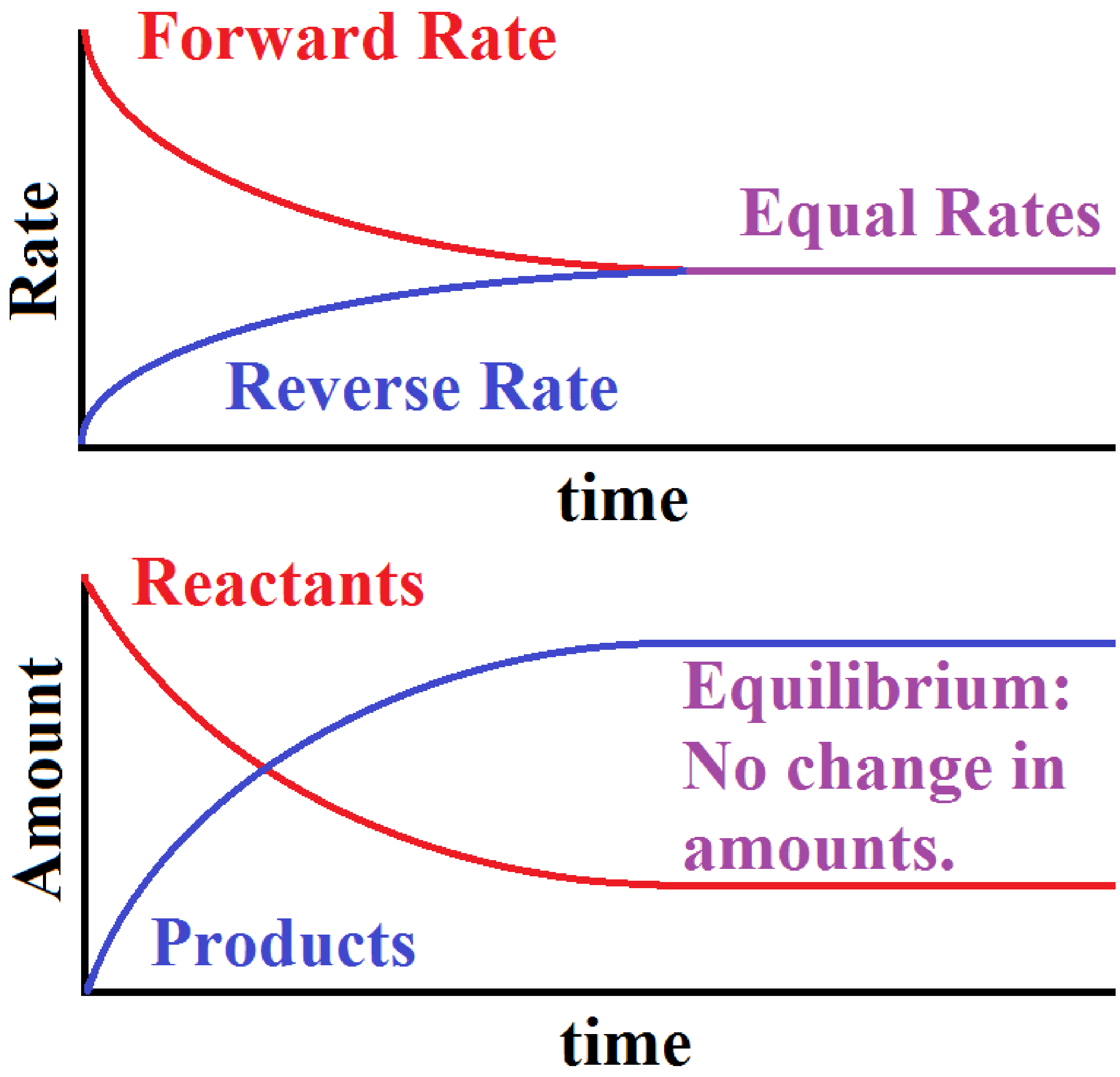
That is, raw materials are constantly being added to make products which are constantly being removed.

However, a steady state system is not equilibrium because the reverse reaction does not happen.

How does the rate of the forward reaction compare to the rate of the reverse reaction?

For example, $A + B \rightleftarrows C$





Important Definitions:

-**Steady State:** an open system where some properties are constant, but equilibrium does not exist. There is a constant feeding of reactants to maintain a constant removal of products.

-**Dynamic Equilibrium:** a system in which change is constantly occurring at the microscopic level, but there is no net change

-**Static State:** a system in which no obvious change is occurring at any level

5.1 - Reversible Reactions and Equilibrium

5.1 Assignment

1. Write reversible reactions for each of the following situations (be sure to balance your equations):

a. Hydrogen iodide gas (HI) decomposes into its elements.

b. Hydrogen and nitrogen gases combine to form ammonia gas, NH_3.

2. If the system represented by the following equation is found to be at equilibrium at a specific temperature, which of the following statements is true? Explain your answers.

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

a. All species must be present in the same concentration.

b. The rate of the forward reaction equals the rate of the reverse reaction.

c. We can measure continual changes in the reactant concentrations.

3. Which of the following are equilibrium systems and which are steady state systems?

a. A playing football team and a bench of reserve players. The number of players o the field is constant and the number of players on the bench is constant

b. A well fed tiger in a cage. The weight of the tiger is constant.

c. The Nipawin Dam and Codette Lake behind the dam. The water level is constant.

d. The liquid alcohol and alcohol vapor in a thermometer. The temperature is constant.

e. A block of wood floating on water

4. Which of the following are chemical equilibria and which are physical equilibria systems?

a. sublimation of dry ice (solid carbon dioxide)

b. a saturated magnesium chloride solution

c. the partial dissociation of 2 moles of HI molecules into 1 mole H_2 and 1 mole of I_2 molecules

5.1 - Reversible Reactions and Equilibrium

5. Which of the following reactions are reversible?

   a. the evaporation of water

   b. the combustion of coal

   c. the magnetization of an iron bar

6. A chemist wished to prepare pure phosgene ($COCl_{2(g)}$) by reacting carbon monoxide and chlorine gas accoridng to the reaction:

$$CO_{(g)} + Cl2_{(g)} \rightleftharpoons COCl_{2(g)}$$

Why will this reaction NOT produce pure phosgene? If the chemist could somehow obtain a sample of pure $COCl_{2(g)}$, would it remain pure? Why?

7. Read the following observations and then answer the questions.

- Two sealed glass tubes containing a mixture of a red–brown gas, $NO_2(g)$, and a colourless gas, $N_2O_4(g)$, are observed. The colour is an identical medium red–brown in each tube and there is no visible change in the colour of the contents as time passes.
- One tube is placed in a beaker of boiling water for a minute. The contents of the tube become much darker red–brown in colour. Upon first placing the tube in the hot water, the colour gets continually darker, but after a few seconds the colour stops changing.
- The second tube is placed in a beaker containing dry ice at –78°C. The colour quickly disappears and the contents of the tube remain colourless.
- The hot and cold tubes are taken out of their beakers, placed side by side and allowed to come to room temperature. The tubes have an identical medium red-brown colour when they both are at room temperature.

a) The gases are involved in the reversible reaction: $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$.
What evidence exists that the forward and reverse rates are equal at room temperature?

b) Can temperature changes affect an equilibrium reaction? How do you know this?

c) What evidence shows that the forward and reverse reaction rates are equal at 100°C? If the temperature were raised above 100°C, what would you expect to happen to the colour?

d) The balanced equation in part (a) should also include "energy". Consider what happened to the colour when a tube was heated. Is the reaction exothermic or endothermic, as written? Explain.

e) What gas was predominantly present at low temperatures? What gas was predominantly present at high temperatures? How would you describe the chemical composition in a tube when it was at room temperature?

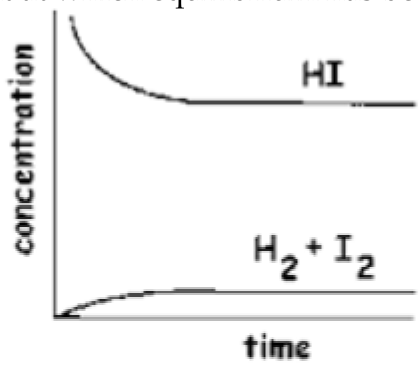
f) If one tube were filled with pure $NO_2(g)$ and another tube with pure $N_2O_4(g)$, what might be true of the colours you would expect to see in the tubes after they sit for a minute at the same temperature? What evidence do you have that your prediction should occur?

Name:______________

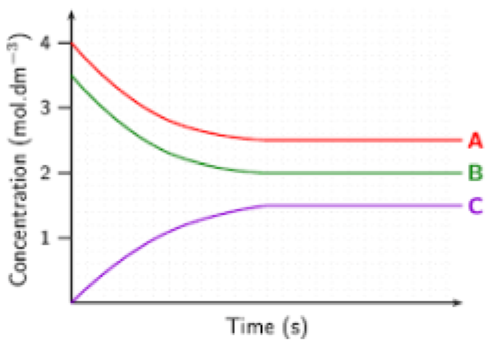
Unit 5 Hand-In Assignment #1 (5.1-5.3)

When using a formula (including keq), write down the formula then substitute values with units. Show all of your work. **Your answer must have the correct units and significant figures in all of your final answers.**

1. Below you can see two graphs that show the concentration of the reactants and products as a function of time. On each graph, draw a vertical line at the point at which equilibrium has been reached.



$\frac{\quad}{2}$ a.



b.

2. Write the equilibrium expression for each of the following reactions. If you are not given a chemical equation, you must first write out a balanced chemical equation. (4 marks)

a) $4\ HCl_{(aq)} + O_{2(g)} \rightleftarrows 2\ H_2O_{(g)} + 2\ Cl_{2\ (g)}$

$\frac{\quad}{2}$

b) $5\ Fe^{+2}_{(aq)} + MnO_4^{-}{}_{(aq)} + 8\ H^{+}_{(aq)} \rightleftarrows 5\ Fe^{+3}_{(aq)} + Mn^{+2}_{(aq)} + 4\ H_2O_{(l)}$

c) Bromine and fluorine participate in a synthesis reaction to produce gaseous bromine pentafluoride.

$\frac{\quad}{2}$

Name:_____________

3. For each of the following, state whether the value of the equilibrium constant favours the formation of reactants, products, or both sides equally. Explain, referencing the ratio of products to reactants, how you know.

a) $K_{eq} = 45.0$

$\overline{3}$

b) $K_{eq} = 1$

c) $K_{eq} = 2.1 \times 10^{-5}$

4. Molecular chlorine decomposes into atoms according to the reaction:

$Cl_{2\,(g)} \rightleftarrows 2\,Cl_{(g)}$

The equilibrium constant for the reaction at 25°C is 1.4×10^{-38}. Would many chlorine atoms be present at this temperature? How do you know?

$\overline{2}$

5. The following table give some values for reactant and product equilibrium concentrations for 700K for the Shift reaction, an important method for the commercial production of hydrogen gas:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)} + \text{heat}$$

Trial	[CO2]	[H2]	[CO]	[H2O]
1	0.600	0.600	0.266	0.266
2	0.600	0.800	0.330	0.286
3	2.00	2.00	0.887	0.887
4	1.00	1.50	0.450	0.655
5	1.80	2.00	0.590	1.20

$\overline{5}$

All concentrations are in moles per litre. Using the data **show that the ratio of the concentration of the products to that of the reactants, is a constant value at equilibrium.**

Name:______________

6. Calculate K_{eq} for the following. The concentration of species at equilibrium is shown below.

$H_{2(g)} + Cl_{2(g)} \rightleftarrows 2\ HCl_{(g)}$

$[H_2] = 1.0 \times 10^{-2}$ M

$[Cl_2] = 2.5 \times 10^{-2}$ M

$[HCl] = 3.0 \times 10^{-2}$ M

$\overline{}$ 3

7. The equilibrium constant for the equilibrium $CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$ is 302 at 600K. Show the keq expression for the reverse reaction then calculate <u>the value</u> of the equilibrium constant reaction at the same temperature.

$\overline{}$ 2

8. For the following reaction at equilibrium at 2000°C, the concentration of N_2 and O_2 are both 5.2 M.

$$N_{2(g)} + O_{2(g)} \rightleftarrows 2\ NO_{(g)} \qquad K_{eq} = 6.2 \times 10^{-4}$$

Calculate the concentration of NO at equilibrium.

$\overline{}$ 3

Name:_____________

9. Sulfur dioxide forms sulfur trioxide according to the following equation:

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

If initially $[SO_2]$ = 0.200 M and $[O_2]$ = 0.250 M, and at equilibrium $[SO_3]$ = 0.130 M, what is the equilibrium constant? All mole to mole ratios that are not 1:1 must be shown.

[Initial]			
[Change]			
[Equilibrium]			

$\overline{5}$

10. A certain amount of NO_2 was initially put into a 5.00 L flask. When equilibrium was attained according to the equation:
$2NO_{(g)} + O_{2(g)} \leftrightarrow 2NO_{2(g)}$,

The concentration of NO at equilibrium was 0.800 M. If K_{eq} for this system is 24.0, what was the initial concentration of the NO_2?

$\overline{6}$

[Initial]			
[Change]			
[Equilibrium]			

5.2 – Equilibrium Constant – K_{eq} – Worksheet

1. Write equilibrium expressions for the following reversible reactions:

a. $2\,NO_{2\,(g)} \leftrightarrow N_2O_{4\,(g)}$

$$Keq = \frac{[N_2O_4]}{[NO_2]^2}$$

b. $N_{2\,(g)} + 3\,H_{2\,(g)} \leftrightarrow 2\,NH_{3\,(g)}$

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

c. $H_2O_{(g)} + \cancel{C_{(s)}} \leftrightarrow H_{2(g)} + CO_{(g)}$

$$Keq = \frac{[H_2O]}{[H_2][CO]} \quad R$$

d. $2\,SO_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2\,SO_{3\,(g)}$

$$Keq = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

e. $\cancel{Cu_{(s)}} + 2Ag^{+}_{(aq)} \leftrightarrow Cu^{2+}_{(aq)} + \cancel{2Ag_{(s)}}$

$$Keq = \frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

2. For the equilibrium system described by $2\,SO_2\,(g) + O_2\,(g) \leftrightarrow 2\,SO_3\,(g)$ at a particular temperature the equilibrium concentrations of SO_2, O_2 and SO_3 were 0.75 M, 0.30 M, and 0.15 M, respectively. At the temperature of the equilibrium mixture, calculate the equilibrium constant, Keq, for the reaction.

$$Keq = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0.15M]^2}{(0.75M)^2(0.3M)} = \boxed{0.13}$$

5.2 – Equilibrium Constant – K_{eq} – Worksheet

3. For the equilibrium system described by: PCl_5 (g) ↔ PCl_3 (g) + Cl_2 (g) Keq equals 35 at 487°C. If the concentrations of the PCl_5 and PCl_3 are 0.015 M and 0.78 M, respectively, what is the concentration of the Cl_2?

$$K_{eq} = \frac{[PCl_3][Cl_2]}{[PCl_5]} \Rightarrow 35 = \frac{(0.78M)[Cl_2]}{(0.015M)}$$

$$[Cl_2] = 0.67M.$$

4. Find the concentration of the products for the following:

$\cancel{NH_4Cl}_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$ when $K_{eq} = 6.0 \times 10^{-9}$

$$K_{eq} = [NH_3][HCl]$$

$$6.0\times10^{-9} = (x)(x)$$

$$\sqrt{6.0\times10^{-9}} = x$$

$$x = 7.7\times10^{-5}M = [NH_3] = [HCl]$$

5. For the equilibrium reaction

$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$

the K_{eq} value at 690°C = 10.0. A reaction mixture is analyzed and found to contain 0.80M CO, 0.050M H_2O, 0.50M CO_2, and 0.40M H_2. Show that the reaction is not at equilibrium.

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.5M)(0.4M)}{(0.8M)(0.05M)} = 5$$

since $K_{eq} \neq 10$, it is not at equilibrium

6. For each of the following reactions, state whether the value of the equilibrium constant favours the formation of reactants or products.

a. $I_{2(g)} + Cl_{2(g)} \rightleftharpoons 2ICl_{(g)}$ $K_{eq} = 2\times10^6$ Products

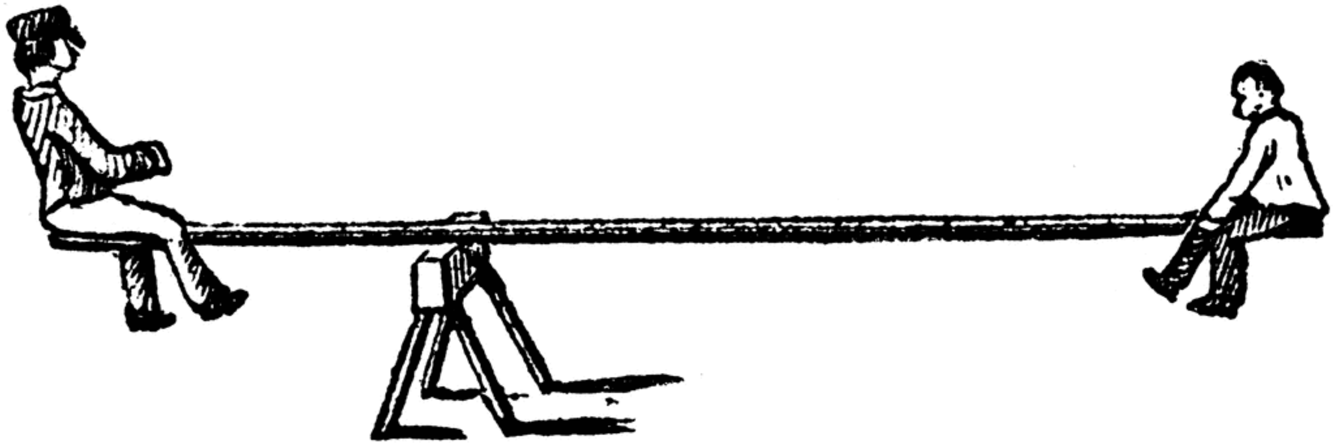
b. $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ $K_{eq} = 1.08$ Neither

c. $I_{2(g)} \rightleftharpoons I_{(g)} + I_{(g)}$ $K_{eq} = 3.8\times10^{-7}$ Reactants.

5.2 - Equilibrium Constant - K_{eq}

pages 562-568 Matter and Change

pages 531-539 Health Chemistry



-Some chemical systems have basically no reaction, while others readily go to completion. However, most chemical systems fall somewhere in between these two extremes.

-Given the following chemical reaction; predict the number of moles of product produced:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The Law of Chemical Equilibrium

-states that a chemical system may reach a point in which a particular ratio of reactant and product concentrations has a constant value called the equilibrium constant (K_{eq} or K_c)

For a general reaction,

$aA + bB \rightleftarrows cC + dD$

where a,b,c,d are balancing coefficients and A,B,C,D are substances, an equilibrium constant (K_{eq}) expression can be written as:

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

This mathematical relationship is true for all equilibrium systems.

Another term for this equation is the **mass-action expression**.

Ex) For the equilibrium reaction

$H_2 + I_2 \rightleftarrows 2\ HI$

find the equilibrium constant if $[H_2] = 0.022$ M, $[I_2] = 0.022$ M, and $[HI] = 0.156$ M.

Since K_{eq} is a constant for a reaction, it does not change unless the temperature of the system changes.

It does not matter on the initial concentrations used to reach equilibrium, just the concentrations **at equilibrium**.

For example, the following data was taken during an experiment with the equation $H_2 + I_2 \rightleftharpoons 2\ HI$ at equilibrium:

Trial	**[HI]**	**[H_2]**	**[I_2]**	**K_{eq}**
1	**0.156**	**0.0220**	**0.0220**	**50.3**
2	**0.750**	**0.106**	**0.106**	**50.1**
3	**1.00**	**0.820**	**0.0242**	**50.4**
4	**1.00**	**0.0242**	**0.820**	**50.4**
5	**1.56**	**0.220**	**0.220**	**50.3**

Note that for this reaction, K_{eq} is always the same (ignoring experimental error) irrespective of the concentration of A, B, C, and D you started with.

When calculating K_{eq} for a given reaction, we do **not** include substances in the liquid or solid phase.

This is because the concentrations of substances in these phases do not change, but are constant no matter how much you have.

So, only include gaseous and aqueous states when calculating K_{eq}.

Homogeneous and Hetergeneous Equilibria Constants

-**Homogeneous Equilibrium** refers to a system with all components in the same phase

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

Write the equilibrium expression for the above reaction:

-**Hetegeneous Equilibrium** refers to a system with components that exist is more than one physical state

ex: $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

Write the equilibrium expression for the above reaction:

What does K_{eq} tell us?

There are 3 situations:

i. If K_{eq} is very large:

The concentration of the products are much greater than the concentration of the reactants. This means that the reaction essentially 'goes to completion'. That is, all - or most of - the reactants are used up to form the products.

Equilibrium lies to the right.
-We will call a number greater than 10^{10} very large.

For example he decomposition of ozone, O_3
$2\,O_{3(g)} \rightleftarrows 3\,O_{2(g)}$ $K_{eq} = 2.0 \times 10^{57}$

ii. If K_{eq} is very small:

The concentration of the products are much smaller than the concentration of the reactants. This means the reaction does not occur to a great extent. That is, most of the reactants remain unchanged because only a few products are formed.

Equilibrium lies to the left.
-We will call a value less than 10^{-10} very small.

For example, The production of nitrogen monoxide

$N_{2(g)} + O_{2(g)} \rightleftarrows 2\,NO_{(g)}$ $K_{eq} = 1.0 \times 10^{-25}$

iii. If K_{eq} is neither very large or very small

This means that there significant amounts of both products and reactants formed at equilibrium.

We call values between 10^{-10} and 10^{10} neither very large or very small.

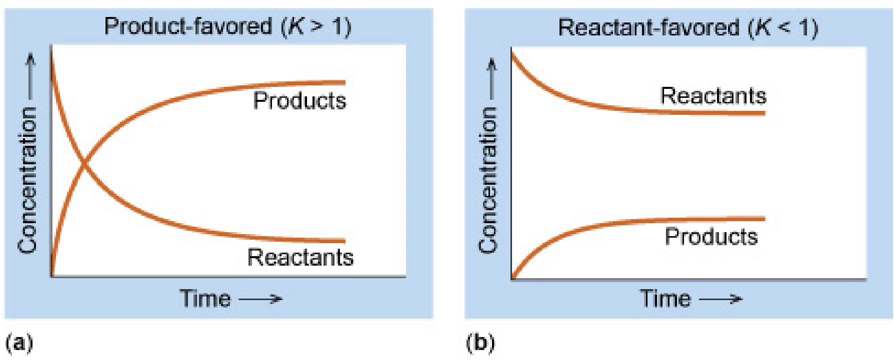
-K_{eq} >1: a bit more product at equilibrium

-K_{eq} >1: a bit more reactant at equilibrium

-K_{eq} =1: neither is favored

For example, the reaction of carbon monoxide and water

$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2\,(g)} + H_{2\,(g)}$ $K_{eq} = 5.09$ (at 700 K)



5.2 – Equilibrium Constant – K_{eq} – Assignment

1. Write equilibrium expressions for the following reversible reactions:

a. $2\ NO_{2\ (g)} \leftrightarrow N_2O_{4\ (g)}$

b. $N_{2\ (g)} + 3\ H_{2\ (g)} \leftrightarrow 2\ NH_{3\ (g)}$

c. $H_2O_{(g)} + C_{(s)} \leftrightarrow H_{2(g)} + CO_{(g)}$

d. $2\ SO_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ SO_{3\ (g)}$

e. $Cu_{(s)} + 2Ag^{+}_{(aq)} \leftrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

2. For the equilibrium system described by $2\ SO_2\ (g) + O_2\ (g) \leftrightarrow 2\ SO_3\ (g)$ at a particular temperature the equilibrium concentrations of SO_2, O_2 and SO_3 were 0.75 M, 0.30 M, and 0.15 M, respectively. At the temperature of the equilibrium mixture, calculate the equilibrium constant, Keq, for the reaction.

5.2 - Equilibrium Constant - Keq

5.2 – Equilibrium Constant – K_{eq} – Assignment

3. For the equilibrium system described by: PCl_5 (g) ↔ PCl_3 (g) + Cl_2 (g) Keq equals 35 at 487°C. If the concentrations of the PCl_5 and PCl_3 are 0.015 M and 0.78 M, respectively, what is the concentration of the Cl_2?

4. Find the concentration of the products for the following:

$NH4Cl_{(s)} \leftrightarrow NH_{3(g)} + HCl_{(g)}$ when $K_{eq} = 6.0 \times 10^{-9}$

5. For the equilibrium reaction

$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$

the K_{eq} value at 690˚C = 10.0. A reaction mixture is analyzed and found to contain 0.80M CO, 0.050M H_2O, 0.50M CO_2, and 0.40M H_2. Show that the reaction is not at equilibrium.

6. For each of the following reactions, state whether the value of the equilibrium constant favours the formation of reactants or products.

a. $I_{2(g)} + Cl_{2(g)} \rightleftharpoons 2ICl_{(g)}$ $\quad K_{eq} = 2 \times 10^6$

b. $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ $\quad K_{eq} = 1.08$

c. $I_{2(g)} \rightleftharpoons I_{(g)} + I_{(g)}$ $\quad K_{eq} = 3.8 \times 10^{-7}$

5.3 – ICE Box Problems – Assignment

1. For the reaction
   $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$
   The initial $[N_2]$ = 0.32 M and the initial $[H_2]$ = 0.66 M. At a certain temperature and pressure the equilibrium $[H_2]$ is found to be 0.30 M. What is K_{eq} under these circumstances?

	$[N_2]$	$[H_2]$	$[NH_3]$
[Initial]	0.32	0.66	0
[Change]	-0.12	-0.36	0.24
[Equilibrium]	0.20	0.3	0.24

$\frac{N_2}{1} = \frac{H_2}{3}$

$\frac{1 mol}{x} = \frac{3 mol}{0.36 M}$

$x = 0.12 M$

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{[0.24]^2}{[0.3]^3[0.2]} = \frac{0.0576}{(0.027)(0.2)}$$

$K_{eq} = 10.7$

$3 H_2 : 2 NH_3$

$0.36 : x$

$x = 0.24 M$

2. Suppose that 2.00 moles of HCl in a 1.00L glass flask slowly decomposes into H_2 and Cl_2. When equilibrium is reached, the concentrations of H_2 and Cl_2 are both 0.214 M. What is the K_{eq}?

	HCl	H_2	Cl_2
[Initial]	2.0	0	0
[Change]	-0.428	+.214	+0.214
[Equilibrium]	1.572	0.214	0.214

$2HCl \leftrightarrow H_2 + Cl_2$

HCl : H_2

$\frac{2 mol}{x} = \frac{1 mol}{0.214}$

$x = 0.428$

$$K_{eq} = \frac{[H_2][Cl_2]}{[HCl]^2} = \frac{[0.214][0.214]}{[1.572]^2}$$

$$= \frac{0.045796}{2.471184}$$

$$= 0.0185$$

$$= 1.85 \times 10^{-2}$$

$4NO \leftrightarrow 2N_2O + O_2$

3. Consider the equilibrium: $2N_2O(g) + O_2(g) \leftrightarrow 4NO(g)$ Keq for this rxn
3.00 moles of NO(g) are introduced into a 1.00-Liter evacuated flask. When the system comes to equilibrium, 1.00 mole of $N_2O(g)$ has formed. Determine the equilibrium concentrations of each substance. Calculate the K_c for the reaction based on these data.

	NO	N_2O	O_2
[Initial]	3.0	0	0
[Change]	-2.0	+1.0	+0.5M
[Equilibrium]	1.0	1.0	0.5M

NO : N_2O

$\frac{4 mol}{x} = \frac{2 mol}{1.0}$

x=2.0M

O_2 : N_2O

$\frac{1 mol}{x} = \frac{2 mol}{1.0}$

x = 0.5M

$$Keq = \frac{[NO]^4}{[N_2O]^2[O_2]}$$

$$= \frac{[1.0]^4}{[1.0]^2[0.5]} = \boxed{2.00}$$

4. At some temperature, $K_{eq} = 33$ for the reaction $H_2 + I_2 \rightarrow 2HI$. If initially, $[H_2]$ = .0600 M and $[I_2]$ = .0300 M, what are all three equilibrium concentrations?

	H_2	I_2	HI
[Initial]	0.06	0.03	0
[Change]	-x	-x	+2x
[Equilibrium]	0.06-x	0.03-x	2x

Eq:
$[H_2] = 0.06 - 0.0273 = 0.0327M$
$[I_2] = 0.03 - 0.0273 = 0.0027M$
$[HI] = 2(0.0273) = 0.0546M$

Keq = 33

$$Keq = \frac{[HI]^2}{[H_2][I_2]} = \frac{[2x]^2}{(0.06-x)(0.03-x)} = \frac{4x^2}{0.0018 - 0.06x - 0.03x + x^2}$$

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

$$33 = \frac{4x^2}{0.0018 - 0.09x + x^2} \Rightarrow 33(0.0018 - 0.09x + x^2) = 4x^2$$

$0.0594 - 2.97x + 33x^2 = 4x^2$
$0.0594 - 2.97x + 29x^2 = 0$
C B A

$$x = \frac{-(2.97) \pm \sqrt{(2.97^2) - 4(0.0594)(29)}}{2(29)}$$

$$x = \frac{2.97 \pm \sqrt{1.9305}}{58}$$

x = 0.0752 or 0.0273

5. Graphite (solid carbon) and carbon dioxide are kept at constant pressure at 1000 K until the following reaction reaches equilibrium.

$C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}$

If $K_{eq} = 0.021$, calculate the equilibrium concentration of CO if the concentration of CO_2 was initially 0.012 M.

$K_{eq} = 0.021$

	C	CO_2	CO
[Initial]		0.012	0
[Change]		-x	+2x
[Equilibrium]		0.012-x	2x ?

$K_{eq} = \frac{[CO]^2}{[CO_2]} = \frac{(2x)^2}{(0.012-x)}$

$0.021 = \frac{4x^2}{0.012-x}$

$(0.021)(0.012-x) = 4x^2$

$\underset{C}{0.000252} - \underset{B}{0.021x} - \underset{A}{4x^2} = 0$

$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{-(0.021) \pm \sqrt{(0.021)^2 - 4(-4)(0.000252)}}{2(-4)}$

$x = \frac{0.021 \pm \sqrt{0.004423}}{-8}$

$x = \frac{0.021 \pm 0.06688049}{-8}$

$\Rightarrow \frac{-0.04588}{-8} = \boxed{0.005735}$

$\Rightarrow \frac{0.08788}{-8} = -\cancel{0.01099}$

$[CO] = 2x$

$= 2(0.005735M)$

$\boxed{[CO] = 0.011 M}$

5.3 - ICE Box Problems

As we already know, a chemical equation tells us several pieces of information.

$$H_2 + I_2 \leftrightarrow 2HI$$

This equation tells us how the number of molecules or moles of each substance relate to each other by looking at the balancing coefficients.

The balancing coefficients also tell us how the concentration of each substance changes as a reaction goes on.

For example, if $[H_2]$ changes by x mols/L, then $[I_2]$ changes by x mols/L, and [HI] changes by 2x mols/L.

However, $[H_2]$ and $[I_2]$ are decreasing while [HI] is increasing. Thus, we say that $\Delta[H_2] = \Delta[I_2] = -x$, and the $\Delta[HI] = 2x$.

Note that the negatives mean decrease (or losing) and a positive value means gaining.

This knowledge of changing concentrations is key for an **ICE box problem**. The ICE is an acronym for:

I - Initial concentration
C - Change in concentration
E - Equilibrium concentration

An ICE box problem deals with initial concentrations **not** at equilibrium. Time passes, and equilibrium is eventually reached with new concentrations kept in check by the equilibrium constant.

You can use an ICE box in any problem where you know some, but not all, equilibrium concentrations

5.3 - ICE Box Problems

The following process can be used to solve an ICE box problem for a general reaction: A + B $\leftrightarrow$ C

1. Balance the equation.
2. Set up the ICE box:

	[A]	[B]	[C]
[Initial]			
[Change]			
[Equilibrium]			

3. Use information from the question to plug values into the ICE box. It is the bottom row that we really want to use; the other rows in the table just help get us there

Some hints you may want to consider:

i. Initially, you should have no product for the forward reaction.

ii. Balanced coefficients (mole to mole ratios) can help you determine unknown values in the "C" column.

iii. E = I - C

Ex) Ammonia is created by the following process:

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

If the initially $[N_2]$ = 0.96 M and $[H_2]$ = 0.72 M, and at equilibrium $[NH_3]$ = 0.24 M what is the equilibrium constant?

[Inial]			
[Change]			
[Equilibrium]			

•

iii. If K_{eq} is known, but you **do not** know [product] then let one of the changes in equilibrium equal x to solve for the missing concentrations at equilibrium.

Ex) Initially, for the reaction below, $[H_2] = [I_2] = 0.200$ M.

$H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$

Calculate all three equilibrium concentrations if $K_{eq} = 64.0$.

[Inial]			
[Change]			
[Equilibrium]			

•

This situation may involve the quadratic formula if you come across a quadratic equation of the for ax ^{2}+ bx + c:

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

Ex) Given this equation,

$PCl_{3(g)} + Cl_{2(g)} \leftrightarrow PCl_{5(g)}$

Calculate all three equilibrium concentrations if initially $[PCl_5]$ = 1.00 M and K_{eq} = 16.0.

[Inial]			
[Change]			
[Equilibrium]			

•

5.3 – ICE Box Problems – Assignment

1. For the reaction
   $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$
   The initial $[N_2]$ = 0.32 M and the initial $[H_2]$ = 0.66 M. At a certain temperature and pressure the equilibrium $[H_2]$ is found to be 0.30 M. What is K_{eq} under these circumstances?

[Initial]			
[Change]			
[Equilibrium]			

2. Suppose that 2.00 moles of HCl in a 1.00L glass flask slowly decomposes into H_2 and Cl_2. When equilibrium is reached, the concentrations of H_2 and Cl_2 are both 0.214 M. What is the K_{eq}?

[Initial]			
[Change]			
[Equilibrium]			

•

5.3 - ICE Box Problems

3. Consider the equilibrium: $2N_2O(g) + O_2(g) \leftrightarrow 4NO(g)$
   3.00 moles of NO(g) are introduced into a 1.00-Liter evacuated flask. When the system comes to equilibrium, 1.00 mole of $N_2O(g)$ has formed. Determine the equilibrium concentrations of each substance. Calculate the K_c for the reaction based on these data.

[Initial]			
[Change]			
[Equilibrium]			

4. At some temperature, $K_{eq} = 33$ for the reaction $H_2 + I_2 \rightarrow 2HI$. If initially, $[H_2] = .0600$ M and $[I_2] = .0300$ M, what are all three equilibrium concentrations?

[Initial]			
[Change]			
[Equilibrium]			

•

5. Graphite (solid carbon) and carbon dioxide are kept at constant pressure at 1000 K until the following reaction reaches equilibrium.

   $C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)}$

   If K_{eq} = 0.021, calculate the equilibrium concentration of CO if the concentration of CO_2 was initially 0.012 M.

[Initial]			
[Change]			
[Equilibrium]			

•

5.4 – Special K's – Equilibrium Solubility - Assignment

1. Write the balanced equation and the solubility product constant expression, K_{sp}, for the each of the following dissociation reactions. All compounds are solids. One has been given as an example.

Reminders
- ion charges MUST BE included.
- solids (and liquids) are NOT included in the equilibrium expression
- don't forget to include exponents when needed
- polyatomic ions (e.g. CO_3^-) do not break apart

Compound	Equation	Ksp
$(NH_4)_2S$	$(NH_4)_2O\ (s) \rightleftharpoons 2\ NH_4^+(aq) + S^{2-}(aq)$	$K_{sp} = [NH_4^+]^2[S^{2-}]$
CaS	$CaS_{(s)} \rightleftharpoons Ca^{2+}_{(aq)} + S^{2-}_{(aq)}$	$Ksp = [Ca^{2+}][S^{2-}]$
K_2SO_4	$K_2SO_{4(s)} \rightleftharpoons 2K^+_{(aq)} + SO_4^{2-}{}_{(aq)}$	$Ksp = [K^+]^2[SO_4^{2-}]$
$Mg(OH)_2$	$Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$	$Ksp = [Mg^{2+}][OH^-]^2$

2. Organize the following salts in order of solubility (highest to lowest):

AgCl; $K_{sp} = 1.8 \times 10^{-10}$ AgI; $K_{sp} = 8.5 \times 10^{-17}$ AgBr; $K_{sp} = 5.4 \times 10^{-13}$

AgCl, AgBr, AgI

3. Calculate K_{sp} for a saturated nickel(II) sulfide, NiS, solution with a solubility of 3.27×10^{-11}. Calculate the K_{sp}.

$$NiS_{(s)} \rightleftharpoons Ni^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$3.27\times10^{-11}\,M \longrightarrow$

$$Ksp = [Ni^{2+}][S^{2-}] = (3.27\times10^{-11}M)(3.27\times10^{-11}M)$$

$$Ksp = 1.07\times10^{-21}$$

4. Calculate the concentration of ions in a saturated solution of $CaCO_3$ in water at 25°C. K_{sp} for $CaCO_3$ is 4.8×10^{-9}.

$$CaCO_3 \rightleftharpoons Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$$[Ca^{2+}] = [CO_3^{2-}] = x$$

$$\underset{Ksp}{4.8\times10^{-9}} = [Ca^{2+}][CO_3^{2-}]$$

$$\sqrt{4.8\times10^{-9}} = \sqrt{x^2}$$

$$\boxed{x = 6.93\times10^{-5}M}$$

5.4 - Special K's - Solubility Equilibrium

5. Calculate the concentrations of ions at 25°C for a saturated solution of silver bromate (Ksp = 5.3 x 10^{-5}).

$AgBrO_3 \rightleftharpoons Ag^+_{(aq)} + BrO_3^-{}_{(aq)}$ let $x = [Ag^+] = [BrO_3^-]$

$Ksp = [Ag^+][BrO_3^-] = (x)(x)$

$5.3 \times 10^{-5} = x^2$

$x = 0.0073M$ $\therefore [Ag^+] = [BrO_3^-] = 0.0073M$.

6. At 25°C, 0.0024 g of $Ce(OH)_3$ is contained in a 2.5 L solution. Calculate K_{sp}.

$C = \frac{wt}{mm \cdot V} = \frac{0.0024g}{(191.15\frac{g}{mol})(2.5L)} = 5.0 \times 10^{-6} M$

$Ce(OH)_{3(s)} \rightleftharpoons Ce^{3+}_{(aq)} + 3OH^-_{(aq)}$

$[Ce^{3+}] = 5.0 \times 10^{-6} M$

$[OH^-] = 3(5.0 \times 10^{-6} M) = 1.5 \times 10^{-5} M$

$Ksp = [Ce^{3+}][OH^-]^3 = (5.0 \times 10^{-6})(1.5 \times 10^{-5})^3$

$\boxed{Ksp = 1.7 \times 10^{-20}}$

7. What is the mass of calcium fluoride present in a saturated 1.5 L solution?

$Ksp = 3.9 \times 10^{-11}$

$CaF_2 \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$ let $x = [Ca^{2+}]$ $\therefore 2x = [F^-]$

$Ksp = [Ca^{2+}][F^-]^2 = (x)(2x)^2$

$3.9 \times 10^{-11} = 4x^3$

$9.75 \times 10^{-12} = x^3$

$x = 2.1 \times 10^{-4} M = [Ca^{2+}] = [CaF_2]$

$wt = C \cdot mm \cdot V$
$= (2.1 \times 10^{-4})(78.076\frac{g}{mol})(1.5L)$
$\boxed{= 0.025g}$

Final Volume = 900mL

8. 400.0 mL of 4.00 x 10^{-10} M $Al(NO_3)_3$ is mixed with 500.0 mL of 3.00 x 10^{-7} M NaOH. If K_{sp} for $Al(OH)_3$ is 5.00 x 10^{-33} at this temperature, will there be a precipitate?

$Al(OH)_3 \rightleftharpoons Al^{3+}_{(aq)} + 3OH^-_{(aq)}$

$Al(NO_3)_3 \rightarrow M_1V_1 = M_2V_2$

$(4.0 \times 10^{-10})(0.4) = M_2(0.9)$

$M_2 = 1.78 \times 10^{-10} M = [Al^{3+}]$

$NaOH \rightarrow M_1V_1 = M_2V_2$

$(3.0 \times 10^{-7})(0.5) = M_2(0.9)$

$M_2 = 1.67 \times 10^{-7} M = [OH^-]$

$Q = [Al^{3+}][OH^-]^3 = (1.78 \times 10^{-10})(1.67 \times 10^{-7})^3 = 8.29 \times 10^{-31}$

$Q > Ksp$ $\therefore$ yes.

$K_{sp} = 2.0 \times 10^{-4}$

9. Will a precipitate form if 20.0 mL of 0.0100 M $CaCl_2$ are mixed with 20.0 mL of 0.00800 M Na_2SO_4 at 25.0 °C?

$CaCl_2 + Na_2SO_4 \rightarrow NaCl_{(aq)} + CaSO_{4(s)}$

$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$CaCl_2 : M_1V_1 = M_2V_2$

$(0.01M)(0.02L) = M_2(0.04L)$

$M_2 = 0.005M = [Ca^{2+}]$

$Na_2SO_4 : (0.008M)(0.02L) = M_2(0.04L)$

$M_2 = 0.004M = [SO_4^{2-}]$

$Q = [Ca^{2+}][SO_4^{2-}] = (0.005M)(0.004M)$

$Q = 2.00 \times 10^{-5}$

$\boxed{Q < K_{sp} \therefore NO}$

10. Will a precipitate form if 40.0 mL of 8.0×10^{-3} M $Mg(NO_3)_2$ are mixed with 60.0 mL of 1.00×10^{-2} M K_2CO_3? (K_{sp} for $MgCO_3 = 2.60 \times 10^{-5}$)

removed

removed

~~$Q < K_{sp} \therefore NO$~~

~~$Q = 2.00 \times 10^{-5}$~~

11. Will a precipitate form if 25 mL of 4.0×10^{-3} M $AgNO_3$ are mixed with 75 mL of 2.0×10^{-4} M Na_2CrO_4 at 25.0 °C?

$K_{sp} = 1.1 \times 10^{-12}$

$AgNO_3 + Na_2CrO_4 \rightarrow NaNO_3 + Ag_2CrO_4$

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$

$M_1V_1 = M_2V_2$

$AgNO_3 : (4.0 \times 10^{-3})(0.025L) = M_2(0.1L)$

$M_2 = 0.001M = [Ag^+]$

$Na_2CrO_4 : (2.0 \times 10^{-4})(0.075L) = M_2(0.1L)$

$M_2 = 1.5 \times 10^{-4}M = [CrO_4^{2-}]$

$Q = [Ag^+]^2[CrO_4^{2-}] = (0.001)^2(1.5 \times 10^{-4}M)$

$= 1.5 \times 10^{-10}$

$\boxed{Q > K_{sp} \therefore yes}$

12. What is the maximum $[Sr^{2+}]$ that can be dissolved in a 0.020 M solution of K_2SO_4 without precipitating $SrSO_4$? (K_{sp} of $SrSO_4 = 7.6 \times 10^{-7}$)

$SrSO_{4(s)} \rightleftharpoons Sr^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

$K_{sp} = [Sr^{2+}][SO_4^{2-}]$

$7.6 \times 10^{-7} = x\ (0.020M)$

$\boxed{x = 3.8 \times 10^{-5}M}$

5.4 - Special K's - Solubility Equilibrium

pages 545-553 in Health

Table 13 in resource package

5.4 - Special K's - Solubility Equilibrium

Since saturated solutions are equilibrium systems, we can apply the equilibrium constant expression to solutions.

Since a solution is a special kind of equilibrium, we will be dealing with a special kind of equilibrium constant, denoted K_{sp}. The sp stands for 'solubility product'.

Recall that in a solution, we often deal with aqueous ions. Therefore, dissociation will need to be used.

For example, consider a saturated silver sulfate solution:

$$Ag_2SO_{4(s)} \rightleftarrows 2Ag^+_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Since solids and liquids are not involved in an K_{eq} calculation,

$$K_{eq} = [Ag^+]^2\,[SO_4^{2-}]$$

This equation only contains the products of a solution. Therefore, it is a special equilibrium constant that shows up a lot in chemistry.

$$K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$$

Note that we **must** include the charges on the ions in this expression. Ag is different from Ag^+.

Note that unless otherwise indicated, K_{sp} calculations will always involve dissolving a solid to produce aqueous ions.

Also note that if you compare two K_{sp}'s together, the larger one will indicate a more soluble salt since the products will be favored. Therefore, a smaller K_{sp} indicates a less soluble salt because the reactants will be favored.

Ex) Write the solubility product constant expression for $Ca_3(PO_4)_2$.

Ex) The concentration of lead ions in a saturated solution of PbI_2 at 25°C is 1.3×10^{-3} M. What is the solubility product constant?

Ex) The K_{sp} for $MgCO_3$ at 25°C is 2.0×10^{-8}. What are the ion concentrations in a saturated solution at this temperature?

Ex) Calculate the solubility for silver chromate in a saturated solution at 25°C. $K_{sp} = 1.1 \times 10^{-12}$.

5.4 - Special K's - Solubility Equilibrium

Recall from Unit 4 that the *solubility* of a substance is the maximum concentration a substance can have in water to make a saturated solution.

Even 'insoluble' substances will dissolve slightly. However, the amount that actually dissolves has such a small concentration that we say that the substance is insoluble (less than 0.1M).

Also recall that we learned how to use a solubility table to determine whether or not a precipitate would form during a double displacement reaction. When doing those predictions, we **assumed** that the concentration of the 'insoluble' substance was great enough that it would accumulate at the bottom of the solution.

However, we could run into a situation where this 'insoluble' substance forms in such a small amount that the water is able to hold it. Therefore, no solid would form.

Remember that equilibrium systems involving solutions are **saturated**. Therefore, K_{sp} values are related to **saturated** solutions. If a solution is unsaturated then more substance can dissolve. If a solution is supersaturated then a solid should form at the bottom of the solution.

So, when we are trying to determine whether or not a precipitate will form when two ions meet each other, we need to determine the level of saturation. We can do this by comparing a **trial K_{sp}** to the **actual K_{sp}**.

The trial K_{sp} can be denoted as Q.

Q can be thought of as '**what we have**' and K_{sp} is '**what we need for saturation**'.

There are three situations that can happen when we compare Q to K_{sp}:

1. $Q < K_{sp}$

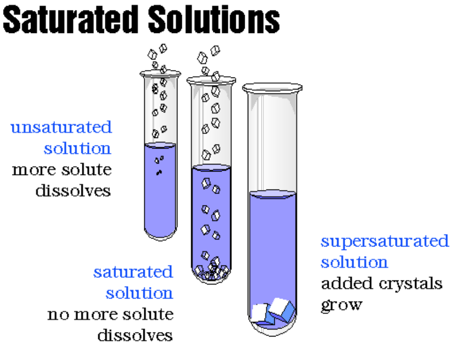
This means that 'what we have' is less than 'what we need'. Therefore, this represents an unsaturated solution and **no precipitate will form.**

2. $Q = K_{sp}$

This means 'what we have' is equal to 'what we need'. Therefore, this represents a saturated solution and **no precipitate will form.**

3. $Q > K_{sp}$

This means 'what we have' is more than 'what we need'. Therefore, this represents a supersaturated solution and **a precipitate will form.**



5.4 - Special K's - Solubility Equilibrium

What if I mix two substances together?.... they dilute each other.

This dilution must be considered when deciding on whether a precipitate will form (remember determining ion concentration from Unit 4...)

Steps:

1. Decide if any possible precipitates can form from the two substances being mixed using a solubility table.

   Write the net ionic equation for this substance to determine what the trial K_{sp} expression is.

2. Calculate the dilution of **both** substances present. Note that the final volume will be the sum of the volumes of both substances ($M_1V_1=M_2V_2$).

   Then, calculate the concentrations of the **ions** that make up your possible precipitate.

3. Using the concentrations of the **ions** above, calculate the trial K_{sp} and compare it to the actual K

Ex) 25.0 mL of 0.00200 M of potassium chromate are mixed with 75.0 mL of 0.000125 M of lead (II) nitrate. Will a precipitate form if K_{sp} of lead (II) chromate is 1.8×10^{-14}?

Ex) If 25.0 mL of 4.50×10^{-3} M $Pb(NO_3)_2$ is mixed with 35.0 mL of 2.80×10^{-3} M MgI_2, will a precipitate form?

•

-We can also use the K_{sp} to determine the maximum concentration of an ion which can exist in solution with another ion without precipitation

Ex) Water hardness is caused by the presence of Ca^{2+} and Mg^{2+} ions. One way of removing these ions is to add washing soda (sodium carbonate Na_2CO_3) which causes the precipitation of $CaCO_3$ and $MgCO_3$. If 5.0L of water has $[Ca^{2+}]$ of 0.0040M, calculate the maximum mass of Na_2CO_3 which can be added without causing any precipitate to form. K_{sp} for $CaCO_3$ = 4.8 x 10-9

•

5.4 - Special K's - Solubility Equilibrium

5.4 – Special K's – Equilibrium Solubility - Assignment

1. Write the balanced equation and the solubility product constant expression, K_{sp}, for the each of the following dissociation reactions. All compounds are solids. One has been given as an example.

Reminders – ion charges MUST BE included.

– solids (and liquids) are NOT included in the equilibrium expression

– don't forget to include exponents when needed

– polyatomic ions (e.g. CO_3^-) do not break apart

Compound	Equation	Ksp
$(NH_4)_2S$	$(NH_4)_2O\ (s) \rightleftarrows 2\ NH_4^+(aq) + S^{2-}(aq)$	$K_{sp} = [NH_4^+]^2[S^{2-}]$
CaS		
K_2SO_4		
$Mg(OH)_2$		

2. Organize the following salts in order of solubility (highest to lowest):

AgCl; $K_{sp} = 1.8 \times 10^{-10}$ AgI; $K_{sp} = 8.5 \times 10^{-17}$ AgBr; $K_{sp} = 5.4 \times 10^{-13}$

3. Calculate K_{sp} for a saturated nickel(II) sulfide, NiS, solution with a solubility of 3.27×10^{-11}. Calculate the K_{sp}.

4. Calculate the concentration of ions in a saturated solution of $CaCO_3$ in water at 25°C. K_{sp} for $CaCO_3$ is 4.8×10^{-9}.

5.4 - Special K's - Solubility Equilibrium

5. Calculate the concentrations of ions at 25°C for a saturated solution of silver bromate (Ksp = 5.3×10^{-5}).

6. At 25°C, 0.0024 g of $Ce(OH)_3$ is contained in a 2.5 L solution. Calculate K_{sp}.

7. What is the mass of calcium fluoride present in a saturated 1.5 L solution?

8. 400.0 mL of 4.00×10^{-10} M $Al(NO_3)_3$ is mixed with 500.0 mL of 3.00×10^{-7} M NaOH. If K_{sp} for $Al(OH)_3$ is 5.00×10^{-33} at this temperature, will there be a precipitate?

5.4 - Special K's - Solubility Equilibrium

9. Will a precipitate form if 20.0 mL of 0.0100 M $CaCl_2$ are mixed with 20.0 mL of 0.00800 M Na_2SO_4 at 25.0 ˚

10. Will a precipitate form if 25 mL of 4.0 x 10^{-3} M $AgNO_3$ are mixed with 75 mL of 2.0 x 10^{-4} M Na_2CrO_4 at 25.0 ˚C?

11. What is the maximum [Sr^{2+}] that can be dissolved in a 0.020 M solution of K_2SO_4 without precipitating $SrSO_4$? (K_{sp} of $SrSO_4$ = 7.6 x 10^{-7})

Name:______________________ **School:** ___________________

Unit 5 Hand In Assignment #2

This assignment covers sections 5.4 and 5.5

For all K_{sp} calculations, the dissociation equation with <u>*states and charges*</u> *must be shown. You do not have to show calculations to find the concentrations of ions; however, you may want to.*

1. Write the dissociation equation and the solubility product expression for the following:
   a) $LiBr_{(s)}$ (2 marks)

   b) Magnesium Phosphate (2 marks)

2. At a certain temperature a saturated solution of BaF_2 has a concentration of 4.59×10^{-2} M. What is the K_{sp} for BaF_2 at this temperature? (3 marks)

3. What is the concentration of the ions present in a saturated $Cd(OH)_2$ solution? $K_{sp} = 5.3 \times 10^{-15}$. (4 marks)

Name:______________________ **School:** ___________________

4. What mass of CuI is present in a 1.2 L saturated solution at 25°C? Ksp = 1.3×10^{-12} (5 marks)

5. Will a precipitate form when 125 mL of 4.0×10^{-2} M of $CaCl_2$ is added to 175 mL of 2.9×10^{-2} M of NaOH? K_{sp} of $Ca(OH)_2 = 4.8 \times 10^{-6}$. Show the dissociation equation for the possible precipitate and all formulas. (10 marks)

Name:______________________ **School:** ___________________

6. The pressure on each of the following systems is increased by decreasing the volume of the container. Explain whether each system would shift left, right, or stay the same.

a. $2\ SO_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2\ SO_{3\,(g)}$ (1 mark)

b. $H_{2\,(g)} + I_{2\,(g)} \leftrightarrow 2\ HI_{(g)}$ (1 mark)

c. $CaCO_{3\,(s)} \leftrightarrow CaO_{(s)} + CO_{2\,(g)}$ (1 mark)

d. $AgCl_{(s)} \leftrightarrow Ag^{1+}{}_{(aq)} + Cl^{1-}{}_{(aq)}$ (1 mark)

7. How could you alter the following to make the equilibrium below shift to the left:

$$2CO_{(g)} + O_{2(g)} \longleftrightarrow 2CO_{2(g)} + 566\ kJ$$

a) [CO] (1 mark)

b) pressure(1 mark)

c) temperature(1 mark)

Name:______________________ **School:** ___________________

8. Given the following equilibrium reaction:

$2\ C_{(s)} + O_{2\ (g)} \leftrightarrow 2\ CO_{(g)}$

what will be the effect of the following disturbances to the system? That is, will it shift to the left or the right? Also mention the effect on the **other participants** in the reaction for a, b, and c.

   a. adding CO (2 marks)

   b. addition of O_2(2 marks)

   c. addition of $C_{(s)}$ (2 marks)

9. Use Le Châtelier's Principle to predict how the changes listed will affect the following equilibrium reaction:

$$2\ HI(g) + 9.4\ kJ \leftrightarrow H_2\ (g) + I_2\ (g)$$

a. Will the concentration of HI increase, decrease, or remain the same if more H_2 is added? (1 mark)

b. What is the effect on the concentration of HI if the pressure of the system is increased? (1 mark)

c. What is the effect on the concentration of HI if the temperature of the system is increased? (1 mark)

d. What is the effect on the concentration of HI if a catalyst is added to the system? (1 mark)

e. Write the equilibrium constant expression for this reaction. (1 mark)

Name:______________________ **School:** ___________________

10. Changing the volume of the system alters the equilibrium position of this equilibrium:

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

    But a similar change has no effect on this equilibrium:

    $H_{2(g)} + Cl_{2(g)} \qquad 2HCl_{(g)}$

    Explain. (2 marks)

5.5 La Chatelier's Principle Assignment

1. For the following system at equilibrium:

$H_{2\,(g)} + Br_{2\,(g)} \leftrightarrow 2\,HBr_{\,(g)} + 36.4\text{ kJ}$

a. Predict the shift in equilibrium when more $HBr_{(g)}$ is added to the system.

↑P = shifts left to make more reactant.

b. How will a temperature increase shift equilibrium?

↑ temp = shifts left to use up extra heat

2. For the reaction below, predict the direction the equilibrium will shift given the following changes. Temperature and volume are held constant.

$2\,NO_{2\,(g)} + 7\,H_{2\,(g)} + \text{energy} \leftrightarrow 2\,NH_{3\,(g)} + 4\,H_2O_{(g)}$

a. addition of ammonia → shifts left
b. removal of nitrogen dioxide → shifts left
c. decrease the temperature → shifts to left
d. removal of water vapour → shifts to right
e. addition of hydrogen → shifts to right

3. At a particular temperature, the following reaction has an equilibrium constant, K_{eq} of 0.18

$PCl_{3\,(g)} + Cl_{2\,(g)} + 87.9\text{ kJ} \leftrightarrow PCl_{5\,(g)}$

a) If more PCl_3 is added to the system. Will the value of K_{eq} increase, decrease, or remain the same? remain the same.

b) How would the equilibrium shift if a catalyst is introduced? No change.

c) Explain how you can shift the equilibrium to the products by separately altering the concentration of one of the substances, the temperature, or the pressure.

↑ temp ; remove PCl_5; add Cl_2 or PCl_3 ; ↑ Pressure

4. For the following reactions, how will equilibrium shift for an increase in pressure?

a) $H_{2(g)} + Cl_{2(g)} \leftrightarrow 2HCl_{(g)}$ – no shift
2 2

b) $PCl_{3\,(g)} + Cl_{2\,(g)} \leftrightarrow PCl_{5\,(g)}$ – shift right
2 1

5. For the following reactions, how will equilibrium shift if the pressure is decreased?
   a) $CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3H_2$ shift right

   b) $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ shift left

6. Methyl alcohol is produced according to the equation:
   $CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(g)} + heat$
   Predict the effect on the equilibrium species distribution if there was an increase in:
   a) Temperature
   shift left

   b) Pressure shift right

7. List three ways that the following equilibrium reaction could be forced to shift to the right:
   $2NO_{2(g)} \leftrightarrow 2NO_{(g)} + O_{2(g)}$
   2 3

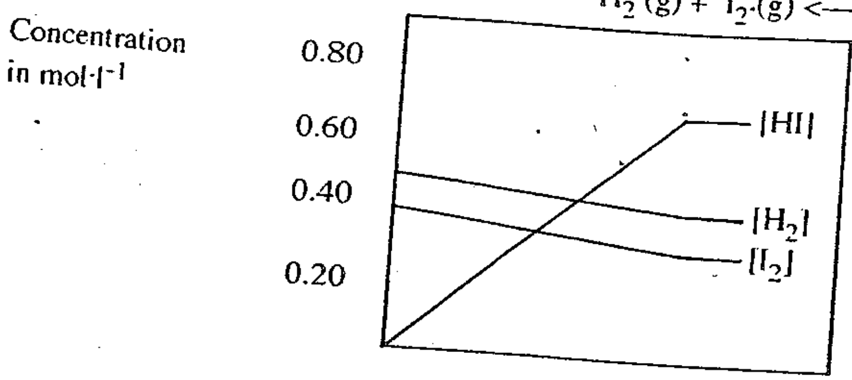
- ↓ Pressure
- ↓ products
- ↑ reactants

9. In each of the following equilibria, would you increase or decrease the temperature to force the reaction in the forward direction?
   c) $H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)}$ $\Delta H = +41kJ$ ↑ temp b/c endo

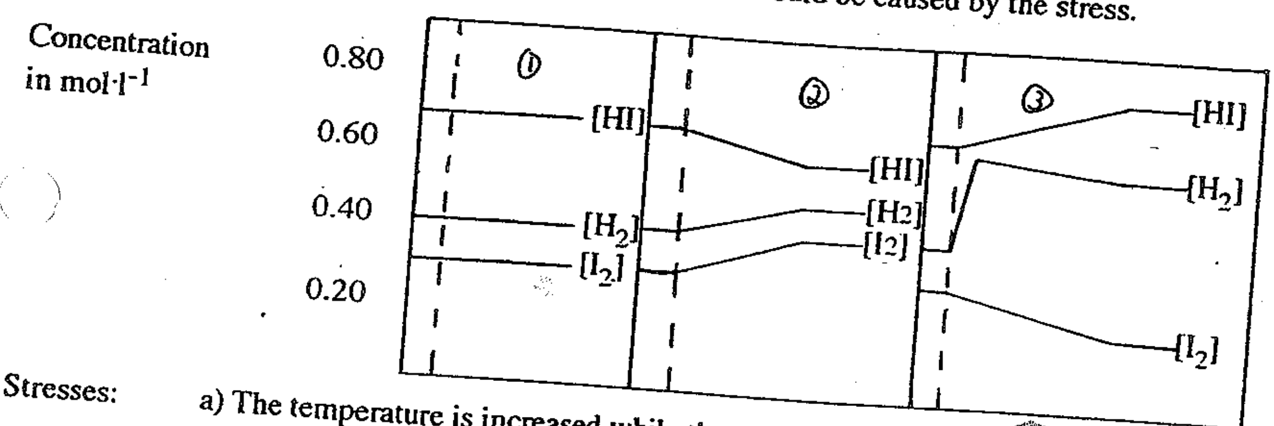
   d) $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$ $\Delta H = -198kJ$ ↓ temp b/c exo

The following graph show how the concentration of the reactants and product changes until equilibrium is established for the reactions: $H_2\,(g) + I_2\,(g) \longleftrightarrow 2\,HI\,(g) + 12.6\,J$

exo



The following graphs begin with the system at equilibrium and then have a stress applied. Select whether graph 1, 2 or 3 best represents the change that would be caused by the stress.



Stresses:

a) The temperature is increased while the pressure is constant. 2

b) The temperature and pressure are increased. 2

c) Some hydrogen gas is added. 3

d) The pressure is increased while the temperature is constant. 1

e) A catalyst is added. 1

5.5 Answers

R ⇌ P   Left: R ⇋ P   Right: R ⇀ P

Factors that Affect Equilibrium

Stress	*Shift and Affect*	*Reason*
Concentration		
↑[reactant]	R → P ↑[prod]	use excess reactant to ↑[prod]
↑[product]	R ← P ↑[react]	excess prod to ↑[react]
↓[reactant]	R ← P ↑[react]	excess prod. to ↑[react]
↓[product]	R → P ↑[prod]	excess react to ↑[prod]
Temperature		
↑T° on endothermic reaction R + NRG ⇌ P	R → P ↑[prod]	excess NRG to use.
↑T° on exothermic reaction R ⇌ NRG + P	R ← P ↑[react]	excess NRG (in reverse)
↓T° on endothermic reaction R + NRG ⇌ P	R ← P ↑[react]	produce more NRG.
↓T° on exothermic reaction R ⇌ NRG + P	R → P ↑[prod]	produce more energy.
*Pressure/Volume *ignore for solids and liquids ** only has affect if unequal # moles on reactant and product sides*		↓ # moles.
↑P(↓V) more #moles on reactant side 2R ⇌ 1P	R → P ↑[prod]	
↑P(↓V) more #moles on product side 1R ⇌ 2P	R ← P ↑[react]	↓ # moles.
↓P(↑V) more #moles on reactant side 2R ⇌ 1P	R ← P ↑[react]	↑ # moles
↓P(↑V) more #moles on product side 1R ⇌ 2P	R → P ↑[prod]	↑ # moles.

5.5 Factors Affecting Chemical Equilibrium (Qualitative factors)

Many things can change a reaction rate (think about unit 4), but only three things have the potential to change the forward and reverse reaction rates ***unequally***. These three things are:

1. Change in Concentration
2. Change in Temperature
3. Change in Pressure (or Volume)

Changes that affect reaction rate but ***do not*** affect equilibrium are:

1. Adding a catalyst (or inhibitor): because it affects the forward and reverse reactions equally. It just helps a reaction reach equilibrium sooner.
2. Change in surface area: also because it affects the forward and reverse reactions equally.

Le Chatelier's Principle

- The French chemist Henri-Louis Le Chatelier is credited with first discovering ways to change the equilibrium of a chemical system.
- A system at equilibrium represents a delicate balance between the forward and reverse reactions.
- Small changes in external conditions can cause a shift in the equilibrium.
    - A shift to the right means more products.
    - A shift to the left means more reactants.
- The system readjusts itself to accommodate the changes forced upon it and the readjustments may alter concentrations.
- *Le Chatelier stated that an equilibrium system subjected to an external stress will shift so as to minimize the stress (or remain in equilibrium).*
    - *A stress is anything changed in a system to upset the equilibrium (concentration, temperature or pressure/volume).*

Stresses:

1) Changes in Concentration
    - Adding a reactant or product will cause the equilibrium to shift in the opposite direction to use up the extra material.
    - Taking away a reactant or product will cause the equilibrium to shift in the same direction as the removal of material
    - Does not change K_c or K_{eq} (which is a quantitative change)

2) Changes in Volume or Pressure
    - Gaseous systems are affected by volume and pressure changes but not solid or liquid systems.
    - Volume and pressure changes will only affect equilibrium if the # of moles on the product and reactant sides are different.
    - Does not change K_c or K_{eq}

3) Changes in Temperature
    - The shift will be to minimize the stress
    - Shifts due to changes in temperature are dependent upon whether the system is endothermic or exothermic.
    - Does change K_c or K_{eq}

Factors that Affect Equilibrium		
Stress	***Shift and Affect***	***Reason***
Concentration		
↑ [reactant]		
↑ [product]		
↓ [reactant]		
↓ [product]		
Temperature		
↑ T° on endothermic reaction		
↑ T° on exothermic reaction		
↓ T° on endothermic reaction		
↓ T° on exothermic reaction		
*Pressure/Volume *ignore for solids and liquids ** only has affect if unequal # moles on reactant and product sides*		
↑ P(↓ V) more #moles on reactant side		
↑ P(↓ V) more #moles on product side		
↓ P(↑ V) more #moles on reactant side		
↓ P(↑ V) more #moles on product side		

5.5 La Chatelier's Principle Assignment

1. For the following system at equilibrium:

$$H_{2\,(g)} + Br_{2\,(g)} \leftrightarrow 2\,HBr_{(g)} + 36.4\text{ kJ}$$

   a. Predict the shift in equilibrium when more $HBr_{(g)}$ is added to the system.

   b. How will a temperature increase shift equilibrium?

2. For the reaction below, predict the direction the equilibrium will shift given the following changes. Temperature and volume are held constant.

$$2\,NO_{2\,(g)} + 7\,H_{2\,(g)} + \text{ energy } \leftrightarrow 2\,NH_{3\,(g)} + 4\,H_2O_{(g)}$$

   a. addition of ammonia
   b. removal of nitrogen dioxide
   c. decrease the temperature
   d. removal of water vapour
   e. addition of hydrogen

3. At a particular temperature, the following reaction has an equilibrium constant, K_{eq} of 0.18

$$PCl_{3\,(g)} + Cl_{2\,(g)} + 87.9\text{ kJ} \leftrightarrow PCl_{5\,(g)}$$

   a) If more PCl_3 is added to the system. Will the value of K_{eq} increase, decrease, or remain the same?

   b) How would the equilibrium shift if a catalyst is introduced?

   c) Explain how you can shift the equilibrium to the products by separately altering the concentration of one of the substances, the temperature, or the pressure.

4. For the following reactions, how will equilibrium shift for an increase in pressure?
   a) $H_{2(g)} + Cl_{2(g)} \leftrightarrow 2HCl_{(g)}$

   b) $PCl_{3\,(g)} + Cl_{2\,(g)} \leftrightarrow PCl_{5\,(g)}$

5. For the following reactions, how will equilibrium shift if the pressure is decreased?
   a) $CH_{4\,(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3H_2$

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

6. Methyl alcohol is produced according to the equation:
   $CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(g)} + heat$
   Predict the effect on the equilibrium species distribution if there was an increase in:
   a) Temperature

   b) Pressure

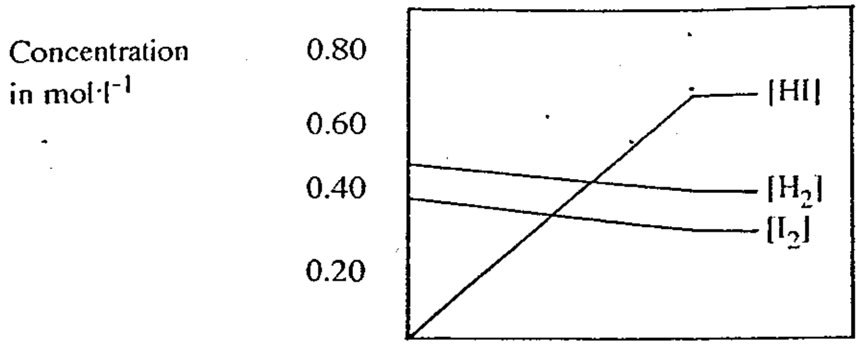
7. List three ways that the following equilibrium reaction could be forced to shift to the right:
   $2NO_{2(g)} \leftrightarrow 2NO_{(g)} + O_{2(g)}$

9. In each of the following equilibria, would you increase or decrease the temperature to force the reaction in the forward direction?
   c) $H_{2(g)} + CO_{2(g)} \leftrightarrow H_2O_{(g)} + CO_{(g)} \qquad \Delta H = +41kJ$

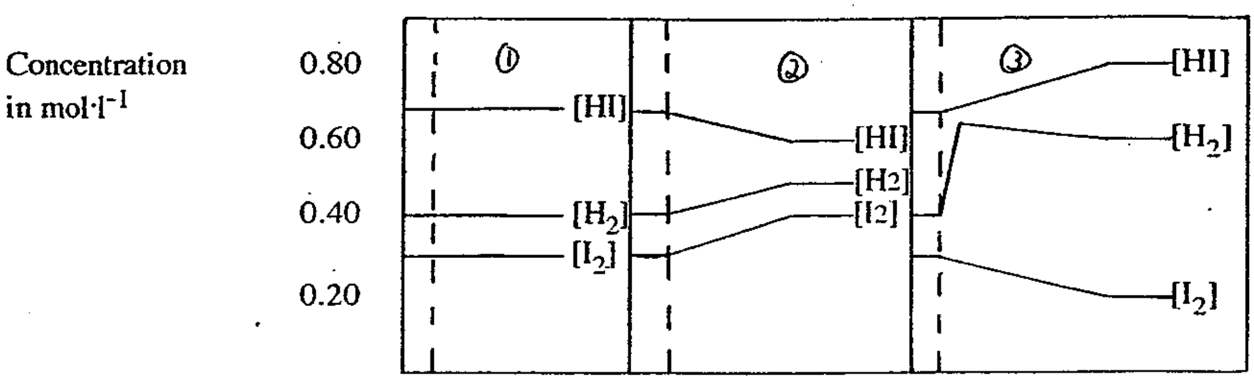
   d) $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)} \qquad \Delta H = -198kJ$

10.

The following graph show how the concentration of the reactants and product changes until equilibrium is established for the reactions: $H_2\,(g) + I_2\,(g) \longleftrightarrow 2\,HI\,(g) + 12.6\ J$



The following graphs begin with the system at equilibrium and then have a stress applied. Select whether graph 1, 2 or 3 best represents the change that would be caused by the stress.



Stresses:
a) The temperature is increased while the pressure is constant.
b) The temperature and pressure are increased.
c) Some hydrogen gas is added.
d) The pressure is increased while the temperature is constant.
e) A catalyst is added.

Additional Practice Problems: Matter and Change Textbook pp. 574 # 11, 12, 13

1)FACTORS THAT CHANGE EQUILIBRIUM: CONCENTRATION

We know that changing the concentration will also change an equilibrium.

Here's Why:

The rate of any chemical reaction actually depends on a factor called the activity of the reacting chemicals. In reasonably dilute solutions the activity is equal to the concentration. In other words, the rate depends on the concentration of the reacting chemicals. The reaction rate depends on the concentration of the reacting chemicals because, with a higher concentration, there will be more collisions. It also depends on a reaction rate constant, and so can be represented by the equation:

$$\textbf{rate} = \textbf{k[substance]}$$

In an equilibrium we have two processes going on at the same time:

- $rate_f = k_f[R]$
- $rate_r = k_r[P]$

where $rate_f$ is the rate in the forward, and $rate_r$ the rate in the reverse directions. At equilibrium we know that $rate_f = rate_r$ since the forward and reverse rates are equal at equilibrium.

What would happen to our reaction at equilibrium if we were to increase the cocentration of the reactants, R? We would expect the forward rate to increase. So, for a while at least, the rate would go faster in the forward direction. This is no longer an equilibrium, since the rates aren't equal any longer. Of course as the reaction goes forward faster it will make more products, P. More P will increase the rate in the reverse direction. Eventually, we'll reach an equilibrium, but it won't be the same one we started with. Similarly, if we increase the concentration of P, then the reaction would initially go faster in the reverse direction. Again though, it would eventually reach a new equilibrium with equal rates.

SO, IN GENERAL, WE EXPECT A CHANGE IN CONCENTRATION TO HAVE AN EFFECT ON EQUILIBRIUM.

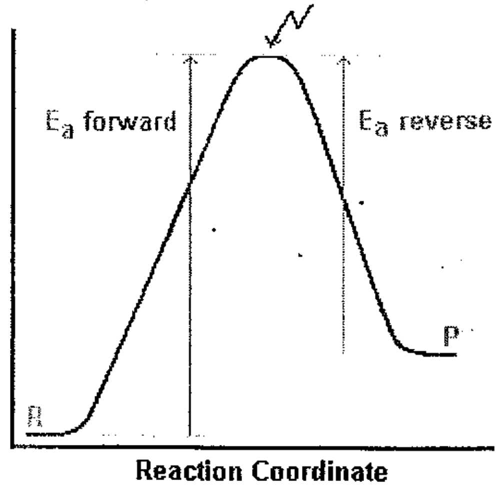
2)FACTORS THAT CHANGE EQUILIBRIUM: TEMPERATURE

We know that changing temperature will change an equilibrium.

Here's Why:

The rate of a chemical reaction depends on the temperature. In order for molecules to react they must collide, and the kinetic energy of the collision must be great enough to change the molecule's potential energy and allow the atoms to rearrange into new substances. The potential energy holding the atoms to each other in the original molecule is a potential energy barrier to change and is called the activation energy. The reaction rate depends on the temperature because, with a higher temperature, more molecules will be traveling faster. More will have enough kinetic energy to make it over the activation energy barrier as they collide. Notice however that as shown in the diagram below, the activation energy in the forward and reverse directions are not the same. Because of this, the reaction rate in the forward and reverse directions will not be affected equally by changing temperature.

Graph:



When the activation energy in the forward direction is larger (as shown here for an endothermic reaction), an increase in temperature will make the forward reaction increase more rapidly than the reverse. So, for a while, the rate will go faster in the forward direction. This is no longer an equilibrium, since the rates aren't equal any longer. Of course, as the reaction goes forward faster it make more products, P. More P will increase the rate in the reverse direction. Eventually, we'll get back to an equilibrium, but it won't be the same one as we started with. Temperature change has caused a change to a new equilibrium.

Exactly the opposite would happen if the reaction was exothermic, so that the activation energy in the reverse direction would be greater. A change in temperature would result in the rate initially going faster in the reverse direction until enough products had decomposed that the rate would slow down to the point where the forward and reverse rates were once again equal. This would once again be a new equilibrium.

SO, IN GENERAL, WE EXPECT A CHANGE IN TEMPERATURE TO HAVE AN EFFECT ON AN EQUILIBRIUM.

3) FACTORS THAT CHANGE EQUILIBRIUM: GAS PRESSURE

The effect of pressure on solids and liquids is so small that we will ignore it. However, there is a very real and important effect when we increase the pressure of reactions that contain gases. Here's why:

It is very important to clear up some confusion that students have about gas phase reactions. Although we write a chemical equation with two sides — the reactants and the products — in reality when the reaction is carried out, both reactants and products will invariably in a single container. This means that it is inappropriate to speak of "increasing the pressure on the products (or reactants)".

In fact, when we refer to changing the pressure in a reaction, it is usually referring to the pressure change caused by changing the volume of the reaction container. Changing the volume doesn't change the number of particles in a container directly, but it does mean that the number in each unit of volume will be different. Therefore, it changes the pressure.

When the volume increases, there are less molecules per unit volume. This means the number of collisions per unit of surface area decreases, so the pressure is lower.

When the volume decreases, there are more molecules per unit volume. This means the number of collisions per unit of surface area increases, so the pressure is higher.

Effectively, increasing the pressure by decreasing the volume increases the concentration. Remember though that is increases the concentration of everything that is in the gas phase, both reactants and products.

We already know that changing the concentration has an effect on an equilibrium, and so we would expect it to do so here. However, we have changed both reactant and product molecule concentrations, so we need to be cautious. Consider this reaction:

$$\underset{\text{2 gas molecules}}{2NO_2\,(g)} \rightleftharpoons \underset{\text{1 gas molecule}}{N_2O_4\,(g)}$$

There are two molecules of gaseous reactants, but only 1 molecule of gaseous produts. Therefore, we expect the effect of an increase in concentration to have a greater effect on the forward reaction. An unbalanced effect on the reaction rate will effect the equilibrium. We would expect this reaction to change with a change in pressure. But look at this reaction:

$$\underset{\text{2 gas molecules}}{H_2\,(g) + I_2\,(g)} \rightleftharpoons \underset{\text{2 gas molecules}}{2\,HI\,(g)}$$

Here there are two gaseous reactant molecules, but also two gaseous product molecules. The rate of the forward reaction should increase if the pressure increased, but there should be just as great an effect on the reverse reaction. If both rates are effected equally, then the equilibrium is not shifted. Remember that this is like running one step forward, and running one step back, as compared to walking one step forward, and walking one step back. Your actual rate is different in the two cases, but the net result is exactly the same — you remain at a standstill.

In reactions where the number of gaseous reactant molecules are the same as the gasious product molecules, changing pressure should have no effect on the equilibrium. The above shows us what to expect if we changed the pressure by changing the volume. There are two other ways to change the pressure of gases:

- change the temperature (since temperature effects other reactions as well)
- add an inert gas (overall pressure is increased – more molecules per unit volume so the total number of collisions increases, so the total pressure increases, the concentration of the original molecules is no different than it was before). Since the inert gas does not change the concentration of reactant and product molecules, it will not effect the rate, so it should have no effect on the equilibrium.

IN GENERAL, WE EXPECT PRESSURE TO HAVE AN EFFECT ON AN EQUILIBRIUM WHEN THERE ARE DIFFERENT NUMBERS OF MOLECULES OF GAS IN THE PRODUCTS AND REACTANTS. WHEN THE NUMBER OF GAS MOLECULES IN THE PRODUCTS AND REACTANTS ARE IDENTICAL, PRESSURE WILL NOT HAVE ANY EFFECT. AN INERT GAS WILL HAVE NO EFFECT ON THE EQUILIBRIUM.

4) FACTORS THAT CHANGE EQUILIBRIUM: CATALYSTS

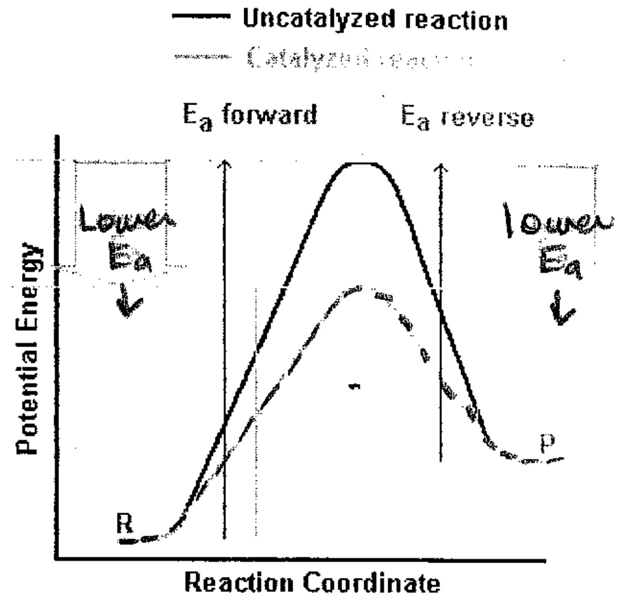
A catalyst has no effect on the final equilibrium condition. If a catalyst exists, then it will cause the reaction to reach an equilibrium more quickly, but the final position reached is the same with, or without the catalyst.

Here's why:

An equilibrium must react in both the forward and reverse directions. There is an activation energy barrier for each of these two reactions — a forward and activation energy and a reverse activation energy. The higher this activation energy barrier, the slower the reaction rate.

A catalyst creates a new reaction pathway, with different reaction steps, with a lower activation energy. Notice though that as shown in the diagram below, the effect on the activation energy in the forward and reverse direction is exactly the same. Because of this, the reaction rates in the forward and reverse directions will be affected equally.

Graph:



The reaction will go faster in the forward direction because of the catalyst. It will go just as fast in the reverse direction. Since both the forward and reverse reaction rates are affected equally, there is no net change to the equilibrium once it has been achieved. What about before you reach equilibrium? Then the rates are not equal, so the catalyst will increase the reaction rate, and an equilibrium will be reached sooner. However, the final equilibrium achieved is exactly the same with or without the catalyst.

SO, IN GENERAL, WE EXPECT A CATALYST TO HAVE NO EFFECT ON AN EQUILIBRIUM, ONCE EQUILIBRIUM IS ESTABLISHED.

5) FACTORS THAT CHANGE EQUILIBRIUM: SURFACE AREA

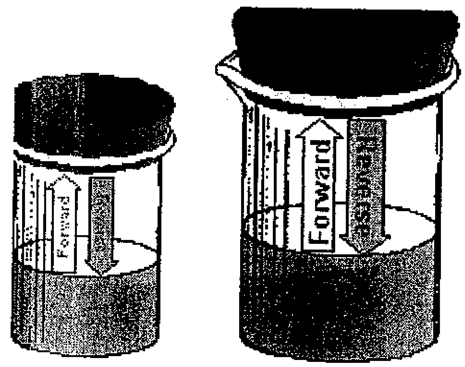
If the surface area is larger, then a reaction will reach an equilibrium more quickly, but the final position reached is the same as with a smaller surface area.

Here's Why:

Increasing the surface area in a heterogeneous reaction will normally increase the reaction rate. It does so because with more surface area exposed between the two reacting states, there will be more collisions and therefore a greater chance for a reaction. For example, if we crush a solid before trying to dissolve it in water, it will have more surfaces exposed. Since it can only dissolve from the outside edge, the larger number of surfaces will dissolve more quickly. At the same time, with more surfaces exposed there will also be more sites available for the molecules int he dissolved state to re-crystallize. Similarly, a large beaker of water has more surface area than a small beaker. The water can evaporate faster from a larger surface. However, the water can also condense faster from the vpor state since there is more surface area available for the reverse reaction as well.

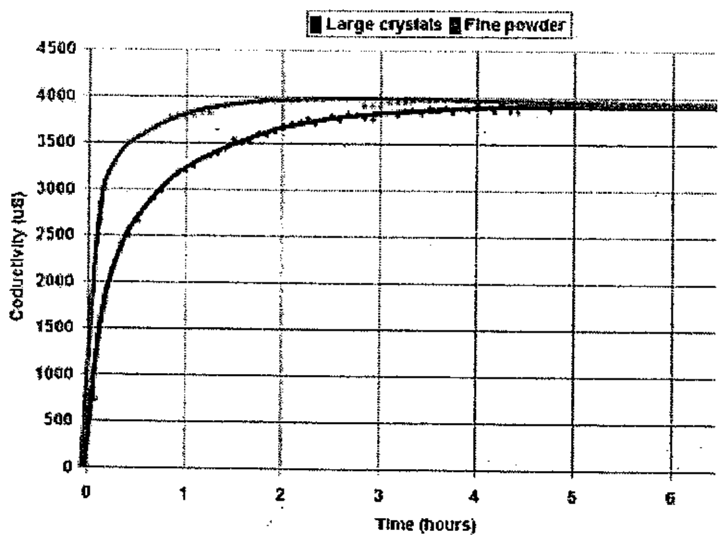
Because of this, the reaction rates in the forward and reverse directions will be affected equally by changing the surface area. The reaction will go faster in the forward direction because of an increase in surface area. It will go just as much faster in the reverse direction. Since both forward and reverse reaction rates are effected the same, there is no net change to the equilibrium once it has been achieved. The net result is that surface area has no effect on equilibrium.

Diagram:



What about before you reach equilibrium? Then the rates are not equal. Increasing the surface area means that you get to equilibrium more quickly. However, eventually you reach a point where the rates in the forward and reverse directions are equal. The approach to equilibrium is different but the final equilibrium achieved is the same with and without the change in surface area.

Graph:



As shown by the red curve, finely crushed crystals dissolve more quickly than do large crystals (the blue graph). However, the final equilibrium concentration reacted is the same for both

SO, IN GENERAL, WE EXPECT SURFACE AREA TO HAVE NO EFFECT ON AN EQUILIBRIUM, ONCE EQUILIBRIUM IS ESTABLISHED.

5.6 Application of le Chatelier's Principle Assignment

1. Consider the following equilibrium system:

   $PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

Describe what happens to the solubility of $PbCl_2$ when the following substances are added to the solution. Why?

a) $Pb(NO_3)_2$

decrease solubity b/c ↑$[Pb^{2+}]$

b) NaCl

↑$[Cl^-]$ ∴ ↓ solubity

c) H_2O

increase solubity b/c more solvent

d) $AgNO_3$

$AgCl_{(s)}$ ∴ ↑ solubility

∴ ↓ $[Ag^+]$

e) NaBr

$PbBr_{2(s)}$

↓ $[Pb^{2+}]$ ∴ ↑ solubility

2. Consider the following equilibrium system:

   $AgBr_{(s)} \rightleftharpoons Ag^{+}_{(aq)} + Br^{-}_{(aq)}$

Describe what happens to the solubility of $AgBr_{(s)}$ when the following substances are added to the solution. Why?

a) $Pb(NO_3)_2$

$PbB_{2(s)}$ ∴ ↓ $[Br^-]$

↑ solubility.

b) $AgNO_3$

↑ $[Ag^+]$

∴ ↓ solubility.

c) NaCl

$AgCl_{(s)}$ ∴ ↓ $[Ag^+]$

∴ ↑ solubity

d) NaBr

↑ $[Br^-]$

∴ ↓ solubility

3. Explain why more $Zn(OH)_2$ dissolves when 3 M HCl is added to a saturated solution of Zn $(OH)_2$. Start by writing the correct equilibrium equation.

$$Zn(OH)_{2(s)} \rightleftharpoons Zn^{2+}_{(aq)} + OH^-_{(aq)}$$

add $HCl \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

$\therefore \downarrow [OH^-]$

$\therefore \uparrow$ solubility of $Zn(OH)_2$

(and more solvent)

4. Explain three ways in which the Haber-Bosch process utilizes Le Chatelier's principle to increase the yield of ammonia in industrial fertilizer production.

- removal of NH_3
- $\downarrow$ temp
- $\uparrow$ pressure

5.6 Application of Le Chatelier's Principle

pages 583-584 and 588 in Matter and Change

pages 553 and 554 in Health

Le Chatelier 1888

5.6 - Application of Le Chatelier's Principle

The Common Ion Effect

The **common ion effect** is an example of Le Chatelier's Principle.

It states that the *solubility of an ionic compound is decreased* (less is dissolved) by the addition of another ionic compound to the solution that contains one of the ions already in the solution.

For example, if $BaSO_{4(s)}$ was in equilibrium in a solution, then we would have the following system:

$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Note - it is dissociated because it is soluble.

If we added barium chloride, another soluble substance to this system, what would happen to the concentration of Ba^{2+}?

Le Chatelier's Principle more $BaSO_{4(s)}$ is being produced. If there is more solid than there initially was, and less ions in the solution, then the solubility of $BaSO_4$ has been decreased.

Note - only the addition of substances with common ions can affect the equilibrium of a soluble substance.

We also need to consider if adding a substance will create an additional precipitate.

This will cause ions from the original system to drop out, increasing the solubility of the solid…

Ex) Determine what would happen to the solubility of sodium sulfate if we added the following to a sodium sulfate solution in equilibrium:

a) NaCl

b) sulfuric acid

c) $Ca(OH)_2$

.

The Haber-Bosch Process

$$N_{2(g)} + H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 46.1KJ$$

- diatomic nitrogen makes up about 79% of the Earth's atmosphere; only a few bacteria species can "fix" ammonia from atmospheric nitrogen
- ammonia can then be changed into nitrates and nitrites
- plants can use nitrates and nitrites (few can use ammonia) to meet their nitrogen needs

- In 1909, Fritz Haber first demonstrated how to synthesize ammonia from nitrogen and hydrogen gas to be used in fertilizer
  > incorporated several operations that increased the yield of ammonia
    - cooled the reaction
    - pressurized reactant chambers
    - the use of a catalyst
    - the removal of ammonia gas (by liquefication)

- The above system was improved by Carl Bosch in 1913

- Using Le Chatelier's Principle, why did the Haber-Bosch process increase the yield of ammonia?

  > increased pressure:

  > lower temperatures:

  > use of catalyst:

  > removal of product:

5.6 - Application of Le Chatelier's Principle

5.6 Application of le Chatelier's Principle Assignment

1. Consider the following equilibrium system:

$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2Cl^{-}{}_{(aq)}$

Describe what happens to the solubility of $PbCl_2$ when the following substances are added to the solution. Why?

a) $Pb(NO_3)_2$

b) NaCl

c) H_2O

d) $AgNO_3$

e) NaBr

2. Consider the following equilibrium system:

$AgBr_{(s)} \rightleftharpoons Ag^{+}{}_{(aq)} + Br^{-}{}_{(aq)}$

Describe what happens to the solubility of $AgBr_{(s)}$ when the following substances are added to the solution. Why?

a) $Pb(NO_3)_2$

b) $AgNO_3$

c) NaCl

d) NaBr

•

5.6 - Application of Le Chatelier's Principle

3. Explain why more $Zn(OH)_2$ dissolves when 3 M HCl is added to a saturated solution of $Zn(OH)_2$. Start by writing the correct equilibrium equation.

4. Explain three ways in which the Haber-Bosch process utilizes Le Chatelier's principle to increase the yield of ammonia in industrial fertilizer production.