Acid/base Equilibria Problems

1. Which of the following has the largest dissociation constant in water?

(1) NH_3 (2) $HClO_4$ (3) H_2O (4) HSO_4^- (5) HCN

$HClO_4$ is the strongest acid. Hence, it has the highest dissociation constant.

2. If the pH of an aqueous solution is 3.75, the $[H_3O^+]$ is

(1) 6.6×10^{-3} M (2) 1.8×10^{3} M (3) 5.6×10^{-4} M (4) 1.8×10^{-4} M (5) 5.6×10^{3} M

Note: throughout this problem set, H^+ and H_3O^+ are used interchangeably.

$pH = -\log[H^+]$

$3.75 = -\log[H^+]$

$[H^+] = 1.8 \times 10^{-4}$ M.

3. K_w for water at normal body temperature, 37 °C, is 2.42×10^{-14}. What is the pH for a neutral solution at this temperature?

(1) 0 (2) 6.8 (3) 7.0 (4) 7.2 (5) 14

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

x x

$K_w = [H^+][OH^-] = 2.42 \times 10^{-14}$

$(x)(x) = 2.42 \times 10^{-14}$

$x^2 = 2.42 \times 10^{-14}$

$x = [H^+] = 1.56 \times 10^{-7}$ M

$pH = -\log(1.56 \times 10^{-7}) = 6.81$

4. The pH of a 0.20 M solution of a weak base ($K_b = 1.8 \times 10^{-5}$) is

(1) 2.4 (2) 2.6 (3) 4.2 (4) 11.3 (5) 12.1

Let B be the base:

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

0.20 – x x x

$$K_b = \frac{[BH^+][OH^-]}{[B]} = 1.8 \times 10^{-5}$$

$$\frac{(x)(x)}{0.20 - x} = 1.8 \times 10^{-5}$$

Assume x << 0.20 M. We expect this to be a reasonable assumption because the value of K_b is relatively small. Therefore, $0.20 - x \approx 0.20$ and we have:

$$\frac{x^2}{0.20} = 1.8 \times 10^{-5}$$

$x = [OH^-] = 1.9 \times 10^{-3}$ M

$pOH = -\log(1.9 \times 10^{-3}) = 2.72$

$pH + pOH = 14$

$pH = 14 - 2.72 = 11.28.$

Check the assumption:

$$\frac{x}{0.20\,M} \times 100\% = \frac{1.9\times10^{-3}\,M}{0.20\,M} \times 100\% = 0.95\%$$

x < 1% of 0.20 M, therefore the assumption is OK.

5. The acid ionization constant for HSO_3^- is 6.24×10^{-8}; therefore the base ionization constant for SO_3^{2-} is
   (1) 1.7×10^{-2} (2) 2.5×10^{-4} (3) 3.1×10^{-8} (4) 1.6×10^{7} (5) 1.6×10^{-7}

$K_w = K_aK_b$

$1 \times 10^{-14} = (6.24 \times 10^{-8}) \times K_b$

$K_b = 1.6 \times 10^{-7}$

6. The pH of a 0.40 M NH_4Br solution is ($K_b = 1.8 \times 10^{-5}$ for NH_3):
   (1) 2.7 (2) 4.8 (3) 7.0 (4) 9.2 (5) 12.1

$K_w = K_aK_b$

$1 \times 10^{-14} = K_a \times (1.8 \times 10^{-5})$

$K_a = 5.6 \times 10^{-10}$

$NH_4^+ + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$0.40 - x$ x x

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

$$\frac{(x)(x)}{0.40 - x} = 5.6 \times 10^{-10}$$

Assume that x << 0.40 M. We expect this to be a reasonable assumption because the value of K_a is relatively small. Therefore, $0.40 - x \approx 0.40$ and we have:

$$\frac{x^2}{0.40} = 5.6 \times 10^{-10}$$

$x = [H_3O^+] = 1.5 \times 10^{-5}$ M

$pH = -\log(H_3O^+) = -\log(1.5 \times 10^{-5}) = 4.8.$

Check the assumption:

$$\frac{x}{0.40\,M} \times 100\% = \frac{1.5\times10^{-5}\,M}{0.40\,M} \times 100\% = 0.00375\%$$

x < 1% of 0.40 M, therefore the assumption is OK.

7. What is the pH of a solution of 0.300 mole of acetic acid ($K_a = 1.80 \times 10^{-5}$) and 1.50 moles of sodium acetate in 1.00 liter of water?
   (1) 0.52 (2) 4.05 (3) 5.44 (4) 7.00 (5) 8.56

$$[H_3O^+] = K_a \frac{[acid]}{[base]}$$

So, $pH = pKa + \log\left(\frac{[base]}{[acid]}\right)$

$pH = -\log(1.80 \times 10^{-5}) + \log\left(\frac{1.50}{0.300}\right) = 5.44$

8. When 10 mL of 5 M HCl are added to the solution from question 7, the change in pH is
(1) +0.08 (2) −0.08 (3) +0.18 (4) −0.18 (5) +0.28

HCl is a strong acid, so the moles of H^+ added is:
moles H^+ added = 5 M × 0.010 L = 0.05 mol
The H^+ added reduce the amount of Ac^- in solution by protonating it to HAc. Therefore, we have:

$$[Ac^-] = \frac{1.50 - 0.05\,mol}{1.010\,L} = 1.44\ M$$

$$[H^+] = \frac{0.300 + 0.05\,mol}{1.010\,L} = 0.35\ M$$

(Note: the total volume is now 1.010 L since 10 mL of acid has been added.)

To calculate the new pH:

Because: $[H_3O^+] = K_a \frac{[acid]}{[base]}$

$$pH = pKa + \log\left(\frac{[base]}{[acid]}\right) = -\log(1.80 \times 10^{-5}) + \log\left(\frac{1.44}{0.35}\right) = 5.36$$

$\Delta pH = 5.36 - 5.44 = -0.08$

9. An equimolar solution of chloroacetic acid ($K_a = 1.4 \times 10^{-3}$) and its potassium salt in water has an approximate pH of
(1) 1.4 (2) 2.9 (3) 7.0 (4) 8.4 (5) 9.9

$[H_3O^+] = K_a \frac{[acid]}{[base]}$

So, $pH = pKa + \log\left(\frac{[base]}{[acid]}\right)$

$= -\log(1.4 \times 10^{-3}) + \log 1$ (equimolar: [salt] = [acid])

$= 2.9$

10. Consider the following bases and their pK_b values:
(a) NH_3 (4.74) (b) acetate ion (9.26) (c) CN^- (4.60) (d) N_2H_4 (5.52)

The order of increasing strength as a base is

(1) a, d, c, b (2) c, a, d, b (3) b, d, a, c (4) d, a, c, b (5) c, b, d, a

The strongest base has the highest K_b. Since $pK_b = -\log K_b$, the highest K_b (greatest base strength) results in the smallest pK_b: K_b(acetate ion) < $K_b(N_2H_4)$ < $K_b(NH_3)$ < $K_b(CN^-)$.

11. Which of the following salts dissolve in water to give acid solutions?

(1) $KClO_4$ (2) $NaHSO_4$ (3) $Ca(CN)_2$ (4) NH_4NO_3 (5) Na_2CO_3

$KClO_4 \rightarrow K^+(aq) + ClO_4^-(aq)$

ClO_4^- is the weak conjugate base of the strong acid $HClO_4$. Because it is weak, it does not react with H_2O appreciably. All the H^+ and OH^- in solution are therefore from water dissociation only. The resulting solution is neutral.

$NaHSO_4 \rightarrow Na^+(aq) + HSO_4^-(aq)$

$HSO_4^- + H_2O \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

HSO_4^- is a strong acid. It reacts with H_2O to give H_3O^+ and the resulting solution is acidic.

$Ca(CN)_2 \rightarrow Ca^{2+}(aq) + 2CN^-(aq)$

$CN^-(aq) + H_2O \rightleftharpoons HCN + OH^-(aq)$

CN^- is the strong conjugate base of the weak acid HCN. It reacts with H_2O to give OH^- and the resulting solution is basic.

$NH_4NO_3 \rightarrow NH_4^+(aq) + NO_3^-(aq)$

$NH_4^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NH_3$

NH_4^+ is the strong conjugate acid of the weak base NH_3. It reacts with H_2O to give H_3O^+ and the resulting solution is acidic.

$Na_2CO_3 \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$

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

CO_3^{2-} is the strong conjugate base of the weak acid HCO_3^-. It reacts with H_2O to give OH^- and the resulting solution is basic.

12. The pH of a 0.158 M solution of NH_3 is 11.22. What is the percent dissociation of NH_3 in this solution?

(1) 0.0105% (2) 1.05% (3) 10.5% (4) 0.166% (5) 9.45%

$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

pOH = 14 − 11.22 = 2.78

$[OH^-] = 10^{-2.87} = 1.66 \times 10^{-3}$ M

One mole of NH_3 produces one mole of OH^-; hence, in 1 L of this solution, 1.66×10^{-3} moles of NH_3 have dissociated.

$$\%\ \text{dissociation} = \frac{\text{moles}\,NH_3\ \text{dissociated}}{\text{initial moles}\,NH_3} \times 100\% = \frac{1.66\times10^{-3}\ \text{mol}}{0.158\,\text{mol}} \times 100\% = 1.05\%$$

13. Given $K_a(HCN) = 4.0 \times 10^{-10}$; $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, then a 1 M solution of sodium acetate is more basic than a 1 M solution of sodium cyanide.
(1) true (2) false

K_a (HCN) < K_a (CH_3COOH), so HCN is a weaker acid than CH_3COOH.

The smaller K_a is for an acid, the larger K_b is for its conjugate base:

K_b (CN^-) > K_b (CH_3COO^-), so CN^- is a stronger base than CH_3COO^-.

Therefore, a 1 M solution of NaCN (1 M CN^-) be more basic than a 1 M solution of $NaCH_3COO$ (1 M CH_3COO^-).

14. The pH of a 1.0×10^{-4} M CH_3CO_2H solution ($K_a = 1.82 \times 10^{-5}$) is
(1) 4.28 (2) 4.37 (3) 4.00 (4) 4.82 (5) 4.46

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

1.0×10^{-4} M – x x x

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]}$$

$$1.82 \times 10^{-5} = \frac{(x)(x)}{1.0\times10^{-4} - x}$$

$$x^2 + 1.82 \times 10^{-5}x - 1.82 \times 10^{-9} = 0$$

Solving quadratic equation gives: $x = 3.45 \times 10^{-5}$ M = $[H^+]$
$pH = -\log(3.45 \times 10^{-5} \text{ M}) = 4.46$

Note: it is not valid to assume $1.0 \times 10^{-4} - x$ is $\approx 1.0 \times 10^{-4}$ for this situation. This leads to the incorrect answer of 4.37.

15. The addition of sodium acetate to a solution of acetic acid in water will
(1) reduce the pH of the solution.
(2) increase the degree of ionization of the acetic acid.
(3) increase the H^+ concentration in the solution.
(4) cause K_a for acetic acid to decrease.
(5) repress the ionization of acetic acid.

The answer is (5)

$$CH_3COOH \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

A – x x x

where x is the degree of dissociation of the acid.

If the acetate ion, CH_3COO^-, and H^+ were present only because of the acetic acid dissociating, then we would have:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(x)(x)}{A - x} = \text{constant}$$

However, when a salt containing the acetate ion is added, the $[CH_3COO^-]$ is larger than x. For example, sodium acetate completely dissociated when added to the solution. If the initial concentration of $NaCH_3COO$ is B, then the concentration of the CH_3COO^- produced from the salt dissociating is also B:

$$NaCH_3COO(s) \rightarrow \underset{B}{CH_3COO^-(aq)} + \underset{B}{Na^+(aq)}$$

This is a case of the **common ion effect**. The CH_3COO^- comes from two sources (acid dissociation and salt dissociation) and the total $[CH_3COO^-]$ is B + x. Now the form for K_a is:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(B + x)(x)}{A - x} = \text{constant}$$

Since $[CH_3COO^-]$ increases when it comes from two sources, then $[H^+]$ must decrease so that K_a remains constant: if the concentration of one ion involved in the acetic acid equilibrium goes up, the concentration of the other ion must go down. Therefore, $[H^+]$ = x is less, i.e. the degree of ionization of the acetic acid is repressed. In addition, the pH wil be higher since $[H^+]$ is lowered.

16. A solution contains 0.20 mol per liter of NH_3 and 0.10 mol per liter of NH_4Cl. What is the OH^- ion concentration in this solution? K_b for ammonia is 1.8×10^{-5}?
(1) 1.8×10^{-3} M (2) 3.6×10^{-5} M (3) 9.0×10^{-3} M (4) 3.6×10^{-6} M (5) 6.0×10^{-3} M

$$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

0.20 – x x x

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

0.10 M 0.10 M 0.10 M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$1.8 \times 10^{-5} = \frac{(0.10 + x)(x)}{0.20 - x}$$

Assume 0.20 − x ≅ 0.20 and 0.10 + x ≅ 0.10:

$$1.8 \times 10^{-5} = \frac{(0.10)(x)}{0.20}$$

$x = 3.6 \times 10^{-5}$ M = $[OH^-]$.

Was assumption valid?

$$\frac{x}{0.10} \times 100\% = \frac{3.6\times10^{-5}}{0.10} \times 100\% = 0.036\% << 5\%.$$ Thus, assumption valid.

Alternative solution using the equation of buffer (note that we have a buffer system with a weak base NH_3 and its conjugate acid NH_4^+):

$$[OH^-] = K_b \frac{[base]}{[acid]}$$

$$\text{So, } pOH = pK_b + \log\left(\frac{[acid]}{[base]}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.10\,M}{0.20\,M}\right) = 4.44$$

$$[OH^-] = 10^{-4.44} = 3.6 \times 10^{-5}\ M$$

17. Hypochlorous acid (HClO) is a weak acid. It ionizes slightly in water to produce hydrogen ions and hypochlorite ions (ClO^-). Which one of the following substances could be used with hypochlorous acid to make a buffer solution?

(1) $NaClO_4$ (2) KaClO (3) KNO_3 (4) NaCl (5) $HClO_4$

To make a buffer solution, mix equal amounts of the weak acid (HClO) and a salt of its conjugate base (ClO^-). NaClO is a salt containing the conjugate base.

18. What is the pH of a buffer solution that contains 0.20 M formic acid and 0.20 M sodium formate? The K_a of monoprotic formic acid is 6.0×10^{-4}.

(1) 4.96 (2) 2.34 (3) 4.56 (4) 3.22 (5) 1.96

$$\text{For buffer, } [H_3O^+] = K_a \frac{[acid]}{[base]}$$

$$\text{So, } pH = pKa + \log\left(\frac{[base]}{[acid]}\right) = -\log(6.0 \times 10^{-4}) + \log\left(\frac{0.20}{0.20}\right) = 3.22$$

19. What mass of sodium hydroxide should be added to 100 mL of a 0.0100 M acetic acid solution in order that the solution should have a pH of 4.74? K_a for acetic acid is 1.8×10^{-5}. Assume that the volume does not change when this sodium hydroxide is added.

(1) 5.0×10^{-4} g (2) 1.0×10^{-3} g (3) 8.00 mg (4) 20.0 mg (5) 80 mg

First react base with acid. Assume all base added reacts completely and is used up.
Let y = $[OH^-]$ added (since we assume no volume change, we can use concentration here instead of #moles)

	CH_3COOH	+ OH^-	$\rightarrow CH_3COO^-$	+ H_2O
initial conc.	0.0100	y	0	0
change	−y	−y	+y	+y
final conc.	0.0100−y	0	y	y

$$[H_3O^+] = K_a \frac{[acid]}{[base]}$$

$$pH = pKa + \log\left(\frac{[base]}{[acid]}\right)$$

$$4.74 = -\log(1.8 \times 10^{-5}) + \log\left(\frac{y}{0.0100 - y}\right)$$

$$\log\left(\frac{y}{0.0100 - y}\right) = 0$$

$$\left(\frac{y}{0.0100 - y}\right) = 1$$

$y = 0.00500$ M = $[OH^-]$ added

mass NaOH = 0.00500 M × 0.100 L × 39.9971 g/mol = 0.0200 g = 20.0 mg

20. A buffer solution is prepared from the weak base ammonia and its conjugate acid such that the concentration of the base is exactly ten times the concentration of its conjugate acid. What is the pH of this buffer solution if K_b for ammonia is 1.8×10^{-5}?
(1) 3.74 (2) 10.26 (3) 8.26 (4) 5.74 (5) 9.26

$$[OH^-] = K_b \frac{[base]}{[acid]}$$

$$\text{So, } pOH = pK_b + \log\left(\frac{[acid]}{[base]}\right) = -\log(1.8 \times 10^{-5}) + \log\left(\frac{1}{10}\right) = 3.74$$

pH = 14 − pOH = 10.26

21. Given 100.0 mL of a buffer that is 0.5 M in HOCl and 0.40 M in NaOCl, what is the pH after 10.0 mL of 1.0 M NaOH has been added? (K_a for HOCl is 3.5×10^{-8})
(1) 6.45 (2) 6.64 (3) 7.36 (4) 7.45 (5) 7.55

initial moles HOCl = 0.5 M × 0.100 L = 0.05 mol
initial moles OH^- = 1.0 M × 0.0100 L = 0.01 mol
initial moles OCl^- = 0.4 M × 0.100 L = 0.04 mol

Assume all added base reacts completely with acid:

	HOCl	+ OH^-	→ OCl^-	+ H_2O
initial moles	0.05	0.01	0.04	0.00
change	−0.01	−0.01	+0.01	+0.01

final moles 0.04 0.00 0.05 0.01

Therefore, the final concentrations are:

$$[HOCl] = \frac{0.04\,mol}{0.110\,L} = 0.364\ M$$

$$[OCl^-] = \frac{0.05\,mol}{0.110\,L} = 0.455\ M$$

Note: one cannot assume the volume change is negligible. Change in volume is 10% when NaOH is added.

$$[H_3O^+] = K_a \frac{[acid]}{[base]}$$

So, $pH = pKa + \log\left(\frac{[base]}{[acid]}\right) = -\log(3.5 \times 10^{-8}) + \log\left(\frac{0.455M}{0.364M}\right) = 7.55$

22. How many millimoles of HCl must be added to 100 mL of a 0.100 M solution of methylamine (pK_b = 3.36) to give a buffer having a pH of 10.0? Assume no volume changes.
(1) 8.1 (2) 18.7 (3) 20.0 (4) 6.1 (5) 12.7

CH_3NH_2 = methylamine. (Note: we do not need to know the formula to do the question! One could simply assume that A is methylamine and HA^+ is its conjugate acid.)

$pOH = 14 - pH = 14 - 10.0 = 4.0$

$$[OH^-] = K_b \frac{[base]}{[acid]}$$

So, $pOH = -\log K_b + \log\left(\frac{[acid]}{[base]}\right)$

$$4.0 = 3.36 + \log\left(\frac{[acid]}{[base]}\right)$$

$$\frac{[acid]}{[base]} = 4.365$$

initial moles CH_3NH_2 = 0.100 M × 0.100 L = 0.01 mol

Let x = moles of HCl added. Assume all the added HCl reacts with CH_3NH_2 (the weak conjugate base) to produce $CH_3NH_3^+$ (the weak acid):

	CH_3NH_2 +	HCl →	$CH_3NH_2^+$ +	Cl^-
initial moles	0.01	x	0	0
change	−x	−x	+x	+x

final moles 0.01−x 0 x x

$$\frac{x}{0.01 - x} = 4.365$$

x = 0.0081 mol = 8.1 mmol

23. Calculate the pH of pure water at 45 °C ($K_w = 4.20 \times 10^{-14}$ at 45 °C). Is this solution acidic, neutral, or basic? Explain your answer.

$[OH^-][H_3O^+] = K_w$
$[OH^-] = [H_3O^+]$ for pure water
$[H_3O^+]^2 = 4.20 \times 10^{-14}$
$[H_3O^+] = 2.049 \times 10^{-7}$
$pH = -\log_{10}[H_3O^+] = 6.69$
This solution is neutral, as $[OH^-] = [H_3O^+]$ (despite the pH being below 7).

24. To 200 mL of 0.100 M benzoic acid (C_6H_5COOH) solution is added 110 mL of 0.100 M NaOH solution. Calculate the pH for the new solution (K_a for benzoic acid = 6.3×10^{-5}). If 2.00×10^{-3} mol of HCl are added to the above solution and equilibrium is reached. Calculate the pH of the resulting solution.

In the beginning, moles of HA = 0.200L × 0.100M = 0.020,
moles of OH^- = 0.110L × 0.100M = 0.011
At equilibrium, moles of HA = 0.020 − 0.011 = 0.009, moles of A− = 0.011
$[H_3O^+]= Ka[HA]/[A^-] = 6.3 \times 10^{-5} \times 0.009/0.011 = 5.15 \times 10^{-5}$
$pH = -\log_{10}[H_3O^+] = -\log_{10}(5.15 \times 10^{-5}) = 4.29$

Once more HCl is added, at new equilibrium, moles of HA = 0.009 + 0.002 = 0.011,
moles of A− = 0.011 − 0.002 = 0.009
$[H_3O^+] = Ka[HA]/[A^-] = 6.3 \times 10^{-5} \times 0.011/0.009 = 7.70 \times 10^{-5}$
$pH = -\log_{10}[H_3O^+] = -\log_{10}(7.70 \times 10^{-5}) = 4.11$