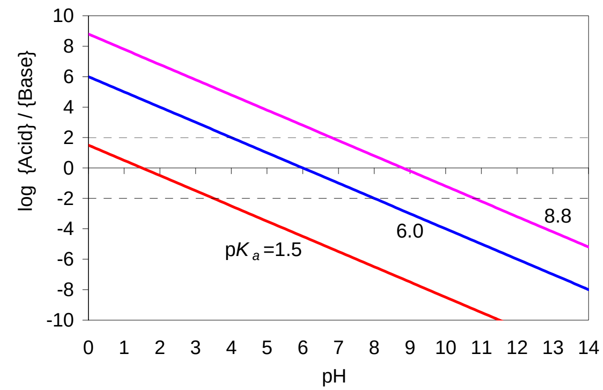
Mathematics of Acid/Base Speciation

$$\frac{\{Acid\}}{\{Base\}} = \frac{\{H^+\}}{K_a} \qquad \log\frac{\{Acid\}}{\{Base\}} = pK_a - pH$$

- The K_a expression requires that:
  - ***Whenever the H^+ activity increases by a factor of x, the activity ratio of the acid to the conjugate base increases by this same factor***
  - ***When H^+ activity equals K_a ($pH=pK_a$), the acid and base have equal activities***
  - ***Each unit increase in pH causes the ratio of Base/ Conjugate Acid to increase by a factor of 10***

Graphical Representation of Acid/Base Speciation

$$\log\frac{\{Acid\}}{\{Base\}} = pK_a - pH$$



Example Applications

- The pK_a of ammonium ion (NH_4^+) is 9.25. In what pH range is ammonia (NH_3) more concentrated than ammonium?
- To what pH must a solution be adjusted to cause >90% of *TOT*NH_3 to be present as the neutral NH_3 molecule?
- A solution is at pH 7.5. What is the dominant species of the carbonic acid group ($H_2CO_3/HCO_3^-/CO_3^{2-}$)? p$K_{a1}$=6.35, p$K_{a2}$=10.33.

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$

Define $\alpha_i \equiv c_i/TOTc$. Then, for monoprotic acids, if γ_i=1.0:

$$\alpha_{Acid} = \frac{(Acid)}{TOTc} = \frac{(Acid)}{(Acid)+(Base)} = \frac{\{Acid\}}{\{Acid\}+\frac{\{Acid\}K_a}{\{H^+\}}}$$

$$= \frac{\{H^+\}}{\{H^+\}+K_a}$$

$$\alpha_{Base} = \frac{(Base)}{TOTc} = 1-\alpha_{Acid} = \frac{K_a}{(H^+)+K_a}$$

The speciation of monoprotic acids depends only on their pK_a and the solution pH (and, if $\gamma_i \neq 1.0$, the ionic strength).

Graphical Representation of Acid/Base Speciation

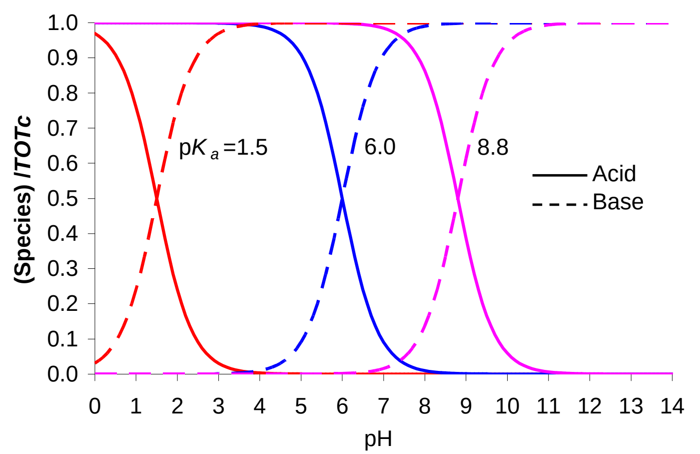
For monoprotic acids, if γ_i=1.0: $\alpha_{Acid} = \frac{(H^+)}{(H^+)+K_a}$

If $(H^+) >> K_a$: $\alpha_{Acid} \approx 1.0; \quad \alpha_{Base} \approx \frac{K_a}{(H^+)}$

If $(H^+) << K_a$: $\alpha_{Acid} \approx \frac{(H^+)}{K_a}; \quad \alpha_{Base} \approx 1.0$

If $(H^+) = K_a$: $\alpha_{Acid} = \alpha_{Base} = \frac{1}{2}$

Graphical Representation of Acid/Base Speciation



Graphical Representation of Acid/Base Speciation

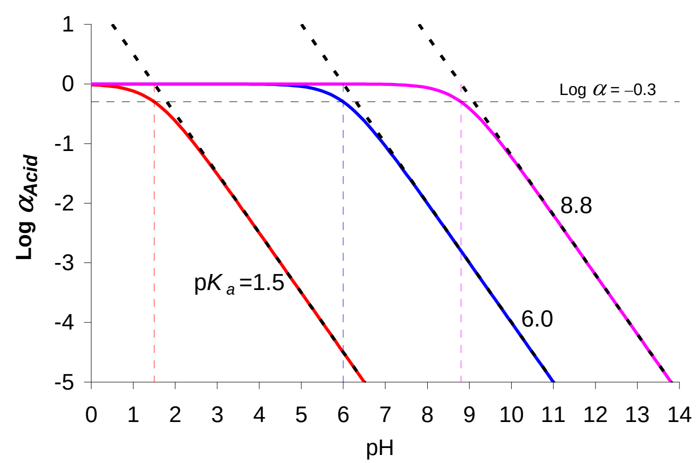
For monoprotic acids, if γ_i=1.0: $\alpha_{Acid} = \frac{(H^+)}{(H^+)+K_a}$

If $(H^+) >> K_a$: $\alpha_{Acid} \approx 1.0; \quad \log \alpha_{Acid} \approx 0.0$

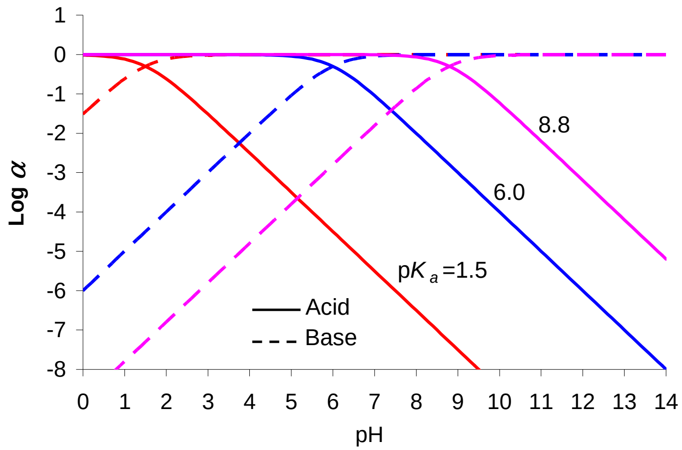
If $(H^+) << K_a$: $\alpha_{Acid} \approx \frac{(H^+)}{K_a} \quad \log \alpha_{Acid} \approx pK_a - pH$

If $(H^+) = K_a$: $\alpha_{Acid} = \frac{1}{2} \quad \log \alpha_{Acid} = \log(0.5) = -0.3$

Graphical Representation of Acid/Base Speciation

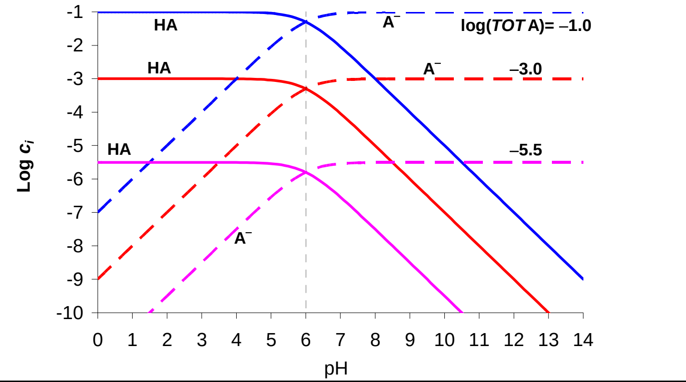


Graphical Representation of Acid/Base Speciation

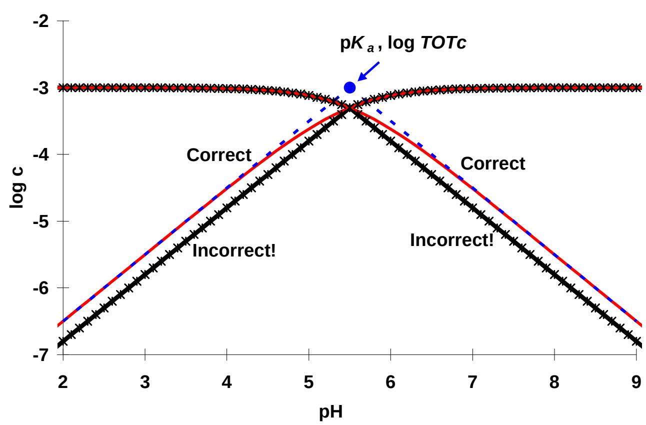


If *TOTc* is known, the species' concentrations are easily computed; e.g.:

$$\left[Acid\right]=\alpha_{Acid}\left(TOTA\right); \quad \log\left[Acid\right]=\log\alpha_{Acid}+\log TOTA$$



The ***most common error*** in drawing log *c* vs. pH graphs. ***Please*** do not make this error!!!



For multiprotic acids, assuming $\gamma_i = 1$:

$$\alpha_0=\frac{(H_nA)}{(H_nA)+(H_{n-1}A)+(H_{n-2}A)+...}=\frac{1}{1+\frac{(H_{n-1}A)}{(H_nA)}+\frac{(H_{n-2}A)}{(H_nA)}+...}$$

Substitute for terms in denominator:

$$\frac{(H_{n-1}A)}{(H_nA)}=\frac{K_{a1}}{(H^+)}$$

$$H_nA \leftrightarrow H_{n-1}A + H^+ \qquad K_{a1}$$

$$H_{n-1}A \leftrightarrow H_{n-2}A + H^+ \qquad K_{a2}$$

$$H_nA \leftrightarrow H_{n-2}A + 2H^+ \qquad K_{a1}K_{a2}$$

$$\frac{(H_{n-2}A)}{(H_nA)}=\frac{K_{a1}K_{a2}}{(H^+)^2}$$

Graphical Representation of Acid/Base Speciation

In general: $H_nA \leftrightarrow H_{n-j}A + jH^+ \qquad K_{a1}K_{a2}...K_{aj}$

$$\frac{(H_{n-j}A)}{(H_nA)} = \frac{K_{a1}K_{a2}...K_{aj}}{(H^+)^j}$$

$$\alpha_0 = \frac{1}{1+\frac{(H_{n-1}A)}{(H_nA)}+\frac{(H_{n-2}A)}{(H_nA)}+...} = \frac{1}{1+\frac{K_{a1}}{(H^+)}+\frac{K_{a1}K_{a2}}{(H^+)^2}+...}$$

Graphical Representation of Acid/Base Speciation

$$\alpha_1 = \frac{(H_{n-1}A)}{(H_nA)+(H_{n-1}A)+(H_{n-2}A)+...} = \frac{1}{\frac{(H_nA)}{(H_{n-1}A)}+1+\frac{(H_{n-2}A)}{(H_{n-1}A)}+...}$$

Substitute for terms in denominator:

$$\frac{(H_nA)}{(H_{n-1}A)} = \frac{(H^+)}{K_{a1}} \qquad \frac{(H_{n-2}A)}{(H_{n-1}A)} = \frac{K_{a2}}{(H^+)}$$

$$\alpha_1 = \frac{1}{\frac{(H_nA)}{(H_{n-1}A)}+1+\frac{(H_{n-2}A)}{(H_{n-1}A)}+...} = \frac{1}{\frac{(H^+)}{K_{a1}}+1+\frac{K_{a2}}{(H^+)}+...}$$

Graphical Representation of Acid/Base Speciation

$$\alpha_0 = \frac{1}{1+\frac{(H_{n-1}A)}{(H_nA)}+\frac{(H_{n-2}A)}{(H_nA)}+...} = \frac{1}{1+\frac{K_{a1}}{(H^+)}+\frac{K_{a1}K_{a2}}{(H^+)^2}+...}$$

$$\alpha_1 = \frac{1}{\frac{(H_nA)}{(H_{n-1}A)}+1+\frac{(H_{n-2}A)}{(H_{n-1}A)}+...} = \frac{1}{\frac{(H^+)}{K_{a1}}+1+\frac{K_{a2}}{(H^+)}+...}$$

$$\alpha_2 = \frac{1}{\frac{(H_nA)}{(H_{n-2}A)}+\frac{(H_{n-1}A)}{(H_{n-2}A)}+1+...} = \frac{1}{\frac{(H^+)^2}{K_{a1}K_{a2}}+\frac{(H^+)}{K_{a2}}+1+...}$$

The speciation of any acid depends only on its pK_a's and the solution pH (and, if $\gamma_i \neq 1.0$, the ionic strength).