

ACID-BASE EQUILIBRIUM PROBLEMS

1. Calculate the *pH* of a solution that contains 0.15 M Oxalic acid. Calculate the *concentration of the oxalate ion* in this solution.



From the first equilibrium:

	$\text{H}_2\text{C}_2\text{O}_4$	H_3O^+	HC_2O_4^-
I	0.15	1.0×10^{-7}	0
C	-x	+x	+x
E	$0.15-x$	$1.0 \times 10^{-7}+x$	x

Because the ratio of [HA] to K_{a1} is about 3, the approximation that x is negligible compared to [HA] is not valid.

$$K_{a1} = 5.9 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} = \frac{(1.0 \times 10^{-7} + x)(x)}{(0.15 - x)} \approx \frac{x^2}{(0.15 - x)}$$

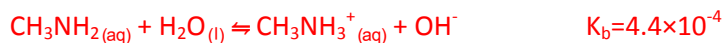
$$x^2 + 5.9 \times 10^{-2}x - 0.00885 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 6.9 \times 10^{-2}, -0.13$$

$$x = 6.9 \times 10^{-2} \approx [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.16$$

2. Calculate the *pH* of a 0.0035 M solution of methylamine.



Again because $0.0035/4.4 \times 10^{-4} = 8$, x will not be negligible compared to [B].

	CH_3NH_2	CH_3NH_3^+	OH^-
I	0.0035	0	1.0×10^{-7}
C	-x	+x	+x
E	$0.0035-x$	x	$1.0 \times 10^{-7}+x$

$$K_{a1} = 4.4 \times 10^{-4} = \frac{[\text{OH}^-][\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]} = \frac{(1.0 \times 10^{-7} + x)(x)}{(0.0035 - x)} \approx \frac{x^2}{(0.0035 - x)}$$

$$x^2 + 4.4 \times 10^{-4}x - 1.54 \times 10^{-6} = 0$$

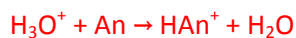
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = 1.04 \times 10^{-3}, -1.48 \times 10^{-3}$$

$$x = 1.0 \times 10^{-3} \approx [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{OH}^-] = 3.00 \therefore \text{pH} = 11.00$$

3. 65.3 mL of 0.156 M hydrochloric acid is added to 145.3 mL of 0.078 M aniline solution.
What is the pH of the resulting solution?

Do Chemistry 101 (neutralization) first.



mmol	10.2	11.3	0
	-10.2	-10.2	+10.2
	0	1.1	10.2

It's a buffer (a fairly poor one, but one nonetheless).

$$pH = pK_a + \log \frac{[B]}{[A]} = 4.63 + \log \frac{10.2}{1.1} = 4.63 + 0.97 = 5.60$$

4. Out of the following, which is the best acid/base to use to make a buffer with a pH of 8.00?
- Cyanic acid $pK_a \sim 4.3$
 - Lactic acid $pK_a \sim 3.2$
 - Hydrazine $pK_a \sim 8.11$

Hydrazine has a pK_a closest to the desired pH so we would use that.

What ratio of masses of the weak acid/base and its conjugate should you use to make the buffer of the required pH ? Use the sodium salt of the conjugate base if you chose a weak acid or the chloride salt of the conjugate acid if you chose the weak base.

$$pH = pK_a + \log \frac{base}{acid}$$

$$\frac{base}{acid} = 10^{pH - pK_a} = 10^{8.00 - 8.11} = 10^{-0.11} = 0.776$$

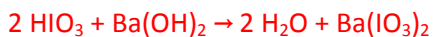
$$\frac{n_{acid}}{n_{base}} = 1.29$$

We can then find the ratio of the mass of the chloride of the conjugate acid to the mass of the base as follows:

$$\frac{m_{acid}}{m_{base}} = \frac{M_{acid} \cdot n_{acid}}{M_{base} \cdot n_{base}} = \frac{M_{acid}}{M_{base}} \cdot \frac{n_{acid}}{n_{base}} = \frac{68.506}{33.0531} \cdot 1.29 = \frac{88.372}{33.0531} \approx \frac{8}{3}$$

5. Calculate the *pH at the equivalence point* when 25.00 mL of 0.10 M Iodic acid is titrated with 0.080 M Barium Hydroxide solution.

We need to find the volume of Ba(OH)₂ at the equivalence point. This is a chemistry 101 problem:



$$? \text{ mL Ba(OH)}_2 = 25.00 \text{ mL HIO}_3 \times \frac{0.10 \text{ mol HIO}_3}{1000 \text{ mL HIO}_3} \times \frac{2 \text{ mol Ba(OH)}_2}{1 \text{ mol HIO}_3} \times \frac{1000 \text{ mL Ba(OH)}_2}{0.080 \text{ mol Ba(OH)}_2} = 62.5 \text{ mL Ba(OH)}_2$$

The total volume at the equivalence point is 87.5 mL. There are 2.50 mmol of IO₃⁻ at this point. The equilibrium is: IO₃⁻ + H₂O ⇌ HIO₃ + OH⁻ and the initial concentration of IO₃⁻ is: $\frac{2.50 \text{ mmol}}{87.5 \text{ mL}} = 0.0286 \text{ M}$

ICE Table:

	IO ₃ ⁻	HIO ₃	OH ⁻
I	0.0829	0	10 ⁻⁷
C	-x	+x	+x
E	0.0829-x	x	10 ⁻⁷ +x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-1}} = 5.6 \times 10^{-14} = \frac{[\text{HIO}_3][\text{OH}^-]}{[\text{IO}_3^-]} = \frac{(x)(10^{-7} + x)}{0.0829 - x}$$

Making the usual assumptions gives:

$$5.6 \times 10^{-14} = \frac{(x)(x)}{0.0829} = \frac{x^2}{0.0829} \text{ and } x = \sqrt{0.0829 \times 5.6 \times 10^{-14}} = 6.9 \times 10^{-8}$$

Assumption (10⁻⁷ << x) not valid:

$$5.6 \times 10^{-14} = \frac{(x)(10^{-7} + x)}{0.0829} \Rightarrow x^2 + 10^{-7}x - 4.642 \times 10^{-15}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(10^{-7}) \pm \sqrt{(10^{-7})^2 - 4(1)(-4.642 \times 10^{-15})}}{2(1)} = 3.45 \times 10^{-8}, -1.345 \times 10^{-7}$$

$$[\text{OH}^-] = x + 10^{-7} = 1.345 \times 10^{-7}$$

$$p\text{OH} = 6.87$$

$$p\text{H} = 7.13$$

6. What is the *pH* of a solution obtained by adding 100.0 g of Sodium Benzoate to enough water to make 1.50 L of solution?



$$[\text{Bz}^-] = \frac{100.0 \text{ g NaC}_7\text{H}_5\text{O}_2}{1.50 \text{ L}} \times \frac{1 \text{ mol NaC}_7\text{H}_5\text{O}_2}{144.1032 \text{ g NaC}_7\text{H}_5\text{O}_2} = 0.463 \text{ M}$$

ICE Table:

	Bz ⁻	HBz	OH ⁻
I	0.463	0	10 ⁻⁷
C	-x	+x	+x
E	0.463-x	x	10 ⁻⁷ +x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10} = \frac{[HBz][OH^-]}{[Bz^-]} = \frac{(x)(10^{-7} + x)}{0.463 - x} \approx \frac{x^2}{0.463}$$

$$x = \sqrt{(0.463)(1.5 \times 10^{-10})} = 8.4 \times 10^{-6}$$

Assumptions are valid.

$$[OH^-] = 8.4 \times 10^{-6} \therefore pOH = 5.08 \therefore pH = 8.92$$

7. 25.00 mL of 0.15 M hydroxylamine is titrated with 0.20 M hydrochloric acid. When 12.56 mL of the acid have been added what should the *pH* be?

$$\text{mmol OHNH}_2 = 25.00 \text{ mL} \times \frac{0.15 \text{ mol}}{1 \text{ L}} = 3.75 \text{ mmol}$$

$$\text{mmol HCl} = 12.56 \text{ mL} \times \frac{0.20 \text{ mol}}{1 \text{ L}} = 2.51 \text{ mmol} \text{ This is the limiting reactant}$$

We are left with a buffer containing 2.51 mmol of the conjugate acid and 1.24 mmol of the weak base.

$$pH = pK_a + \log \frac{\text{base}}{\text{acid}} = 6.04 + \log \frac{1.24}{2.51} = 5.94$$

8. If K_w at 40.0°C is 2.916×10^{-14} , what is the *pH of pure water* at this temperature?

$$K_w = 2.916 \times 10^{-14} = [H_3O^+][OH^-] = x^2$$

$$x = 1.71 \times 10^{-7} = [H_3O^+]$$

$$pH = 6.77$$

9. The pH of a 0.15 M solution of butanoic acid is 2.82. What is the K_b of the butanoate ion?

	HBu	H_3O^+	Bu^-
I	0.15	1.0×10^{-7}	0
C	-x	+x	+x
E	$0.15-x$	$1.0 \times 10^{-7} + x$	x

$$[H_3O^+] = 10^{-pH} = 10^{-2.82} = 0.00151 \text{ M} = 1.0 \times 10^{-7} + x$$

$$x \cong 0.0151 \text{ M}$$

$$[HBu] = 0.15 - x = 0.13$$

$$[Bu^-] = x = 0.0151$$

$$K_a = \frac{[Bu^-][H_3O^+]}{[HBu]} = \frac{(0.0151)(0.0151)}{0.13} = 1.8 \times 10^{-3}$$

$$K_b = 5.7 \times 10^{-12}$$

10. Ethanolammonium ion has pK_a of 9.498. What is the pH of a 0.050 M solution of ethanolamine?



ICE Table:

	Ea	HEa^+	OH^-
I	0.050	0.00	1.0×10^{-7}
C	-x	+x	+x
E	$0.050-x$	x	$1.0 \times 10^{-7} + x$

$$K_b = 3.15 \times 10^{-5} = \frac{x(1.0 \times 10^{-7} + x)}{(0.050 - x)} \cong \frac{x^2}{0.050}$$

$$x = \sqrt{(0.050)(3.15 \times 10^{-5})} = 0.00125 \text{ approximation is valid (2\%).}$$

$$[OH^-] = 0.00125$$

$$pOH = 2.90$$

$$pH = 11.10$$