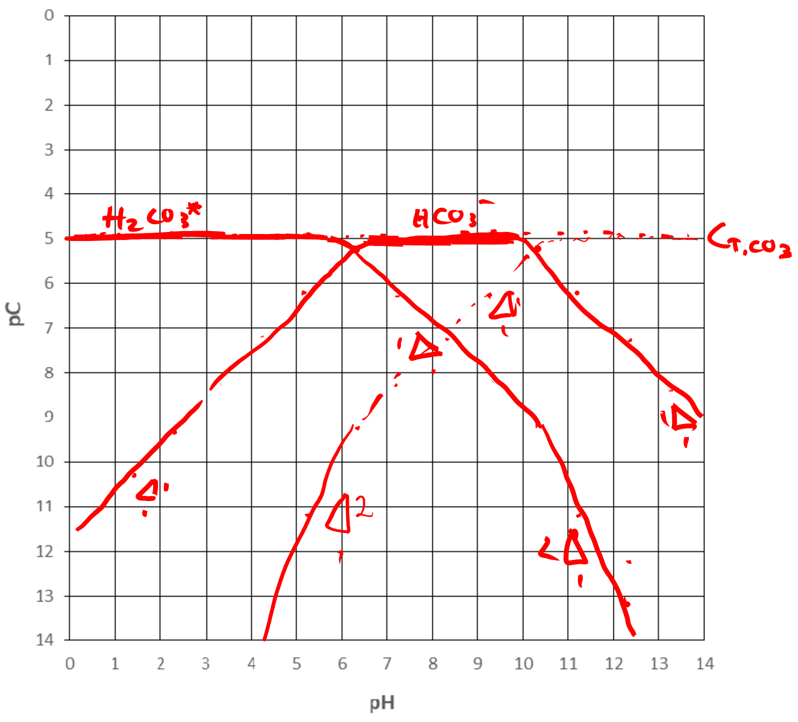
Advanced Water Quality

Class 10: Acid Base Chemistry III

Review of Last Class

E.g., for 10^{-5} M carbonic acid

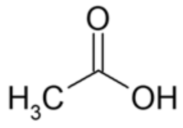


Procedure for solving problems

1. List components (irreducible “building block” groups)
2. List species (component species + combinations of components)
3. Equations (need “x” eqns to solve for “x” unknowns)
    A. Equilibrium Expressions
    B. Mass balance for each component (other than H_2O, H^+)
    C. Electroneutrality
4. List known and unknown quantities
6. Check if #eqns $\geq$ #unknowns
7. Make any simplifying assumptions
8. Solve problem using assumptions
9a. Check validity of your assumptions
9b. If assumptions invalid, make new ones and repeat 7-8

Problem 1. Calculate the equilibrium pH and speciation of acetate after 10^{-3} M acetic acid is added to deionized water (nothing else initially present in the water). *Assume dilute solution approximates “infinite dilution” reference state condition.*

Acetic Acid



$pK_a = 4.7$

Problem 2: Calculate the equilibrium pH and speciation of chloride after 10^{-3} hydrochloric acid (HCl; pK_a = -3) is added to deionized water (nothing else initially present in the water). ***Assume dilute solution approximates "infinite dilution" assumption of the reference state.***

Step 1: components

Step 2: species

Step 3: equations

Step 4: knowns

Step 5: unknowns

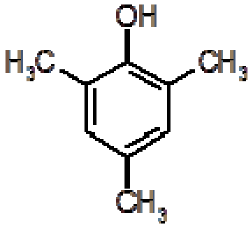
Step 6: #eqns $\geq$ unknowns?

Step 7: simplifying assumptions:

Step 8: Solve!

Step 9a: Check assumptions

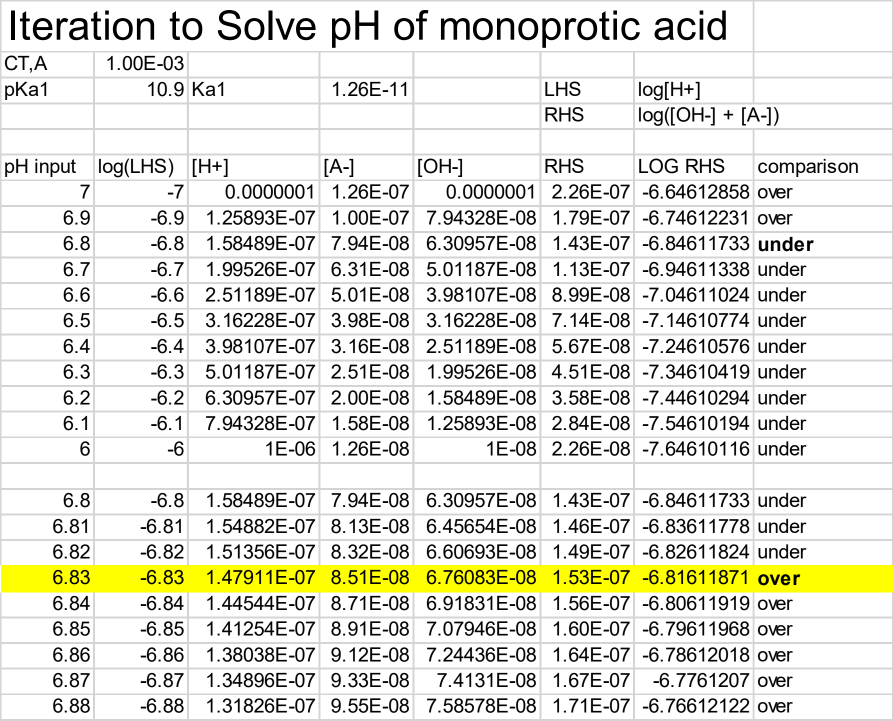
Problem 3: Calculate the equilibrium pH and speciation of trimethylphenol (pK_a = 10.9) after 10^{-3} M is added to deionized water (nothing else initially present in the water). ***Assume dilute solution approximates "infinite dilution" assumption of the reference state.***



Alternative: Solve for pH by iteration

Calculate charge balance at all pH values, compare Log(LHS) vs Log(RHS)

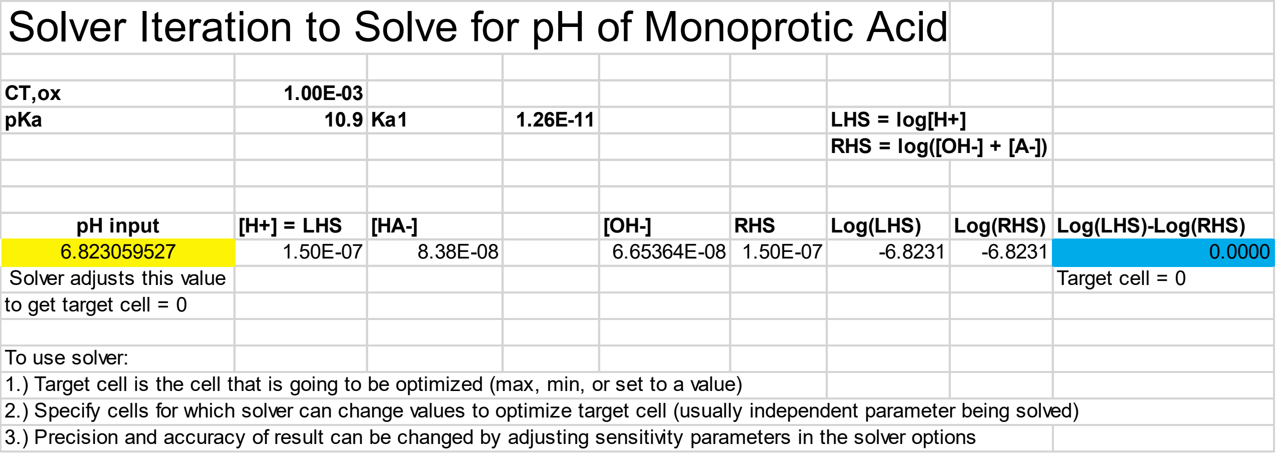
$$\log([H^+]) = \log([OH^-]+[\mathrm{Ph}^-])$$



Iteration to Solve pH of monoprotic acid							
CT,A	1.00E-03						
pKa1	10.9	Ka1	1.26E-11		LHS	log[H+]	
					RHS	log([OH-] + [A-])	
pH input	log(LHS)	[H+]	[A-]	[OH-]	RHS	LOG RHS	comparison
7	-7	0.0000001	1.26E-07	0.0000001	2.26E-07	-6.64612858	over
6.9	-6.9	1.25893E-07	1.00E-07	7.94328E-08	1.79E-07	-6.74612231	over
6.8	-6.8	1.58489E-07	7.94E-08	6.30957E-08	1.43E-07	-6.84611733	**under**
6.7	-6.7	1.99526E-07	6.31E-08	5.01187E-08	1.13E-07	-6.94611338	under
6.6	-6.6	2.51189E-07	5.01E-08	3.98107E-08	8.99E-08	-7.04611024	under
6.5	-6.5	3.16228E-07	3.98E-08	3.16228E-08	7.14E-08	-7.14610774	under
6.4	-6.4	3.98107E-07	3.16E-08	2.51189E-08	5.67E-08	-7.24610576	under
6.3	-6.3	5.01187E-07	2.51E-08	1.99526E-08	4.51E-08	-7.34610419	under
6.2	-6.2	6.30957E-07	2.00E-08	1.58489E-08	3.58E-08	-7.44610294	under
6.1	-6.1	7.94328E-07	1.58E-08	1.25893E-08	2.84E-08	-7.54610194	under
6	-6	1E-06	1.26E-08	1E-08	2.26E-08	-7.64610116	under
6.8	-6.8	1.58489E-07	7.94E-08	6.30957E-08	1.43E-07	-6.84611733	under
6.81	-6.81	1.54882E-07	8.13E-08	6.45654E-08	1.46E-07	-6.83611778	under
6.82	-6.82	1.51356E-07	8.32E-08	6.60693E-08	1.49E-07	-6.82611824	under
6.83	-6.83	1.47911E-07	8.51E-08	6.76083E-08	1.53E-07	-6.81611871	**over**
6.84	-6.84	1.44544E-07	8.71E-08	6.91831E-08	1.56E-07	-6.80611919	over
6.85	-6.85	1.41254E-07	8.91E-08	7.07946E-08	1.60E-07	-6.79611968	over
6.86	-6.86	1.38038E-07	9.12E-08	7.24436E-08	1.64E-07	-6.78612018	over
6.87	-6.87	1.34896E-07	9.33E-08	7.4131E-08	1.67E-07	-6.7761207	over
6.88	-6.88	1.31826E-07	9.55E-08	7.58578E-08	1.71E-07	-6.76612122	over

Or using the solver tool in Excel

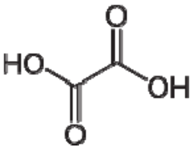
$$\log([H^+]) = \log([OH^-]+[\mathrm{Ph}^-])$$



Solver Iteration to Solve for pH of Monoprotic Acid								
CT,ox	**1.00E-03**							
pKa	**10.9**	**Ka1**	**1.26E-11**			**LHS = log[H+]**		
						RHS = log([OH-] + [A-])		
pH input	**[H+] = LHS**	**[HA-]**		**[OH-]**	**RHS**	**Log(LHS)**	**Log(RHS)**	**Log(LHS)-Log(RHS)**
6.823059527	1.50E-07	8.38E-08		6.65364E-08	1.50E-07	-6.8231	-6.8231	0.0000
Solver adjusts this value								Target cell = 0
to get target cell = 0								
To use solver:								
1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)								
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)								
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options								

- **Objectives:** In class today, you will learn how to
- use spreadsheets to iterate and solve problems that cannot be directly solved.
- Extend the approach begun last class to solve more complex solutions containing
  - Multiprotic acids
  - Non-ideal solution conditions
  - Mixtures of acids & bases

Problem 4: Calculate the equilibrium pH and speciation of oxalic acid (pK_{a1} = 0.9; pK_{a2} = 4.2) after 10^{-3} M is added to deionized water (nothing else initially present in the water). *Assume dilute solution approximates "infinite dilution" assumption of the reference state.*



Step 1: components

Step 2: species

Step 3: equations

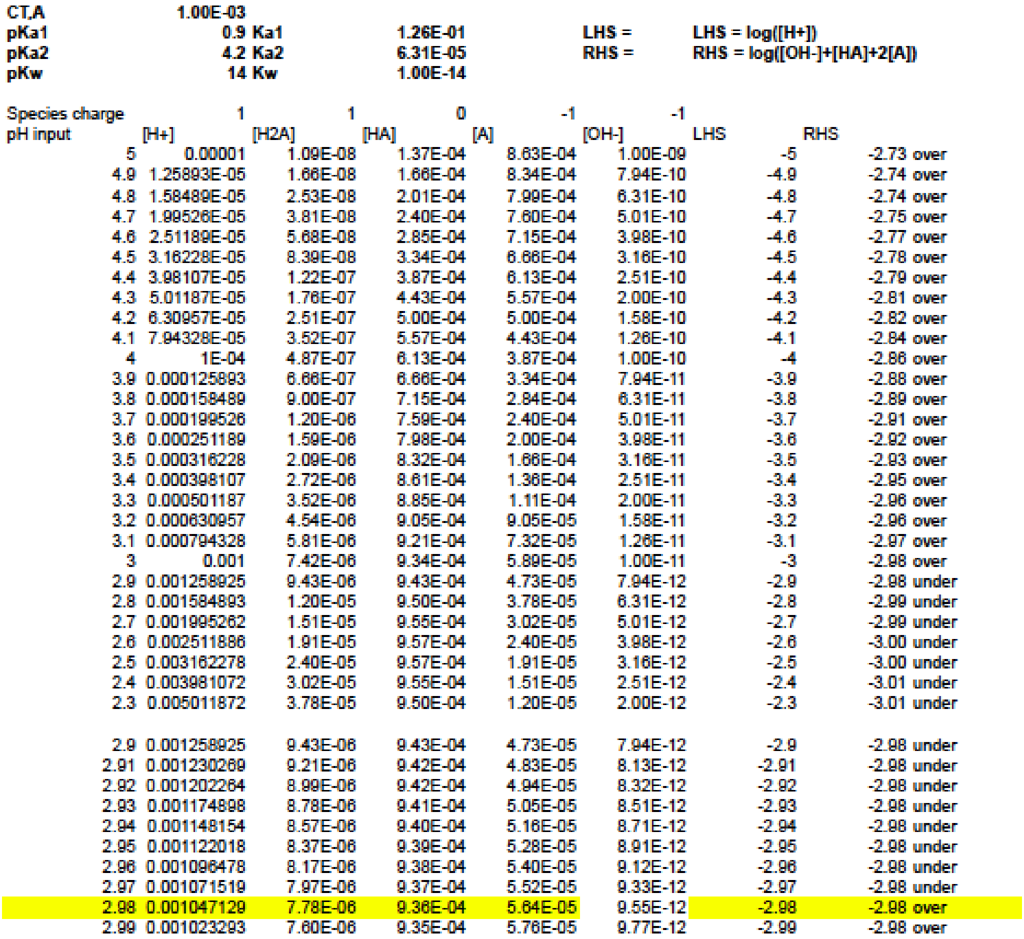
Step 4: knowns

Step 5: unknowns

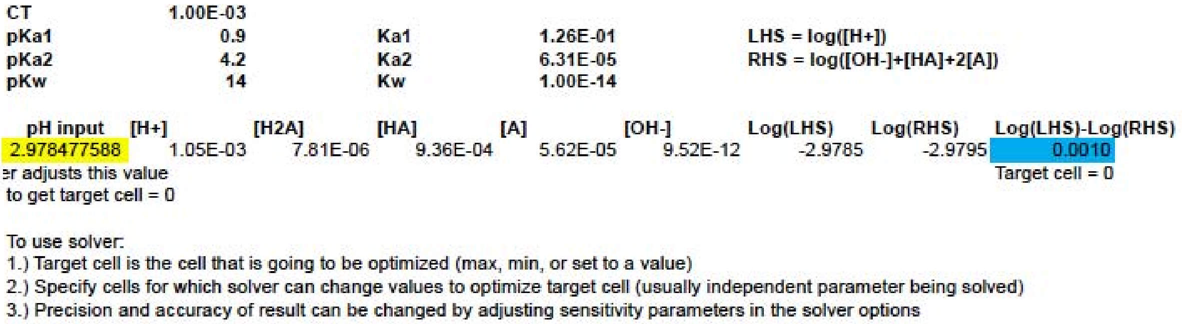
Step 6: #eqns $\geq$ unknowns?

Step 7: simplifying assumptions (let’s skip this time)

Step 8: solve



CT,A	**1.00E-03**							
pKa1	**0.9**	**Ka1**	**1.26E-01**		**LHS =**	**LHS = log([H+])**		
pKa2	**4.2**	**Ka2**	**6.31E-05**		**RHS =**	**RHS = log([OH-]+[HA]+2[A])**		
pKw	**14**	**Kw**	**1.00E-14**					
Species charge	1	1	0	-1	-1			
pH input	[H+]	[H2A]	[HA]	[A]	[OH-]	LHS	RHS	
5	0.00001	1.09E-08	1.37E-04	8.63E-04	1.00E-09	-5	-2.73	over
4.9	1.25893E-05	1.66E-08	1.66E-04	8.34E-04	7.94E-10	-4.9	-2.74	over
4.8	1.58489E-05	2.53E-08	2.01E-04	7.99E-04	6.31E-10	-4.8	-2.74	over
4.7	1.99526E-05	3.81E-08	2.40E-04	7.60E-04	5.01E-10	-4.7	-2.75	over
4.6	2.51189E-05	5.68E-08	2.85E-04	7.15E-04	3.98E-10	-4.6	-2.77	over
4.5	3.16228E-05	8.39E-08	3.34E-04	6.66E-04	3.16E-10	-4.5	-2.78	over
4.4	3.98107E-05	1.22E-07	3.87E-04	6.13E-04	2.51E-10	-4.4	-2.79	over
4.3	5.01187E-05	1.76E-07	4.43E-04	5.57E-04	2.00E-10	-4.3	-2.81	over
4.2	6.30957E-05	2.51E-07	5.00E-04	5.00E-04	1.58E-10	-4.2	-2.82	over
4.1	7.94328E-05	3.52E-07	5.57E-04	4.43E-04	1.26E-10	-4.1	-2.84	over
4	1E-04	4.87E-07	6.13E-04	3.87E-04	1.00E-10	-4	-2.86	over
3.9	0.000125893	6.66E-07	6.66E-04	3.34E-04	7.94E-11	-3.9	-2.88	over
3.8	0.000158489	9.00E-07	7.15E-04	2.84E-04	6.31E-11	-3.8	-2.89	over
3.7	0.000199526	1.20E-06	7.59E-04	2.40E-04	5.01E-11	-3.7	-2.91	over
3.6	0.000251189	1.59E-06	7.98E-04	2.00E-04	3.98E-11	-3.6	-2.92	over
3.5	0.000316228	2.09E-06	8.32E-04	1.66E-04	3.16E-11	-3.5	-2.93	over
3.4	0.000398107	2.72E-06	8.61E-04	1.36E-04	2.51E-11	-3.4	-2.95	over
3.3	0.000501187	3.52E-06	8.85E-04	1.11E-04	2.00E-11	-3.3	-2.96	over
3.2	0.000630957	4.54E-06	9.05E-04	9.05E-05	1.58E-11	-3.2	-2.96	over
3.1	0.000794328	5.81E-06	9.21E-04	7.32E-05	1.26E-11	-3.1	-2.97	over
3	0.001	7.42E-06	9.34E-04	5.89E-05	1.00E-11	-3	-2.98	over
2.9	0.001258925	9.43E-06	9.43E-04	4.73E-05	7.94E-12	-2.9	-2.98	under
2.8	0.001584893	1.20E-05	9.50E-04	3.78E-05	6.31E-12	-2.8	-2.99	under
2.7	0.001995262	1.51E-05	9.55E-04	3.02E-05	5.01E-12	-2.7	-2.99	under
2.6	0.002511886	1.91E-05	9.57E-04	2.40E-05	3.98E-12	-2.6	-3.00	under
2.5	0.003162278	2.40E-05	9.57E-04	1.91E-05	3.16E-12	-2.5	-3.00	under
2.4	0.003981072	3.02E-05	9.55E-04	1.51E-05	2.51E-12	-2.4	-3.01	under
2.3	0.005011872	3.78E-05	9.50E-04	1.20E-05	2.00E-12	-2.3	-3.01	under
2.9	0.001258925	9.43E-06	9.43E-04	4.73E-05	7.94E-12	-2.9	-2.98	under
2.91	0.001230269	9.21E-06	9.42E-04	4.83E-05	8.13E-12	-2.91	-2.98	under
2.92	0.001202264	8.99E-06	9.42E-04	4.94E-05	8.32E-12	-2.92	-2.98	under
2.93	0.001174898	8.78E-06	9.41E-04	5.05E-05	8.51E-12	-2.93	-2.98	under
2.94	0.001148154	8.57E-06	9.40E-04	5.16E-05	8.71E-12	-2.94	-2.98	under
2.95	0.001122018	8.37E-06	9.39E-04	5.28E-05	8.91E-12	-2.95	-2.98	under
2.96	0.001096478	8.17E-06	9.38E-04	5.40E-05	9.12E-12	-2.96	-2.98	under
2.97	0.001071519	7.97E-06	9.37E-04	5.52E-05	9.33E-12	-2.97	-2.98	under
2.98	0.001047129	7.78E-06	9.36E-04	5.64E-05	9.55E-12	-2.98	-2.98	over
2.99	0.001023293	7.60E-06	9.35E-04	5.76E-05	9.77E-12	-2.99	-2.98	over



CT	1.00E-03			
pKa1	0.9	Ka1	1.26E-01	LHS = log([H+])
pKa2	4.2	Ka2	6.31E-05	RHS = log([OH-]+[HA]+2[A])
pKw	14	Kw	1.00E-14	

pH input	[H+]	[H2A]	[HA]	[A]	[OH-]	Log(LHS)	Log(RHS)	Log(LHS)-Log(RHS)
2.978477588	1.05E-03	7.81E-06	9.36E-04	5.62E-05	9.52E-12	-2.9785	-2.9795	0.0010
er adjusts this value to get target cell = 0								Target cell = 0

To use solver:

1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options

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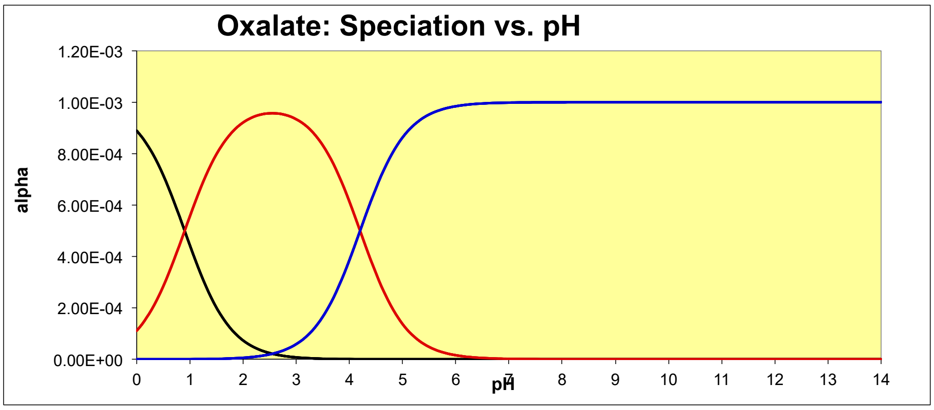
Problem 5: Repeat Problem 4, but do after making simplifying assumptions

Step 7: simplifying assumptions



Step 8: solve

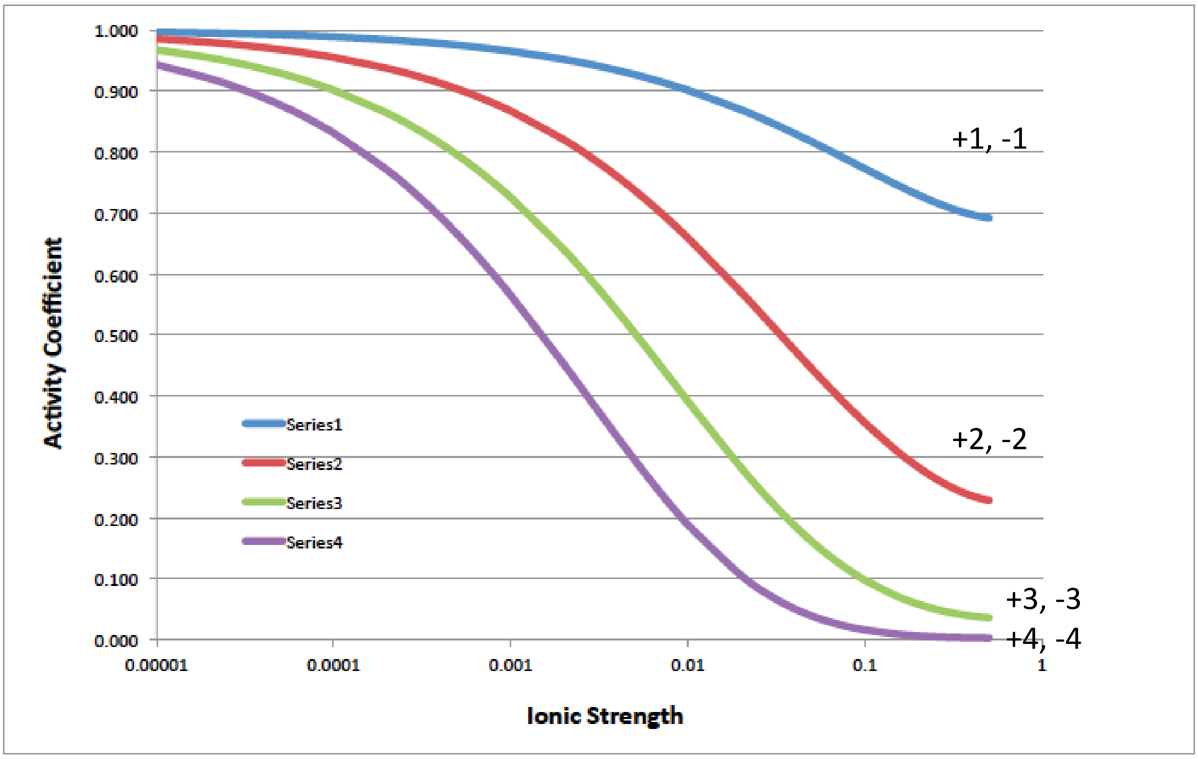
Step 9a: check assumptions

Problem 6: Repeat Problem 4, but do not assume ideal solution conditions. Instead, the water has an ionic strength of 0.2.

Step 1: components

Step 2: species

Step 3: equations (write the same way as if we were assuming ideal solution conditions, i.e., *write everything in terms of molar concentrations, not activities*)



At IS = 0.2, γ_1 = 0.73 and γ_2 = 0.28

Step 3b: Obtain “conditional” equilibrium constants to replace “intrinsic” to use in problem solution.

Step 4: knowns

Step 5: unknowns

Step 6: #eqns $\geq$ unknowns?

Step 7: simplifying assumptions (let’s skip this time)

Step 8: solve

CT,A	**1.00E-03**				
pKa1	**0.63**	**Ka1**	**2.34E-01**	**LHS =**	**LHS = log([H+])**
pKa2	**3.65**	**Ka2**	**2.24E-04**	**RHS =**	**RHS = log([OH-]+[HA]+2[A])**
pKw	**13.7**	**Kw**	**2.00E-14**		

Species charge	1	1	0	-1	-1			
pH input	[H+]	[H2A]	[HA]	[A]	[OH-]	LHS	RHS	
5	0.00001	1.82E-09	4.28E-05	9.57E-04	2.00E-09	-5	-2.71	over
4.9	1.2589E-05	2.86E-09	5.32E-05	9.47E-04	1.58E-09	-4.9	-2.71	over
4.8	1.5849E-05	4.47E-09	6.61E-05	9.34E-04	1.26E-09	-4.8	-2.71	over
4.7	1.9953E-05	6.96E-09	8.18E-05	9.18E-04	1.00E-09	-4.7	-2.72	over
4.6	2.5119E-05	1.08E-08	1.01E-04	8.99E-04	7.94E-10	-4.6	-2.72	over
4.5	3.1623E-05	1.67E-08	1.24E-04	8.76E-04	6.31E-10	-4.5	-2.73	over
4.4	3.9811E-05	2.56E-08	1.51E-04	8.49E-04	5.01E-10	-4.4	-2.73	over
4.3	5.0119E-05	3.91E-08	1.83E-04	8.17E-04	3.98E-10	-4.3	-2.74	over
4.2	6.3096E-05	5.92E-08	2.20E-04	7.80E-04	3.16E-10	-4.2	-2.75	over
4.1	7.9433E-05	8.87E-08	2.62E-04	7.38E-04	2.51E-10	-4.1	-2.76	over
4	1E-04	1.32E-07	3.09E-04	6.91E-04	2.00E-10	-4	-2.77	over
3.9	0.00012589	1.93E-07	3.60E-04	6.40E-04	1.58E-10	-3.9	-2.79	over
3.8	0.00015849	2.80E-07	4.14E-04	5.85E-04	1.26E-10	-3.8	-2.80	over
3.7	0.00019953	4.01E-07	4.71E-04	5.29E-04	1.00E-10	-3.7	-2.82	over
3.6	0.00025119	5.66E-07	5.28E-04	4.71E-04	7.94E-11	-3.6	-2.83	over
3.5	0.00031623	7.89E-07	5.85E-04	4.14E-04	6.31E-11	-3.5	-2.85	over
3.4	0.00039811	1.09E-06	6.39E-04	3.60E-04	5.01E-11	-3.4	-2.87	over
3.3	0.00050119	1.48E-06	6.90E-04	3.08E-04	3.98E-11	-3.3	-2.88	over
3.2	0.00063096	1.98E-06	7.37E-04	2.61E-04	3.16E-11	-3.2	-2.90	over
3.1	0.00079433	2.64E-06	7.78E-04	2.19E-04	2.51E-11	-3.1	-2.91	over
3	0.001	3.47E-06	8.14E-04	1.82E-04	2.00E-11	-3	-2.93	over
2.9	0.00125893	4.54E-06	8.45E-04	1.50E-04	1.58E-11	-2.9	-2.94	under
2.8	0.00158489	5.89E-06	8.71E-04	1.23E-04	1.26E-11	-2.8	-2.95	under
2.7	0.00199526	7.59E-06	8.92E-04	1.00E-04	1.00E-11	-2.7	-2.96	under
2.6	0.00251189	9.74E-06	9.09E-04	8.10E-05	7.94E-12	-2.6	-2.97	under
2.5	0.00316228	1.24E-05	9.22E-04	6.53E-05	6.31E-12	-2.5	-2.98	under
2.4	0.00398107	1.58E-05	9.32E-04	5.24E-05	5.01E-12	-2.4	-2.98	under
2.3	0.00501187	2.01E-05	9.38E-04	4.19E-05	3.98E-12	-2.3	-2.99	under
2.9	0.00125893	4.54E-06	8.45E-04	1.50E-04	1.58E-11	-2.9	-2.94	under
2.91	0.00123027	4.42E-06	8.42E-04	1.53E-04	1.62E-11	-2.91	-2.94	under
2.92	0.00120226	4.30E-06	8.39E-04	1.56E-04	1.66E-11	-2.92	-2.94	under
2.93	0.0011749	4.19E-06	8.36E-04	1.59E-04	1.70E-11	-2.93	-2.94	under
2.94	0.00114815	4.08E-06	8.33E-04	1.63E-04	1.74E-11	-2.94	-2.94	over
2.95	0.00112202	3.97E-06	8.30E-04	1.66E-04	1.78E-11	-2.95	-2.93	over
2.96	0.00109648	3.87E-06	8.27E-04	1.69E-04	1.82E-11	-2.96	-2.93	over
2.97	0.00107152	3.77E-06	8.24E-04	1.72E-04	1.86E-11	-2.97	-2.93	over
2.98	0.00104713	3.67E-06	8.21E-04	1.75E-04	1.91E-11	-2.98	-2.93	over
2.99	0.00102329	3.57E-06	8.18E-04	1.79E-04	1.95E-11	-2.99	-2.93	over

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CT	**1.00E-03**			
pKa1	**0.63**	**Ka1**	**2.34E-01**	**LHS = log([H+])**
pKa2	**3.65**	**Ka2**	**2.24E-04**	**RHS = log([OH-]+[HA]+2[A])**
pKw	**13.7**	**Kw**	**2.00E-14**	

pH input	**[H+]**	**[H2A]**	**[HA]**	**[A]**	**[OH-]**	**Log(LHS)**	**Log(RHS)**	**Log(LHS)-Log(RHS)**
2.93566205	1.16E-03	4.13E-06	8.35E-04	1.61E-04	1.72E-11	-2.9357	-2.9367	0.0010
er adjusts this value to get target cell = 0								Target cell = 0

To use solver:
1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options

Mixtures of Acids + Bases

- **Problem 7:** Calculate the pH of a solution containing 10^{-3} M sodium acetate ($pK_a = 4.7$). Assume that ideal solution conditions

CT,A 1.00E-03
pKa1 4.7 Ka1 2.00E-05 LHS log([H+]+[Na+])
RHS log([OH-] + [A-])

pH input	log(LHS)	[H+]	[Na+]	[A-]	[OH-]	RHS	LOG RHS	comparison
7	-2.99996	0.0000001	1.00E-03	9.95E-04	0.0000001	9.95E-04	-3.0021275	under
7.1	-2.99997	7.94328E-08	1.00E-03	9.96E-04	1.25893E-07	9.96E-04	-3.0016706	under
7.2	-2.99997	6.30957E-08	1.00E-03	9.97E-04	1.58489E-07	9.97E-04	-3.0013021	under
7.3	-2.99998	5.01187E-08	1.00E-03	9.97E-04	1.99526E-07	9.98E-04	-3.0010027	under
7.4	-2.99998	3.98107E-08	1.00E-03	9.98E-04	2.51189E-07	9.98E-04	-3.0007564	under
7.5	-2.99999	3.16228E-08	1.00E-03	9.98E-04	3.16228E-07	9.99E-04	-3.0005502	under
7.6	-2.99999	2.51189E-08	1.00E-03	9.99E-04	3.98107E-07	9.99E-04	-3.0003733	under
7.7	-2.99999	1.99526E-08	1.00E-03	9.99E-04	5.01187E-07	1.00E-03	-3.0002163	under
7.8	-2.99999	1.58489E-08	1.00E-03	9.99E-04	6.30957E-07	1.00E-03	-3.0000707	under
7.9	-2.99999	1.25893E-08	1.00E-03	9.99E-04	7.94328E-07	1.00E-03	-2.9999289	over
8	-3	1E-08	1.00E-03	9.99E-04	1E-06	1.00E-03	-2.9997833	over
8.1	-3	7.94328E-09	1.00E-03	1.00E-03	1.25893E-06	1.00E-03	-2.9996262	over
8.2	-3	6.30957E-09	1.00E-03	1.00E-03	1.58489E-06	1.00E-03	-2.9994493	over
8.3	-3	5.01187E-09	1.00E-03	1.00E-03	1.99526E-06	1.00E-03	-2.9992432	over
8.4	-3	3.98107E-09	1.00E-03	1.00E-03	2.51189E-06	1.00E-03	-2.9989969	over
8.5	-3	3.16228E-09	1.00E-03	1.00E-03	3.16228E-06	1.00E-03	-2.9986974	over
8.6	-3	2.51189E-09	1.00E-03	1.00E-03	3.98107E-06	1.00E-03	-2.9983289	over
8.7	-3	1.99526E-09	1.00E-03	1.00E-03	5.01187E-06	1.00E-03	-2.997872	over
8.8	-3	1.58489E-09	1.00E-03	1.00E-03	6.30957E-06	1.01E-03	-2.9973027	over
8.9	-3	1.25893E-09	1.00E-03	1.00E-03	7.94328E-06	1.01E-03	-2.9965911	over
9	-3	1E-09	1.00E-03	1.00E-03	1E-05	1.01E-03	-2.9957002	over
9.1	-3	7.94328E-10	1.00E-03	1.00E-03	1.25893E-05	1.01E-03	-2.9945838	over
9.2	-3	6.30957E-10	1.00E-03	1.00E-03	1.58489E-05	1.02E-03	-2.9931844	over
9.3	-3	5.01187E-10	1.00E-03	1.00E-03	1.99526E-05	1.02E-03	-2.9914307	over
9.4	-3	3.98107E-10	1.00E-03	1.00E-03	2.51189E-05	1.03E-03	-2.9892342	over
9.5	-3	3.16228E-10	1.00E-03	1.00E-03	3.16228E-05	1.03E-03	-2.9864857	over
9.6	-3	2.51189E-10	1.00E-03	1.00E-03	3.98107E-05	1.04E-03	-2.983051	over
9.7	-3	1.99526E-10	1.00E-03	1.00E-03	5.01187E-05	1.05E-03	-2.9787657	over
	-3		1.00E-03					
7.8	-2.99999	1.58489E-08	1.00E-03	9.99E-04	6.30957E-07	1.00E-03	-3.0000707	under
7.81	-2.99999	1.54882E-08	1.00E-03	9.99E-04	6.45654E-07	1.00E-03	-3.0000565	under
7.82	-2.99999	1.51356E-08	1.00E-03	9.99E-04	6.60693E-07	1.00E-03	-3.0000423	under
7.83	-2.99999	1.47911E-08	1.00E-03	9.99E-04	6.76083E-07	1.00E-03	-3.0000281	under
7.84	-2.99999	1.44544E-08	1.00E-03	9.99E-04	6.91831E-07	1.00E-03	-3.0000139	under
7.85	-2.99999	1.41254E-08	1.00E-03	9.99E-04	7.07946E-07	1.00E-03	-2.9999998	under
7.86	-2.99999	1.38038E-08	1.00E-03	9.99E-04	7.24436E-07	1.00E-03	-2.9999856	over
7.87	-2.99999	1.34896E-08	1.00E-03	9.99E-04	7.4131E-07	1.00E-03	-2.9999715	over
7.88	-2.99999	1.31826E-08	1.00E-03	9.99E-04	7.58578E-07	1.00E-03	-2.9999573	over
7.89	-2.99999	1.28825E-08	1.00E-03	9.99E-04	7.76247E-07	1.00E-03	-2.9999431	over
7.9	-2.99999	1.25893E-08	1.00E-03	9.99E-04	7.94328E-07	1.00E-03	-2.9999289	over

CT,A 1.00E-03
pKa 4.7 Ka1 2.00E-05 LHS = log([H+]+[Na+])
RHS = log([OH-] + [A-])

pH input	**[H+] = LHS**	**[HA-]**	**[Na+)**	**[OH-]**	**RHS**	**Log(LHS)**	**Log(RHS)**	**Log(LHS)-Log(RHS)**
7.85458666	1.40E-08	9.99E-04	1.00E-03	7.15462E-07	1.00E-03	-3.0000	-3.0000	0.0000

Solver adjusts this value
to get target cell = 0

Target cell = 0

To use solver:
1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options

Problem 8: Calculate the pH of a solution to which 10^{-3} M acetic acid and 10^{-3} M NaOH are added. Assume ideal solution conditions.

Problem 9: How do you expect addition to 10^{-3} M NaCl to affect the pH of the solution from problem #1 (10^{-3} M of acetic acid in deionized water)?

Procedure for solving problems

1. List components (irreducible "building block" groups)
2. List species (component species + combinations of components)
3. Equations (need "x" eqns to solve for "x" unknowns)
    - A. Equilibrium Expressions
    - B. Mass balance for each component (other than H_2O, H^+)
    - C. Electroneutrality
4. List known and unknown quantities
6. Check if #eqns $\geq$ #unknowns
7. Make any simplifying assumptions
8. Solve problem using assumptions

9a. Check validity of your assumptions

9b. If assumptions invalid, make new ones and repeat 7-8

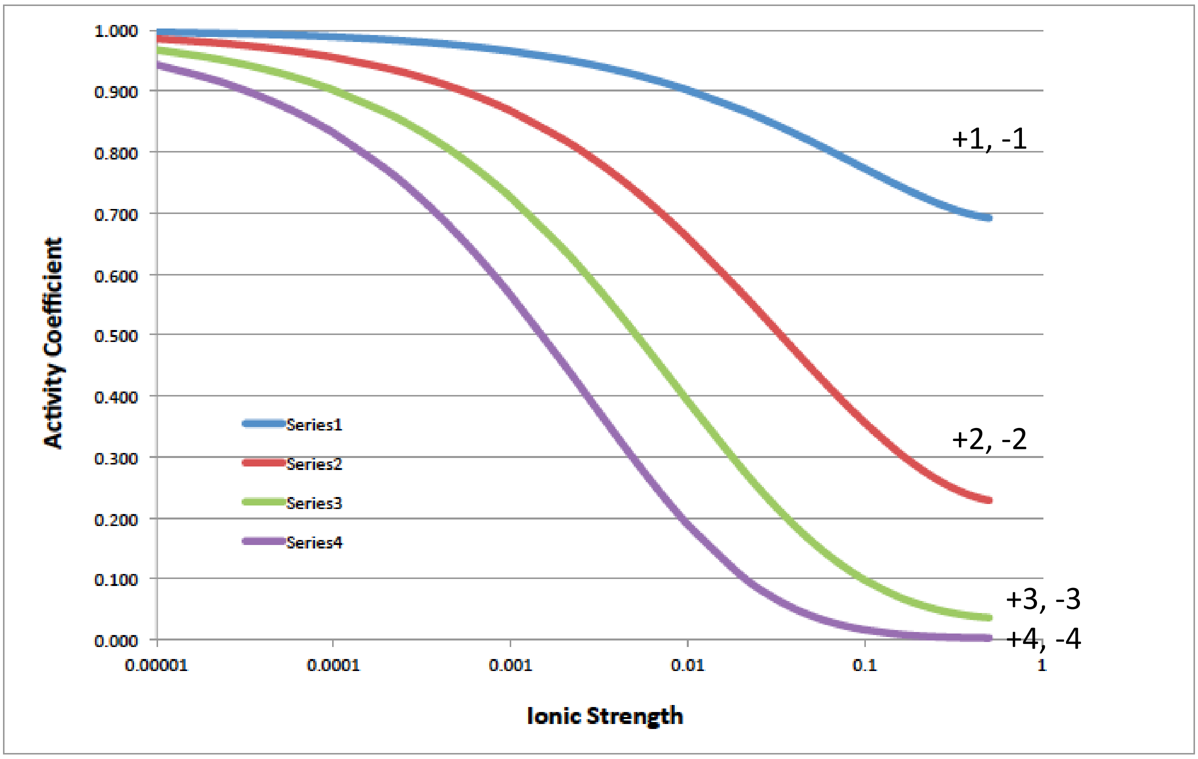
Problem 6: Repeat Problem 4, but do not assume ideal solution conditions. Instead, the water has an ionic strength of 0.2.

Problem 4: Calculate the equilibrium pH and speciation of oxalic acid ($pK_{a1} = 0.9$; $pK_{a2} = 4.2$) after 10^{-3} M is added to deionized water (nothing else initially present in the water). *Assume dilute solution approximates "infinite dilution" assumption of the reference state.*

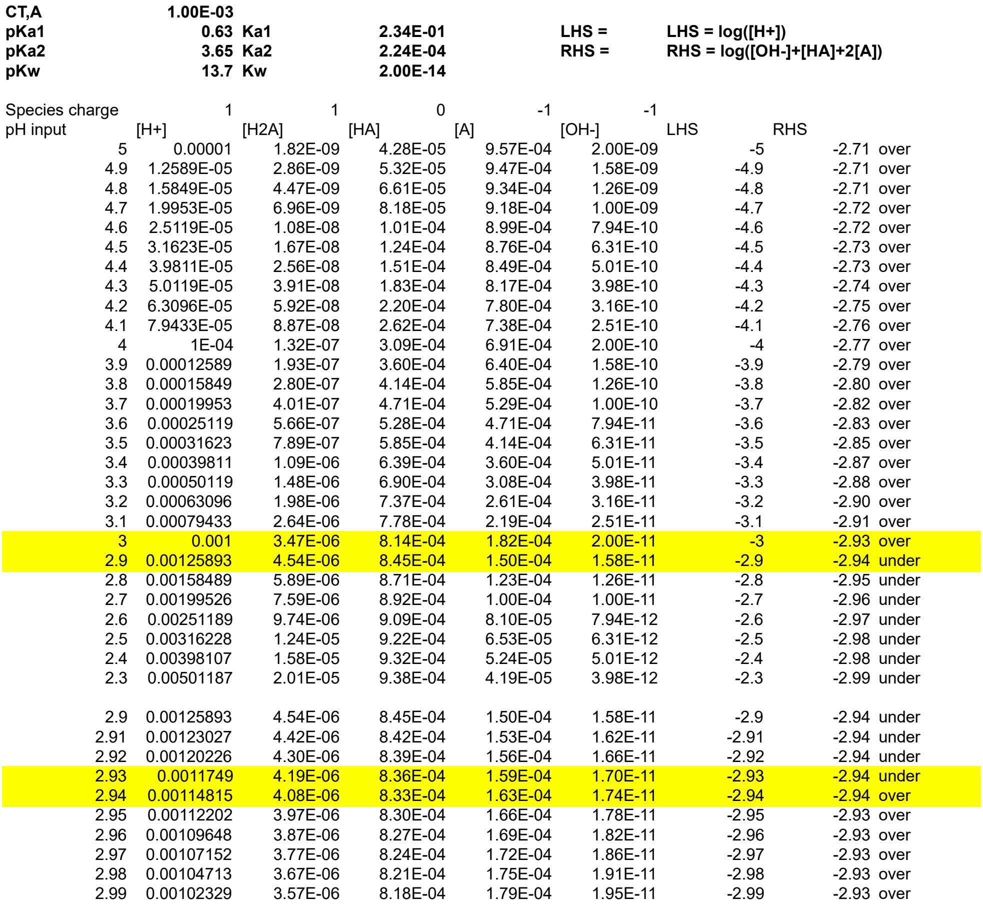
Step 1: components

Step 2: species

Step 3: equations (write the same way as if we were assuming ideal solution conditions, i.e., *write everything in terms of molar concentrations, not activities*)

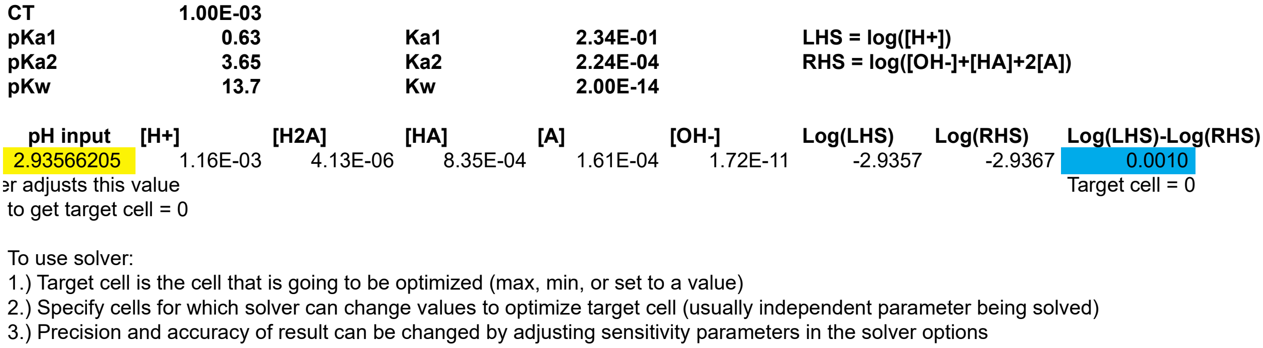


At IS = 0.2, γ_1 = 0.73 and γ_2 = 0.28



CT,A	**1.00E-03**					
pKa1	**0.63**	**Ka1**	**2.34E-01**	**LHS =**	**LHS = log([H+])**	
pKa2	**3.65**	**Ka2**	**2.24E-04**	**RHS =**	**RHS = log([OH-]+[HA]+2[A])**	
pKw	**13.7**	**Kw**	**2.00E-14**			

Species charge	1	1	0	-1	-1			
pH input	[H+]	[H2A]	[HA]	[A]	[OH-]	LHS	RHS	
5	0.00001	1.82E-09	4.28E-05	9.57E-04	2.00E-09	-5	-2.71	over
4.9	1.2589E-05	2.86E-09	5.32E-05	9.47E-04	1.58E-09	-4.9	-2.71	over
4.8	1.5849E-05	4.47E-09	6.61E-05	9.34E-04	1.26E-09	-4.8	-2.71	over
4.7	1.9953E-05	6.96E-09	8.18E-05	9.18E-04	1.00E-09	-4.7	-2.72	over
4.6	2.5119E-05	1.08E-08	1.01E-04	8.99E-04	7.94E-10	-4.6	-2.72	over
4.5	3.1623E-05	1.67E-08	1.24E-04	8.76E-04	6.31E-10	-4.5	-2.73	over
4.4	3.9811E-05	2.56E-08	1.51E-04	8.49E-04	5.01E-10	-4.4	-2.73	over
4.3	5.0119E-05	3.91E-08	1.83E-04	8.17E-04	3.98E-10	-4.3	-2.74	over
4.2	6.3096E-05	5.92E-08	2.20E-04	7.80E-04	3.16E-10	-4.2	-2.75	over
4.1	7.9433E-05	8.87E-08	2.62E-04	7.38E-04	2.51E-10	-4.1	-2.76	over
4	1E-04	1.32E-07	3.09E-04	6.91E-04	2.00E-10	-4	-2.77	over
3.9	0.00012589	1.93E-07	3.60E-04	6.40E-04	1.58E-10	-3.9	-2.79	over
3.8	0.00015849	2.80E-07	4.14E-04	5.85E-04	1.26E-10	-3.8	-2.80	over
3.7	0.00019953	4.01E-07	4.71E-04	5.29E-04	1.00E-10	-3.7	-2.82	over
3.6	0.00025119	5.66E-07	5.28E-04	4.71E-04	7.94E-11	-3.6	-2.83	over
3.5	0.00031623	7.89E-07	5.85E-04	4.14E-04	6.31E-11	-3.5	-2.85	over
3.4	0.00039811	1.09E-06	6.39E-04	3.60E-04	5.01E-11	-3.4	-2.87	over
3.3	0.00050119	1.48E-06	6.90E-04	3.08E-04	3.98E-11	-3.3	-2.88	over
3.2	0.00063096	1.98E-06	7.37E-04	2.61E-04	3.16E-11	-3.2	-2.90	over
3.1	0.00079433	2.64E-06	7.78E-04	2.19E-04	2.51E-11	-3.1	-2.91	over
3	0.001	3.47E-06	8.14E-04	1.82E-04	2.00E-11	-3	-2.93	over
2.9	0.00125893	4.54E-06	8.45E-04	1.50E-04	1.58E-11	-2.9	-2.94	under
2.8	0.00158489	5.89E-06	8.71E-04	1.23E-04	1.26E-11	-2.8	-2.95	under
2.7	0.00199526	7.59E-06	8.92E-04	1.00E-04	1.00E-11	-2.7	-2.96	under
2.6	0.00251189	9.74E-06	9.09E-04	8.10E-05	7.94E-12	-2.6	-2.97	under
2.5	0.00316228	1.24E-05	9.22E-04	6.53E-05	6.31E-12	-2.5	-2.98	under
2.4	0.00398107	1.58E-05	9.32E-04	5.24E-05	5.01E-12	-2.4	-2.98	under
2.3	0.00501187	2.01E-05	9.38E-04	4.19E-05	3.98E-12	-2.3	-2.99	under
2.9	0.00125893	4.54E-06	8.45E-04	1.50E-04	1.58E-11	-2.9	-2.94	under
2.91	0.00123027	4.42E-06	8.42E-04	1.53E-04	1.62E-11	-2.91	-2.94	under
2.92	0.00120226	4.30E-06	8.39E-04	1.56E-04	1.66E-11	-2.92	-2.94	under
2.93	0.0011749	4.19E-06	8.36E-04	1.59E-04	1.70E-11	-2.93	-2.94	under
2.94	0.00114815	4.08E-06	8.33E-04	1.63E-04	1.74E-11	-2.94	-2.94	over
2.95	0.00112202	3.97E-06	8.30E-04	1.66E-04	1.78E-11	-2.95	-2.93	over
2.96	0.00109648	3.87E-06	8.27E-04	1.69E-04	1.82E-11	-2.96	-2.93	over
2.97	0.00107152	3.77E-06	8.24E-04	1.72E-04	1.86E-11	-2.97	-2.93	over
2.98	0.00104713	3.67E-06	8.21E-04	1.75E-04	1.91E-11	-2.98	-2.93	over
2.99	0.00102329	3.57E-06	8.18E-04	1.79E-04	1.95E-11	-2.99	-2.93	over



CT	**1.00E-03**			
pKa1	**0.63**	**Ka1**	**2.34E-01**	**LHS = log([H+])**
pKa2	**3.65**	**Ka2**	**2.24E-04**	**RHS = log([OH-]+[HA]+2[A])**
pKw	**13.7**	**Kw**	**2.00E-14**	

pH input	**[H+]**	**[H2A]**	**[HA]**	**[A]**	**[OH-]**	**Log(LHS)**	**Log(RHS)**	**Log(LHS)-Log(RHS)**
2.93566205	1.16E-03	4.13E-06	8.35E-04	1.61E-04	1.72E-11	-2.9357	-2.9367	0.0010
er adjusts this value								Target cell = 0
to get target cell = 0								

To use solver:

1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options

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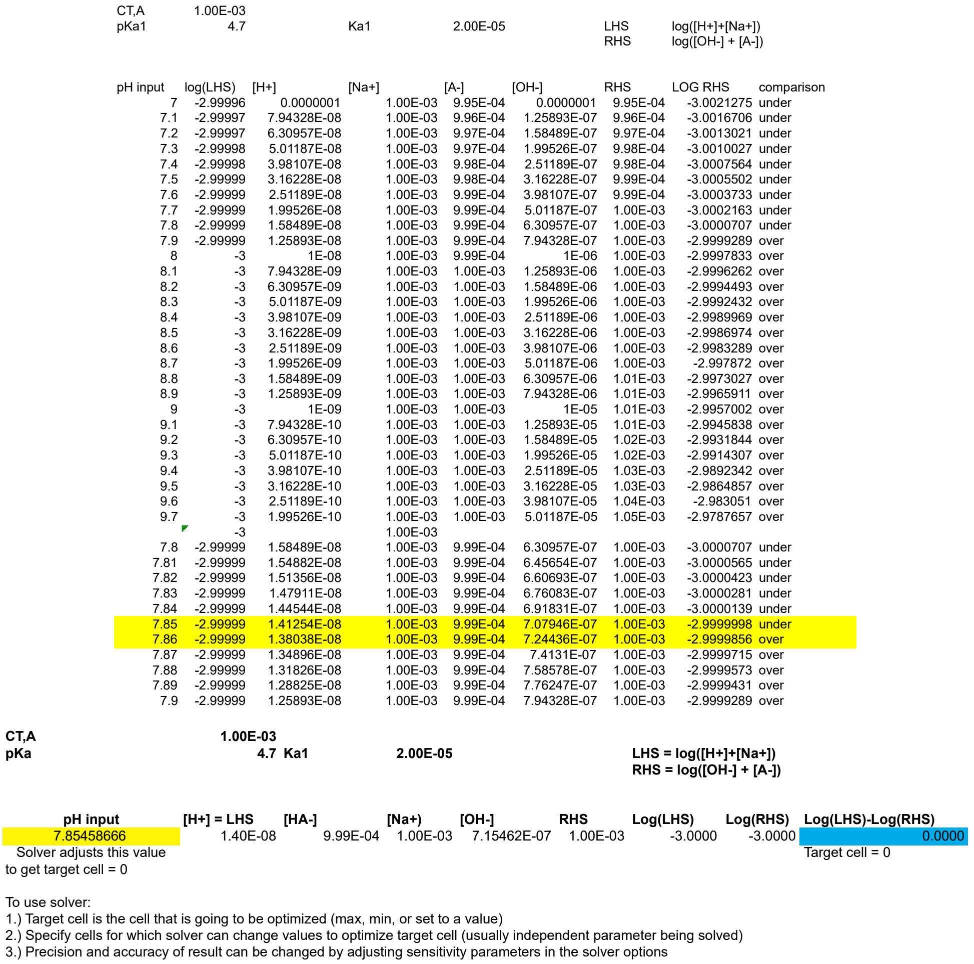
Mixtures of Acids + Bases

- **Problem 7:** Calculate the pH of a solution containing 10^{-3} M sodium acetate (pK_a = 4.7). Assume that ideal solution conditions



CT,A	1.00E-03							
pKa1	4.7		Ka1		2.00E-05		LHS	log([H+]+[Na+])
							RHS	log([OH-] + [A-])

pH input	log(LHS)	[H+]	[Na+]	[A-]	[OH-]	RHS	LOG RHS	comparison
7	-2.99996	0.0000001	1.00E-03	9.95E-04	0.0000001	9.95E-04	-3.0021275	under
7.1	-2.99997	7.94328E-08	1.00E-03	9.96E-04	1.25893E-07	9.96E-04	-3.0016706	under
7.2	-2.99997	6.30957E-08	1.00E-03	9.97E-04	1.58489E-07	9.97E-04	-3.0013021	under
7.3	-2.99998	5.01187E-08	1.00E-03	9.97E-04	1.99526E-07	9.98E-04	-3.0010027	under
7.4	-2.99998	3.98107E-08	1.00E-03	9.98E-04	2.51189E-07	9.98E-04	-3.0007564	under
7.5	-2.99999	3.16228E-08	1.00E-03	9.98E-04	3.16228E-07	9.99E-04	-3.0005502	under
7.6	-2.99999	2.51189E-08	1.00E-03	9.99E-04	3.98107E-07	9.99E-04	-3.0003733	under
7.7	-2.99999	1.99526E-08	1.00E-03	9.99E-04	5.01187E-07	1.00E-03	-3.0002163	under
7.8	-2.99999	1.58489E-08	1.00E-03	9.99E-04	6.30957E-07	1.00E-03	-3.0000707	under
7.9	-2.99999	1.25893E-08	1.00E-03	9.99E-04	7.94328E-07	1.00E-03	-2.9999289	over
8	-3	1E-08	1.00E-03	9.99E-04	1E-06	1.00E-03	-2.9997833	over
8.1	-3	7.94328E-09	1.00E-03	1.00E-03	1.25893E-06	1.00E-03	-2.9996262	over
8.2	-3	6.30957E-09	1.00E-03	1.00E-03	1.58489E-06	1.00E-03	-2.9994493	over
8.3	-3	5.01187E-09	1.00E-03	1.00E-03	1.99526E-06	1.00E-03	-2.9992432	over
8.4	-3	3.98107E-09	1.00E-03	1.00E-03	2.51189E-06	1.00E-03	-2.9989969	over
8.5	-3	3.16228E-09	1.00E-03	1.00E-03	3.16228E-06	1.00E-03	-2.9986974	over
8.6	-3	2.51189E-09	1.00E-03	1.00E-03	3.98107E-06	1.00E-03	-2.9983289	over
8.7	-3	1.99526E-09	1.00E-03	1.00E-03	5.01187E-06	1.00E-03	-2.997872	over
8.8	-3	1.58489E-09	1.00E-03	1.00E-03	6.30957E-06	1.01E-03	-2.9973027	over
8.9	-3	1.25893E-09	1.00E-03	1.00E-03	7.94328E-06	1.01E-03	-2.9965911	over
9	-3	1E-09	1.00E-03	1.00E-03	1E-05	1.01E-03	-2.9957002	over
9.1	-3	7.94328E-10	1.00E-03	1.00E-03	1.25893E-05	1.01E-03	-2.9945838	over
9.2	-3	6.30957E-10	1.00E-03	1.00E-03	1.58489E-05	1.02E-03	-2.9931844	over
9.3	-3	5.01187E-10	1.00E-03	1.00E-03	1.99526E-05	1.02E-03	-2.9914307	over
9.4	-3	3.98107E-10	1.00E-03	1.00E-03	2.51189E-05	1.03E-03	-2.9892342	over
9.5	-3	3.16228E-10	1.00E-03	1.00E-03	3.16228E-05	1.03E-03	-2.9864857	over
9.6	-3	2.51189E-10	1.00E-03	1.00E-03	3.98107E-05	1.04E-03	-2.983051	over
9.7	-3	1.99526E-10	1.00E-03	1.00E-03	5.01187E-05	1.05E-03	-2.9787657	over
	-3		1.00E-03					
7.8	-2.99999	1.58489E-08	1.00E-03	9.99E-04	6.30957E-07	1.00E-03	-3.0000707	under
7.81	-2.99999	1.54882E-08	1.00E-03	9.99E-04	6.45654E-07	1.00E-03	-3.0000565	under
7.82	-2.99999	1.51356E-08	1.00E-03	9.99E-04	6.60693E-07	1.00E-03	-3.0000423	under
7.83	-2.99999	1.47911E-08	1.00E-03	9.99E-04	6.76083E-07	1.00E-03	-3.0000281	under
7.84	-2.99999	1.44544E-08	1.00E-03	9.99E-04	6.91831E-07	1.00E-03	-3.0000139	under
7.85	-2.99999	1.41254E-08	1.00E-03	9.99E-04	7.07946E-07	1.00E-03	-2.9999998	under
7.86	-2.99999	1.38038E-08	1.00E-03	9.99E-04	7.24436E-07	1.00E-03	-2.9999856	over
7.87	-2.99999	1.34896E-08	1.00E-03	9.99E-04	7.4131E-07	1.00E-03	-2.9999715	over
7.88	-2.99999	1.31826E-08	1.00E-03	9.99E-04	7.58578E-07	1.00E-03	-2.9999573	over
7.89	-2.99999	1.28825E-08	1.00E-03	9.99E-04	7.76247E-07	1.00E-03	-2.9999431	over
7.9	-2.99999	1.25893E-08	1.00E-03	9.99E-04	7.94328E-07	1.00E-03	-2.9999289	over

CT,A	**1.00E-03**				
pKa	**4.7**	**Ka1**	**2.00E-05**		**LHS = log([H+]+[Na+])**
					RHS = log([OH-] + [A-])

pH input	**[H+] = LHS**	**[HA-]**	**[Na+)**	**[OH-]**	**RHS**	**Log(LHS)**	**Log(RHS)**	**Log(LHS)-Log(RHS)**
7.85458666	1.40E-08	9.99E-04	1.00E-03	7.15462E-07	1.00E-03	-3.0000	-3.0000	0.0000
Solver adjusts this value to get target cell = 0								Target cell = 0

To use solver:
1.) Target cell is the cell that is going to be optimized (max, min, or set to a value)
2.) Specify cells for which solver can change values to optimize target cell (usually independent parameter being solved)
3.) Precision and accuracy of result can be changed by adjusting sensitivity parameters in the solver options

---

Can we solve Problem 7 directly using charge balance and assumptions?

$$[H^+] + [Na^+] = [OH^-] + [Ac^-]$$

- Na^+ completely dissociates, so $[Na^+] \approx C_{T,Na} = 10^{-3}$ M
- Adding a base, so let's assume pH >> 7, so $[OH^-] >> [H^+]$
- Since pH > 7, $[Ac^-] >> [HAc]$, so $[Ac^-] \approx C_{T,AC} = 10^{-3}$ M (pK_a = 4.7)

$$\cancel{[H^+]} + [Na^+] = [OH^-] + [Ac^-]$$

$$[10^{-3}M] = [OH^-] + [10^{-3}M]$$

We cannot solve directly for [H⁺] using charge balance.

Need a new electroneutrality constraint where the dominant terms are eliminated

Recognize that $[Na^+] \approx C_{T,Na} = C_{T,Ac} = [HAc] + [Ac^-]$

So: $[H^+] + [Na^+] = [OH^-] + [Ac^-]$

$[H^+] + [HAc] + [Ac^-] = [OH^-] + [Ac^-]$

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

This expression is equivalent to a TOT*H* expression we will derive later (eliminated the dominant terms)

$$[H^+] + \frac{C_{T,Ac}}{\frac{K_a}{[H^+]} + 1} = \frac{K_w}{[H^+]}$$

Multiply both sides by $(K_a/[H^+] + 1)$:

$$[H^+] + K_a + C_{T,Ac} = \frac{K_w}{[H^+]} + \frac{K_a K_w}{[H^+]^2}$$

Multiply both sides by $[H^+]^2$ to clear the denominator:

$$[H^+]^3 + \left(K_a + C_{T,Ac}\right)[H^+]^2 - K_w[H^+] - K_a K_w = 0$$

Solve the cubic, or recognize the $[H^+] < 10^{-7}$, so first cubic term much smaller than second squared term (so you can neglect) :

$a = 10^{-3}$
$b = -10^{-14}$
$c = -10^{-18.7}$

$[H^+] = 10^{-7.85}$

Check assumption: $(10^{-7.85})^3 << 10^{-3}(10^{-7.85})^2$

Problem 8: Calculate the pH of a solution to which 10^{-3} M acetic acid and 10^{-3} M NaOH are added. Assume ideal solution conditions.

Problem 9: How do you expect addition to 10^{-3} M NaCl to affect the pH of the solution from problem #1 (10^{-3} M of acetic acid in deionized water)?

Replacing Charge Balance with the TOT*H* Expression for Electroneutrality

- Mathematically useful because it can be derived in such a way to eliminate dominant terms
- Can be derived by combining C.B. and M.B.
- Derived directly using mass balance on H, (TOT*H*)
  - Using a “non-zero baseline” or “proton reference level species”
    - H_2O contains H
    - Easier to track *changes* in concentrations of H-bearing species
  - H^+ excess (+)
    - Species containing more H than reference level
  - H^+ deficiency (-)
    - Species containing less H than reference level
  - Write the Hydrogen M.B. equation the same way

$$TOTH_{in} = TOTH_{eq}$$

Choosing the baseline: proton reference level (P.R.L.) species

- Choose species expected to be present at highest concentration at *equilibrium*
  - To eliminate species of high concentration in the final equation
  - Baseline species vary from one system to another

- H_2O is always chosen as the baseline for H^+ and OH^-

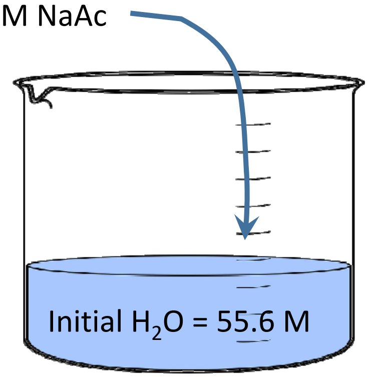
- Salts (e.g. Na^+, Cl^-) are always chosen as reference level species

---

- **Problem 7 (Repeat):** Calculate the pH of a solution containing 10^{-3} M sodium acetate (pK_a = 4.7). Assume that ideal solution conditions. Derive TOT*H* expression and solve for equilibrium pH

Component Groups: H^+, OH^-
Na^+
Ac^-

Add10^{-3} M NaAc



Ref Level Species (try to pick the dominant one from each component group):

H_2O (always, based on the previous slide)
Na^+ (same here)
Ac^-

H^+ Excess

	-3	-2	-1	RLS = 0	+1	+2	+3	Conc. (M)
@Equilibrium			OH^-	H_2O	H^+			
				Na^+				
				Ac^-	HAc			
Initial Conditions or added at t = 0				H_2O				55.6
				NaAc				10^{-3}

$$\mathrm{TOT}H_{eq} = [OH^-](-1)+\cancel{[H_2O]}(0)+[H^+](+1)+\cancel{[Na^+]}(0)+[HAc](1)+\cancel{[Ac^-]}(0)$$

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

$$\mathrm{TOT}H_{in} = [H_2O](0)+[NaAc](0)$$

$$= (55.6M)(0)+(10^{-3}M)\ (0)$$

$$= 0$$

Now we can express each term as a function of $[H^+]$, C_T, K_a values, and solve by (a) iteration (b) rearrange to cubic and solve

$$[\mathrm{H}^+] + \left(\frac{C_{T,AC}}{\frac{K_a}{[\mathrm{H}^+]} + 1} \right) = \frac{K_w}{[\mathrm{H}^+]}$$

$$[\mathrm{H}^+]^3 + (K_a + C_{T,AC})[\mathrm{H}^+]^2 - K_w[\mathrm{H}^+] - \mathrm{K_a K_w}$$

pH = 7.85

What if I had chosen HAc as the RLS instead of Ac^-?

H^+ Excess

	-3	-2	-1	RLS = 0	+1	+2	+3	Conc. (M)
@Equilibrium			OH^-	H_2O	H^+			
				Na^+				
			Ac^-	HAc				
Initial Conditions or added at t = 0				H_2O				55.6
			NaAc					10^{-3}

$$TOT\mathit{H}_{eq} = [OH^-](-1) + [H^+](+1) + [Ac^-](-1)$$

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

$$TOT\mathit{H}_{in} = [H_2O](0) + [NaAc](-1)$$

$$= (55.6M)(0) + (10^{-3}M)(-1)$$

$$= -10^{-3}\ M$$

$$TOT\mathit{H}_{in} = TOT\mathit{H}_{eq}$$

$$-10^{-3}M = [H^+] – [OH^-] – [Ac^-]$$

$$[H^+] + 10^{-3}M = [OH^-] + [Ac^-]$$

Exactly same form as charge balance
because $[Na^+] = 10^{-3}$ M

Is still a valid EN constraint, but not as useful as when we select $[Ac^-]$ as the RLS

Okay, so how do we guess which species dominate for each component group?

- We will guess by collecting all the H^+ available into a "basket" and then we will add these H^+ sequentially to the available bases in order of strength (strongest to weakest) until the basket is empty
- Consider our example (10^{-3} M NaAc):
- H^+ Available = 0

Acid/Base Pair	pKa	$C_{T,A}$	H^+ Available (M)
H_2O/OH^-	14.0	10^{-7} M	0
HAc/Ac^-	4.7	10^{-3} M	0
H^+/H_2O	0	55.6 M	0

RLS = Ac^-, H_2O, Na^+

- Consider another example (10^{-3} M HAc):
- H^+ Available = 10^{-3} M

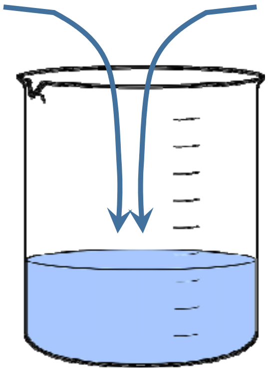
Acid/Base Pair	pKa	$C_{T,A}$	H^+ Available (M)
H_2O/OH^-	14.0	10^{-7} M	10^{-3} M
HAc/Ac^-	4.7	10^{-3} M	10^{-3} M ($10^{-3} - 10^{-7}$)
H^+/H_2O	0.0	55.6 M	0 M

RLS = HAc, H_2O

Let’s consider a slightly more complicated mixture of weak base and strong acid

Component Groups:

CO_3^{2-}, Na^+, Cl^-, H^+, OH^-



Add $1.9x10^{-3}$ M HCl

Add 10^{-3} M Na_2CO_3

Let’s try to select the reference level species that will dominate for each component group:

H^+ available = $1.9x10^{-3}$ M

Acid/Base Pair	pKa	$C_{T,A}$	H^+ Available (M)
H_2O/OH^-	14.0	10^{-7} M	$1.9x10^{-3}$ M
HCO_3^-/CO_3^{2-}	10.33	10^{-3} M	$1.9x10^{-3}$ M
H_2CO_3/HCO_3^-	6.35	10^{-3} M	$0.9x10^{-3}$ M
H^+/H_2O	0	55.6 M	0 M

RLS = H_2CO_3, Na^+, Cl^-, H_2O

	H^+ Excess							
	-3	-2	-1	RLS = 0	+1	+2	+3	
@Equilibrium			OH^-	H_2O	H^+			
				Na^+				
				Cl^-				
		CO_3^{2-}	HCO_3^-	H_2CO_3				
								Conc. (M)
Initial Conditions or added at t = 0				H_2O				55.6
		Na_2CO_3						10^{-3}
					HCl			$1.9x10^{-3}$

$\mathrm{TOT}H_{eq} = [H^+]-[HCO_3^-]-2[CO_3^{2-}]-[OH^-]$

$\mathrm{TOT}H_{in} = [H_2CO_3](-2)+[HCl](+1)$

$= 10^{-3}(-2) + 1.9\mathrm{x}10^{-3}(1)$

$= -10^{-4}\,\mathrm{M}$

$[H^+]+10^{-4}\mathrm{M} = [OH^-] +[HCO_3^-]+2[CO_3^{2-}]$

$$\frac{K_W}{[H^+]}+\frac{C_{T,CO3}}{\frac{[H^+]}{Ka1}+1+\frac{Ka2}{[H^+]}}+\frac{2C_{T,CO3}}{\frac{[H^+]^2}{Ka1Ka2}+\frac{[H^+]}{Ka2}+1}$$

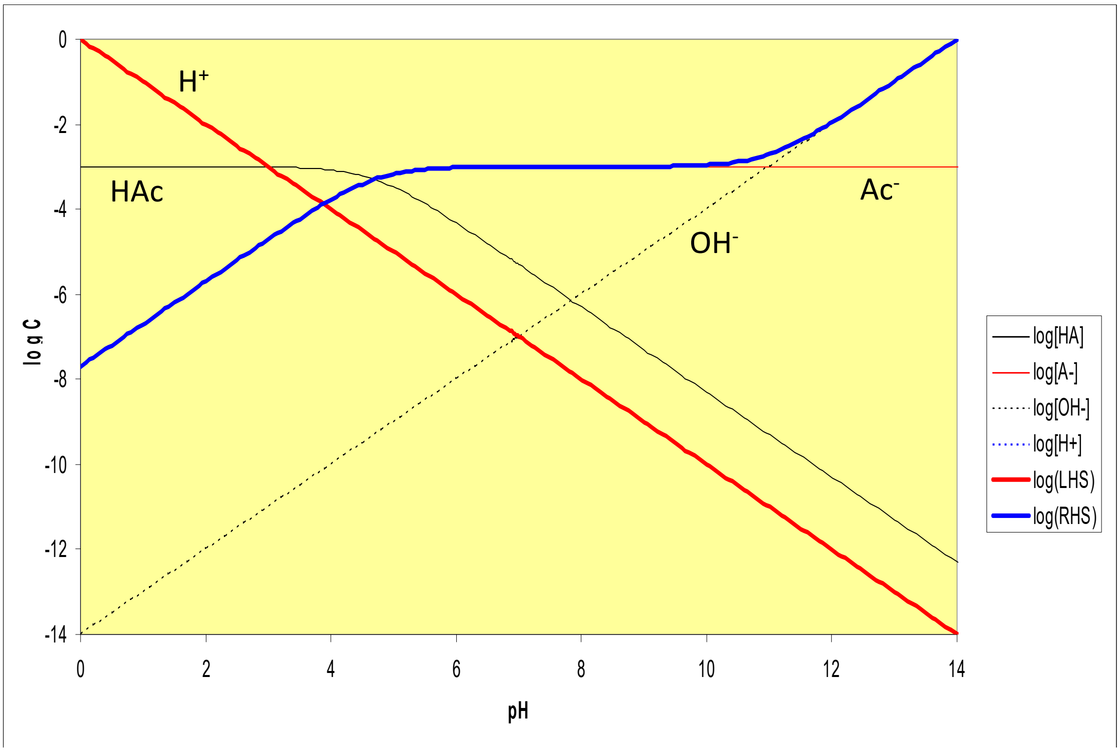
Graphical Solution

- If all possible components & species in solution are known, then you can use such plot to solve for the equilibrium pH and composition
  - Draw 2 lines:
    - Sum of all positive charged species (follow dominant term since log scale)
    - Sum of all negative charged species
  - Where lines cross is the only point that satisfies the charge balance “constraint”, and therefore represents to pH at equilibrium.

Graphical Solution

- E.g. 10^{-3} M acetic acid (pKa = 4.7)

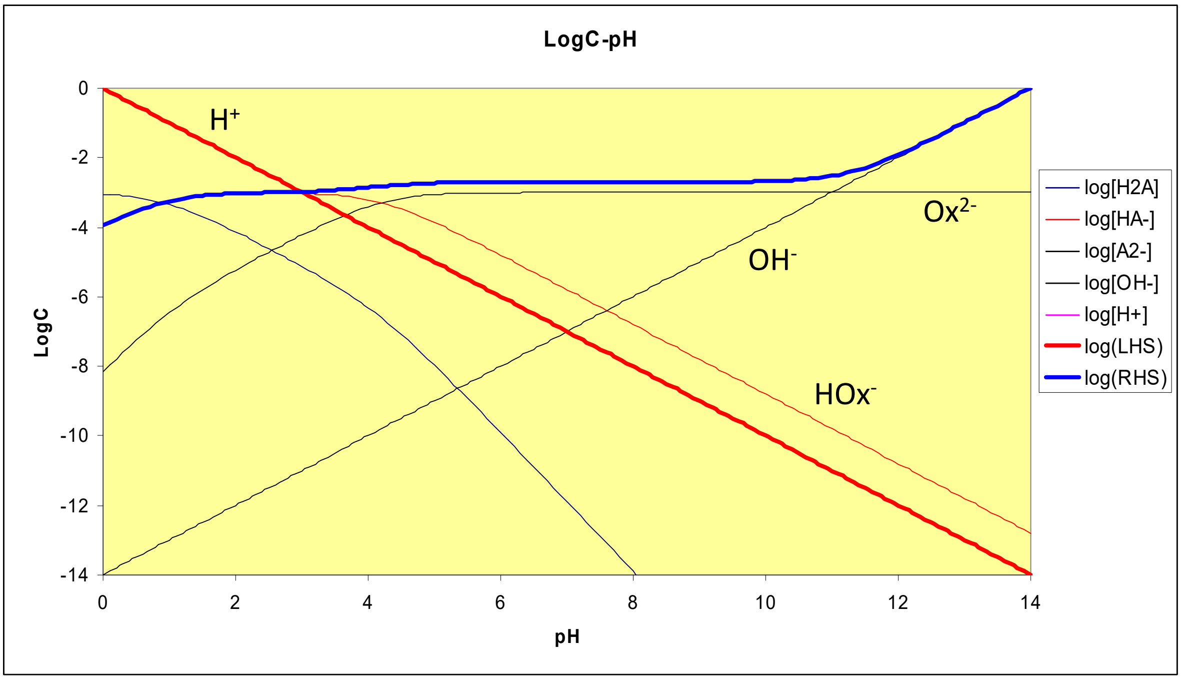
$$[H^+] = [Ac^-] + [OH^-]$$



Graphical Solution

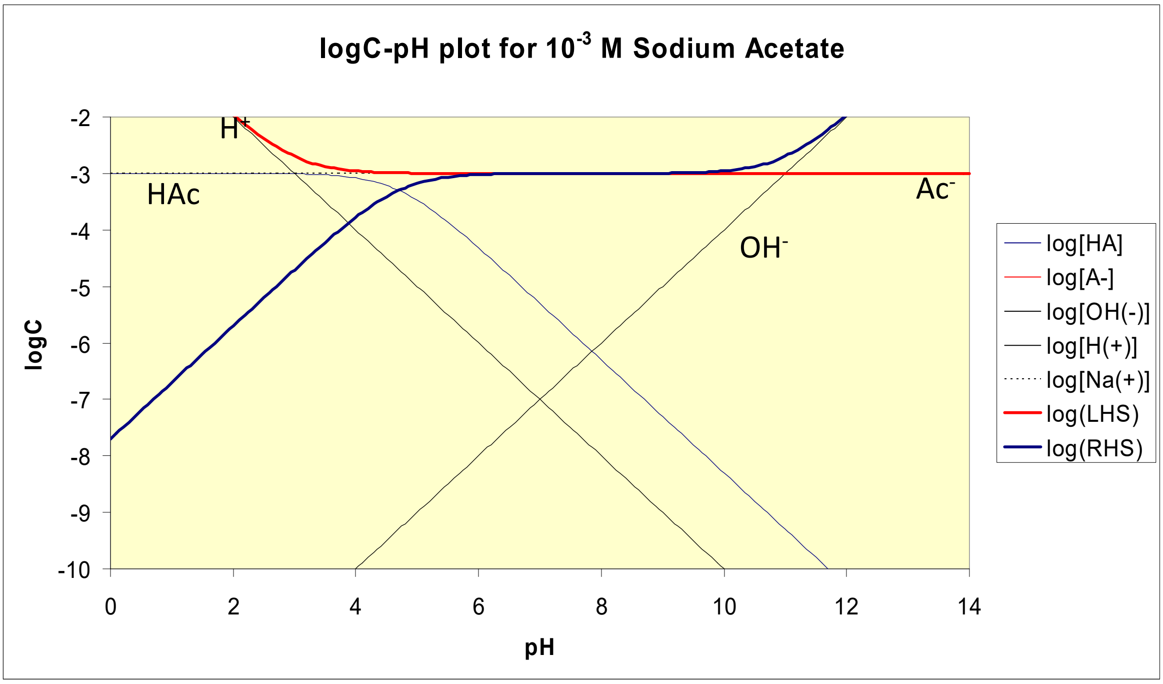
- E.g. 10^{-3} M oxalic acid ($pK_{a1} = 0.9$; $pK_{a2} = 4.2$)

$$[H^+] = [OH^-] + [HOx^-] + 2[Ox^-]$$



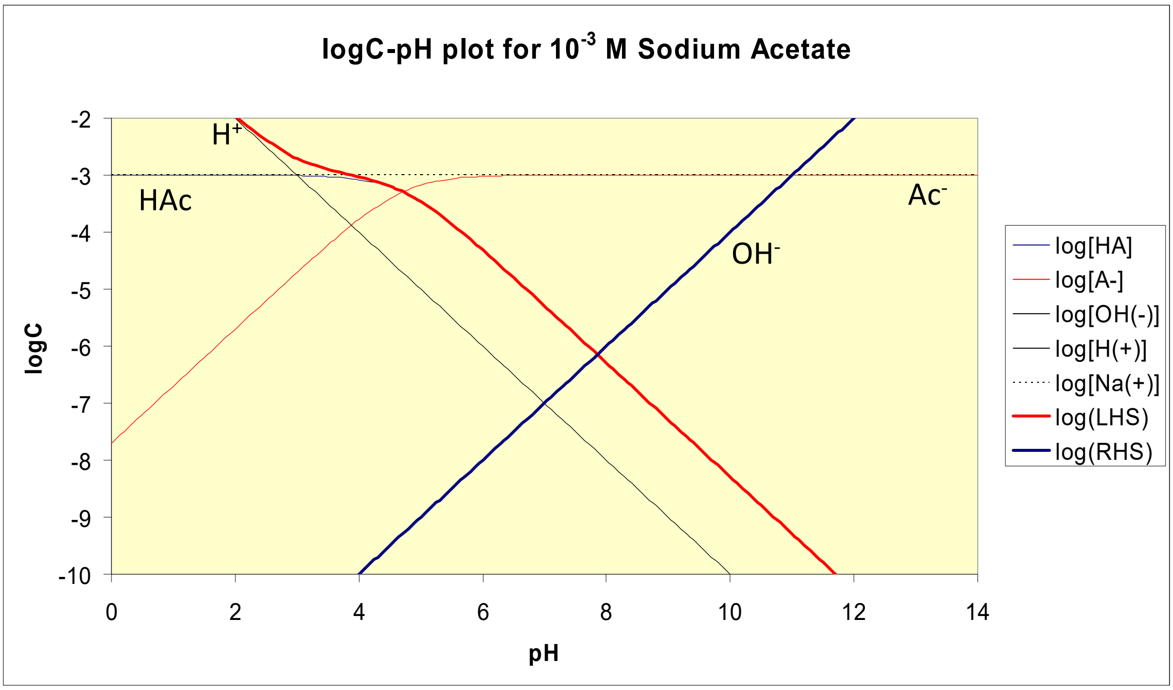
Graphical Solution

- Sometimes, you may find the crossing point hard to define precisely using (sum + = sum -); rearrange charge balance terms, and add up each side of rearranged expression (Use TOTH concept)
- 10^{-3} M sodium acetate

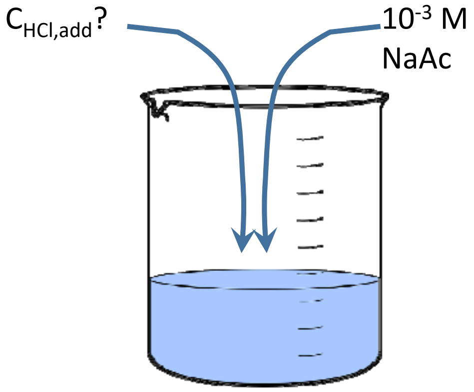


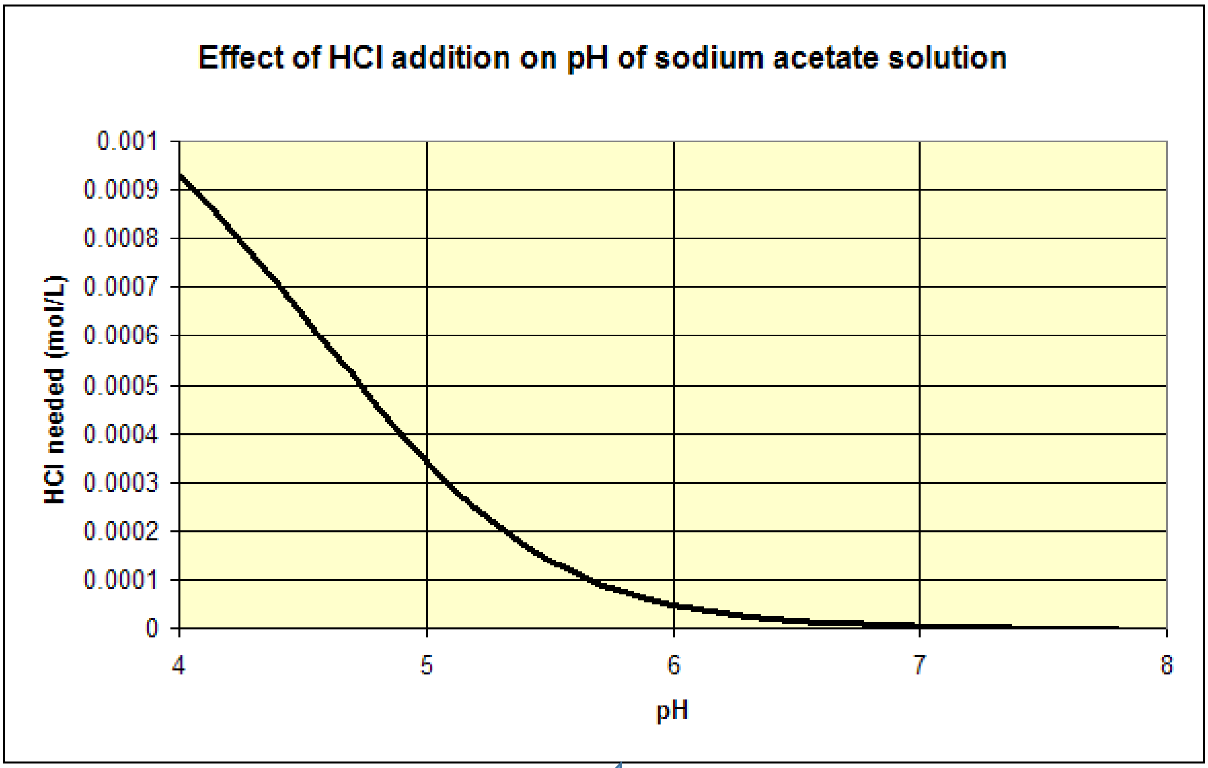
Graphical Solution

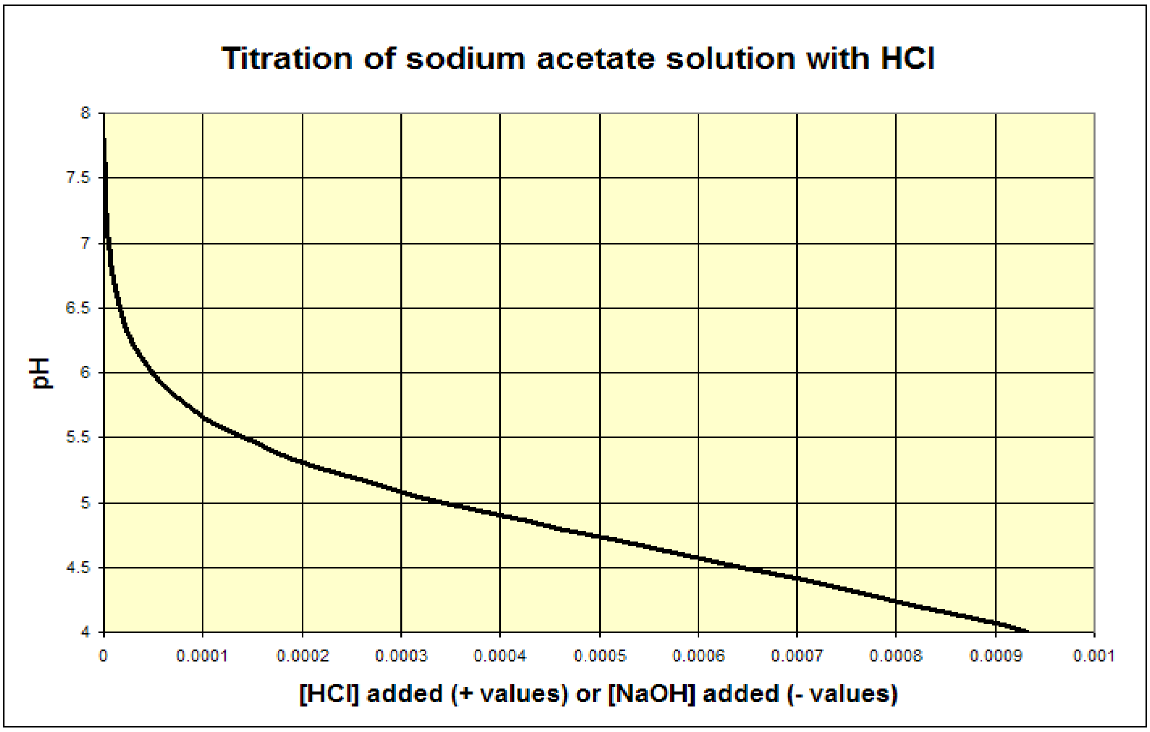
- Sometimes, you may find the crossing point hard to define precisely using (sum + = sum -); rearrange charge balance terms, and add up each side of rearranged expression (Use TOTH concept)
- 10^{-3} M sodium acetate



Problem 10: Determine how much HCl, a strong acid, must be added to the solution created by addition of 10^{-3} M sodium acetate (pK_a = 4.7) to convert the solution pH to 5.0. Assume ideal solution conditions.




Effect of HCl addition on pH of sodium acetate solution
HCl needed (mol/L)
0.001
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
4
5
6
7
8
pH


Titration of sodium acetate solution with HCl
pH
8
7.5
7
6.5
6
5.5
5
4.5
4
0
0.0001
0.0002
0.0003
0.0004
0.0005
0.0006
0.0007
0.0008
0.0009
0.001
[HCl] added (+ values) or [NaOH] added (- values)

Titration:

Summary

- TOT*H* expression – mass balance on protons introduced to solution:

$$\mathrm{TOT}H_{\mathrm{in}} = \mathrm{TOT}H_{\mathrm{eq}}$$

- To be most useful, pick RLS to be dominant member of each component group
- All the H^+ introduced to the solution (relative to the RLS) must be distributed among the species at equilibrium
- Titrations – plot of the pH response to incremental addition of strong acid or strong base to a solution mixture
  - Setup CB, then vary $[H^+]$ and determine $C_{SA} - C_{SB}$