Acid-Base Equilibria

Section 95 – Hydrolysis of Salts

95-1 Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$
(b) RbI
(c) $KHCO_2$
(d) CH_3NH_3Br

Solution

(a) $Al(NO_3)_3$ dissociates into Al^{3+} ions (acidic metal cation) and NO_3^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.
(b) RbI dissociates into Rb^+ ions (neutral metal cation) and I^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore neutral.
(c) $KHCO_2$ dissociates into K^+ ions (neutral metal cation) and HCO_2^- ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic.
(d) CH_3NH_3Br dissociates into $CH_3NH_3^+$ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore acidic.

95-2 Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$
(b) K_2CO_3
(c) NH_4Br
(d) $KClO_4$

Solution

(a) $FeCl_3$ dissociates into Fe^{3+} ions (acidic metal cation) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.
(b) K_2CO_3 dissociates into K^+ ions (neutral metal cation) and CO_3^{2-} ions (the conjugate base of a weak acid and therefore basic). The aqueous solution is therefore basic.
(c) NH_4Br dissociates into NH_4^+ ions (a weak acid) and Br^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.
(d) $KClO_4$ dissociates into K^+ ions (neutral metal cation) and ClO_4^- ions (the conjugate base of a strong acid and therefore neutral). The aqueous solution is therefore neutral.

95-3 Determine whether the following 0.10 M aqueous solutions are acidic, basic or neutral. For each solution, indicate what the pH-determining reaction, the major species present, and the pH at 25 °C. Note that Ka and Kb values for the weak acids and bases are available in the Appendices to this text.

(a) ammonium chloride, NH_4Cl

(b) hydrogen chloride, HCl

(c) lithium nitrite, $LiNO_2$

(d) sodium hydroxide, NaOH

(e) barium hydroxide, $Ba(OH)_2$

Solution:

(a) NH_4Cl dissociates into NH_4^+ ions (a weak acid) and Cl^- ions (the conjugate base of a strong acid and therefore essentially neutral). The aqueous solution is therefore acidic.

- The pH-determining reaction is $NH_4^+ \rightleftharpoons NH_3 + H^+$
- Major species present: H_2O (the solvent), NH_4^+, Cl^-.
- pH determination:

	$NH_4^+ \rightleftharpoons$	NH_3	$+ H^+$
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

We first need to calculate the Ka for NH_4^+ from the K_b for NH_3 (1.8×10^{-5})

$$K_w = K_a \times K_b$$

$$Ka = 10^{-14} / 1.8 \times 10^{-5} = 5.56 \times 10^{-10}$$

Then,

$$Ka = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$5.56\ x\ 10^{-10} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Ka, we can assume that the “x” is neglible compared to 0.100 M, therefore the equation becomes:

$$5.56\ x\ 10^{-10} = \frac{x^2}{0.10}$$

$$5.56 \times 10^{-11} = x^2$$

$$\sqrt{5.56\ x\ 10^{-1}} = \sqrt{x^2}$$

x = 7.45 x 10^{-6}

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

pH = -log(7.45 x 10^{-6})

pH = 5.13

(b) HCl is a strong acid and fully dissociates in aqueous solution. The Cl^- ions are pH neutral and so the solution is acidic.

- The pH-determining reaction is HCl(aq) → H^+(aq) + Cl^-(aq)
- Major species present: H_2O (the solvent), H^+, Cl^-.
- pH determination: Since the HCl dissociates completely, the [H^+] = 0.10 M.
  pH = -log[H^+] = -log(0.10) = 1.00

(c) $LiNO_2$ dissociates into Li^+ ions (Group I metal, pH neutral) and NO_2^- ions (the conjugate base of a weak acid and therefore a weak base). The aqueous solution is therefore basic.

- The pH-determining reaction is NO_2^-+ H_2O ⇌ HNO_2 + OH^-
- Major species present: H_2O (the solvent), Li^+, NO_2^-.
- pH determination:

We first need to calculate the Kb for NO_2^- from the K_a for HNO_2 (4.6 x 10^{-4})

$K_w = K_a \times K_b$
Kb = 10^{-14} / 4.6 x 10^{-4} = 2.17 x 10^{-11}

Then,

	NO_2^-	⇌ HNO_2	+ OH^-
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

$$Kb = \frac{[\mathrm{HNO_2}][\mathrm{OH^-}]}{[\mathrm{NO_2^-}]}$$

$$2.17\ x\ 10^{-1} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.17\ x\ 10^{-11} = \frac{x^2}{0.10}$$

$$2.17 \text{ x } 10^{-12} = x^2$$

$$\sqrt{2.17\ x\ 10^{-12}} = \sqrt{x^2}$$

$$x = 1.47 \text{ x } 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(1.47 \text{ x } 10^{-6})$$

$$pOH = 5.83$$

$$pH + pOH = pKw$$

$$pH = 14.00-5.83$$

$$pH = 8.17$$

(d) sodium hydroxide dissociates completely into Na^+ ions (a group I metal, pH neutral) and OH^- (a strong base), and so the solution will be basic.

- The pH-determining reaction is $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
- Major species present: H_2O (the solvent), Na^+, OH^-.
- pH determination: Since the NaOH dissociates completely, the $[OH^-]$ = 0.10 M.
  pOH = -log$[OH^-]$ = -log(0.10) = 1.00
  pH = pKw – pOH = 14.00 - 1.00 = 13.00

(e) barium hydroxide dissociates completely into Ba^{2+} ions (a group II metal, pH neuetral0 and OH^- ions (a strong base), and so the solution will be basic.

- The pH determining reaction is $Ba(OH)_2\,(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$
- Major species present: H_2O (the solvent), Ba^{2+}, OH^-.
- pH determination: Since the $Ba(OH)_2$ dissociates completely, each mole of $Ba(OH)_2$ produces TWO moles of OH^-. Thus the $[OH^-]$ = 2 x 0.10 M = 0.20 M

$$pOH = -\log[OH^-] = -\log(0.20) = 0.70$$

$$pH = pKw - pOH = 14.00 - 0.70 = 13.30$$

95-4 Determine whether the following 0.10 M aqueous solutions are acidic, basic or neutral. For each solution, indicate what the pH-determining reaction, the major species present, and the pH at 25 °C. Note that Ka and Kb values for the weak acids and bases are available in the Appendices to this text.

(a) sodium nitrate, $NaNO_3$

(b) sodium benzoate, $NaC_6H_5CO_2$

(c) potassium fluoride, KF

(d) methylammonium chloride, CH_3NH_3Cl

(e) sodium cyanide, NaCN

Solution:

(a) sodium nitrate dissociates completely into Na^+ (a group I neutral metal ion) and NO_3^- (the conjugate base of the strong acid HNO_3, so NO_3^- is an extremely weak base that is essentially pH neutral in aqueous solution). The solution will be neutral.

- The pH determining reaction is $H_2O\,(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
- Major species present: H_2O (the solvent), Na^+, and NO_3^-.
- pH determination: since the only source of protons is through the autoionization of water, we know that the pH can be determined using the Kw of water at 25 oC,

$$Kw = [OH^-][H^+] = 10^{-14}$$

Since the

$$[OH^-] = [H^+],$$

$$([H^+])^2 = 10^{-14}$$

$$\sqrt{[H^+]} = \sqrt{10^{-14}}$$

$$[H^+] = 10^{-7}$$

$$pH = -\log 10^{-7} = 7.0$$

(b) $NaC_6H_5CO_2$ dissociates completely into Na^+ (a group I neutral metal ion) and $C_6H_5CO_2^-$ (the conjugate base of the weak acid benzoic acid, so $C_6H_5CO_2^-$ is a weak base). The solution will be basic.

- The pH-determining reaction is $C_6H_5CO_2^- + H_2O \rightleftharpoons C_6H_5CO_2H + OH^-$
- Major species present: H_2O (the solvent), Na^+, $C_6H_5CO_2^-$.
- pH determination:

We first need to calculate the Kb for $C_6H_5CO_2^-$ from the K_a for $C_6H_5CO_2H$ (6.3×10^{-5})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 6.3 \times 10^{-5} = 1.59 \times 10^{-10}$

Then,

	$C_6H_5CO_2^- \rightleftharpoons$	$C_6H_5CO_2H$	$+ OH^-$
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

$$Kb = \frac{[C_6H_5CO_2-][OH^-]}{[C_6H_5CO_2H]}$$

$$1.59 \text{ x } 10^{-10} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$1.59 \text{ x } 10^{-10} = \frac{x^2}{0.10}$$

$$1.59 \text{ x } 10^{-11} = x^2$$

$$\sqrt{1.59 \text{ x } 10^{-11}} = \sqrt{x^2}$$

$$x = 3.99 \text{ x } 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(3.99 \text{ x } 10^{-6})$$

$$pOH = 5.40$$

$$pH + pOH = pKw$$

$$pH = 14.00-5.40$$

$$pH = 8.60$$

(c) KF dissociates dissociates completely into K^+ (a group I neutral metal ion) and F^- (the conjugate base of the weak acid HF, so F^- is a weak base). The solution will be basic.

- The pH-determining reaction is $F^- + H_2O \rightleftharpoons HF + OH^-$
- Major species present: H_2O (the solvent), K^+, F^-.
- pH determination:

We first need to calculate the Kb for F^- from the K_a for HF ($6.4 \text{ x } 10^{-4}$)

$K_w = K_a \text{ x } K_b$
$Kb = 10^{-14} / 6.4 \text{ x } 10^{-4} = 1.56 \text{ x } 10^{-11}$

Then,

	$F^- \rightleftharpoons$	HF	+ OH^-
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

$$Kb = \frac{[F-][\mathrm{OH}^-]}{[\mathrm{HF}]}$$

$$1.56 \text{ x } 10^{-11} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$1.56 \text{ x } 10^{-11} = \frac{x^2}{0.10}$$

$$1.56 \text{ x } 10^{-12} = x^2$$

$$\sqrt{1.56 \text{ x } 10^{-12}} = \sqrt{x^2}$$

$$x = 1.25 \text{ x } 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$\mathrm{pOH} = -\log(1.25 \text{ x } 10^{-6})$$

$$\mathrm{pOH} = 5.90$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{pKw}$$

$$\mathrm{pH} = 14.00-5.90$$

$$\mathrm{pH} = 8.10$$

(d) CH_3NH_3Cl dissociates completely into $CH_3NH_3^+$ (the conjugate acid of a weak base) and Cl^- (the conjugate base of a very strong acid, so Cl^- is essentially pH neutral). The solution will be acidic.

- The pH-determining reaction is $CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$
- Major species present: H_2O (the solvent), $CH_3NH_3^+$, Cl^-.

- pH determination:

	$CH_3NH_3^+ \rightleftharpoons$	CH_3NH_2	$+ H^+$
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

We first need to calculate the Ka for $CH_3NH_3^+$ from the K_b for CH_3NH_2 (4.4×10^{-4})

$$K_w = K_a \times K_b$$

$$Ka = 10^{-14} / 4.4 \times 10^{-4} = 2.27 \times 10^{-11}$$

Then,

$$Ka = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]}$$

$$2.27\ x\ 10^{-1} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Ka, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.27\ x\ 10^{-11} = \frac{x^2}{0.10}$$

$$2.27 \times 10^{-12} = x^2$$

$$\sqrt{2.27\ x\ 10^{-12}} = \sqrt{x^2}$$

$$x = 1.51 \times 10^{-6}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pH = -\log(1.51 \times 10^{-6})$$

$$pH = 5.82$$

(e) NaCN dissociates dissociates completely into Na^+ (a group I neutral metal ion) and CN^- (the conjugate base of the weak acid HCN, so CN^- is a weak base). The solution will be basic.

- The pH-determining reaction is $CN^- + H_2O \rightleftharpoons HCN + OH^-$
- Major species present: H_2O (the solvent), Na^+, CN^-.
- pH determination:

We first need to calculate the Kb for CN^- from the K_a for HCN (4.9×10^{-10})

$K_w = K_a \times K_b$
$Kb = 10^{-14} / 4.9 \times 10^{-10} = 2.04 \times 10^{-5}$

Then,

	$CN^- \rightleftharpoons$	HCN	+ OH^-
I	0.100	0	~0
C	-*x*	+*x*	+*x*
E	0.100-*x*	*x*	*x*

$$Kb = \frac{[CN-][\mathrm{OH^-}]}{[\mathrm{HCN}]}$$

$$2.04 \text{ x } 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

Given the very small value for Kb, we can assume that the "x" is neglible compared to 0.100 M, therefore the equation becomes:

$$2.04 \text{ x } 10^{-5} = \frac{x^2}{0.10}$$

$$2.04 \times 10^{-6} = x^2$$

$$\sqrt{2.04 \text{ x } 10^{-6}} = \sqrt{x^2}$$

$$x = 1.43 \times 10^{-3}$$

Note that x is < 5% of 0.100, therefore our assumption was correct (we can neglect it in 0.100-x).

$$pOH = -\log(1.43 \times 10^{-3})$$

$$pOH = 2.84$$

$$pH + pOH = pKw$$

$$pH = 14.00-2.84$$

$$pH = 11.16$$

95-5 Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[\mathrm{H_3O^+}]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

Solution

Using the abbreviation Pc for $C_{13}H_{20}O_2N_2$ (procaine), the formula for novocaine is PcHCl, which ionizes to form PcH^+ and Cl^-. The molar mass of novocaine is 272.774 g/mol. For convenience, start with 1.00 L of a 2.0% solution by mass:

$1.00 \times 10^3\ cm^3 \times 1.0\ g\ cm^{-3} = 1.00 \times 10^3\ g$

$$\frac{2.0}{100} \times 1.00 \times 10^3\ \text{g} = 20\ \text{g novocaine}$$

$$= \frac{20\ \text{g}}{272.774\ \text{g mol}^{-1}}$$

$$= 0.073\ \text{mol}$$

In exactly 1 L, there is 0.073 *M*. The cation reacts with water:

$$\text{PcH}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Pc}(aq) + \text{H}_3\text{O}^+(aq)$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-1}}{7 \times 10^{-6}} = 1.4 \times 10^{-9}$$

It is convenient to set up a table of concentrations:

	$[C_{13}H_{21}O_2N_2H^+]$ or $[PcH^+]$	$[H_3O^+]$	$[C_{13}H_{21}O_2N_2]$ or [Pc]
Initial concentration (*M*)	0.073	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.073 - x$	x	x

$$1.4 \times 10^{-9} = \frac{[\text{Pc}][H_3O^+]}{[\text{PcH}^+]} = \frac{x^2}{0.073}$$

The change x compared with 0.073 *M* is small and, therefore, neglected:

$[H_3O^+] = x = 1.0 \times 10^{-5} = 1 \times 10^{-5}\ M$

The solution is acidic. The hydroxide ion concentration is:

$$[\text{OH}^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1 \times 10^{-9}\ M$$

$$\text{pH} = -\log(1.0 \times 10^{-5}) = 5.00 = 5.0$$