Systematic Approach to pH, Equilibrium, and Titrimetry

Use any tools you wish to perform these calculations. Some of these problems can best be solved by using mathematical or technological aids (successive approximations, quadratic formula, calculator solver, etc.). Computer use is recommended wherever appropriate and possible.

Complex Equilibria

16. What is the approximate pH of a solution of 0.015 M arsenic acid (H_3AsO_4)?

Only the 1st ionization needs to be considered.

$$6.0\times10^{-3} = \frac{[H_3O^+][H_2AsO_4^-]}{[H_3AsO_4]}$$

Without proof...

$$6.0\times10^{-3} = \frac{[H_3O^+]^2}{C_{H_3AsO_4} - [H_3O^+]}$$

Which must be solved rigorously...

$[H_2O] = 6.95\times10^{-3}$ M   pH = 2.16

17. Determine the pH of 0.05 M sulfuric acid and show that the 2nd ionization contributes to the pH of the solution.

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$ K_1 = large

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ $K_1 = 1.1 \times 10^{-2}$

Now… treat it just like any diprotic system, except don't ignore the pH contribution by H_2SO_4.

$$K_2 = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$C_{H_2SO_4} = [HSO_4^-] + [SO_4^{2-}]$$

Now for the hard one: mass balance H_3O^+. 2 contributors:
The sulfuric acid (100% ionized) and HSO_4^- (H_3O^+ contribution stoichiometrically tied to SO_4^-).

$$[H_3O^+] = C_{H_2SO_4} + [SO_4^{2-}]$$

Now do all of the algebra...

$$K_2 = \frac{[H_3O^+]([H_3O^+]-C_{H_2SO_4})}{[HSO_4^-]}$$

$$K_2 = \frac{[H_3O^+]([H_3O^+]-C_{H_2SO_4})}{C_{H_2SO_4}-[SO_4^-]}$$

$$K_2 = \frac{[H_3O^+]([H_3O^+]-C_{H_2SO_4})}{C_{H_2SO_4}-([H_3O^+]-C_{H_2SO_4})} = \frac{[H_3O^+]([H_3O^+]-C_{H_2SO_4})}{2C_{H_2SO_4}-[H_3O^+]}$$

Solve it numerically...

$[H_3O^+] = 0.058$ M pH=1.24

Assuming no contribution yields

$$\frac{0.05}{0.058} \times 100 = 86\% \text{ error}$$

18. What is the pH of the malonic acid buffer in which the malonic acid is 0.1 M and the sodium hydrogen malonate is 0.15 M? Demonstrate mathematically that the malonate concentration is negligible.

$$H_2mal + H_2O \rightleftharpoons Hmal^- + H_3O^+$$

$$K_1 = 1.5 \times 10^{-3} = [H_3O^+]\frac{0.15}{0.1}$$

$[H_3O^+] = 0.0010$ M pH=3.0

19. Calculate the pH of 0.001 M sodium hydrogen carbonate.

$$[H_3O^+] = \sqrt{K_1 K_2}$$
$$[H_3O^+] = \sqrt{(4.4\times10^{-7})(4.7\times10^{-11})} = 4.5\times10^{-9}$$
$$pH = 8.3$$

20. Determine the approximate pH of the solution prepared by mixing 3.8 g of oxalic acid dihydrate with 1.3 g of sodium oxalate ($Na_2C_2O_4$), placing the powder in a 100 mL volumetric flask, and diluting to the mark with deionized water.

$$H_2C_2O_4 \quad + \quad C_2O_4^{2-} \longrightarrow 2\ C_2O_4^{2-}$$

$$n_{H_2C_2O_4} = 3.8\text{g} / 126.1\ \text{g/mol} = 0.0301\ \text{mol} = 30.1\ \text{mmol}\ H_2C_2O_4$$
$$n_{Na_2C_2O_4} = 1.3\text{g} / 134.0\ \text{g/mol} = 0.00970\ \text{mol} = 9.70\ \text{mmol}\ H_2C_2O_4$$
$$n_{HC_2O_4^-\ \text{made}} = 9.70\ \text{mmol}\ C_2O_4^{2-} \times \frac{2\ HC_2O_4^-}{1\ C_2O_4^{2-}} = 19.4\ \text{mmol}\ HC_2O_4^-$$
$$n_{H_2C_2O_4\ \text{remaining}} = 30.1\ \text{mmol}\ H_2C_2O_4 - 9.70\ \text{mmol}\ C_2O_4^{2-} \times \frac{1\ H_2C_2O_4}{1\ C_2O_4^{2-}}$$
$$n_{H_2C_2O_4\ \text{remaining}} = 20.4\ \text{mmol}\ H_2C_2O_4$$

$$H_2C_2O_4 \ + \ H_2O \rightleftharpoons H_3O^+ \ + \ HC_2O_4^-$$

$$K_1 = [H_3O^+]\frac{n_{HC_2O_4^-}}{n_{H_2C_2O_4}}$$
$$5.4\times10^{-2} = [H_3O^+]\frac{19.4}{20.4}$$
$$[H_3O^+] = 0.0568\ \text{M}$$
$$pH = 1.25$$

21. Generate the complete titration curve for the titration of 10 mL of 0.1 M maleic acid with 0.1 M NaOH.

Titration curve of 10 mL of 0.1 M malonic acid with 0.1 M NaOH

K_1 =	1.4E-02		2.82
K_2 =	8.6E-07		5.7
V_{acid} =	10	mL	
C_{acid} =	0.1	M	
C_{base} =	0.1	M	

V_{base} (mL)	n_{base} (mmol)	V_{Total} (mL)	n_{H2mal} Remaining (mmol)	C_{H2mal} (M)	n_{Hmal^-} produced (mmol)	C_{Hmal^-} (M)	n_{Hmal^-} Remaining (mmol)	C_{Hmal^-} (M)	$n_{mal^{2-}}$ produced (mmol)	$C_{mal^{2-}}$ (M)	$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	
0.00	0.00	10.00	1.00	0.100	------	------			------	------	0.031	3.22E-13	1.51	Weak acid (K_1) [rigorous soln]
2.00	0.20	12.00	0.80	0.067	0.20	0.017					0.0188	5.31E-13	1.73	Buffer (K1) [rigorous soln]
4.00	0.40	14.00	0.60	0.043	0.40	0.029					0.0112	8.91E-13	1.95	| [rigorous soln]
6.00	0.60	16.00	0.40	0.025	0.60	0.038					0.0093	1.07E-12	2.03	|
8.00	0.80	18.00	0.20	0.011	0.80	0.044					0.0035	2.86E-12	2.46	|
9.00	0.90	19.00	0.10	0.0053	0.90	0.047					0.0016	6.43E-12	2.81	|
9.20	0.92	19.20	0.08	0.0042	0.92	0.048					0.0012	8.21E-12	2.91	|
9.40	0.94	19.40	0.06	0.0031	0.94	0.048					0.00089	1.12E-11	3.05	|
9.60	0.96	19.60	0.04	0.0020	0.96	0.049					0.00058	1.71E-11	3.23	|
9.80	0.98	19.80	0.02	0.0010	0.98	0.049					0.00029	3.50E-11	3.54	|
9.84	0.98	19.84	0.02	0.00081	0.98	0.050					0.00023	4.39E-11	3.64	|
9.88	0.99	19.88	0.01	0.00060	0.99	0.050					0.00017	5.88E-11	3.77	|
10.00	1.00	20.00	0.00	0.00000	1.00	0.050	1	0.05			0.00011	9.11E-11	3.96	Amphoteric salt: sqrt(K_1K_2)
10.20	1.02	20.20					0.98	0.048515	0.02	0.00099	4.2E-05	2.37E-10	4.38	Buffer (K_2)
10.24	1.02	20.24					0.976	0.048221	0.024	0.001186	3.5E-05	2.86E-10	4.46	|
10.28	1.03	20.28					0.972	0.047929	0.028	0.001381	3E-05	3.35E-10	4.52	|
10.40	1.04	20.40					0.96	0.047059	0.04	0.001961	2.1E-05	4.84E-10	4.69	|
10.80	1.08	20.80					0.92	0.044231	0.08	0.003846	9.9E-06	1.01E-09	5.00	|
11.00	1.10	21.00					0.9	0.042857	0.1	0.004762	7.7E-06	1.29E-09	5.11	|
12.00	1.20	22.00					0.8	0.036364	0.2	0.009091	3.4E-06	2.91E-09	5.46	|
14.00	1.40	24.00					0.6	0.025	0.4	0.016667	1.3E-06	7.75E-09	5.89	|
16.00	1.60	26.00					0.4	0.015385	0.6	0.023077	5.7E-07	1.74E-08	6.24	|
18.00	1.80	28.00					0.2	0.007143	0.8	0.028571	2.1E-07	4.65E-08	6.67	|
19.00	1.90	29.00					0.1	0.003448	0.9	0.031034	9.6E-08	1.05E-07	7.02	|
19.20	1.92	29.20					0.08	0.00274	0.92	0.031507	7.5E-08	1.34E-07	7.13	|
19.40	1.94	29.40					0.06	0.002041	0.94	0.031973	5.5E-08	1.82E-07	7.26	|
19.60	1.96	29.60					0.04	0.001351	0.96	0.032432	3.6E-08	2.79E-07	7.45	|
19.80	1.98	29.80					0.02	0.000671	0.98	0.032886	1.8E-08	5.70E-07	7.76	|
20.00	2.00	30.00					0	0	1	0.033333	5.1E-10	1.97E-05	9.29	Weak conj base (K_{b1})
20.20	2.02	30.20									1.5E-11	0.000662	10.82	Excess NaOH
20.40	2.04	30.40									7.6E-12	0.001316	11.12	|
20.60	2.06	30.60									5.1E-12	0.001961	11.29	|
20.80	2.08	30.80									3.8E-12	0.002597	11.41	|
21.00	2.10	31.00									3.1E-12	0.003226	11.51	|
22.00	2.20	32.00									1.6E-12	0.00625	11.80	|
23.00	2.30	33.00									1.1E-12	0.009091	11.96	|
24.00	2.40	34.00									8.5E-13	0.011765	12.07	|
25.00	2.50	35.00									7E-13	0.014286	12.15	|