Problem: (a) Calculate pH and (b) the fraction of CH_3CO_2H ionized at equilibrium.

$$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$$

	CH_3CO_2H	H^+	$CH_3CO_2^-$
Initial	**1.0M**	**~ 0**	**0**
Equilibrium	**1.0 – x**	**x**	**x**

$$K_a = \frac{(x)(x)}{(1.0 - x)}$$

$$\text{assume } x << 1.0$$

$$K_a = \frac{(x)(x)}{(1.0)}$$

$$K_a = 1.8x10^{-5} = \frac{(x)(x)}{(1.0)}$$

$$x = \sqrt{1.8x10^{-5}}$$

$$x = 4.3x10^{-3}$$

$$pH = -\log[4.3x10^{-3}] = 2.3$$

Question

The pH of 0.1M CH_3COOH is 2.87. What is the value of the acid dissociation constant, K_a?

pH = -log $[H_3O^+]$ = 2.87 $\Rightarrow [H_3O^+] = 1.35 \times 10^{-3}$

$$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$$

$$K_a = \frac{[H_3O+][CH_3COO^-]}{[CH_3COOH]}$$

	CH_3COOH	H_3O^+	CH_3COO^-
Initial conc	0.1	0	0
Equil. Conc	0.1 – x	x	x

$$K_a = \frac{[1.35\times10^{-3}][1.35\times10^{-3}]}{[0.1]}$$

$$K_a = 1.8 \times 10^{-5}$$

Calculate the pH at 25°C of a 0.18 *M* solution of a weak acid that has $K_a = 9.2 \times 10^{-6}$.

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

	$HA(aq)$	$H^+(aq)$	$A^-(aq)$
Initial concentration (*M*):	0.18	0	0
Change in concentration (*M*):	$-x$	$+x$	$+x$
Equilibrium concentration (*M*):	.18 − x	x	x

$$9.2 \times 10^{-6} = \frac{(x)(x)}{0.18\ M - x}$$

Use the approximation since K_a is small compared to C_i.

$$9.2 \times 10^{-6} = \frac{x^2}{0.18\ M}$$

$$9.2 \text{ x } 10^{-6} = \frac{x^2}{0.18\ M}$$

$$1.3 \text{ x } 10^{-3}\ M = x$$

Check the approximation:

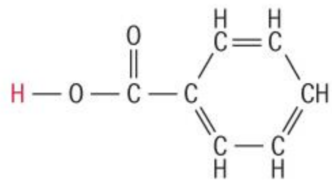
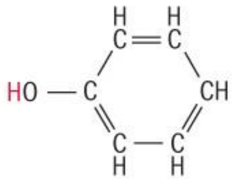
$$\frac{1.3 \text{ x } 10^{-3}\ M}{0.18\ M} x 100 = 0.72\%$$

$$0.72\% < 5\%$$

Approximation is valid.

$$\text{pH} = -\log(1.3 \text{ x } 10^{-3}\ M) = 2.89$$

Acid ionization constants of some monoprotic weak acids at 25 ºC

Acid	Formula	Structural Formula	Ionization Reaction	K_a
Chlorous acid	$HClO_2$	H—O—Cl=O	$HClO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$	1.1×10^{-2}
Nitrous acid	HNO_2	H—O—N=O	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.6×10^{-4}
Hydrofluoric acid	HF	H—F	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	3.5×10^{-4}
Formic acid	$HCHO_2$	H—O—C(=O)—H	$HCHO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$	1.8×10^{-4}
Benzoic acid	$HC_7H_5O_2$		$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.5×10^{-5}
Acetic acid	$HC_2H_3O_2$	H—O—C(=O)—CH_3	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous acid	HClO	H—O—Cl	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	2.9×10^{-8}
Hydrocyanic acid	HCN	H—C≡N	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol	HC_6H_5O		$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

Weak Bases and Base Ionization Constants

To define the base ionization constant K_b we write:

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

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

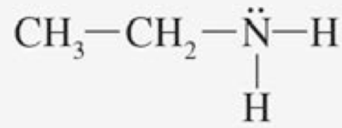
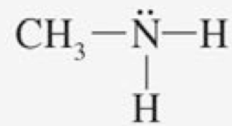
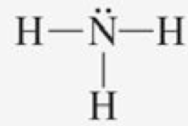
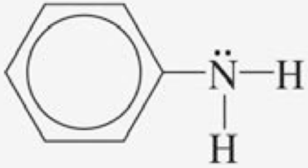
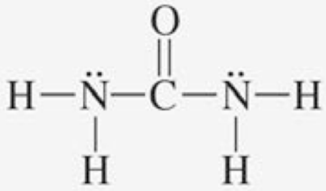
where HB+ is the conjugate acid of base B

$$[OH^-] = \sqrt{C_b * K_b}$$

pK

- A way of expressing the strength of an acid or base is **p*K*.**
- $pK_a = -\log(K_a)$, $K_a = 10^{-pKa}$
- $pK_b = -\log(K_b)$, $K_b = 10^{-pKb}$
- **The stronger the acid, the smaller the pK_a.**
  - Larger K_a = smaller pK_a
  - Because it is the –log
- **The stronger the base, the smaller the pK_b.**
  - Larger K_b = smaller pK_b

Ionization constants of some weak bases at 25 ºC

Name of base	Formula	Structure	K_b
Ethylamine	$C_2H_5NH_2$		5.6×10^{-4}
Methylamine	CH_3NH_2		4.4×10^{-4}
Ammonia	NH_3		1.8×10^{-5}
Pyridine	C_5H_5N		1.7×10^{-9}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}
Urea	H_2NCONH_2		1.5×10^{-14}

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = 1.8 \times 10^{-5}$$

Step 1. Define equilibrium concentrations.

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.010	0	0
change	-x	+x	+x
equilib	0.010 - x	x	x

Equilibria Involving A Weak Base

You have 0.010 M NH_3. Calculate the pH.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$K_b = 1.8 \times 10^{-5}$

Step 2. Solve the equilibrium expression

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.010 - x}$$

Assume x is small ($100 \cdot K_b < C_o$), so

$x = [OH^-] = [NH_4^+] = 4.2 \times 10^{-4}$ M

and $[NH_3] = 0.010 - 4.2 \times 10^{-4} = 0.010$ M

The approximation is valid !