

Worksheet 6

1. A 7.0 mass % solution of H_3PO_4 in water has a density of 1.0353 g / mL. Calculate the pH and the concentrations of all species present (H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , H_3O^+ , and OH^-) in the solution. You will need to look up the equilibrium constants.

H_3PO_4 , 98.0 amu

Assume 1.000 L of solution

Mass of solution = 1.000 L \times 1000 mL / 1 L \times 1.0353 g / mL = 1035.3 g

Mass of H_3PO_4 = (0.070)(1035.3 g) = 72.47 g H_3PO_4

mol H_3PO_4 = 72.47 g H_3PO_4 \times 1 mol H_3PO_4 / 98.00 g H_3PO_4 = 0.740 mol H_3PO_4

$[\text{H}_3\text{PO}_4] = 0.740 \text{ mol } \text{H}_3\text{PO}_4 / 1.000 \text{ L} = 0.740 \text{ M}$

For the dissociation of the first proton, the following equilibrium must be considered:

	$\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq)$		
initial (M)	0.740	$\cong 0$	0
change (M)	-x	+x	+x
equil (M)	0.740 - x	x	x

$$K_{a1} = [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{PO}_4] = 7.5 \times 10^{-3} = x^2 / 0.740 - x$$

$$x^2 + (7.5 \times 10^{-3})x - (5.55 \times 10^{-3}) = 0$$

Solve for x using the quadratic formula.

x = 0.0708 and -0.0783, only the positive value of x has a physical meaning

x = 0.0708 M = $[\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+]$

For the dissociation of the second proton, the following equilibrium must be considered:

	$\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq)$		
initial (M)	0.0708	0.0708	0
change (M)	-y	+y	+y
equil (M)	0.0708 - y	0.0708 + y	y

$$K_{a2} = [\text{H}_3\text{O}^+][\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-] = 6.2 \times 10^{-8} = (0.0708 + y)(y) / 0.0708 - y$$

$$\cong (0.0708)(y) / 0.0708 = y$$

$$y = 6.2 \times 10^{-8} \text{ M} = [\text{HPO}_4^{2-}]$$

For the dissociation of the third proton, the following equilibrium must be considered:

	$\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq)$		
initial (M)	6.2×10^{-8}	0.0708	0
change (M)	-z	+z	+z
equil (M)	$(6.2 \times 10^{-8}) - z$	0.0708 + z	z

$$K_{a3} = [\text{H}_3\text{O}^+][\text{PO}_4^{3-}] / [\text{HPO}_4^{2-}] = 4.8 \times 10^{-13} = (0.0708 + z)(z) / (6.2 \times 10^{-8}) - z$$

$$\cong (0.0708)(z) / 6.2 \times 10^{-8}$$

$$z = 4.2 \times 10^{-19} \text{ M} = [\text{PO}_4^{3-}]$$

$$[\text{H}_3\text{PO}_4] = 0.740 - x = 0.740 - 0.0708 = 0.67 \text{ M}$$

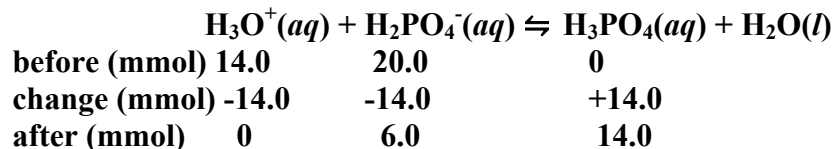
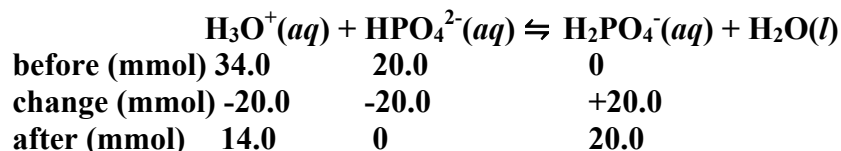
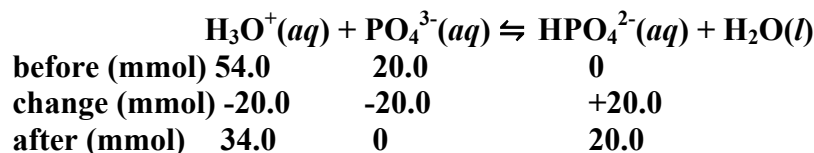
Worksheet 6

$$\begin{aligned}
 [\text{H}_2\text{PO}_4^-] &= [\text{H}_3\text{O}^+] = 0.0708 \text{ M} = 0.071 \text{ M} \\
 [\text{HPO}_4^{2-}] &= 6.2 \times 10^{-8} \text{ M} \\
 [\text{PO}_4^{3-}] &= 4.2 \times 10^{-19} \text{ M} \\
 [\text{OH}^-] &= K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 0.0708 = 1.4 \times 10^{-13} \text{ M} \\
 \text{pH} &= -\log[\text{H}_3\text{O}^+] = -\log(0.0708) = 1.15
 \end{aligned}$$

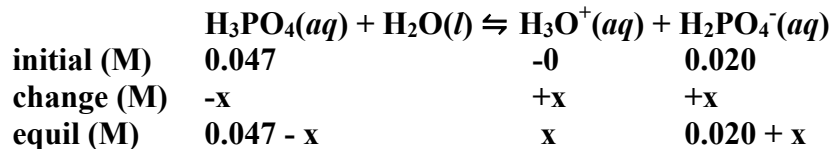
2. Neutralization reactions involving either a strong acid or a strong base go essentially to completion, and therefore we must take such neutralizations into account before calculating concentrations in mixtures of acids and bases. Consider a mixture of 3.28 g of Na_3PO_4 and 300.0 mL of 0.180 M HCl . Write balanced net ionic equations for the neutralization reactions, and calculate the pH of the solution.

Na_3PO_4 , 163.94 amu

$$\begin{aligned}
 3.28 \text{ g Na}_3\text{PO}_4 \times 1 \text{ mol Na}_3\text{PO}_4 / 163.94 \text{ g Na}_3\text{PO}_4 &= 0.0200 \text{ mol} = 20.0 \text{ mmol Na}_3\text{PO}_4 \\
 300.0 \text{ mL} \times 0.180 \text{ mmol / mL} &= 54.0 \text{ mmol HCl}
 \end{aligned}$$



$$[\text{H}_3\text{PO}_4] = 14.0 \text{ mmol} / 300.0 \text{ mL} = 0.047 \text{ M}; [\text{H}_2\text{PO}_4^-] = 6.0 \text{ mmol} / 300.0 \text{ mL} = 0.020 \text{ M}$$



$$\begin{aligned}
 K_a &= [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^{2-}] / [\text{H}_3\text{PO}_4] = 7.5 \times 10^{-3} = x(0.020 + x) / (0.047 - x) \\
 x^2 + 0.0275x - (3.525 \times 10^{-4}) &= 0
 \end{aligned}$$

Solve using the quadratic formula.

$$x = 0.00952$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.00952) = 2.02$$

Worksheet 6

3. A 1.000 L sample of HF gas at 20.0°C and 0.601 atm pressure was dissolved in enough water to make 50.0 mL of hydrofluoric acid. What is the pH of the solution?

$$PV = nRT, n = PV / RT = (0.601 \text{ atm})(1.000 \text{ L}) / (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(293.1 \text{ K})$$

$$n = 0.0250 \text{ mol HF}$$

$$50.0 \text{ mL} \times 1.00 \text{ L} / 1000 \text{ mL} = 0.0500 \text{ L}$$

$$[\text{HF}] = 0.0250 \text{ mol HF} / 0.0500 \text{ L} = 0.500 \text{ M}$$

	$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$		
initial (M)	0.500	$\cong 0$	0
change (M)	-x	+x	+x
equil (M)	0.500 - x	x	x

$$K_a = [\text{H}_3\text{O}^+][\text{F}^-] / [\text{HF}] = 3.5 \times 10^{-4} = x^2 / 0.500 - x$$

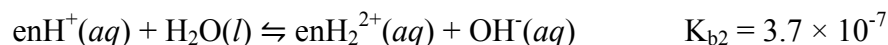
$$x^2 + (3.5 \times 10^{-4})x - (1.75 \times 10^{-4}) = 0$$

Solve for x using the quadratic formula.

$$x = 0.0131$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0131) = 1.883 = 1.88$$

4. Ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, abbreviated en) is an organic base that can accept protons:



Consider the titration of 30.0 mL of 0.100 M ethylenediamine with 0.100 M HCl. Calculate the pH after additions of the following volumes of acid, and construct a qualitative plot of pH versus milliliters of HCl added.

(a) 0.0 mL

	$\text{en}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{enH}^+(aq) + \text{OH}^-(aq)$		
initial (M)	0.100	0	$\cong 0$
change (M)	-x	+x	+x
equil (M)	0.100 - x	x	x

$$K_b = [\text{enH}^+][\text{OH}^-] / [\text{en}] = 5.2 \times 10^{-4} = (x)(x) / 0.100 - x$$

$$x^2 + (5.2 \times 10^{-4})x - (5.2 \times 10^{-5}) = 0$$

Use the quadratic formula to solve for x.

$$x = 0.0070$$

$$[\text{OH}^-] = x = 0.0070 \text{ M}$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 0.0070 = 1.43 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.43 \times 10^{-12}) = 11.84$$

Worksheet 6

(b) 15.0 mL

$$(30.0 \text{ mL})(0.100 \text{ mmol / mL}) = 3.00 \text{ mmol en}$$

$$(15.0 \text{ mL})(0.100 \text{ mmol / mL}) = 1.50 \text{ mmol en}$$

Halfway to the first equivalence point, $[\text{OH}^-] = K_{b1}$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 5.2 \times 10^{-4} = 1.92 \times 10^{-11}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.92 \times 10^{-11}) = 10.72$$

(c) 30.0 mL

At the first equivalence point $\text{pH} = \text{p}K_{a1} + \text{p}K_{a2} / 2 = 9.14$

(d) 45.0 mL

Halfway to the first and second equivalence points, $[\text{OH}^-] = K_{b2} = 3.7 \times 10^{-7} \text{ M}$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 3.7 \times 10^{-7} = 2.70 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.70 \times 10^{-8}) = 7.57$$

(e) 60.0 mL

At the second equivalence point only the acidic enH_2Cl_2 is in solution.

For enH_2^{2+} , $K_a = K_w / K_b$ for $\text{enH}^+ = K_w / K_{b2} = 1.0 \times 10^{-14} / 3.7 \times 10^{-7} = 2.70 \times 10^{-8}$

$$[\text{enH}_2^{2+}] = 3.00 \text{ mmol} / (30.0 \text{ mL} + 60.0 \text{ mL}) = 0.0333 \text{ M}$$

	$\text{enH}_2^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{enH}^+(\text{aq})$
initial (M)	0.0333 $\cong 0$ 0
change (M)	-x +x +x
equil (M)	0.0333 - x x x

$$K_a = [\text{H}_3\text{O}^+][\text{enH}^+] / [\text{enH}_2^{2+}] = 2.70 \times 10^{-8} = (x)(x) / 0.0333 - x \cong x^2 / 0.0333$$

$$\text{Solve for } x. \quad x = [\text{H}_3\text{O}^+] = \sqrt{(2.70 \times 10^{-8})(0.0333)} = 3.00 \times 10^{-5} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.00 \times 10^{-5}) = 4.52$$

(f) 75.0 mL

excess HCl

$$(75.0 \text{ mL} - 60.0 \text{ mL})(0.100 \text{ mmol / mL}) = 1.50 \text{ mmol HCl} = 1.50 \text{ mmol H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = 1.50 \text{ mmol} / (30.0 \text{ mL} + 75.0 \text{ mL}) = 0.0143 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0143) = 1.84$$

5. A 40.0 mL sample of a mixture of HCl and H_3PO_4 was titrated with 0.100 M NaOH. The first equivalence point was reached after 88.0 mL of base, and the second equivalence point was reached after 126.4 mL of base.

Worksheet 6

(a) What is the concentration of H_3O^+ at the first equivalence point?

The first equivalence point is reached when all the H_3O^+ from HCl and H_3O^+ from the first ionization of H_3PO_4 is consumed.

At the first equivalence point $\text{pH} = \text{pK}_{a1} + \text{pK}_{a2} / 2 = 4.66$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-(4.66)} = 2.2 \times 10^{-5} \text{ M}$$

$(88.0 \text{ mL})(0.100 \text{ mmol / mL}) = 8.80 \text{ mmol NaOH}$ are used to get to the first equivalence point.

(b) What are the initial concentrations of HCl and H_3PO_4 in the mixture?

$$\text{mmol (HCl + H}_3\text{PO}_4) = \text{mmol NaOH} = 8.8 \text{ mmol}$$

$$\text{mmol H}_3\text{PO}_4 = (126.4 \text{ mL} - 88.0 \text{ mL})(0.100 \text{ mmol / mL}) = 3.84 \text{ mmol}$$

$$\text{mmol HCl} = (8.8 - 3.84) = 4.96 \text{ mmol}$$

$$[\text{HCl}] = 4.96 \text{ mmol} / 40.0 \text{ mL} = 0.124 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 3.84 \text{ mmol} / 40.0 \text{ mL} = 0.0960 \text{ M}$$

(c) What percent of the HCl is neutralized at the first equivalence point?

100% of the HCl is neutralized at the first equivalence point.

(d) What is the pH of the mixture before addition of any base?

	$\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq)$		
initial (M)	0.0960	0.124	0
change (M)	-x	+x	+x
equil (M)	$0.0960 - x$	$0.124 + x$	x

$$\text{K}_{a1} = [\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-] / [\text{H}_3\text{PO}_4] = 7.5 \times 10^{-3} = (0.124 + x)(x) / 0.0960 - x$$

$$x^2 + 0.132x - (7.2 \times 10^{-4}) = 0$$

Use the quadratic formula to solve for x.

$$x = 0.005$$

$$[\text{H}_3\text{O}^+] = 0.124 + x = 0.124 + 0.005 = 0.129 \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.129) = 0.89$$

(e) Sketch the pH titration curve, and label the buffer regions and equivalence points.

(f) What indicators would you select to signal the equivalence points?

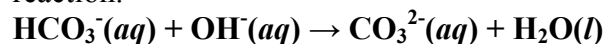
Bromcresol green or methyl orange are suitable indicators for the first equivalence point.

Thymolphthalein is a suitable indicator for the second equivalence point.

6. In qualitative analysis, Ca^{2+} and Ba^{2+} are separated from Na^+ , K^+ , and Mg^{2+} by adding aqueous $(\text{NH}_4)_2\text{CO}_3$ to a solution that also contains aqueous NH_3 . Assume that the concentrations after mixing are 0.080 M $(\text{NH}_4)_2\text{CO}_3$ and 0.16 M NH_3 .

Worksheet 6

(a) List all the Bronsted-Lowry acids and bases present initially, and identify the principal reaction.



(b) Calculate the pH and the concentrations of all species present in the solution.

$$\text{mol HCO}_3^- = (0.560 \text{ mol / L})(0.0500 \text{ L}) = 0.0280 \text{ mol HCO}_3^-$$

$$\text{mol OH}^- = (0.400 \text{ mol / L})(0.0500 \text{ L}) = 0.0200 \text{ mol OH}^-$$

	$\text{HCO}_3^-(aq) + \text{OH}^-(aq) \rightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l)$		
before rxn (mol)	0.0280	0.0200	0
change (mol)	-0.0200	-0.0200	+0.0200
after rxn (mol)	0.0280 - 0.0200	0	0.0200

$$\text{mol HCO}_3^- = 0.0280 - 0.0200 = 0.0080 \text{ mol}$$

$$[\text{HCO}_3^-] = 0.0080 \text{ mol} / 0.1000 \text{ L} = 0.080 \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.0200 \text{ mol} / 0.1000 \text{ L} = 0.200 \text{ M}$$

	$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$		
initial (M)	0.080	$\cong 0$	0.200
change (M)	-x	+x	+x
equil (M)	0.080 - x	x	0.200 + x

$$K_a = [\text{H}_3\text{O}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-] = 5.6 \times 10^{-11} = x(0.200 + x) / 0.080 - x \cong x(0.200) / 0.080$$

$$\text{Solve for } x. \quad x = [\text{H}_3\text{O}^+] = 2.24 \times 10^{-11} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(2.24 \times 10^{-11}) = 10.65$$