# Chapter 9 Homework

**9-5.** (a) $H_2M = H^+ + HM^-$ $\quad K_1 = 1.42 \times 10^{-3}$

$\quad F - x \quad x \quad x$

$$\frac{x^2}{0.100 - x} = K_1 \Rightarrow x = 1.12 \times 10^{-2} \Rightarrow pH = -\log x = 1.95$$

$$[H_2M] = 0.100 - x = 0.089 \text{ M}$$

$$[HM^-] = x = 1.12 \times 10^{-2} \text{ M} \quad [M^{2-}] = \frac{[HM^-]K_2}{[H^+]} = 2.01 \times 10^{-6} \text{ M}$$

(b) $$[H^+] = \sqrt{\frac{K_1K_2(0.100) + K_1K_w}{K_1 + 0.100}} = 5.30 \times 10^{-5} \Rightarrow pH = 4.28$$

$$[HM^-] \approx 0.100 \text{ M} \qquad [H_2M] = \frac{[HM^-][H^+]}{K_1} = 3.7 \times 10^{-3} \text{ M}$$

$$[M^{2-}] = \frac{K_2[HM^-]}{[H^+]} = 3.8 \times 10^{-3} \text{ M}$$

The method of Box 9-2 would give more accurate answers, since $[HM^-]$ is not that much greater than $[H_2M]$ or $[M^{2-}]$ in this case.

(c) $M^{2-} + H_2O \rightleftharpoons HM^- + OH^-$ $\qquad K_{b1} = K_w/K_{a2} = 4.98 \times 10^{-9}$

$\quad F - x \qquad x \quad x$

$$\frac{x^2}{0.100 - x} = K_{b1} \Rightarrow x = 2.23 \times 10^{-5} \Rightarrow pH = -\log\frac{K_w}{x} = 9.35$$

$$[M^{2-}] = 0.100 - x = 0.100 \text{ M} \qquad [HM^-] = x = 2.23 \times 10^{-5} \text{ M}$$

$$[H_2M] = \frac{[H^+][HM^-]}{K_1} = 7.04 \times 10^{-12} \text{ M}$$

**9-9.** Case (a): $pH = 6.002$, $[HM^-] = 9.80 \times 10^{-3}$ M, $[H_2M] = 9.76 \times 10^{-5}$ M, $[M^{2-}] = 9.85 \times 10^{-5}$ M

Case (b):

| | A | B | C | D | E | F | G | H | I | J |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Box 9-1 Successive Approximations | | | | | | | | | |
| 2 | | | | | | | | | | |
| 3 | $pK_{a1}$ = | 4 | | 1st approx. | 2nd approx. | 3rd approx. | 4th approx. | 5th approx. | | 15th approx. |
| 4 | $pKa_2$ = | 5 | $[HA^-]$ = | 0.01000 | 0.003675 | 0.007675 | 0.005146 | 0.006745 | | 0.00613201 |
| 5 | $K_{a1}$ = | 0.0001 | $[H^+]$ = | 3.15E-05 | 3.12E-05 | 3.14E-05 | 3.13E-05 | 3.14E-05 | | 3.14E-05 |
| 6 | $K_{a2}$ = | 0.00001 | $[H_2A]$ = | 3.15E-03 | 1.15E-03 | 2.41E-03 | 1.61E-03 | 2.12E-03 | | 1.92E-03 |
| 7 | F = | 0.01 | $[A^{2-}]$ = | 3.18E-03 | 1.18E-03 | 2.44E-03 | 1.64E-03 | 2.15E-03 | | 1.95E-03 |
| 8 | $K_w$ = | 1.00E-14 | pH = | 4.50 | 4.51 | 4.50 | 4.50 | 4.50 | | 4.50 |
| 9 | | | | | | | | | | |
| 10 | Cell D4: $[HA^-]$ = F | | | | | | | | | |
| 11 | Cell D5: $[H^+]$ =SQRT((Ka1*Ka2*D4+Ka1*Kw)/(Ka1+D4)) | | | | | | | | | |
| 12 | Cell D6: $[H_2A]$ = D4*D5/Ka1 | | | | | | | | | |
| 13 | Cell D7: $[A^{2-}]$ = Ka2*D4/D5 | | | | | | | | | |
| 14 | Cell D8: pH = -log10(D5) | | | | | | | | | |
| 15 | Cell E4: $[HA^-]$ = F-D6-D7 | | | | | | | | | |
| 16 | After computing E4, then highlight cells D5:E8 and FILL RIGHT | | | | | | | | | |
| 17 | After completing column E, highlight cells E4:F:8 and FILL RIGHT | | | | | | | | | |
| 18 | Continue to highlight each column and FILL RIGHT | | | | | | | | | |

**9-13.** $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$

$$10.00 = 10.329 + \log\frac{(x\text{ g})/(105.99\text{ g/mol})}{(5.00\text{ g})/(84.01\text{ g/mol})} \Rightarrow x = 2.96\text{ g}$$

**9-15.** Picolinic acid is HA, the intermediate form of a diprotic system with $\mathrm{p}K_1 = 1.01$ and $\mathrm{p}K_2 = 5.39$. To achieve pH 5.50, we need a mixture of $HA + A^-$.

| | HA | + | $OH^-$ | → | $A^-$ |
|---|---|---|---|---|---|
| Initial mmol: | 10.0 | | $x$ | | — |
| Final mmol: | $10.0 - x$ | | — | | $x$ |

$$5.50 = 5.39 + \log\frac{x}{10.0 - x} \Rightarrow x = 5.63\text{ mmol} \approx 5.63\text{ mL NaOH}$$

Procedure: Dissolve 10.0 mmol (1.23 g) picolinic acid in ≈ 75 mL $H_2O$ in a beaker. Add NaOH (≈ 5.63 mL) until the measured pH is 5.50. Transfer to a 100 mL volumetric flask and use small portions of $H_2O$ to rinse the contents of the beaker into the flask. Dilute to 100.0 mL and mix well.

**9-17.** $\mathrm{p}K_2$ for phosphoric acid is 7.20, so it has a high buffer capacity at pH 7.45 (from the buffer pair $H_2PO_4^-/HPO_4^{2-}$). At pH 8.5, the buffer capacity of phosphate would be low and it would not be very useful.

**9-20.** (a)

$$H_3PO_4 \xrightarrow{\mathrm{p}K_1 = 2.148} H_2PO_4^- \xrightarrow{\mathrm{p}K_2 = 7.198} HPO_4^{2-} \xrightarrow{\mathrm{p}K_3 = 12.375} PO_4^{3-}$$

$H_2PO_4^-$: $\mathrm{pH} \approx (2.148+7.198)/2 = 4.67$

$HPO_4^{2-}$: $\mathrm{pH} \approx (7.198+12.375)/2 = 9.79$

pH 7.45 corresponds to a mixture of $NaH_2PO_4$ and $Na_2HPO_4$. (You could get the same result by mixing other combinations such as $H_3PO_4$ and $Na_3PO_4$ or $H_3PO_4$ and $Na_2HPO_4$.)

(b) $\mathrm{pH} = \mathrm{p}K_2 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$$7.45 = 7.198 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \Rightarrow \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.78_6$$

Combining this last result with $[HPO_4^{2-}] + [H_2PO_4^-] = 0.050\,0$ M gives $[HPO_4^{2-}] = 0.032\,0_5$ M and $[H_2PO_4^-] = 0.017\,9_5$ M. Use 4.55 g of $Na_2HPO_4$ and 2.15 g of $NaH_2PO_4$.

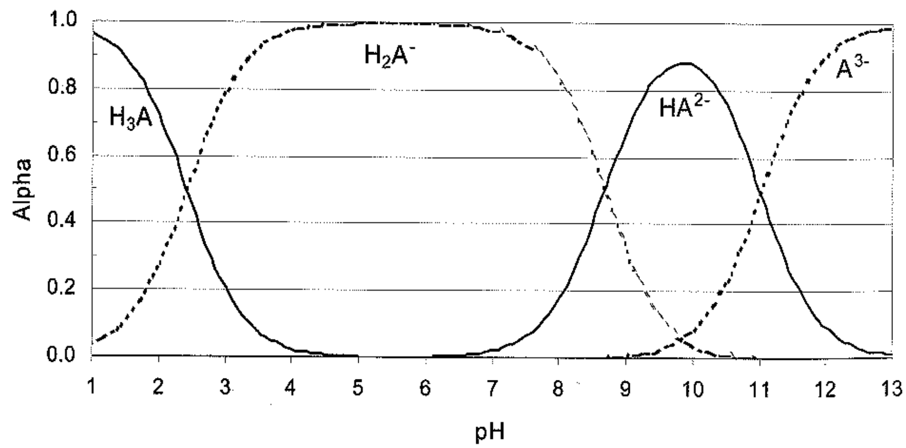
**9-25.** (a) 4.00 (b) 8.00 (c) $H_2A$ (d) $HA^-$ (e) $A^{2-}$

**9-28.** Fraction in form HA $= \alpha_{HA} = \frac{[H^+]}{[H^+]+K_a} = \frac{10^{-5}}{10^{-5}+10^{-4}} = 0.091.$

Fraction in form $A^- = \alpha_{A^-} = \frac{K_a}{[H^+]+K_a} = 0.909.$

$\frac{[A^-]}{[HA]} = \frac{\alpha_{A^-}}{\alpha_{HA}} = 10$, which makes sense.

**9-36.**




| | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 1 | Fractional composition for triprotic acid | | | | | | |
| 2 | | | | | | | |
| 3 | K1 = | pH | [H+] | α(H3A) | α(H2A⁻) | α(HA²⁻) | α(A³⁻) |
| 4 | 3.89E-03 | 1 | 1.00E-01 | 9.63E-01 | 3.74E-02 | 8.01E-10 | 7.82E-20 |
| 5 | K2 = | 2 | 1.00E-02 | 7.20E-01 | 2.80E-01 | 5.99E-08 | 5.85E-17 |
| 6 | 2.14E-09 | 3 | 1.00E-03 | 2.04E-01 | 7.96E-01 | 1.70E-06 | 1.66E-14 |
| 7 | K3 = | 4 | 1.00E-04 | 2.51E-02 | 9.75E-01 | 2.08E-05 | 2.04E-12 |
| 8 | 9.77E-12 | 5 | 1.00E-05 | 2.56E-03 | 9.97E-01 | 2.13E-04 | 2.08E-10 |
| 9 | pK1 = | 6 | 1.00E-06 | 2.56E-04 | 9.98E-01 | 2.13E-03 | 2.08E-08 |
| 10 | 2.41 | 7 | 1.00E-07 | 2.52E-05 | 9.79E-01 | 2.09E-02 | 2.05E-06 |
| 11 | pK2 = | 8 | 1.00E-08 | 2.12E-06 | 8.24E-01 | 1.76E-01 | 1.72E-04 |
| 12 | 8.67 | 9 | 1.00E-09 | 8.14E-08 | 3.17E-01 | 6.77E-01 | 6.61E-03 |
| 13 | pK3 = | 10 | 1.00E-10 | 1.05E-09 | 4.09E-02 | 8.74E-01 | 8.54E-02 |
| 14 | 11.01 | 11 | 1.00E-11 | 6.07E-12 | 2.36E-03 | 5.05E-01 | 4.93E-01 |
| 15 | | 12 | 1.00E-12 | 1.12E-14 | 4.34E-05 | 9.28E-02 | 9.07E-01 |
| 16 | | 13 | 1.00E-13 | 1.22E-17 | 4.74E-07 | 1.01E-02 | 9.90E-01 |
| 17 | A4 = 10^-A10 | | | | | | |
| 18 | C4 = 10^-B4 | | | | | | |
| 19 | D4 = $C4^3/($C4^3+$C4^2*$A$4+$C4*$A$4*$A$6+$A$4*$A$6*$A$8) | | | | | | |
| 20 | E4 = $C4^2*$A$4/($C4^3+$C4^2*$A$4+$C4*$A$4*$A$6+$A$4*$A$6*$A$8) | | | | | | |
| 21 | F4 = $C4*$A$4*$A$6/($C4^3+$C4^2*$A$4+$C4*$A$4*$A$6+$A$4*$A$6*$A$8) | | | | | | |
| 22 | G4 = $A$4*$A$6*$A$8/($C4^3+$C4^2*$A$4+$C4*$A$4*$A$6+$A$4*$A$6*$A$8) | | | | | | |