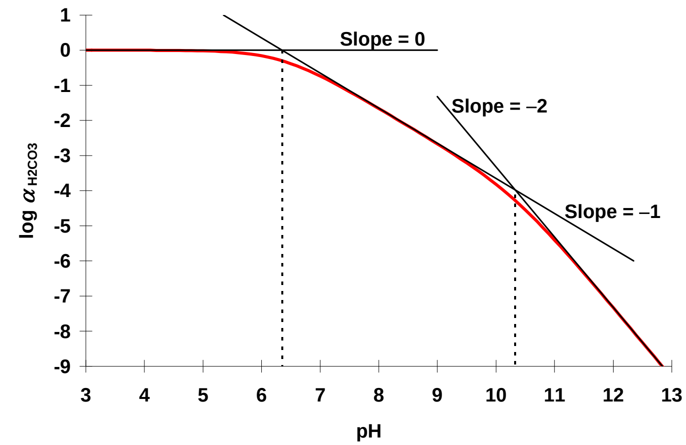
Graphical Representation of Acid/Base Speciation

Example: Carbonic acid (H_2CO_3), pK_{a1}=6.35, pK_{a2}=10.33

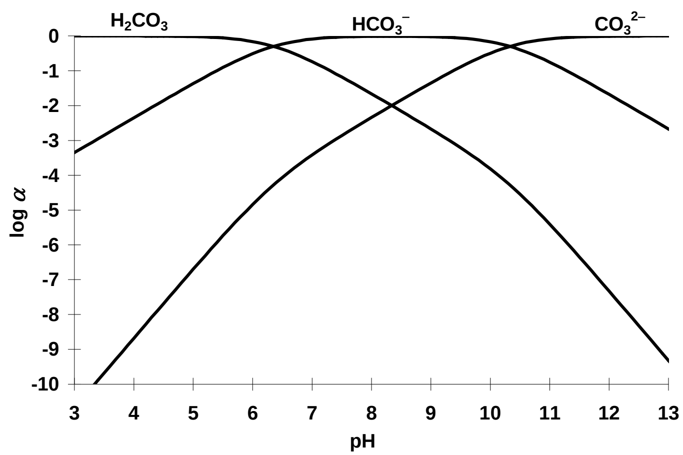
$$\alpha_0 = \frac{1}{1+\frac{K_{a1}}{(\mathrm{H}^+)}+\frac{K_{a1}K_{a2}}{(\mathrm{H}^+)^2}} = \frac{1}{1+\frac{10^{-6.35}}{(\mathrm{H}^+)}+\frac{10^{-16.68}}{(\mathrm{H}^+)^2}}$$

If $(\mathrm{H}^+)>\sim 10^{-5}$, the first term in the denominator is much bigger than the other two. If $10^{-9}<(\mathrm{H}^+)<10^{-7.5}$, the second term is dominant. And, if $(\mathrm{H}^+)<\sim 10^{-11.5}$, the third term dominates. In these regions, the slope of $\log\alpha_0$ vs pH is 0, -1, and -2, respectively.

Graphical Representation of Acid/Base Speciation



Graphical Representation of Acid/Base Speciation



Graphical Representation of Acid/Base Speciation

$$\mathrm{H}_n\mathrm{A} \leftrightarrow \mathrm{H}_{n-j}\mathrm{A} + j\mathrm{H}^+ \quad K_{a1}K_{a2}\ldots K_{aj} \quad \frac{(\mathrm{H}_{n-j}\mathrm{A})}{(\mathrm{H}_n\mathrm{A})} = \frac{K_{a1}K_{a2}\ldots K_{aj}}{(\mathrm{H}^+)^j}$$

$$\log(\mathrm{H}_{n-j}\mathrm{A}) - \log(\mathrm{H}_n\mathrm{A}) = \log(K_{a1}K_{a2}\ldots K_{aj}) + j\mathrm{pH}$$

For every increase of 1 pH unit, the difference $\log(H_{n-j}A) - \log(H_nA)$ increases by j. Hence, on a plot of $\log c_i$ vs. pH, the slopes of the curves for $H_{n-j}A$ and H_nA must differ by j.

Numerical Solution of Acid/Base Problems

If a known mix of acids and bases is added to pure water, the speciation can be determined by identifying the unknowns (broadly speaking, the concentrations and activity coefficients of all dissolved species) and an equal number of equations relating the unknowns.

Unknowns:

- (*a*) H^+ and OH^-
- (*b*) *n* species for each (*n*–1)-protic acid/base group
- (*c*) Salt ions that do not undergo acid/base reactions
- (*d*) Combinations of species from groups *b* and *c*
- (*e*) Ionic strength and activity coefficients

Numerical Solution of Acid/Base Problems

Equations relating the unknowns:

- Equilibrium constants
  - (*a*) K_w
  - (*b*) (*n*-1) K_{eq} values for each (*n*–1)-protic acid/base group
  - (*c*) No *K*'s
  - (*d*) One K_{eq} for each new *b-c* species
- Mass balances: one for each acid/base group and each salt ion (categories *b* and *c*)
- Charge balance: one for the whole solution
- Ionic strength: one for the whole solution
- Activity coefficients vs. *I*: One for each species

Numerical Solution of Acid/Base Problems

Example: Speciation of 0.01 *M* Na_2HPO_4 + 0.003 *M* H_3PO_4 (assuming all γ_i are 1.0). Find pH and concentrations of all solutes

- Species: ??
- Equilibrium constants
  - (*a*) ??
  - (*b*) ??
  - (*c*) ??
  - (*d*) ??
- Mass balances: ??
- Charge balance: ??

Numerical Solution of Acid/Base Problems

Example: Speciation of 0.01 *M* Na_2HPO_4 + 0.003 *M* H_3PO_4

- Species: H^+, OH^-, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, Na^+
- Equilibrium constants
  - (*a*) $K_w = 10^{-14.0}$
  - (*b*) $K_{a1} = 10^{-2.2}$, $K_{a2} = 10^{-7.2}$, $K_{a3} = 10^{-12.2}$
  - (*c*) N/A
  - (*d*) None
- Mass balances: $TOTPO_4=0.013=10^{-1.89}$, $TOTNa=0.02$
- Charge balance:

$$[Na^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Numerical Solution of Acid/Base Problems

Example: Speciation of 0.01 *M* Na_2HPO_4 + 0.003 *M* H_3PO_4

$$[Na^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

$$TOT\text{Na} + \left[\text{H}^+\right] = \frac{K_w}{\left[\text{H}^+\right]} + \alpha_1 * TOT\text{PO}_4 + 2\alpha_2 * TOT\text{PO}_4 + 3\alpha_3 * TOT\text{PO}_4$$

K_w, *TOT*Na and *TOT*PO_4 are known; α_i's depend only on $[H^+]$ and K_a's, and K_a's are known. Therefore, every unknown depends only on $[H^+]$, and the equation has only one unknown…**$[H^+]$ (or pH) is a *Master Variable***

$$TOT\text{Na} + \left[\text{H}^+\right] = \frac{K_w}{\left[\text{H}^+\right]} + \alpha_1 * TOT\text{PO}_4 + 2\alpha_2 * TOT\text{PO}_4 + 3\alpha_3 * TOT\text{PO}_4$$

pH	Na	H	OH	H2PO4	HPO4	PO4	Sum (+)	Sum (-)	Net Charge
1	2.00E-02	1.00E-01	1.00E-13	7.72E-04	4.87E-10	3.07E-21	1.20E-01	7.72E-04	1.19E-01
3	2.00E-02	1.00E-03	1.00E-11	1.12E-02	7.08E-07	4.47E-16	2.10E-02	1.12E-02	9.78E-03
5	2.00E-02	1.00E-05	1.00E-09	1.29E-02	8.14E-05	5.13E-12	2.00E-02	1.31E-02	6.95E-03
7	2.00E-02	1.00E-07	1.00E-07	7.97E-03	5.03E-03	3.17E-08	2.00E-02	1.80E-02	**1.97E-03**
9	2.00E-02	1.00E-09	1.00E-05	2.03E-04	1.28E-02	8.07E-06	2.00E-02	2.58E-02	**-5.82E-03**
11	2.00E-02	1.00E-11	1.00E-03	1.94E-06	1.22E-02	7.71E-04	2.00E-02	2.78E-02	-7.77E-03
13	2.00E-02	1.00E-13	1.00E-01	2.82E-09	1.78E-03	1.12E-02	2.00E-02	1.37E-01	-1.17E-01
7	2.00E-02	1.00E-07	1.00E-07	7.97E-03	5.03E-03	3.17E-08	2.00E-02	1.80E-02	1.97E-03
7.1	2.00E-02	7.94E-08	1.26E-07	7.24E-03	5.75E-03	4.57E-08	2.00E-02	1.88E-02	1.25E-03
7.2	2.00E-02	6.31E-08	1.58E-07	6.50E-03	6.50E-03	6.50E-08	2.00E-02	1.95E-02	**5.00E-04**
7.3	2.00E-02	5.01E-08	2.00E-07	5.75E-03	7.24E-03	9.12E-08	2.00E-02	2.02E-02	**-2.45E-04**
7.21	2.00E-02	6.17E-08	1.62E-07	6.43E-03	6.57E-03	6.73E-08	2.00E-02	1.96E-02	4.25E-04
7.22	2.00E-02	6.03E-08	1.66E-07	6.35E-03	6.65E-03	6.96E-08	2.00E-02	1.96E-02	3.50E-04
7.23	2.00E-02	5.89E-08	1.70E-07	6.28E-03	6.72E-03	7.21E-08	2.00E-02	1.97E-02	2.75E-04
7.24	2.00E-02	5.75E-08	1.74E-07	6.20E-03	6.80E-03	7.46E-08	2.00E-02	1.98E-02	2.01E-04
7.25	2.00E-02	5.62E-08	1.78E-07	6.13E-03	6.87E-03	7.71E-08	2.00E-02	1.99E-02	1.26E-04
7.26	2.00E-02	5.50E-08	1.82E-07	6.05E-03	6.95E-03	7.98E-08	2.00E-02	1.99E-02	**5.15E-05**
7.27	2.00E-02	5.37E-08	1.86E-07	5.98E-03	7.02E-03	8.25E-08	2.00E-02	2.00E-02	**-2.29E-05**