Lecture 2

pH Calculations

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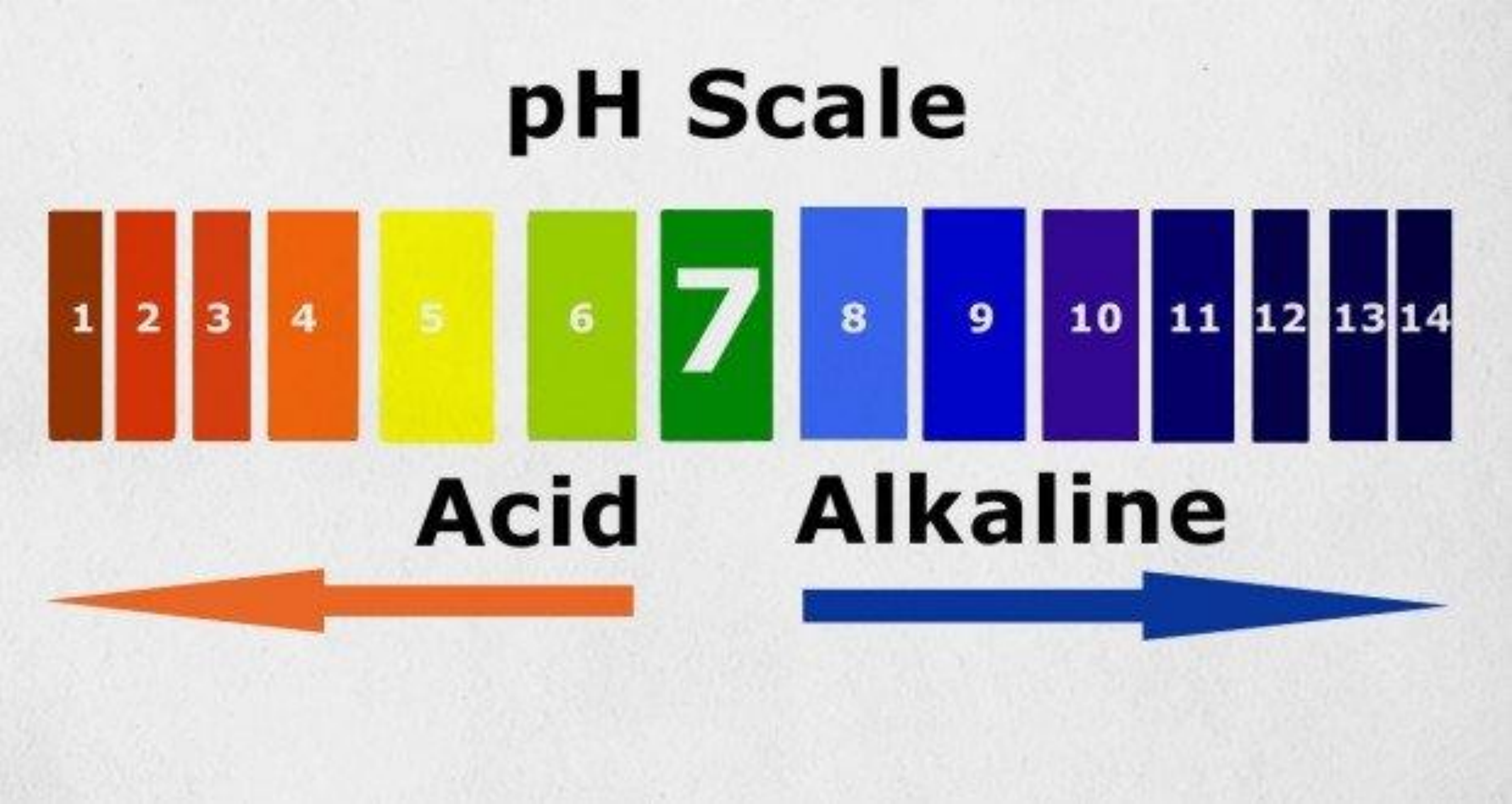

What is pH?

$$pH = -\log_{10} [H^+_{(aq)}]$$

where $[H^+]$ is the concentration of hydrogen ions in mol dm^{-3}

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to convert pH into
hydrogen ion concentration

$$[H^+(aq)] = \text{antilog}\ (-pH)$$

IONIC PRODUCT OF WATER $K_w = [H^+(aq)]\ [OH^-(aq)]\ \text{mol}^2\ \text{dm}^{-6}$

$= 1 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ (at 25°C)

Autoionization of H_2O

$$H_2O \quad + \quad H_2O \rightleftharpoons H_3O^+ \quad + \quad OH^-$$

	H_2O	H_2O	H_3O^+	OH^-
Pairs	**1**	**2**	**2**	**1**
	acid	base	acid	base

$$H_2O \quad + \quad H_2O \rightleftharpoons H_3O^+ \quad + \quad OH^-$$

H_2O # 1	H_2O # 2	H_3O^+	OH^-
acid	base	Conjugate acid of H_2O #2	Conjugate base of H_2O #1

$$H_2O \quad + \quad H_2O \rightleftharpoons H_3O^+ \quad + \quad OH^-$$

H_2O	H_2O	H_3O^+	OH^-
Conjugate acid of OH^-	Conjugate base of H_3O^+	acid	base

Amphoterism - an ion or molecule can act as an acid or base depending upon the reaction conditions

Calculating pH - weak acids

A weak acid is one which only partially dissociates in aqueous solution

A weak acid, HA, dissociates as follows $HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)}$ **(1)**

Calculating pH - weak acids

A weak acid is one which only partially dissociates in aqueous solution

A weak acid, HA, dissociates as follows $$HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)} \qquad (1)$$

Applying the Equilibrium Law $$K_a = \frac{[H^{+}_{(aq)}]\,[A^{-}_{(aq)}]}{[HA_{(aq)}]} \quad \text{mol dm}^{-3} \qquad (2)$$

The ions are formed in equal amounts, so $$[H^{+}_{(aq)}] = [A^{-}_{(aq)}]$$

therefore $$K_a = \frac{[H^{+}_{(aq)}]^2}{[HA_{(aq)}]} \qquad (3)$$

Rearranging (3) gives $$[H^{+}_{(aq)}]^2 = [HA_{(aq)}]\,K_a$$

therefore $$[H^{+}_{(aq)}] = \sqrt{[HA_{(aq)}]\,K_a}$$

$$pH = -\log\ [H^{+}_{(aq)}]$$

Calculating pH - weak acids

Calculate the pH of a weak acid HX of concentration 0.1M ($K_a = 4\times10^{-5}\ \text{mol dm}^{-3}$)

HX dissociates as follows $HX_{(aq)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)}$

Dissociation constant for a weak acid $K_a = \dfrac{[H^+_{(aq)}]\,[X^-_{(aq)}]}{[HX_{(aq)}]}$ mol dm^{-3}

Substitute for X⁻ as ions are formed in equal amounts and the rearrange equation $[H^+_{(aq)}] = \sqrt{[HX_{(aq)}]\,K_a}$ mol dm^{-3}

ASSUMPTION
HA is a weak acid so it will not have dissociated very much. You can assume that its equilibrium concentration is approximately that of the original concentration

$$[H^+_{(aq)}] = \sqrt{0.1 \times 4 \times 10^{-5}} \ \text{mol dm}^{-3}$$

$$= \sqrt{4.00 \times 10^{-6}} \ \text{mol dm}^{-3}$$

$$= 2.00 \times 10^{-3} \ \text{mol dm}^{-3}$$

ANSWER $pH = -\log [H^+_{(aq)}] = 2.699$

Format for solving problems of weak acids using an equilibrium table

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

	$HA(aq)$	$H^+(aq)$	$A^-(aq)$
Initial concentration (*M*):			
Change in concentration (*M*):			
Equilibrium concentration (*M*):			

- Fill in initial concentrations
- Determine concentration changes in terms of x
- Determine equilibrium concentrations in terms of initial concentrations (C_i) and x
- Substitute into the K_a expression and solve for x

Percent Ionization

- Another way to measure the strength of an acid is to determine the percentage of acid molecules that ionize when dissolved in water; this is called the **percent ionization**.
  - The higher the percent ionization, the stronger the acid.

$$\text{Percent Ionization} = \frac{\text{molarity of ionized acid}}{\text{initial molarity of acid}} \times 100\%$$

- Because $[\text{ionized acid}]_{\text{equil}} = [H_3O^+]_{\text{equil}}$

$$\text{Percent Ionization} = \frac{[H_3O^+]_{\text{equil}}}{[HA]_{\text{init}}} \times 100\%$$

Problem: (a) Calculate pH and (b) the fraction of CH_3CO_2H ionized at equilibrium. The concentration of CH_3CO_2H is 1 M (initial, or total). The K_a for acetic acid is 1.8×10^{-5}

Estimate major species in solution **CH_3CO_2H** (a weak acid) and **H_2O.**

$$\mathbf{CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^- \qquad K_a = 1.8 \times 10^{-5}}$$

$$\mathbf{H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}}$$

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

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

Initial	**1.0M**	**~ 0**	**0**
Equilibrium	**1.0 – x**	**x**	**x**

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

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

	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?

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

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

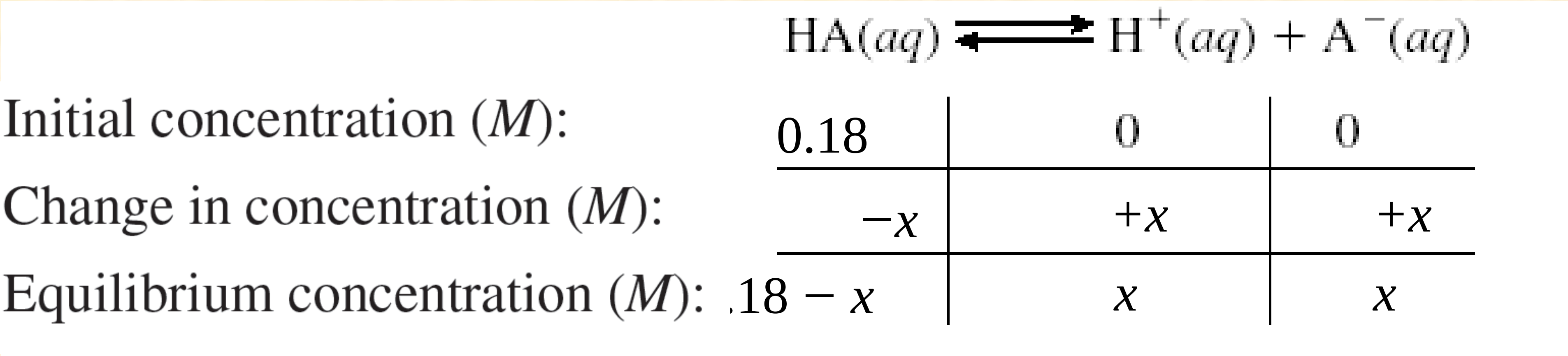
$$K_a = \frac{[H_3O+][CH_3COO^-]}{[CH_3COOH]}$$

	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:

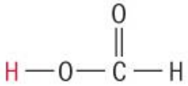
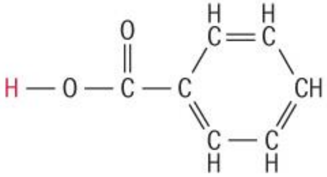
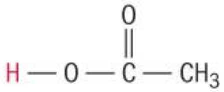
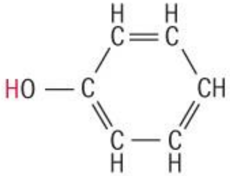
$$\frac{1.3 \text{ x } 10^{-3}\ M}{0.18\ M} x 100 = 0.72\%$$

$$0.72\% < 5\%$$

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	$HCHO_2$	 $H-O-\overset{\overset{\displaystyle O}{\Vert}}{C}-H$	$HCHO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CHO_2^-(aq)$	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	$HC_2H_3O_2$	 $H-O-\overset{\overset{\displaystyle O}{\Vert}}{C}-CH_3$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	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	$H-C\equiv N$	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	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:

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

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

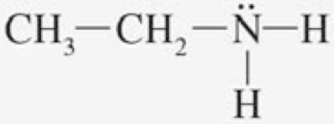
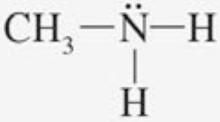
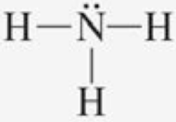
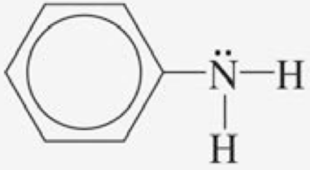
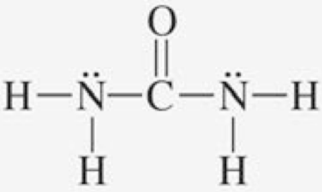
where HB+ is the conjugate acid of base B

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

p*K*

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

Ionization constants of some weak bases at 25 ºC

Name of base	**Formula**	**Structure**	K_b
Ethylamine	$C_2H_5NH_2$	 $CH_3{-}CH_2{-}\underset{\overset{\mid}{H}}{\ddot{N}}{-}H$	5.6×10^{-4}
Methylamine	CH_3NH_2	 $CH_3{-}\underset{\overset{\mid}{H}}{\ddot{N}}{-}H$	4.4×10^{-4}
Ammonia	NH_3	 $H{-}\underset{\overset{\mid}{H}}{\ddot{N}}{-}H$	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	 $H{-}\underset{\overset{\mid}{H}}{\ddot{N}}{-}\overset{\overset{O}{\|}}{C}{-}\underset{\overset{\mid}{H}}{\ddot{N}}{-}H$	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 !

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 3. Calculate pH

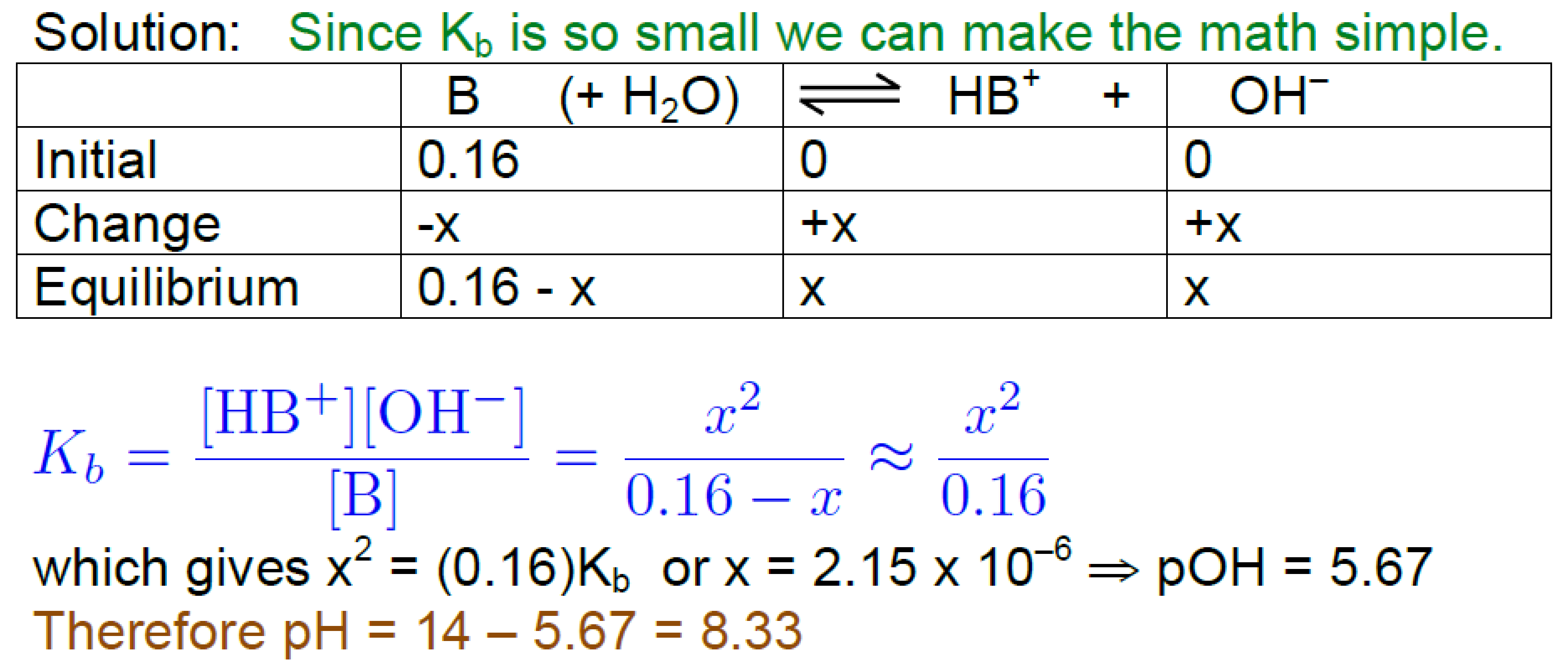
$[OH^-] = 4.2 \times 10^{-4}$ M

so pOH = - log $[OH^-]$ = 3.37

Because pH + pOH = 14

pH = 10.63

Calculate the pH at 25ºC of a 0.16 *M* solution of a weak base with a Kb of 2.9×10^{-11}.



Solution: Since K_b is so small we can make the math simple.

	B (+ H_2O)	$\rightleftharpoons$ HB^+ +	OH^-
Initial	0.16	0	0
Change	-x	+x	+x
Equilibrium	0.16 - x	x	x

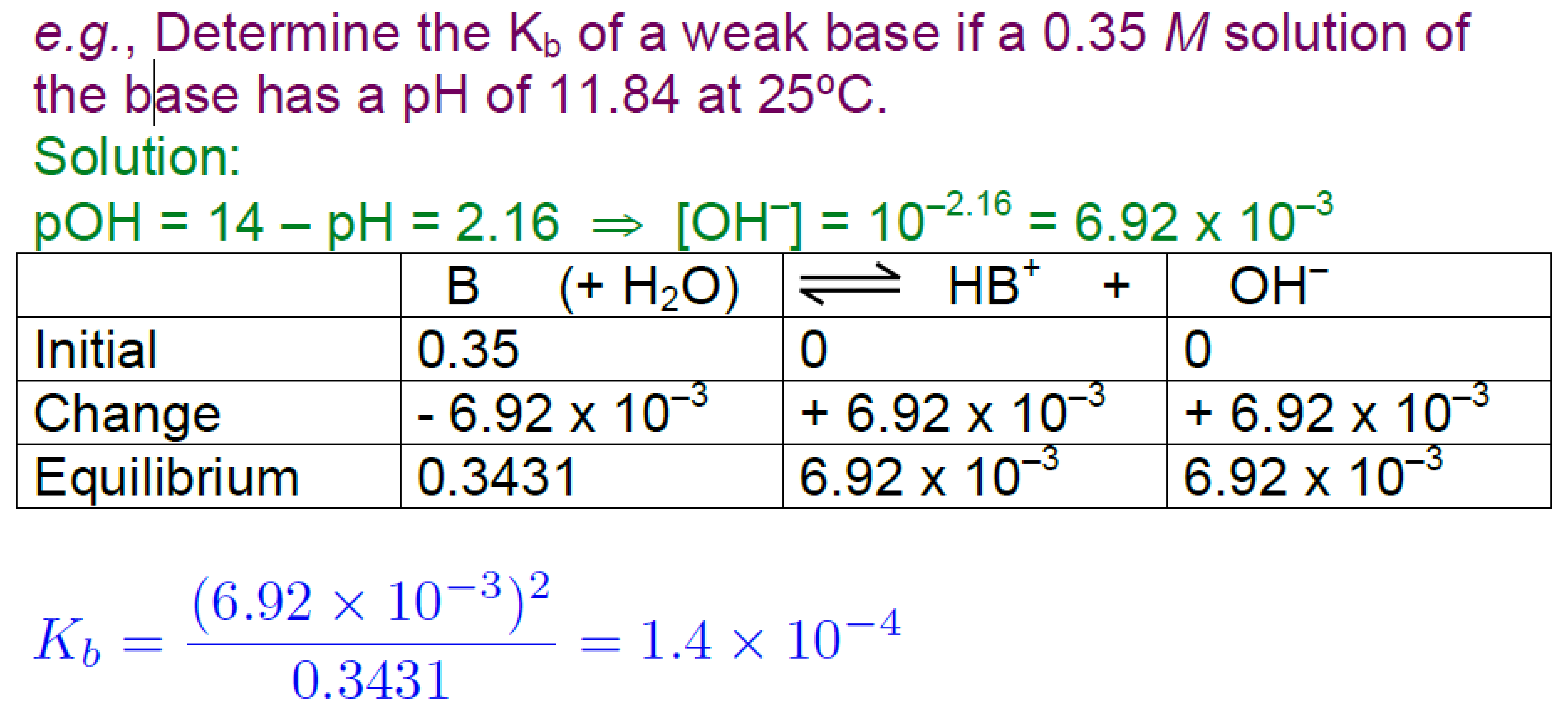
$$K_b = \frac{[\mathrm{HB}^+][\mathrm{OH}^-]}{[\mathrm{B}]} = \frac{x^2}{0.16 - x} \approx \frac{x^2}{0.16}$$

which gives $x^2 = (0.16)K_b$ or $x = 2.15 \times 10^{-6} \Rightarrow \mathrm{pOH} = 5.67$

Therefore pH = 14 – 5.67 = 8.33

Using pH to Determine K_b

This is very similar the weak acid calculation



e.g., Determine the K_b of a weak base if a 0.35 *M* solution of the base has a pH of 11.84 at 25°C.

Solution:

$\text{pOH} = 14 - \text{pH} = 2.16 \Rightarrow [OH^-] = 10^{-2.16} = 6.92 \times 10^{-3}$

	$B \quad (+ H_2O)$	$\rightleftharpoons \quad HB^+ \quad +$	OH^-
Initial	0.35	0	0
Change	$- 6.92 \times 10^{-3}$	$+ 6.92 \times 10^{-3}$	$+ 6.92 \times 10^{-3}$
Equilibrium	0.3431	6.92×10^{-3}	6.92×10^{-3}

$$K_b = \frac{(6.92 \times 10^{-3})^2}{0.3431} = 1.4 \times 10^{-4}$$

Determine the K_b of a weak base if a 0.50 M solution of the base has a pH of 9.59 at 25°C.

$$\text{pH} + \text{pOH} = 14.00$$

$$9.59 + \text{pOH} = 14.00$$

$$\text{pOH} = 4.41$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$[\text{OH}^-] = 10^{-4.41} = 3.89 \text{ x } 10^{-5} M$$

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

Initial concentration (*M*):	0.050 M		
Change in concentration (*M*):	$-3.89\text{x}10^{-5}$ M	$+3.89\text{x}10^{-5}$ M	$+3.89\text{x}10^{-5}$ M
Equilibrium concentration (*M*):	0.050 M*	$3.89\text{x}10^{-5}$ M	$3.89\text{x}10^{-5}$ M

$$^{*}0.050\ M - (3.89 \text{ x } 10^{-5}\ M) \approx 0.050\ M$$

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

$$K_b = \frac{(3.89\text{x}10^{-5}\ M)2}{0.50\ M} = 3.0 \text{ x } 10^{-9}$$

Equilibria Involving Weak Acids and Bases

1. The pH of a 0.10 M nicotinic acid solution is 2.92. Calculate K_a and the % ionization.

   1.4×10^{-5} 1.2%

2. One liter of ammonia solution has pH 11 and degree of ionazition is 0.02. Calculate number of moles in solution.

3. A solution of hydrazine, N_2H_4, is 0.025 M. $K_b = 8.5 \times 10^{-5}$. Calculate the pH and % ionization.

   11.15   5.6%