Acid Ionization Constant: K_a

Equilibrium constant for acid dissociation

Dissociation of acid in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

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

K_a is the acid ionization (aka acid dissociation) constant

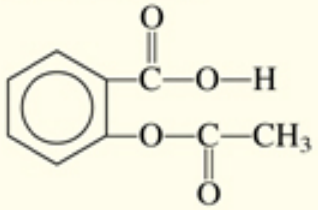
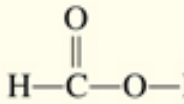
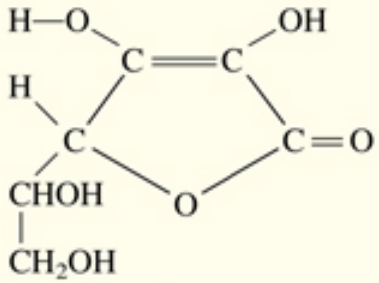
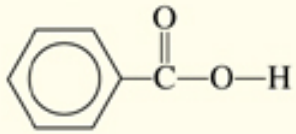
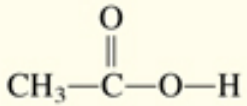
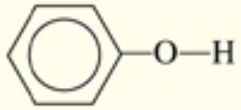
- Quantitative measure of acid strength
- Higher K_a = stronger acid
- Sometimes discussed in terms of pK_a

$$pK_a = -\log K_a$$

K_a ↑ Weak acid strength ↑

pK_a ↑ Weak acid strength ↓

K_a Values for Some Common Weak Acids

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Hydrofluoric acid	HF	H—F	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	O=N—O—H	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	HCOOH		1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH		1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

Calculations Using K_a

1.) 0.100mol of HF is dissolved in 1.00L of water at 25˚C. The pH at equilibrium was found to be 2.08. Calculate K_a.

A: 7.5×10^{-4}

2.) What is the pH of a 0.122M monoprotic acid whose K_a is 5.7×10^{-4}?

A: pH = 2.06

Determining Relative Acidity

1.) Which is the stronger acid, HF or HNO_2?

Look up K_a in table:
HF: 7.5×10^{-4}
HNO_2: 4.6×10^{-4}

A: HF

Making Approximations in Equilibrium Calculations (do we need to use the Quadratic Equation?)

Answer: Only if the percent difference between X and the equilibrium concentration is >5%

Example A:

Find $[HNO_2]$ for a 0.010M solution of Nitrous acid (HNO_2) at 25°C. $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$ where $K_a = 2.9 \times 10^{-8}$.

	HClO	H_3O^+	ClO^-
I	0.010	0	0
C	-X	+X	+X
E	0.010-X	X	X

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

$$2.9 \times 10^{-8} = \frac{[X][X]}{[0.010-X]}$$

Ignore this X

$$2.9 \times 10^{-8} = \frac{X^2}{0.010}$$

$$X^2 = 2.9 \times 10^{-10}$$

$$X = 0.000017$$

$[HClO] = 0.010 - 0.000017 \sim 0.010$

$(0.000017/0.010)*100 = 0.17\%$

Approximation OK

Making Approximations in Equilibrium Calculations (do we need to use the Quadratic Equation?)

Answer: Only if the percent difference between X and the equilibrium concentration is >5%

Example B:

Find [HClO] for a 0.010M solution of Hypochlorous acid (HClO) at 25°C. $HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$ where $K_a = 4.5x10^{-4}$.

	HNO_2	H_3O^+	NO_2^-
I	0.010	0	0
C	-X	+X	+X
E	0.010-X	X	X

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

$$4.5x10^{-4} = \frac{[X][X]}{[0.010-X]}$$

Ignore this X

$$4.5x10^{-4} = \frac{X^2}{0.010}$$

$$X^2 = 4.5x10^{-6}$$

$$X = 0.0021$$

$[HNO_2] = 0.010 - 0.0021 \sim 0.008$

$(0.0021/0.008)*100 = 26\%$

Approximation **NOT** acceptable

Making Approximations

1.) Find the pH of a 0.10M solution of Formic Acid ($HCHO_2$)

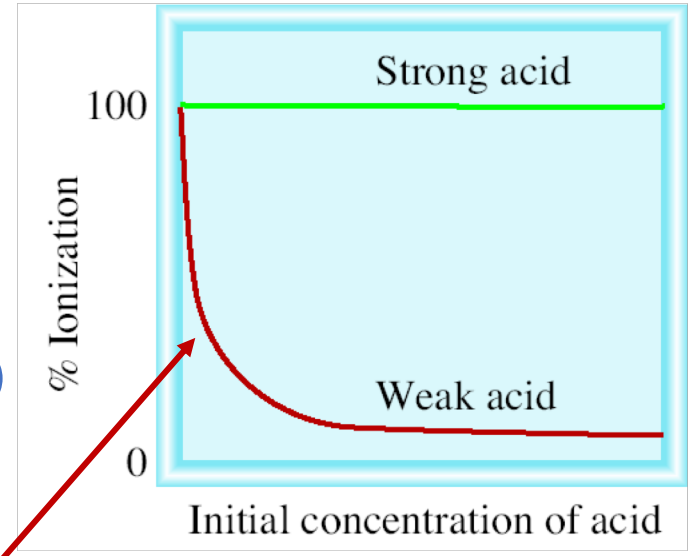
Look up K_a in table:

A: pH=2.37

Percent Ionization and K_a

- Indicates the extent to which an acid is ionized
- Only matters for weak acids (100% for strong)
- Higher percent ionization = more ions = stronger acid
  - Ex: 0.1M HCl, pH = 1.00
  - 0.1M HCOOH, pH = 2.38

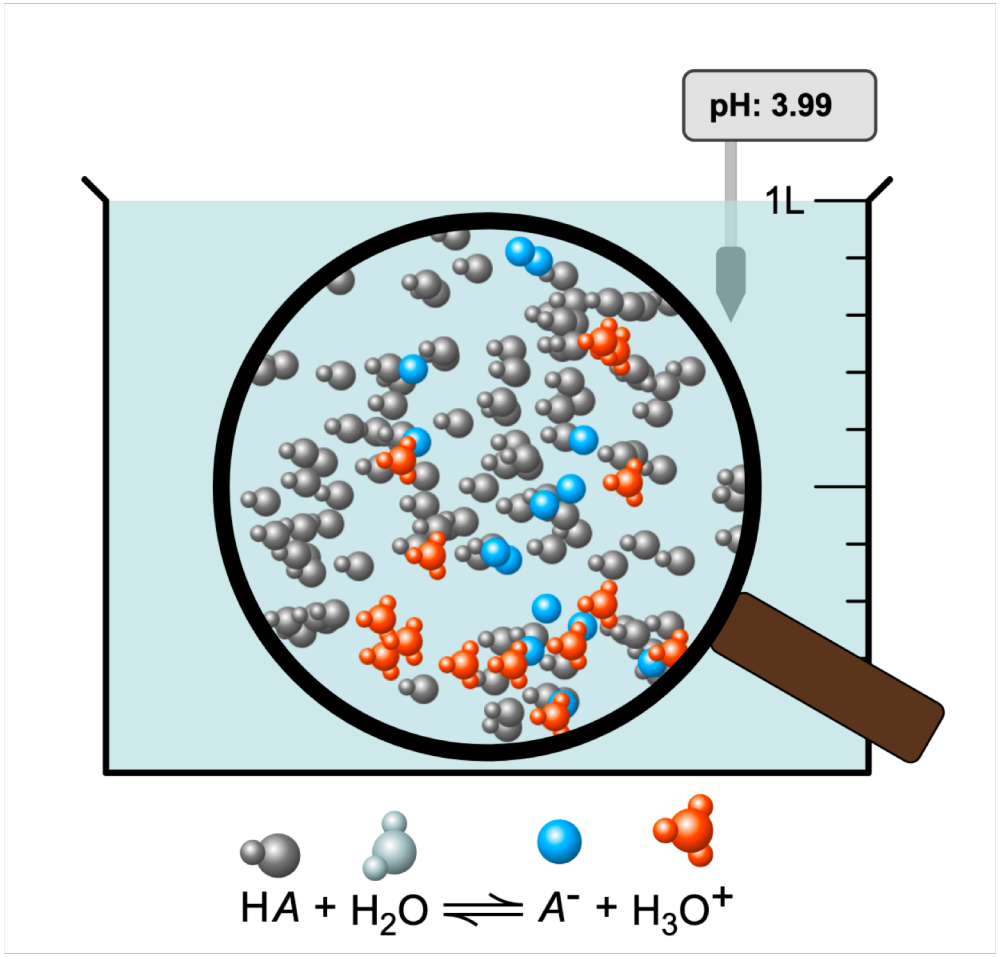
$$\text{Percent Ionization} = \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$$



% ionization of a weak acid decreases as the initial concentration of the acid increases

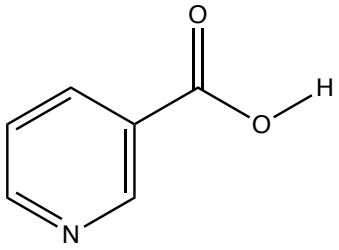
2 Factors affect pH of solution:

- nature of acid/base
- concentration



Calculations Using Percent Ionization

1.) Niacin, one of the B vitamins, has the following structure:



a.) If a 0.020M solution has a pH of 3.26, what is the K_a for niacin?

A:1.6×10^{-5}

b.) What is the percent ionization of the 0.020M solution?

A: 2.7%

2.) A 0.0100M solution of HNO_2 is 19% ionized at equilibrium. What is the K_a?

A:4.46×10^{-4}

Polyprotic Acids

Acids that have more than one ionizable proton

- Ionize in successive steps

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$HCO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

- Each step has its own K_a
- Easier to remove the first proton than the second, etc.
  - $K_{a1} > K_{a2} > K_{a3}$.....
- Successive equilibrium constants have less and less impact on pH
  - May not need to use all K values to solve a problem

Polyprotic Acids

If the difference between the K_a values for the first and 2nd, 3rd, etc. K_a values is 10^3 or more, the pH generally depends on only the first dissociation.

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-3}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	4.6×10^{-5}	

Polyprotic Acid Calculations

Calculate the pH of a 0.0050M solution of sulfuric acid.

A: pH=2.10

Base Ionization Constant: K_b

Equilibrium constant for base dissociation

Weak bases react with water to produce hydroxide ions:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_{eq} = \frac{[HB^+][OH^-]}{[B]} = K_b$$

K_b is the base ionization constant

- Quantitative measure of base strength
- Higher K_b = stronger base
- Sometimes discussed in terms of pK_b

$$pK_b = -\log K_b$$

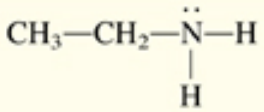
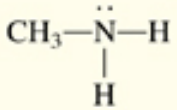
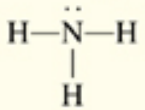
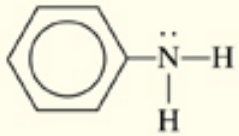
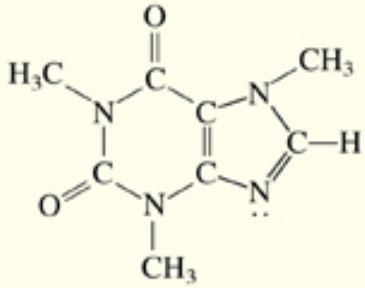
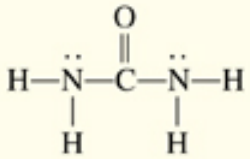
K_b ↑ Weak base strength ↑

pK_b ↑ Weak base strength ↓

Types of Weak Bases

- Neutral substances that have an atom with a non-bonding pair of electrons
  - Examples include ammonia (NH_3) & amines
  - Amines described at beginning of chapter (slide 5)
- Anions (conjugate bases) of weak acids
  - Examples include HCO_3^-, ClO^-, HS^-
  - Act as H^+ acceptors in water
  - Anions of strong acids do not act as bases – not an equilibrium process
- Insoluble/slightly soluble hydroxides
  - Soluble hydroxides are strong bases
  - $Ca(OH)_2$, $Fe(OH)_3$
  - Solubility equilibriums (K_{sp}) will be discussed in the next chapter

K_b Values for Some Common Weak Bases

Name of Base	Formula	Structure	K_b*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$		5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2		4.4×10^{-4}	$CH_3\overset{+}{N}H_3$	2.3×10^{-11}
Ammonia	NH_3		1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$		1.5×10^{-14}	$H_2NCO\overset{+}{N}H_3$	0.67

K_a & K_b Relationship for Conjugate Acid/Base Pairs in Water

Base & water

$NH_3\ (aq) + H_2O(l) \rightleftharpoons NH_4(aq) + OH^-(aq)$ $K_b = 1.8x10^{-5}$

$pK_b = 4.74$

Conjugate acid & water

$NH_4^+\ (aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ $K_a = 5.6x10^{-10}$

$pK_a = 9.26$

Add the two reactions together: multiply K values (Ch15)

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$K_w = K_a x K_b = 1.0x10^{-14}$$

$$1.8x10^{-5} \times 5.6x10^{-10} = 1.0x10^{-14}$$

$$pK_a + pK_b = 14$$

$$9.26 + 4.74 = 14$$

Calculations Using K_b

1.) What is the pH of a 0.15M solution of NH_3? $K_b = 1.8 \times 10^{-5}$

A: pH = 14.21

2.) Codeine is a weak organic base. A 5.0×10^{-3}M solution of codeine has a pH of 9.95. Calculate the pK_b and the value of K_b for this base.

A: $K_b = 1.62 \times 10^{-6}$
$pK_b = 5.79$

3.) A solution of ammonia in water has a pH of 11.17. What is the molarity of the solution? $K_b = 1.8 \times 10^{-5}$

A: 0.123M