

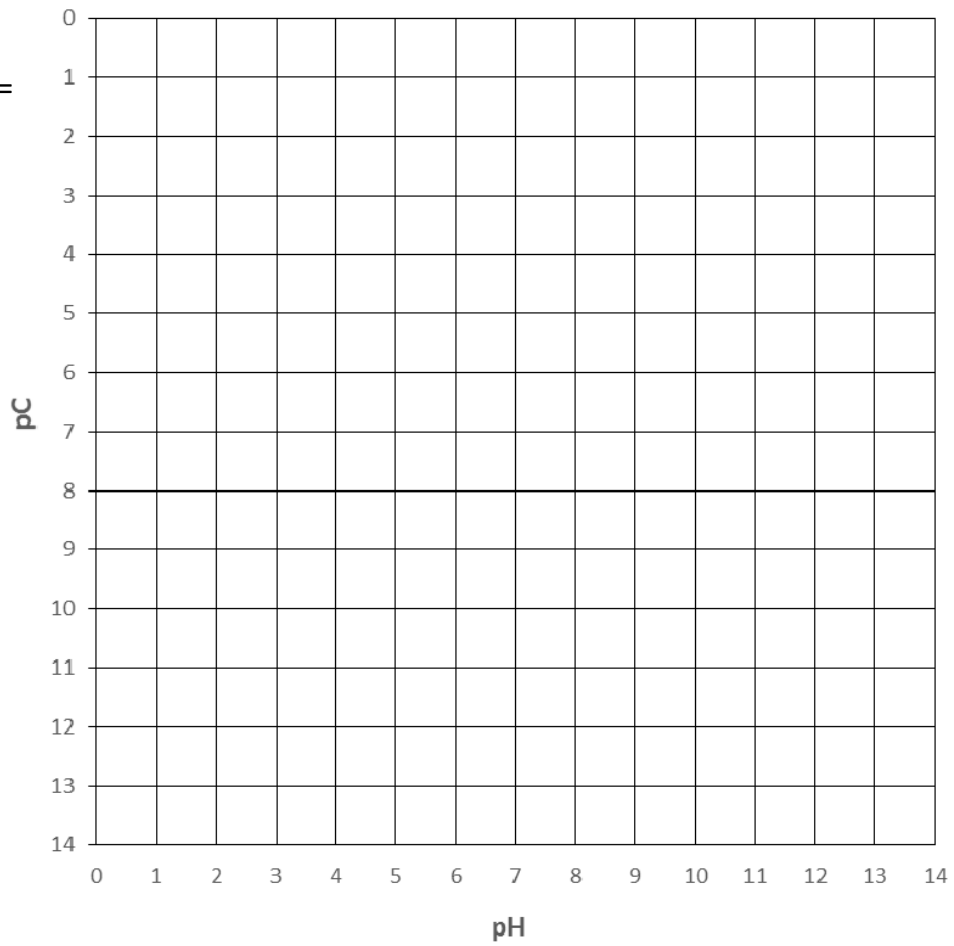
Advanced Water Quality

Class 13: Buffers and Carbonate System

Graphical Solution

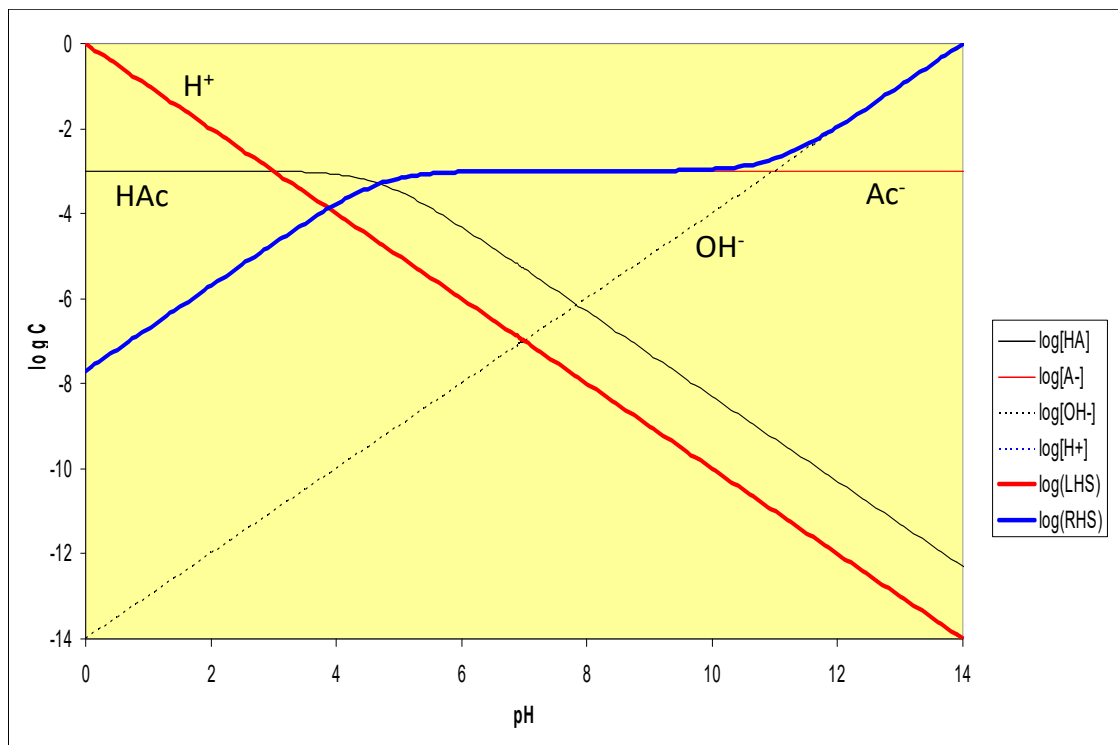
- If all possible components & species in solution are known, then you can use such plot to solve for the equilibrium pH and composition
 - Draw 2 lines:
 - Sum of all positive charged species (follow dominant term since log scale)
 - Sum of all negative charged species
 - Where lines cross is the only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

E.g., for 10^{-3} M acetic acid ($pK_a = 4.7$)



Graphical Solution

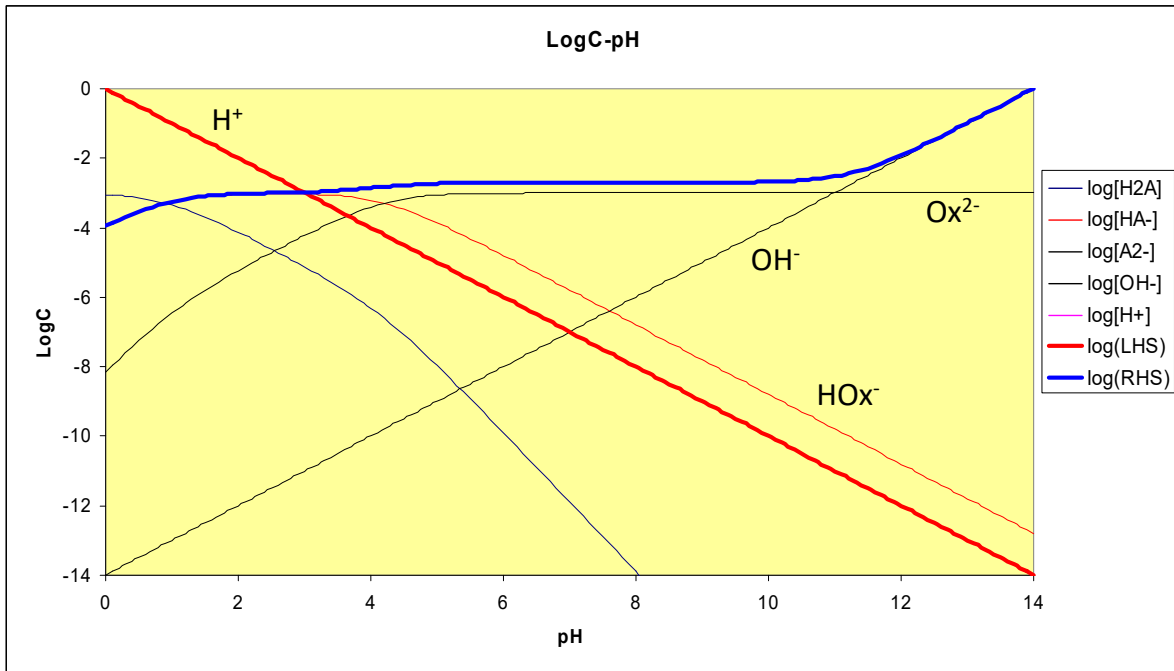
- E.g. 10^{-3} M acetic acid ($pK_a = 4.7$)



Graphical Solution

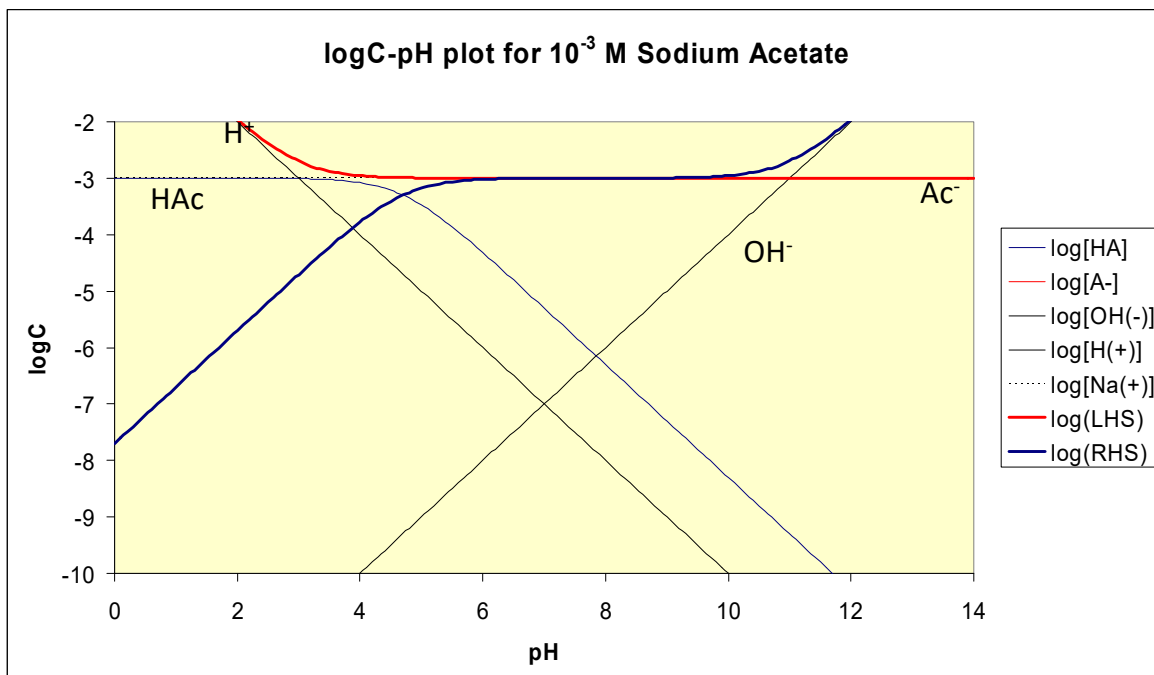
- E.g. 10^{-3} M oxalic acid ($pK_{a1} = 0.9$; $pK_{a2} = 4.2$)

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



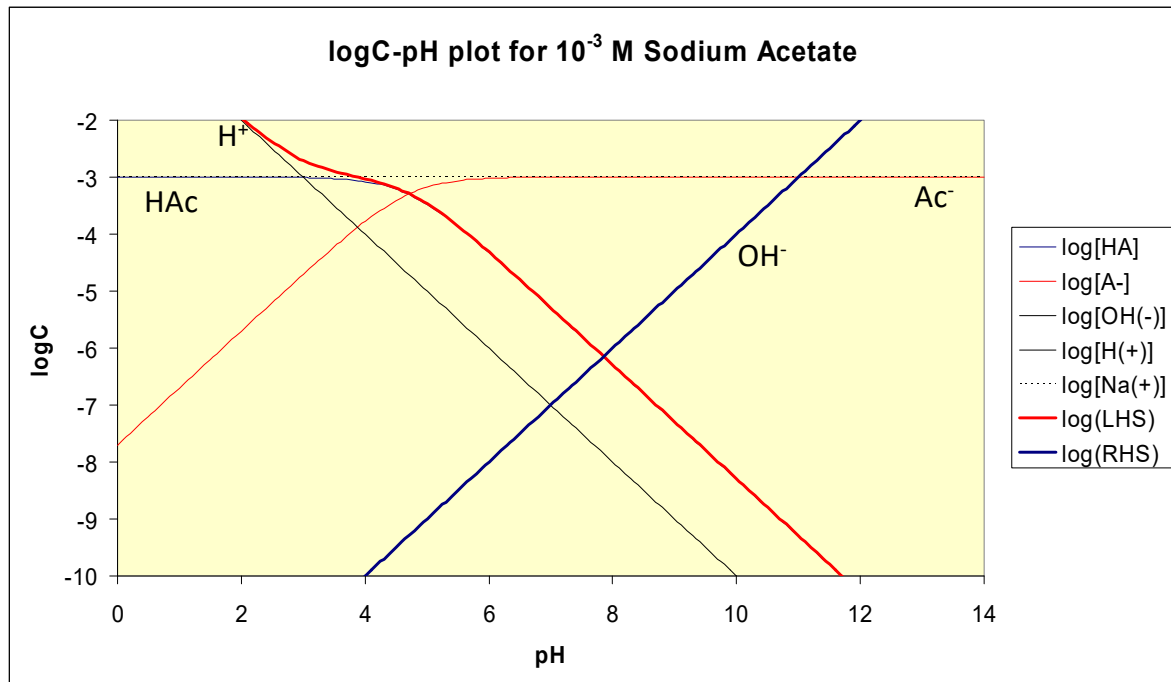
Graphical Solution

- 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



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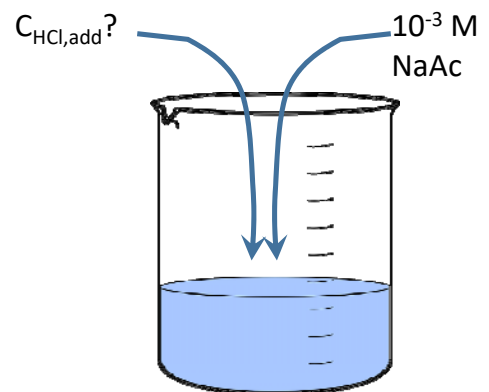
Problem 1: Determine how much HCl, a strong acid, must be added to the solution created by addition of 10^{-3} M sodium acetate ($pK_a = 4.7$) to convert the solution pH to 5.0. Assume ideal solution conditions.

C.B.:

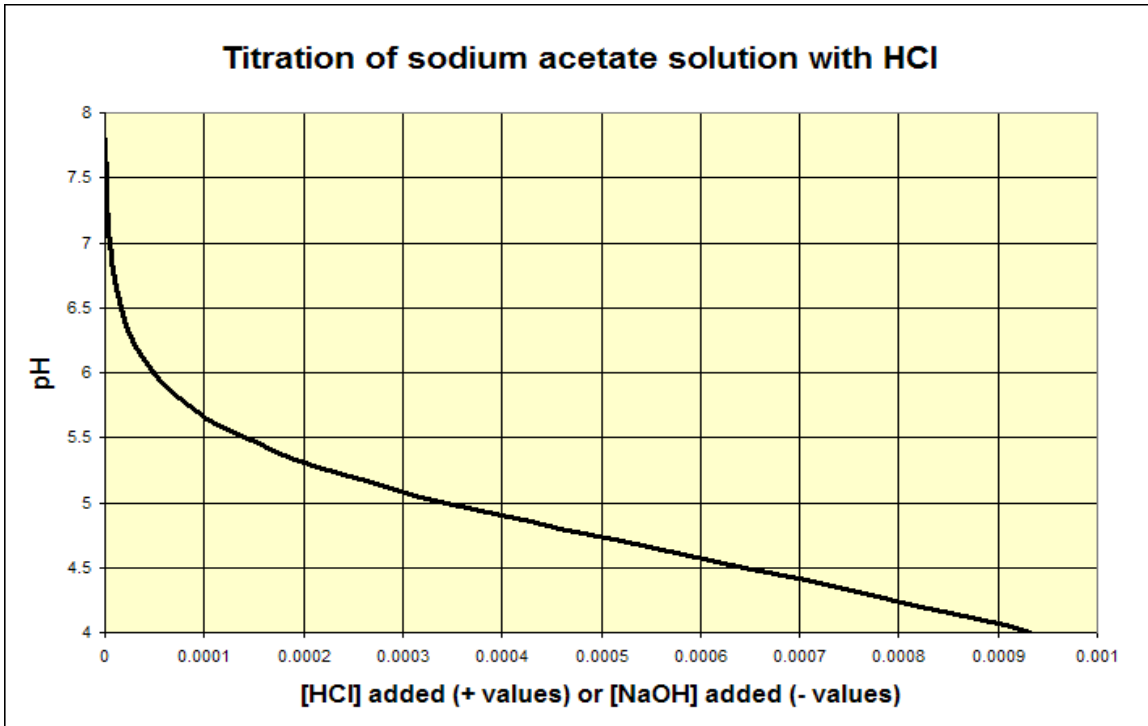
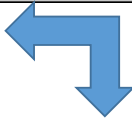
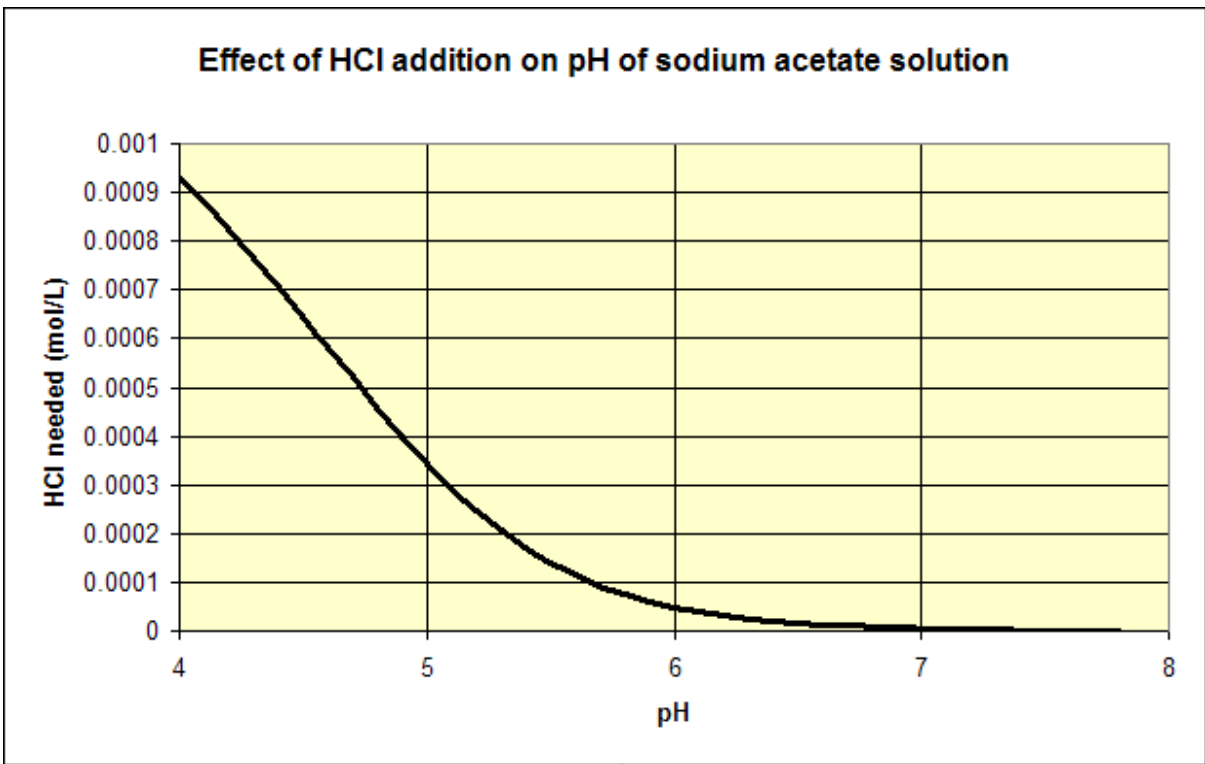
$$[H^+] + [Na^+] = [Cl^-] + [Ac^-] + [OH^-]$$

HCl addition

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

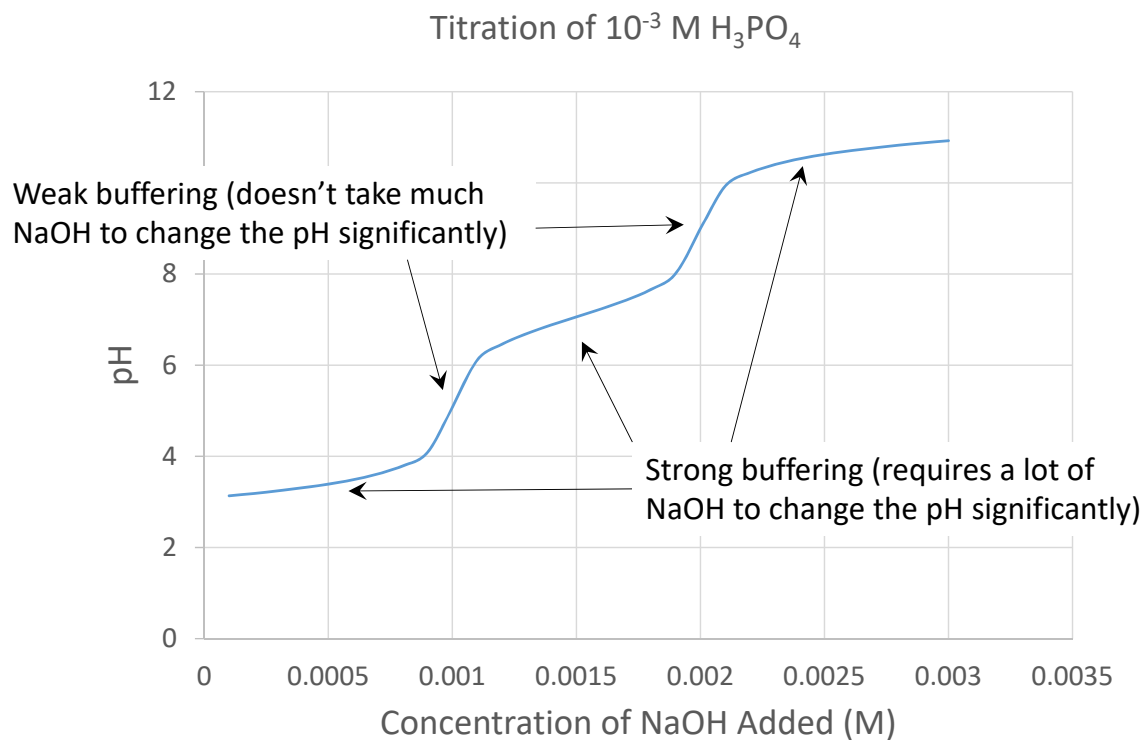


$$[Cl^-] = [H^+] + [10^{-3}] - \left[\frac{C_{T,Ac}}{\frac{\{H^+\}}{K_a} + 1} \right] - \frac{K_w}{[H^+]}$$

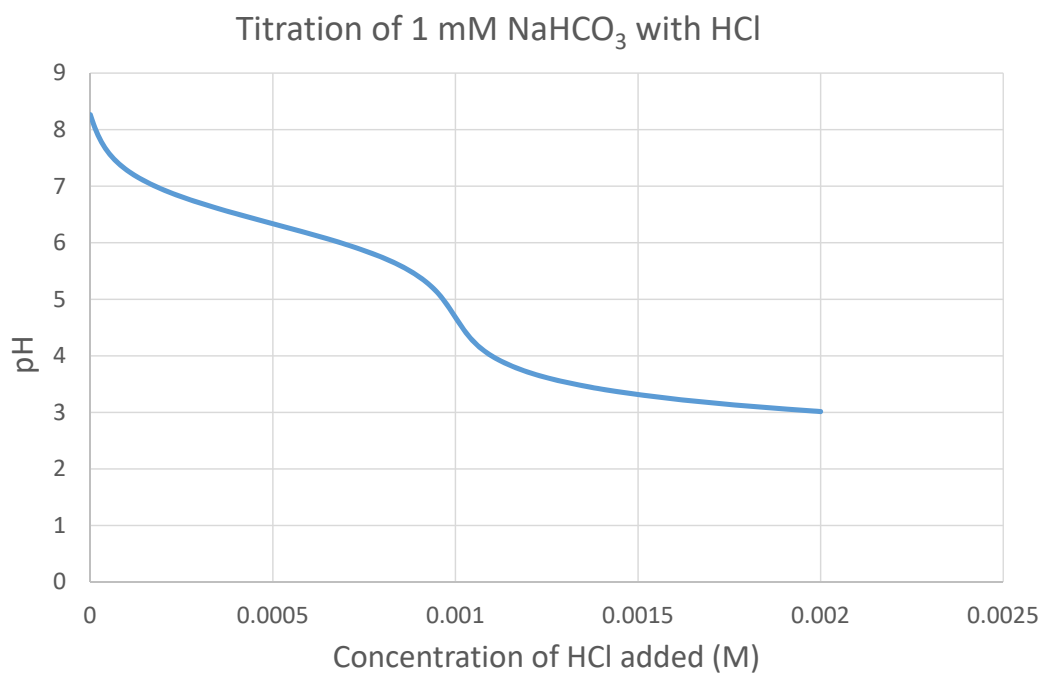


Titration:

From Last Class – Titrations calculated with Visual Minteq



From Last Class – Titrations calculated with Visual Minteq



Can derive this titration curve for 10^{-2} M NaHCO_3 from the equations we've already learned

- Use strong acid (e.g., HCl) to reduce pH
 - Use strong base (e.g., NaOH) raise pH
1. Components: H_2O , H^+ , CO_3^{2-} , Na^+ , Cl^-
 2. Species: H^+ , OH^- , H_2CO_3^* , HCO_3^- , CO_3^{2-} , Na^+ , Cl^-
 3. Knowns: C_{T,CO_3} , K_{a1} , K_{a2} , K_w , $[\text{H}^+]$
 4. Unknowns: $[\text{OH}^-]$, $[\text{H}_2\text{CO}_3^*]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $[\text{Cl}^-]$,
 $[\text{Na}^+]$, $C_{\text{NaOH}}^{\text{added}}$ (or $C_{\text{HCl}}^{\text{added}}$)
- Need 7 equations

$$1 \quad K_w = 10^{-14.00} = [\text{H}^+][\text{OH}^-]$$

$$2 \quad K_{a1} = 10^{-6.35} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

$$3 \quad K_{a2} = 10^{-10.33} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$4 \quad C_{T,\text{CO}_3} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$5 \quad C_{T,\text{Na}} = [\text{Na}^+] = C_{T,\text{CO}_3} + C_{\text{NaOH}}^{\text{added}}$$

$$6 \quad C_{T,\text{Cl}} = [\text{Cl}^-] = C_{\text{HCl}}^{\text{added}}$$

$$7 \quad [\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Cl}^-]$$

I'm not going to make any assumptions since I'm calculating over a wide range of conditions

- Reorganize the charge balance

$$[H^+] + C_{T,CO_3} + C_{NaOH}^{added} = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] + C_{HCl}^{added}$$

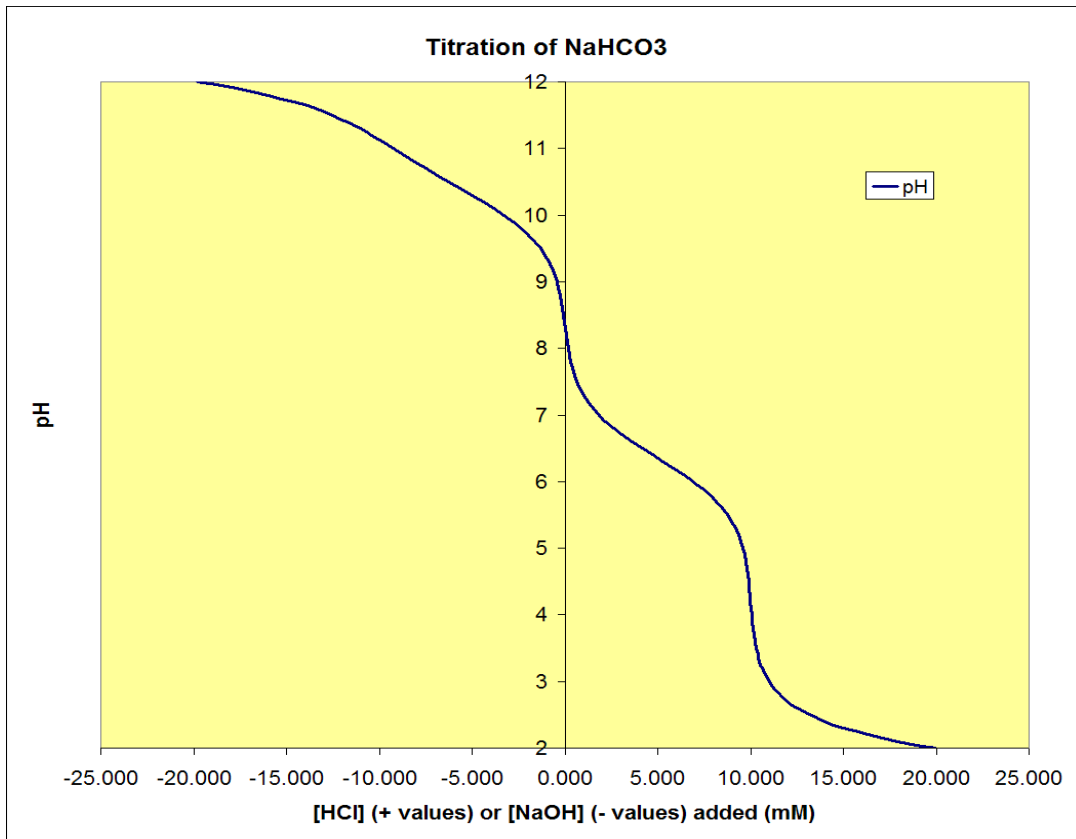
Rearrange to solve for conc. of NaOH or HCl added:

$$(C_{HCl}^{added} - C_{NaOH}^{added}) = [H^+] + C_{T,CO_3} - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}]$$

$$(C_{HCl}^{added} - C_{NaOH}^{added}) = [H^+] + 10^{-2} M - \frac{K_w}{[H^+]} - \frac{C_{T,CO_3}}{\frac{[H^+]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+]}} - \frac{2C_{T,CO_3}}{\frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}} + 1}$$

- Now we can just plug in different pH values and calculate the necessary HCl or NaOH to add to reach each condition

Titration of 10 mM NaHCO ₃			
pH	mM C _{HCl} - C _{NaOH}	6.8	2.616
		6.9	2.195
2	20.000	7	1.825
2.1	17.943	7.1	1.504
2.2	16.309	7.2	1.230
2.3	15.011	7.3	0.999
2.4	13.980	7.4	0.806
2.5	13.161	7.5	0.646
2.6	12.510	7.6	0.513
2.7	11.993	7.7	0.404
2.8	11.582	7.8	0.313
2.9	11.255	7.9	0.236
3	10.996	8	0.171
3.1	10.789	8.1	0.115
3.2	10.624	8.2	0.064
3.3	10.492	8.3	0.017
3.4	10.387	8.4	-0.030
3.5	10.302	8.5	-0.079
3.6	10.233	8.6	-0.131
3.7	10.177	8.7	-0.190
3.8	10.130	8.8	-0.258
3.9	10.091	8.9	-0.338
4	10.056	9	-0.435
4.1	10.024	9.1	-0.551
4.2	9.993	9.2	-0.692
4.3	9.962	9.3	-0.862
4.4	9.929	9.4	-1.068
4.5	9.892	9.5	-1.313
4.6	9.850	9.6	-1.604
4.7	9.801	9.7	-1.945
4.8	9.742	9.8	-2.338
4.9	9.670	9.9	-2.786
5	9.582	10	-3.285
5.1	9.476	10.1	-3.830
5.2	9.345	10.2	-4.415
5.3	9.187	10.3	-5.026
5.4	8.995	10.4	-5.653
5.5	8.765	10.5	-6.282



pH buffer = solution mixture that stabilizes pH against changes when strong acids or bases are added

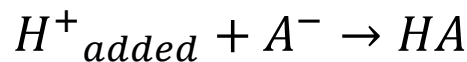
- Weak acid/base conjugate pairs serve as pH buffers at conditions near their pK_a values
 - If both [C.A.] and [C.B.] are present in sufficient concentration
- Carbonate system is the most important pH buffer of natural waters
 - Major source of alkalinity and acidity in water

How do weak acid-base conjugate pair accomplish buffering?

- 1st, a buffer is most effective near its pK_a value, and is only effective within 1 – 2 pH units above and below the pK_a .
- This is because near the pK_a of the a-b conjugate pair, ample conjugate acid is present to react with any strong base added:



- Also, ample conjugate base is present to react with any strong acid added to solution:



- ▶ It is the stability of ratio between [HA] and [A⁻] that stabilizes pH

$$K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}}$$

$$\{H^+\} = K_a \frac{\{HA\}}{\{A^-\}}$$

$$pH = -\log \left[K_a \frac{\{HA\}}{\{A^-\}} \right]$$

- ▶ Important for pH to be near pKa and for [HA] and [A⁻] to both be large compared to amount of H⁺ or OH⁻ added:

$$\{H^+\} = K_a \frac{\{HA\}}{\{A^-\}} \quad pH = -\log \left(K_a \frac{\{HA\}}{\{A^-\}} \right)$$

Initial Conditions			After adding 1 unit of H ⁺			
[HA]	[A ⁻]	[HA]/[A ⁻]	[HA]	[A ⁻]	[HA]/[A ⁻]	Strong buffering?
100	100	1.0				
198	2	99				
3	3	1.0				

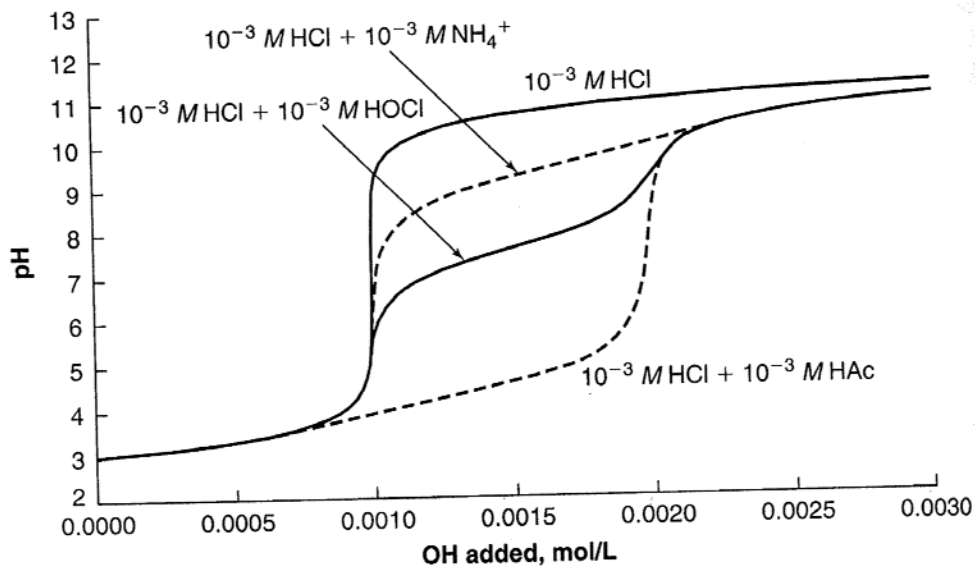


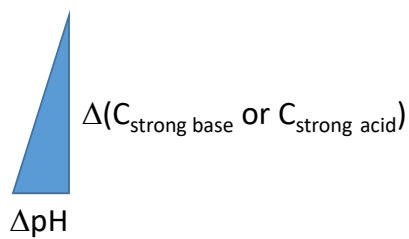
Figure 5.3 Titration curves for four solutions containing either 10⁻³ M HCl alone or in addition to 10⁻³ M of a weaker acid. Source: Benjamin Water Chemistry (2002)

Buffers add acid/base neutralizing capacity up to their concentration near each pKa

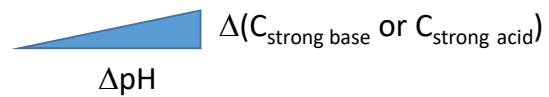
- Acetic acid/acetate adds buffering from
- HOCl/OCl⁻ adds buffering from
- NH₄⁺/NH₃ adds buffering from

Buffer intensity:  $\Delta(C_{\text{strong base or } C_{\text{strong acid}}})$

$$\beta = \frac{\Delta(C_B - C_A)}{\Delta pH}$$

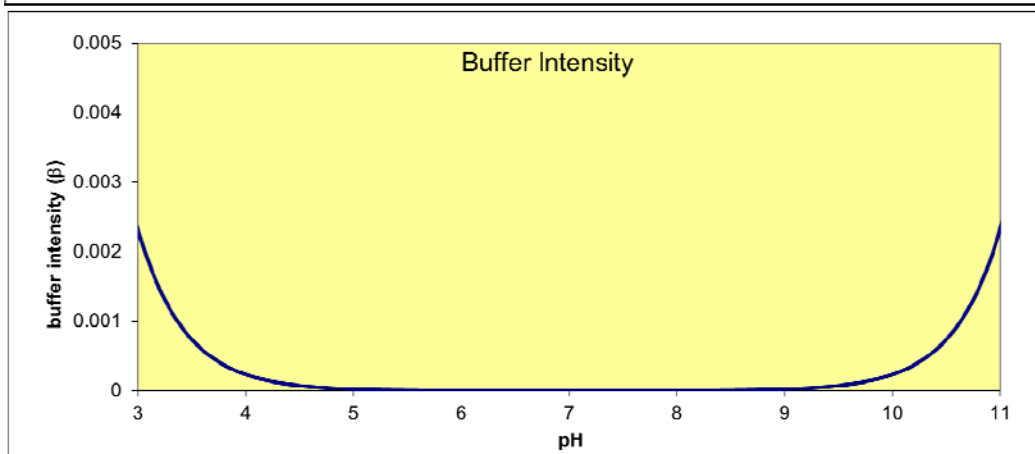
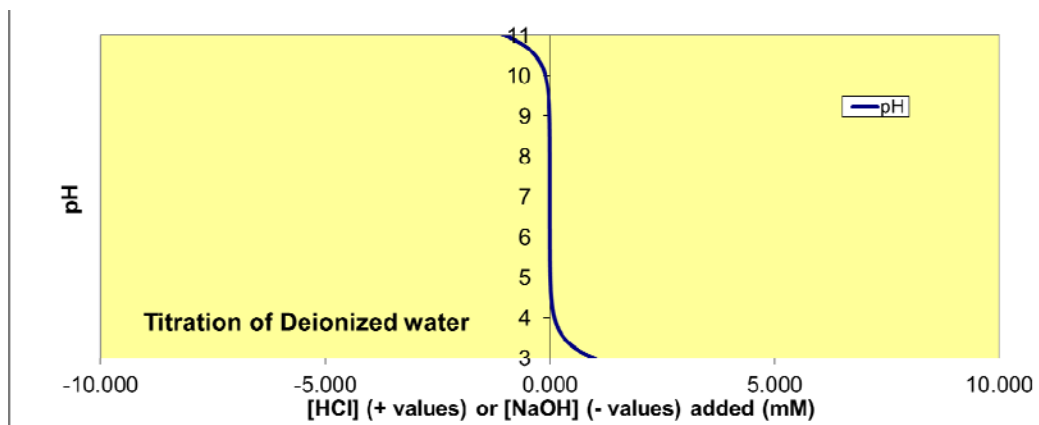


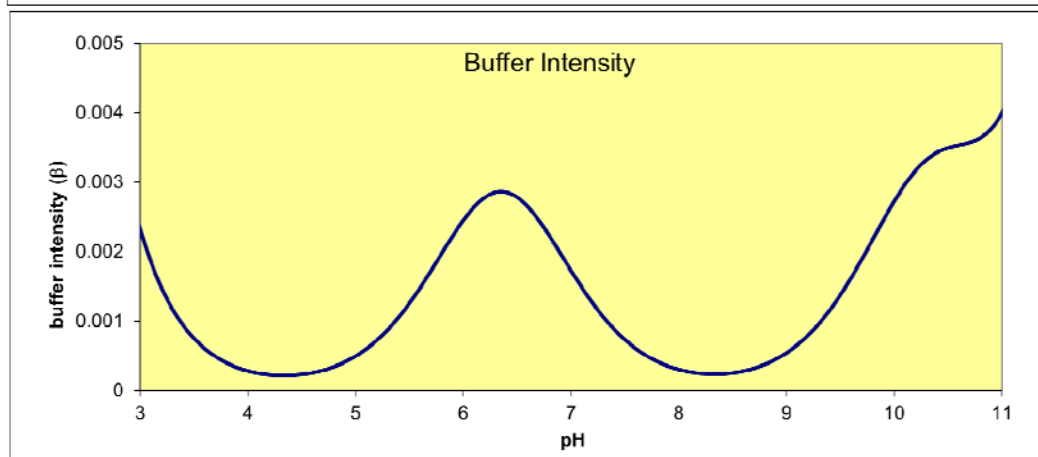
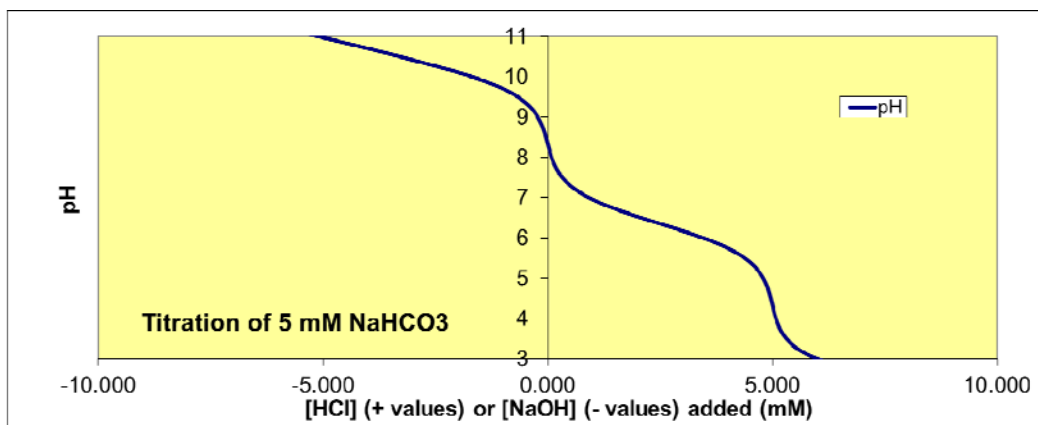
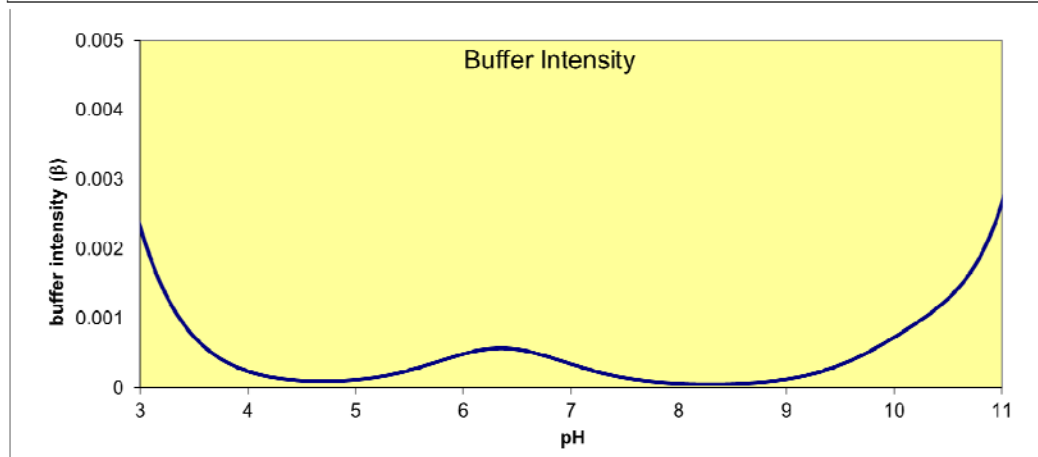
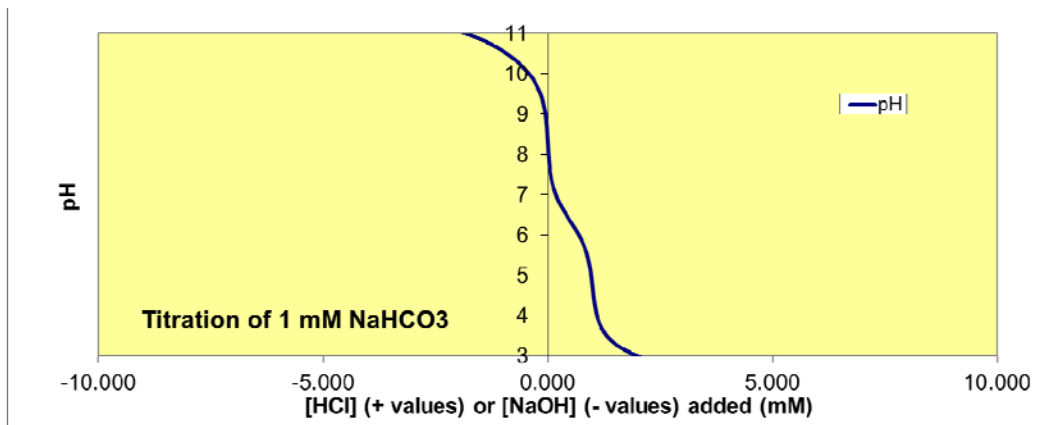
High β = strong pH buffering



Small β = weak pH buffering

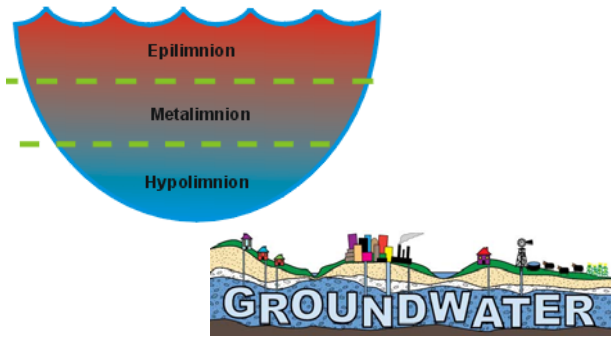
β increases as you near pKa and as the concentration of conj. acid/base pair increases





Closed Systems

- No aq/gas mass exchange



- Good approximation
 - Groundwater
 - sealed reactor
 - Stratified lake
 - Open reactor with short residence time
- Can often use mass balance constraint

Open Systems

- ▶ Aq/gas mass exchange allowed



- ▶ Good approximation
 - ▶ Surface waters
 - ▶ Well mixed open reactors
- ▶ Cannot use mass balance constraint for component undergoing exchange
- ▶ Use K_H constraint instead

$$H = \frac{\{i\}_g}{\{i\}_{aq}} = \frac{P_i}{[i]_{aq}}$$

$$K_H = \frac{\{i\}_{aq}}{\{i\}_g} = \frac{[i]_{aq}}{P_i}$$

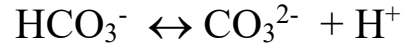
Table of H and K_H values for important gases at 25 °C

Compound	H (atm L mol ⁻¹)	K_H (atm ⁻¹ L ⁻¹ mol)
Nitrogen (N ₂)	1513	10 ^{-3.18}
Hydrogen (H ₂)	1260	10 ^{-3.10}
Carbon Monoxide (CO)	1047	10 ^{-3.02}
Oxygen (O ₂)	794	10 ^{-2.90}
Methane (CH ₄)	775	10 ^{-2.89}
Ozone (O ₃)	107	10 ^{-1.23}
Carbon Dioxide (CO₂)	29.5	10^{-1.47}
Ammonia (NH ₃)	0.017	58.8
Hydrogen Sulfide (H ₂ S)	9.5	0.105
Tetrachloroethylene (PCE)	18.5	0.054
Trichloroethylene (TCE)	9.7	0.103
Benzene (C ₆ H ₆)	5.4	0.185

Review of carbonate chemistry in a “closed” system



$$K_w = 10^{-14.0} = \{\text{H}^+\} \{\text{OH}^-\} = \gamma_1[\text{H}^+] \gamma_1[\text{OH}^-]$$



$$K_{a1} = 10^{-6.35} = \frac{\gamma_1[\text{H}^+] \gamma_1[\text{HCO}_3^-]}{\gamma_0[\text{H}_2\text{CO}_3^*]} \quad K_{a2} = 10^{-10.33} = \frac{\gamma_1[\text{H}^+] \gamma_2[\text{CO}_3^{2-}]}{\gamma_1[\text{HCO}_3^-]}$$

$$C_{\text{T,CO}_3} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

$$C_{\text{T,Na}} = [\text{Na}^+] = C_{\text{NaCl(added)}} + C_{\text{NaOH(added)}}$$

$$C_{\text{T,Cl}} = [\text{Cl}^-] = C_{\text{NaCl(added)}} + C_{\text{HCl(added)}}$$

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{Cl}^-]$$

What do we change for an open system?

- All expressions still valid, but likely we do not know $C_{\text{T,CO}_3}$ as a fixed constraint, and it will vary with pH conditions.
- Add Henry's constant constraint now

$$K_H = 10^{-1.47} = \frac{[\text{H}_2\text{CO}_3^*]}{P_{\text{CO}_2}}$$

- Expressions for $[\text{H}_2\text{CO}_3^*]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ vs. pH revised to be a function of K_H and P_{CO_2} rather than $C_{\text{T,CO}_3}$

$$[\text{HCO}_3^-] = \frac{K_{a1}[\text{H}_2\text{CO}_3^*]}{[\text{H}^+]} = \frac{K_{a1}K_H P_{\text{CO}_2}}{[\text{H}^+]}$$

Estimate the pH of rainwater in equilibrium with our current atmosphere containing 400 ppm_v CO₂, and the expected pH in equilibrium with the atmosphere in the year 2300 with a projected CO₂ level of 1900 ppm_v
-Assume T=25C, no other weak acid or bases present

Components:

Species:

Knowns:

Unknowns:

Governing Equations:

Formulate charge balance as a function of [H⁺] and knowns:

Present Day ($P_{\text{CO}_2} = 400 \text{ ppm}_v$):

Year 2300 ($P_{\text{CO}_2} = 1900 \text{ ppm}_v$ projected):

pC-pH diagram for water in equilibrium
with 1900 ppm_v CO₂

$p[H_2CO_3^*]$ set by $K_H P_{CO_2}$

$p[H_2CO_3^*] =$

- Use rules we established for pC-pH diagrams in closed systems.

