## PART 1 CHEMICAL EQUILIBRIUM Chapter 14

## I Dynamic Equilibrium

I. In a closed system a liquid obtains a dynamic equilibrium with its vapor state


Dynamic equilibrium: rate of evaporation = rate of condensation
II. In a closed system a solid obtains a dynamic equilibrium with its dissolved state


Dynamic equilibrium: rate of dissolving = rate of crystallization

## II Chemical Equilibrium

I. EQUILIBRIUM
A. BACKGROUND

Consider the following reversible reaction:

$$
a A+b B \rightleftharpoons c C+d D
$$

1. The forward reaction $(\rightarrow)$ and reverse $(-)$ reactions are occurring simultaneously.
2. The rate for the forward reaction is equal to the rate of the reverse reaction and a dynamic equilibrium is achieved.
3. The ratio of the concentrations of the products to reactants is constant.
B. THE EQUILIBRIUM CONSTANT - Types of K's

| Solutions | $\mathrm{K}_{\mathrm{c}}$ |
| :--- | :--- |
| Gases | $\mathrm{Kc} \& \mathrm{Kp}$ |
| Acids | Ka |
| Bases | Kb |
| Solubility | Ksp |
| Ionization of water | Kw |
| Hydrolysis | $\mathrm{K}_{\mathrm{h}}$ |
| Complex ions | $\beta_{\eta}$ |

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## C. EQUILIBRIUM CONSTANT

For the reaction, $\mathrm{aA}+\mathrm{bB} \rightleftharpoons \mathrm{cC}+\mathrm{dD}$ The equilibrium constant, K , has the form:

$$
\mathrm{K}_{\mathrm{C}}=\frac{[\mathrm{C}]^{\mathrm{C}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{~A}]^{\mathrm{a}}[\mathrm{~B}]^{\mathrm{b}}}
$$

D. WRITING K's

1. $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
2. $2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})$

## E. MEANING OF K

1. If $K>1$, equilibrium favors the products
2. If $K<1$, equilibrium favors the reactants
3. If $K=1$, neither is favored

## F. ACHIEVEMENT OF EQUILIBRIUM

Chemical equilibrium is established when the rates of the forward and reverse reactions are equal.

$$
\mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$



## G. OBTAINING EQUILIBRIUM CONSTANTS FOR REACTIONS

1. For the reaction: $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$
the concentrations of the substances present in an equilibrium mixture at $25^{\circ} \mathrm{C}$ are:
$\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]=4.27 \times 10^{-2} \mathrm{~mol} / \mathrm{L}$
$\left[\mathrm{NO}_{2}\right]=1.41 \times 10^{-2} \mathrm{~mol} / \mathrm{L}$
What is the value of $\mathrm{K}_{\mathrm{c}}$ for this temperature?
2. For the reaction: $2 \mathrm{ONCCl}(\mathrm{g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{g})+\mathrm{Cl}_{2}(\mathrm{~g})$
1.00 mol of $\mathrm{ONCI}(\mathrm{g})$ at $500^{\circ} \mathrm{C}$ is introduced into a one-liter container. At equilibrium, the ONCL is $9.0 \%$ dissociated. What is the value of $\mathrm{K}_{\mathrm{C}}$ at $500^{\circ} \mathrm{C}$ ?

$$
2 \mathrm{ONCl}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})
$$

## Initial

Change
at Equilibrium

## H. HETEROGENEOUS EQUILIBRIA

When equilibrium between substances involve two or more phases it is called Heterogeneous Equilibria.
The concentration of a pure solid or a pure liquid in their standard states is constant (at constant $\mathrm{T}^{\circ}$ and $\mathrm{P})$.
Therefore, the concentrations of solids or liquids involved in a heterogeneous equilibrium are included in the value of $\mathrm{K}_{\mathrm{c}}$ and do not appear in the equilibrium constant expression.
Write the $K_{C}$ expression for:

1. $\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$
2. $3 \mathrm{Fe}(\mathrm{s})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightleftharpoons \mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g})$

Solids do not appear in the equilibrium constant.
Pure liquids do not appear in the equilibrium constant.
$\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ for example.
I. THE EQUILIBRIUM CONSTANT, Kp FOR GASES

Amounts of gases are often measure by pressure. The partial pressure of a gas is a measure if its concentration. The equilibrium constant, $\mathrm{K}_{\mathrm{p}}$, is written in terms of the partial pressures of gases.

$$
\mathrm{CaCO}_{3}(\mathrm{~s}) \rightleftharpoons \mathrm{CaO}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

The $K_{p}$ expression is:

$$
3 \mathrm{Fe}(\mathrm{~s})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g})
$$

The $K_{p}$ expression is:

Example: For the reaction: $\mathrm{FeO}(\mathrm{s})+\mathrm{CO}(\mathrm{g}) \rightleftharpoons \mathrm{Fe}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$ at $1000 .{ }^{\circ} \mathrm{C}, \mathrm{K}_{\mathrm{p}}$ is 0.403 . If $\mathrm{CO}(\mathrm{g})$, at a pressure of 1.000 atm , and excess $\mathrm{FeO}(\mathrm{s})$ are placed in a container at $1000^{\circ} \mathrm{C}$, what are the pressures of $\mathrm{CO}(\mathrm{g})$ and $\mathrm{CO}_{2}(\mathrm{~g})$ when equilibrium is attained?

$$
\mathrm{FeO}(\mathrm{~s})+\mathrm{CO}(\mathrm{~g}) \rightleftharpoons \mathrm{Fe}(\mathrm{~s})+\mathrm{CO}_{2}(\mathrm{~g})
$$

## Initial

Change
at Equilibrium

## J. THE RELATIONSHIP BETWEEN KC_AND K $\underset{\underline{p}}{ }$

$$
K_{p}=K_{c}(R T)^{\Delta n}
$$

Where: $\quad \mathbf{R}$ is the gas constant
T is the temperature of the system
$\Delta \mathrm{n}$ is the change in the number of moles of gas
\{ $\sum$ moles of products gases $-\sum$ moles of reactants gases \}

Example 1: For the reaction: $2 \mathrm{SO}_{3}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
at $1100 . \mathrm{K}, \mathrm{K}_{\mathrm{C}}$ is $0.0271 \mathrm{~mol} / \mathrm{L}$. What is $\mathrm{K}_{\mathrm{p}}$ at this temperature?

Example 2: For the reaction: $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
at $500 .{ }^{\circ} \mathrm{C}, \mathrm{K}_{\mathrm{p}}$ is $1.50 \times 10^{-5} / \mathrm{atm}^{2}$. What is $\mathrm{K}_{\mathrm{C}}$ at this temperature?

## K. THE EQUILIBRIUM CONSTANT FOR THE SUM OF REACTIONS

When a new chemical equation is obtained by summing individual equations, the equilibrium constant, Koverall, is the product of the individual equations.

Consider the following:

$$
\begin{array}{cl}
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) & \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})
\end{array} \begin{aligned}
& \mathrm{K}_{1}= \\
& 2 \mathrm{SO}_{3}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{aligned} \stackrel{2 \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{~g})}{ } \quad \begin{aligned}
& \mathrm{K}_{2}= \\
&
\end{aligned}
$$

$$
\mathrm{K}_{3}=\mathrm{K}_{\text {overall }}=
$$

L. PREDICTING THE DIRECTION OF REACTION

Given the inital concentrations of reactants and products, how would you predict which direction the reaction will "go" to obtain equilibrium? Left ? or Right?

1. Calculate Reaction Quotient, $\mathrm{Q}_{\mathrm{C}}$

$$
\mathrm{Q}_{\mathrm{C}}=\frac{[C]_{\text {ini }}[D]_{\text {ini }}}{[A]_{\text {ini }}[B]^{\mathrm{b}_{\text {ini }}}}
$$

2. Compare $\mathrm{Q}_{\mathrm{C}}$ with $\mathrm{K}_{\mathrm{C}}$
3. If $Q_{c}>K_{C}$, the reaction will go to the left to obtain equilibrium.

If $Q_{c}<K_{c}$, the reaction will go to the right to obtain equilibrium.
If $Q_{C}=K_{C}$, the reaction is at equilibrium.
Example: $\quad \mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \quad \mathrm{K}_{\mathrm{C}}=0.0415 \mathrm{~mol} / \mathrm{L}$

Initially, 0.100 mol of $\mathrm{PCl}_{5}(\mathrm{~g}), 0.0500 \mathrm{~mol}$ of $\mathrm{PCl}_{3}(\mathrm{~g})$, and 0.0300 mol of $\mathrm{Cl}_{2}(\mathrm{~g})$ is placed in a 1.00 L container. Is this system at equilibrium? If not, which way will the reaction go to obtain equilibrium?

## M. CALCULATING EQUILIBRIUM CONCENTRATIONS

For the Reaction: $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\mathrm{CO}(\mathrm{g}) \quad \mathrm{K}_{\mathrm{C}}=0.771$ at $75 .{ }^{\circ} \mathrm{C}$
If 0.0100 mol of $\mathrm{H}_{2}$ and 0.0100 mol of $\mathrm{CO}_{2}$ are mixed in a one-liter container at $750^{\circ} \mathrm{C}$, what are the concentrations of all substances present at equilibrium?

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g}) \neq \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})
$$

## Initial

Change
at Equilibrium

## N. Le CHATELIER'S PRINCIPLE

Le Chatelier's principle states: Any change to a system in equilibrium causes a shift in the system to reduce the effect of the change (until equilibrium is again reached)

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

If more $\mathrm{H}_{2}$ were added to a mixture at equilibrium, the system is no longer at equilibrium.
$\mathrm{Q}_{\mathrm{c}}<\mathrm{K}_{\mathrm{c}}$. The net reaction would be to the right to restore equilibrium.

If more HI were added to a mixture at equilibrium, the system is no longer at equilibrium.
$\mathrm{Q}_{\mathrm{c}}>\mathrm{K}_{\mathrm{c}}$. The net reaction would be to the left to restore equilibrium.

1. Changing the Concentration
$\mathrm{COCl}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{g})+\mathrm{Cl}_{2}(\mathrm{~g})$
a. Adding more CO
b. Removing some $\mathrm{Cl}_{2}$
c. Adding more $\mathrm{COCl}_{2}$
d. How will any of the above effect the numerical value of $K_{c}$ ?
2. Changing the Pressure
a. $\Delta \mathrm{n}>0$
$\mathrm{COCl}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{g})+\mathrm{Cl}_{2}(\mathrm{~g})$
(1) Increase Pressure
(2) Decrease Pressure
b. $\Delta \mathrm{n}<0$
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
(1) Increase Pressure
(2) Decrease Pressure
c. $\Delta \mathrm{n}=0$
$\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$
3. Changing the Temperature
$2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})$
$\Delta \mathrm{H}=-92 \mathrm{~kJ}$
a. Increase Temperature
b. Decrease Temperature
4. Adding a catalyst

A catalyst increases the rate of reaction and is not consumed in a reaction: The catalyst increases the rate by lowering the energy of activation, $\mathrm{E}_{\mathrm{a}}$

$$
\mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{I}) \stackrel{\mathrm{MnO}_{2}}{\rightleftharpoons} \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{O}_{2}(\mathrm{~g})
$$

Adding a catalyst to a system has no effect on the equilibrium.

1. A mixture of 0.500 mole of hydrogen and 0.500 mole of lodine gas was placed in a oneliter flask at $430^{\circ} \mathrm{C}$. Calculate the concentration of the hydrogen gas, lodine gas and hydrogen iodide gas at equilibrium. The Kc for the reaction is 54.3 at $430{ }^{\circ} \mathrm{C}$

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

## Initial

Change
at Equilibrium
2. Starting with 4.20 moles of $\mathrm{HI}(\mathrm{g})$ in a 9.60 liter reaction vessel, calculate the concentration of the hydrogen gas, lodine gas and hydrogen iodide gas at equilibrium. at $430^{\circ} \mathrm{C}$. The Kc for the reaction is 54.3 at $430^{\circ} \mathrm{C}$

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

Initial
Change
at Equilibrium
3. For the reaction: $\mathrm{C}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{CO}(\mathrm{g})$
$\mathrm{Kp}=167.5 \mathrm{~atm}$ at $1000^{\circ} \mathrm{C}$. What is the partial pressure of $\mathrm{CO}(\mathrm{g})$ in an equilibrium system in which the partial pressure of carbon dioxide gas is 0.100 atm?

## CHAPTER 15

I. ACIDS AND BASES
A. Acidic Characteristics

1. Tart/Sour taste
2. Produces color changes with indicators
3. Will react with and neutralize a base to form water
4. Will react with certain metals with $\mathrm{H}_{2}$ as a product
B. Basic Characteristics $\rightarrow$ Ionic Compounds that contains $\mathrm{OH}-$
5. Bitter taste
6. Slippery feeling
7. Produces color changes with indicators
8. Will neutralize an acid to form water
9. Will form a precipitate (ppt) with certain cations
D. Acid-Base reaction
$\mathrm{HCl}(\mathrm{aq})+\mathrm{KOH}(\mathrm{aq}) \rightarrow \mathrm{KCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
E. Salts- A salt is an ionic compound which is produced in an acid-base reaction.
$\mathrm{HCl}(\mathrm{aq})+\mathrm{KOH}(\mathrm{aq}) \rightarrow \mathrm{KCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}$
Acid + Base $\rightarrow$ Salt $+\mathrm{H}_{2} \mathrm{O}$
How to recognize:
A salt is an ionic compound that does not contain $\mathrm{OH}^{-}$and is not a metal oxide

| $\mathrm{HCl}(\mathrm{aq})$ | NaBr | $\mathrm{Zn}\left(\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)_{2}$ |
| :--- | :--- | :--- |

$\mathrm{Sn}(\mathrm{OH})_{2} \quad \mathrm{HClO}(\mathrm{aq}) \quad \mathrm{HC}_{6} \mathrm{H}_{6} \mathrm{O}_{2}(\mathrm{aq})$

## F. STRENGTH OF ACIDS AND BASES

Strong Acids - Those acids which are 100\% ionized (reacted with water)
Weak Acids - Those acids which are less than 100\% ionized (reacted with water)
Strong Bases - Those bases which are $100 \%$ dissociated in water
Weak Bases - Those bases which are less than $100 \%$ dissociated in water
STRONG BASES

| LiOH | NaOH |
| :--- | :--- |
| KOH | RbOH |
| CsOH | $\mathrm{Sr}(\mathrm{OH})_{2}$ |
| $\mathrm{Ba}(\mathrm{OH})_{2}$ | $\mathrm{Ca}(\mathrm{OH})_{2}$ |

STRONG ACIDS

| $\mathrm{HNO}_{3}$ | $\mathrm{H}_{2} \mathrm{SO}_{4}$ |
| :--- | :--- |
| HClO 4 | HCl |
| HBr | HI |

## Part 4: Concepts of Acids and Bases

I. ARRHENIUS CONCEPT

Arrhenius Acid $\Rightarrow$ A substance that INCREASES the concentration of $\underline{\mathrm{H}}^{+}$in water ex.

Arrehenius base $\Rightarrow$ A substance that INCREASES the concentration of $\mathrm{OH}^{-}$in water ex.
II. BRONSTED-LOWRY CONCEPT
A. DEFINITIONS

Bronsted Acid $\Rightarrow$ A substance that can donate a proton $\left(\mathrm{H}^{+}\right)$
Monoprotic

Polyprotic

Bronsted Base $\Rightarrow$ A substance that can accept a proton $\left(\mathrm{H}^{+}\right)$

An Acid-Base Reaction:
B. CONJUGATED ACID-BASE PAIRS

When a Bronsted-Lowry acid loses a proton, the species formed is a base:

The two species differ by the loss or gain of a proton. These pairs are called: conjugated acidbase pairs.

1. Identifying Bronsted Acid and Base Species

Acid $1+$ Base $2 \rightleftharpoons$ Base $1+$ Acid 2
2. Bronsted Amphiprotic substances

Substances which can act as a Brontsted acid or a Bronsted base
3. Strengths of Bronsted Acids and Bases

The strength of an acid is its tendency to donate a proton
The strength of a base is its tendency to accept a proton

$$
\begin{aligned}
& \text { Acid } 1+\text { Base } 2 \rightleftharpoons \text { Base } 1+\text { Acid } 2 \\
& \mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
\end{aligned}
$$

| RELATIVE STRENGTHS OF ACIDS AND BASES |  |  |  |
| :---: | :---: | :---: | :---: |
| ACID |  | BASE |  |
| STRONGEST ACIDS | $\mathrm{HClO}_{4}$ | $\mathrm{ClO}_{4}{ }^{-}$ | WEAKEST BASES |
|  | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $\mathrm{HSO}_{4}{ }^{-}$ |  |
|  | HI | $\mathrm{I}^{-}$ |  |
|  | HBr | $\mathrm{Br}^{-}$ |  |
|  | HCl | $\mathrm{Cl}^{-}$ |  |
|  | $\mathrm{HNO}_{3}$ | $\mathrm{NO}_{3}{ }^{-}$ |  |
|  | $\mathrm{H}_{3} \mathrm{O}^{+}$ | $\mathrm{H}_{2} \mathrm{O}$ |  |
|  | $\mathrm{HSO}_{4}$ | $\mathrm{SO}_{4}{ }^{-}$ |  |
|  | $\mathrm{H}_{2} \mathrm{SO}_{3}$ | $\mathrm{HSO}_{3}{ }^{-}$ |  |
|  | $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ |  |
|  | $\mathrm{HNO}_{2}$ | $\mathrm{NO}_{2}{ }^{-}$ |  |
|  | HF | $\mathrm{F}^{-}$ |  |
|  | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$ |  |
|  | $\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ | $\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}{ }^{2+}$ |  |
|  | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $\mathrm{HCO}_{3}{ }^{-}$ |  |
|  | $\mathrm{H}_{2} \mathrm{~S}$ | $\mathrm{HS}^{-}$ |  |
|  | HClO | $\mathrm{ClO}^{-}$ |  |
|  | HBrO | $\mathrm{BrO}^{-}$ |  |
|  | $\mathrm{NH}_{4}{ }^{+}$ | $\mathrm{NH}_{3}$ |  |
| $\downarrow$ | HCN | $\mathrm{CN}^{-}$ | $\checkmark$ |
|  | $\mathrm{HCO}_{3}$ | $\mathrm{CO}_{3}{ }^{-2}$ |  |
|  | $\mathrm{H}_{2} \mathrm{O}_{2}$ | $\mathrm{HO}_{2}{ }^{-}$ |  |
| WEAKEST | $\mathrm{HS}^{-}$ | $\mathrm{S}_{2}{ }^{-}$ | STRONGEST |
| ACIDS | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{OH}^{-}$ | BASES |

The stronger acid will have the weaker conjugated base
The stronger base will have the weaker conjugated acid
The direction of the acid-base reaction always favors the weaker acid and base:
"The stronger acid plus the stronger base produces the weaker acid and weaker base"
III. Lewis Acid-Base Concept
A. DEFINITION

Lewis Acid $\Rightarrow$ A substance that is an electron pair acceptor (A covalent bond is made)
ex.

Lewis Base $\Rightarrow$ A substance that is an electron pair donator (A covalent bond is made) ex.

An Acid-Base Reaction:

## Papt 5: Autoionization of Water

## I. THE CONCEPT

Experiments have shown that a very small percentage of water will undergo the following ionization to produce ions:

$$
\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}
$$

Experimentally, it was determined that the product between the molar concentrations of the hydronium ion and hydroxide ion is a constant:

$$
\begin{gathered}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \times\left[\mathrm{OH}^{-}\right]=10^{-14} \text { क. ion product for water (constant) }} \\
\text { or }\left[\mathrm{H}^{+}\right] \times\left[\mathrm{OH}^{-}\right]=10^{-14} \text { as an abbreviation }
\end{gathered}
$$

Therefore, in pure water, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]=10^{-7}$
Problems:

1. What is the hydrogen (hydronium) ion concentration when $\left[\mathrm{OH}^{-}\right]=2 \times 10^{-3} \mathrm{M}$ ?
2. What is the hydroxide ion concentration in a 0.002 M HCl solution?
3. What is the hydrogen ion concentration in a $1.00 \times 10^{-2} \mathrm{M} \mathrm{NaOH}$ solution?

## II. THE pH SCALE

Hydrogen ion concentrations, $\left[\mathrm{H}^{+}\right]$and hydroxide ion concentrations, $\left[\mathrm{OH}^{-}\right]$are usually very small numbers...

Example: $\left[\mathrm{H}^{+}\right]=2 \times 10^{-1} \mathrm{M}$ and $\left[\mathrm{H}^{+}\right]=1 \times 10^{-11} \mathrm{M}$.
The pH scale was developed to handle these very small numbers over a wide range.
( $2 \times 10^{-1}$ is 20 trillion times larger than $1 \times 10^{-11}$ !)

$$
\begin{gathered}
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
\text {and } \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]
\end{gathered}
$$

## Problems:

1. What is the pH when $\left[\mathrm{H}^{+}\right]=10^{-3} \mathrm{M}$ ?
2. What is the what is the pH of a 0.002 M HCl solution?
3. What is the pH of a $1.00 \times 10^{-2} \mathrm{M} \mathrm{NaOH}$ solution?
4. What is the $\left[\mathrm{H}^{+}\right]$if the $\mathrm{pH}=2.56$
5. What is the $\left[\mathrm{H}^{+}\right]$of a NaOH solution with a pOH of 9.983 ?

Acidic, Basic, and Neutral solutions:

| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $\left[\mathrm{OH}^{-}\right]$ | pH | acidic/basic or/neutral |
| :--- | :--- | :--- | :--- |
| $10^{0}$ | $10^{-14}$ | 0 |  |
| $10^{-1}$ | $10^{-13}$ | 1 |  |
| $10^{-2}$ | $10^{-12}$ | 2 |  |
| $10^{-3}$ | $10^{-11}$ | 3 |  |
| $10^{-4}$ | $10^{-10}$ | 4 |  |
| $10^{-5}$ | $10^{-9}$ | 5 |  |
| $10^{-6}$ | $10^{-8}$ | 6 |  |
| $10^{-7}$ | $10^{-7}$ | 7 |  |
| $10^{-8}$ | $10^{-6}$ | 8 |  |
| $10^{-9}$ | $10^{-5}$ | 9 |  |
| $10^{-10}$ | $10^{-4}$ | 10 |  |
| $10^{-11}$ | $10^{-3}$ | 11 |  |
| $10^{-12}$ | $10^{-2}$ | 12 |  |
| $10^{-13}$ | $10^{-1}$ | 13 |  |
| $10^{-14}$ | $10^{-0}$ | 14 |  |

Problem: Is $2 \times 10^{-10} \mathrm{M}\left[\mathrm{H}^{+}\right]$a basic, acidic or neutral solution?
III. INDICATORS

Indicators are often used to determine the approximate pH of solutions. Indicators are weak acids or weak bases whose conjugated species is a different color than it is:

## I. WEAK ACID IONIZATION

A. Equilibria of a weak acid.
$\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$
Or
$\mathrm{HA}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}-(\mathrm{aq})$
ex.
B. Acid lonization constant, Ka
C. $\mathrm{PKa}=-\log \mathrm{K}_{\mathrm{a}}$
D. Degree of lonization, $\alpha$

The degree of ionization, $\alpha$, of a weak acid or base in water is the fraction of the total concentration that has formed ions:
A 0.10 M HA solution undergoes equilibrium (Ionization)
$\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}+(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})$

Ka TABLE

## ACID-IONIZATION CONSTANTS AT $25^{\circ}{ }^{\circ}$ *

| Substance | Formula | Ka |
| :---: | :---: | :---: |
| Acetic acid | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $1.7 \times 10^{-5}$ |
| Benzoic acid | $\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{5}$ | $6.3 \times 10^{-5}$ |
| Boric acid | $\mathrm{H}_{3} \mathrm{BO}_{3}$ | Ka, $5.9 \times 10^{-10}$ |
| Carbonic acid | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $K a_{1}=4.3 \times 10^{-7}$ |
|  | $\mathrm{HCO}_{3}{ }^{-}$ | $\mathrm{Ka}_{2}=4.8 \times 10^{-11}$ |
| Cyanic acid | HOCN | $3.5 \times 10^{-4}$ |
| Formic acid | $\mathrm{HCHO}_{2}$ | $1.7 \times 10^{-4}$ |
| Hydrocyanic acid | HCN | $4.9 \times 10^{-10}$ |
| Hydrofluoric acid | HF | $6.8 \times 10^{-4}$ |
| Hydrogen sulfate ion | $\mathrm{HSO}_{4}{ }^{-}$ | $1.1 \times 10^{-2}$ |
| Hydrogen sulfide | $\mathrm{H}_{2} \mathrm{~S}$ | $K a_{1}=8.9 \times 10^{-8}$ |
|  | HS ${ }^{-}$ | $\mathrm{Ka}_{2}=1.2 \times 10^{-13 \dagger}$ |
| Hypochlorous acid | HClO | $3.5 \times 10^{-8}$ |
| Nitrous acid | $\mathrm{HNO}_{2}$ | $4.5 \times 10^{-4}$ |
| Oxalic acid | $\mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ | $K \mathrm{a}_{1}=5.6 \times 10^{-2}$ |
|  | $\mathrm{HC}_{2} \mathrm{O}_{4}{ }^{-}$ | $\mathrm{Ka}_{2}=5.1 \times 10^{-5}$ |
| Phosphoric acid | $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $K a_{1}=6.9 \times 10^{-3}$ |
|  | $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | $\mathrm{Ka}_{2}=6.2 \times 10^{-8}$ |
|  | $\mathrm{HPO}_{4}{ }^{2-}$ | $\mathrm{Ka}_{3}=4.8 \times 10^{-13}$ |
| Phosphorous acid | $\mathrm{H}_{3} \mathrm{PO}_{3}$ | $K \mathrm{a}_{1}=1.6 \times 10^{-2}$ |
|  | $\mathrm{H}_{2} \mathrm{PO}_{3}{ }^{-}$ | $\mathrm{Ka}_{2}=7 \times 10^{-7}$ |
| Propionoic acid | $\mathrm{HC}_{3} \mathrm{H}_{5} \mathrm{O}_{2}$ | $1.3 \times 10^{-5}$ |
| Pyruvic acid | $\mathrm{HC}_{3} \mathrm{H}_{3} \mathrm{O}_{3}$ | $1.4 \times 10^{-4}$ |
| Sulfurous acid | $\mathrm{H}_{2} \mathrm{SO}_{3}$ | $K a_{1}=1.3 \times 10^{-2}$ |
|  | $\mathrm{HSO}_{3}{ }^{-}$ | $\mathrm{Ka}_{2}=6.3 \times 10^{-8}$ |

*The ionization constants for polyprotic acids are for successive ionizations. Thus, for $\mathrm{H}_{3} \mathrm{PO}_{4}$, the equilibrium is $\mathrm{H}_{3} \mathrm{PO}_{4} \rightleftharpoons \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$. For $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}$, the equilibrium is $\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \stackrel{\rightleftharpoons}{\rightleftharpoons} \mathrm{H}^{+}+$ $\mathrm{HPO}_{4}{ }^{2-}$.
${ }^{\dagger}$ This value is in doubt. Some evidence suggests that it is about 10-19.
F. ACID EQUILIBRIUM CALCULATIONS:

1. Calculation of equilibrium concentrations from Ka

Calculate the pH of a 1.0 M Acetic acid solution, using approimations. $\mathrm{Ka}=1.8 \times 10-5$

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2^{-}}
$$

Initial
Change
at Equilibrium
2. Calculation of species concentrations from Ka , using the quadratic formula

Calculate the pH of a 0.000010 M Acetic acid solution

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2^{-}}
$$

Initial
Change
at Equilibrium
3. Calculation of Ka from the pH of a weak acid solution Calculate the Ka of $\mathrm{HNO}_{2}$ if a $0.10 \mathrm{M} \mathrm{HNO}_{2}$ solution has a pH of 2.187

Initial
Change
at Equilibrium
4. Calculation of Ka from the percent ionization.

Calculate the Ka of Glycine if a 0.10 M Glycine solution is $4.1 \times 10^{-3}$ ionized $\mathrm{HGly}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+} \quad+\quad \mathrm{Gly}^{-}$

Initial
Change
AT EQUILIBRIUM

## II. WEAK BASE IONIZATION

A. Equilibria of a weak base.
$\mathrm{B}(\mathrm{aq}) \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{BH}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
ex.
B. Types of weak bases

1. Insoluble
2. Soluble

Molecular-Nitrogen based Bases
C. Base lonization constant, Kb
D. Ammonia Equilibrium
F. Degree of lonization, $\alpha$

The degree of ionization, $\underline{\alpha}$, of a weak acid or base in water is the fraction of the total concentration that has formed ions: A 1.0 MB solution undergoes equilibrium (Ionization)

$$
\mathrm{B}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HB}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})
$$

Kb table
DISSOCIATION CONSTANTS FOR BASES

| Base | Formula | Dissocaiation Constants at $25^{\circ} \mathrm{C}$ |
| :---: | :---: | :---: |
| Ammonia | $\mathrm{NH}_{3}$ | $1.76 \times 10^{-5}$ |
| Anniline | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ | $3.94 \times 10^{-10}$ |
| 1-Butylamine | $\mathrm{CH}_{3}\left(\mathrm{CH}_{2}\right)_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ | $4.0 \times 10^{-4}$ |
| Dimethylamine | $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NH}$ | $5.9 \times 10^{-4}$ |
| Ethanolamine | $\mathrm{HOC}_{2} \mathrm{H}_{4} \mathrm{NH}_{2}$ | $3.18 \times 10^{-5}$ |
| Ethylamine | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$ | $4.28 \times 10^{-4}$ |
| Ethylenediamine | $\mathrm{NH}_{2} \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{NH}_{2}$ | $\mathrm{K}=8.5 \times 10^{-5}$ |
|  |  | $\mathrm{K}=7.1 \times 10^{-8}$ |
| Hydrazine | $\mathrm{H}_{2} \mathrm{NNH}_{2}$ | $1.3 \times 10^{-6}$ |
| Hydroxlamine | $\mathrm{HONH}_{2}$ | $1.07 \times 10^{-8}$ |
| Methylamine | $\mathrm{CH}_{3} \mathrm{NH}_{2}$ | $4.8 \times 10^{-4}$ |
| Piperidine | $\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{~N}$ | $1.3 \times 10^{-3}$ |
| Pyridine | $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ | $1.7 \times 10^{-9}$ |
| Trimethyl amine | $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$ | $6.25 \times 10^{-5}$ |

G. Base Equilibrium Calculations:

1. Calculation of species concentrations from Kb

Calculate the pH of a $0.100 \mathrm{M} \mathrm{NH}_{3}$ solution $\mathrm{Kb}=1.8 \times 10-5$

## Initial

Change
at Equilibrium
2. Calculation of Kb from species concentrations

Calculate the Kb for methylamine, $\mathrm{CH}_{3} \mathrm{NH}_{2}$, if the pOH of $\mathrm{a} 0.0100 \mathrm{M} \mathrm{CH}_{3} \mathrm{NH}_{2}$ solution is 7.66

Initial
Change
at Equilibrium
3. Calculation of species concentrations from Kb

Calculate the pH of a $0.100 \mathrm{M} \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N} \quad \mathrm{~Kb}=1.3 \times 10^{-3}$

Initial
Change
at Equilibrium
III. THE EFFECT OF DILUTION ON THE \% IONIZATION

The percent ionization of a weak acid or base increase as the acid/base concentration decreases (dilution)

1. Calculate the percent ionization for 0.10 M HF
2. Calculate the percent ionization for 0.00010 M HF Equilibrium problems
