Acid-Base Equilibrium Constants & Expressions

- **Strong acids** are defined as proton donors that will *completely* ionize in water. This means that *all* reactants get consumed to produce lots of products. Therefore a strong acid *cannot form equilibrium* because the products are so heavily favoured.

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow Cl^-_{(aq)} + H_3O^+_{(aq)}$$

none left at the end of rxn.

  - There are only six strong acids and are the top six acids listed on pg. 8-9 in data booklet (very large K values)

- **Strong bases** are defined as proton acceptors that will *completely* dissociate in water. This means that *all* reactants get consumed to produce products. Therefore a strong base *cannot form equilibrium* because the products are so heavily favoured.
  - A strong base is an ionic compound that contains the hydroxide ion (OH^-)

$$Mg(OH)_{2(aq)} + H_2O_{(l)} \longrightarrow Mg^{2+}_{(aq)} + 2OH^-_{(aq)}$$

none left at the end of rxn.

- **Weak acids** in water will establish equilibrium and *produce small amounts* of H^+/H_3O^+. This means not much of the weak acid actually ionizes (ie. not many products form).

- **Weak bases** in water will establish equilibrium and *produce small amounts* of OH^- ions. This means not much of the weak base actually dissociates (ie. not many products form).

- If very few products are produced with weak acids and weak bases, the equilibrium constant must be small for all weak acids and weak bases.
  - The equilibrium constant for weak acids and weak bases is used to determine exactly how many H^+/H_3O^+ ions will be produced when a weak acid breaks down or how many OH^- ions will be produced when a weak base breaks down

ACID IONIZATION EXPRESSIONS

- The general reaction written below represents the equilibrium for a weak acid

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)}$$

still lots at equilibrium — not many at equilibrium

  - The equilibrium expression can be written for any weak acid equilibrium based on the general reaction above and is known as the <u>*acid ionization expression*</u> or <u>*K_a expression*</u>

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

- ICE tables can be applied to <u>*weak*</u> acids in equilibrium, but the general outcome is the same for all weak acids

	$HA_{(aq)}$	+ $H_2O_{(l)}$	$\rightleftharpoons$ $A^-_{(aq)}$	+ $H_3O^+_{(aq)}$
I	$[HA]_{initial}$	—	0	0
C	$-x$	—	$+x$	$+x$
E	$[HA]_{initial} - x$	—	x	x

$$\therefore K_a = \frac{[A^-][H_3O^+]}{[HA]_{equil.}} = \frac{(x)(x)}{([HA]_{initial} - x)}$$

but for weak acids, K_a is small, so use approximation rule $[HA]_{initial} - x \approx [HA]_{initial}$

$$K_a = \frac{(x)(x)}{[HA]_{initial}} = \frac{x^2}{[HA]_{initial}}$$

where $x = [H_3O^+]/[H^+]$ or $[A^-]$

$$\therefore \boxed{K_a = \frac{[H_3O^+]^2}{[HA]_{initial}}}$$

- Recall other acid-base equations that will also be used:

$[H_3O^+_{(aq)}] = 10^{-pH}$ and $pH = -\log[H_3O^+_{(aq)}]$ *memorize!

EXAMPLES:

1. Methanoic acid, $CHOOH_{(aq)}$, is present in the sting of certain ants. What is the pH of a 0.25 mol/L solution of methanoic acid?

pH = ?

[HA] = 0.25 mol/L

$K_a = 1.8 \times 10^{-4}$

from data book

② $pH = -\log[H_3O^+]$

① $K_a = \dfrac{[H_3O^+]^2}{[HA]}$

approximation rule good!

① $K_a = \dfrac{[H_3O^+]^2}{[HA]} \Rightarrow [H_3O^+] = \sqrt{K_a[HA]}$

$[H_3O^+] = \sqrt{(1.8 \times 10^{-4})(0.25)} = 6.708\ldots \times 10^{-3}$ mol/L

② $pH = -\log[H_3O^+]$

$pH = -\log(6.708\ldots \times 10^{-3}) = 2.17339\ldots$

$\boxed{pH = 2.17}$

2. Propanoic acid, $CH_3CH_2COOH_{(aq)}$, is a weak monoprotic acid that is used to inhibit mould formation in bread. A student prepared a 0.10 mol/L solution of propanoic acid and found the pH was 2.96. What is the acid ionization constant for propanoic acid?

$[HA] = 0.10\,mol/L$

$pH = 2.96$

$K_a = ?$

(assume approximation rule is good)

② $K_a = \frac{[H_3O^+]^2}{[HA]}$

$[H_3O^+] = 10^{-pH}$ ①

① $[H_3O^+] = 10^{-pH}$

$[H_3O^+] = 10^{-2.96} = 0.00109\ldots\,mol/L$

② $K_a = \frac{[H_3O^+]^2}{[HA]} = \frac{(0.00109\ldots\,mol/L)^2}{0.10}$

$K_a = 1.20226\ldots \times 10^{-5}$

$\boxed{K_a = 1.2 \times 10^{-5}}$

Now try the Practice Problems

Practice Problems

1. Write the equilibrium expression for each acid ionizing in an aqueous solution.

    a. nitrous acid, $HNO_{2(aq)}$

    b. benzoic acid, $C_6H_5COOH_{(aq)}$

    c. carbonic acid, $H_2CO_{3(aq)}$

2. Phenol, $C_6H_6O_{(aq)}$, is a weak monoprotic acid used as a disinfectant. The K_a expression is $K_a = \frac{[C_6H_5O^-][H_3O^+]}{[C_6H_6O]}$. Write the ionization reaction for phenol in an aqueous solution.

3. Calculate the pH of a sample of vinegar that contains 0.83mol/L ethanoic acid.

4. Hypochlorous acid, $HOCl_{(aq)}$ is used to make bleach. A chemist finds that a 0.40mol/L solution of $HOCl_{(aq)}$ will ionize and produce $1.08\text{x}10^{-4}$ mol/L of $OCl^-_{(aq)}$. What is the K_a for the acid?

5. Hexanoic acid, commonly known as caproic acid, $C_5H_{11}COOH_{(s)}$, occurs naturally in coconut and palm oil. It is a weak monoprotic acid, with $K_a = 1.3\text{x}10^{-5}$. A certain aqueous solution of hexanoic acid has a pH of 2.94. What was the initial concentration of the hexanoic acid solution?

6. Lactic acid is a monoprotic acid produced by muscle activity. It is also produced in milk by the action of bacteria. What is the pH of a 0.16mol/L solution of lactic acid?

7. What is the acid ionization constant for gallic acid if a 0.68mol/L solution has a pH of 2.29?

Practice Problem: Answers

1.

a. $K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$

b. $K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]}$

c. $K_{a1} = \frac{[HCO_3^-][H_3O^+]}{[H_2CO_3]}$ and $K_{a2} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$

2. $C_6H_6O_{(aq)} + H_2O_{(l)} \Leftrightarrow C_6H_5O^-{}_{(aq)} + H_3O^+{}_{(aq)}$

3. 2.41

4. 2.9×10^{-8}

5. 0.10 mol/L

6. 2.32

7. 3.87×10^{-5}

Base Equilibrium Expressions

- The general reaction written below represents the equilibrium for a weak base

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

still lots at equilibrium — not many at equilibrium

  - The equilibrium expression can be written for any weak base equilibrium based on the general reaction above and is known as the <u>*base equilibrium expression*</u> or <u>*K_b expression*</u>

$$K_b = \frac{[OH^-][HB^+]}{[B]_{equil.}}$$

- ICE tables can be applied to <u>*weak*</u> bases in equilibrium, but the general outcome is the same for all weak bases

	$B_{(aq)}$ +	$H_2O_{(l)}$ $\rightleftharpoons$	$HB^+_{(aq)}$ +	$OH^-_{(aq)}$
I	$[B]_{inital}$	—	0	0
C	$[B]_{inital} - x$	—	$+x$	$+x$
E	$[B]_{inital} - x$	—	x	x

$$K_b = \frac{[HB^+][OH^-]}{[B]_{equil.}} = \frac{(x)(x)}{[B]_{inital} - x}$$

but for weak bases, K_b will be small, ∴ use approximation rule $[B]_{inital} - x \simeq [B]_{inital}$

$$K_b = \frac{(x)(x)}{[B]_{inital}} \quad \text{where } x = [OH^-] = [HB^+]$$

$$\boxed{K_b = \frac{[OH^-]^2}{[B]_{inital}}}$$

- Calculations are need to relate acidic information to basic information (because as acidic properties increase, basic properties decrease and vice versa)
  - The relationship between pH and pOH is

$$14 = pOH + pH$$

and recall $pOH = -\log[OH^-_{(aq)}]$ & $[OH^-_{(aq)}] = 10^{-pOH}$

memorize!

  - Water can ionization and create an equilibrium reaction shown below

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

$$\boxed{K_w = [H^+][OH^-]}$$

memorize!

where $K_w = 1.0 \times 10^{-14}$ at 25°C

pg. 3 of data book

  - There is a relationship between the K_a and K_b for a <u>*conjugate acid-base pair*</u>

$$K_w = K_a \times K_b$$

memorize!

EXAMPLES:

1. The characteristic bitter taste of tonic water is due to the addition of quinine, $C_{20}H_{24}N_2O_{2(s)}$, a naturally occurring, white crystalline compound. It is also used to treat malaria. The base equilibrium constant, K_b, for quinine is 3.3×10^{-6}. What is the hydroxide ion concentration of a 3.6×10^{-2} mol/L solution of quinine?

$K_b = 3.3 \times 10^{-6}$

$[B]_{initial} = 3.6 \times 10^{-2}$ mol/L

$[OH^-] = ?$

$$K_b = \frac{[OH^-]^2}{[B]_{initial}}$$

approximation rule good!

$$[OH^-] = \sqrt{K_b [B]_{initial}}$$

$$[OH^-] = \sqrt{(3.3 \times 10^{-6})(3.6 \times 10^{-2})}$$

$$\boxed{[OH^-] = 1.1 \times 10^{-4} \text{ mol/L}}$$

NH_3

2. An aqueous solution of ammonia has a pOH of 3.15. What is the concentration of the ammonia solution?

basic!

pOH = 3.15

$[B]_{initial} = ?$

$K_a = 5.6 \times 10^{-10}$ for NH_4^+ $\Rightarrow$ $\therefore K_b$ (for NH_3) $= \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.7857... \times 10^{-5}$

from data book

② $K_b = \frac{[OH^-]}{[B]_{initial}}$

① $[OH^-] = 10^{-pOH}$

① $[OH^-] = 10^{-pOH} = 10^{-(3.15)} = 7.07945... \times 10^{-4}$ mol/L

② $K_b = \frac{[OH^-]^2}{[B]_{initial}} \Rightarrow [B]_{initial} = \frac{[OH^-]^2}{K_b}$

$$[B]_{initial} = \frac{(7.07945... \times 10^{-4})^2}{1.7857... \times 10^{-5}} = 0.02806...$$

$$\boxed{[B]_{initial} = 0.028 \text{ mol/L}}$$

3. One of the uses for aniline, $C_6H_5NH_{2(l)}$, is in the manufacture of dyes. Aniline is soluble in water and acts as a weak base. When a 0.054mol/L solution of aniline was prepared, the pH was found to be 8.68. Calculate the base equilibrium constant for aniline.

↳ basic

$[B]_{initial} = 0.054\ mol/L$

$pH = 8.68$

$K_b = ?$

assume approximation rule is good!

③ $K_b = \dfrac{[OH^-]^2}{[B]_{initial}}$

② $[OH^-] = 10^{-pOH}$ or $K_w = [OH^-][H^+]$

$[H^+] = 10^{-pH}$

① $14 = pH + pOH$

* going to go with green path *

① $pOH + pH = 14 \Rightarrow pOH = 14 - pH$

$pOH = 14 - 8.68 = 5.32$

② $[OH^-] = 10^{-pH} = 10^{-5.32} = 4.7863... \times 10^{-6}\ mol/L$

③ $K_b = \dfrac{[OH^-]^2}{[B]_{initial}} = \dfrac{(4.7863... \times 10^{-6})^2}{(0.054)} = 4.2423... \times 10^{-10}$

$\boxed{K_b = 4.2 \times 10^{-10}}$

Now try pg. 698 #19 (b,c), 20 (b,c), 22 & pg. 701 #29-31, 33 & pg. 703 #35-38