pC-pH Diagrams
## Equilibrium Diagrams for Weak Acid and Base Systems

The concentration of a weak acid or base (for example H_2CO_3, HCO_3^-, or CO_3^{2-}) can be calculated using simple equilibrium expressions at any given pH. In some cases it is useful to look at the equilibrium distribution of each of the protonated and nonprotonated species in solution at the same time. A pC-pH diagram, such as the one shown below, is an excellent tool for viewing these concentrations simultaneously. As the name implies, the concentrations of all chemical species (including the hydronium ion) are expressed as the negative log of concentration. To construct a pC-pH diagram, the total concentration of the acid or base is needed along with the corresponding equilibrium equations and constants (K).

All pC-pH diagrams have two lines in common, the line describing the concentration of hydroxide (OH⁻) as a function of pH and the line describing the concentration of hydronium ion (H⁺) as a function of pH. These are based on the equilibrium relation

$$H_2O \Leftrightarrow H^+ + OH^-$$
and
$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$
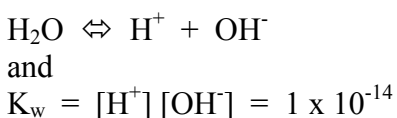
By rearranging and taking the negative log of each side

$$-\log K_w = -\log[H^+] - \log[OH^-]$$
$$pOH = 14 - pH$$

The slope of the line can be expressed as

$$\frac{\Delta pOH}{\Delta pH} = -1 \, ,$$

and when pH equals 0, the pOH equals 14. This results in a line being drawn from (pH=0.0, pC=14.0) to (pH=14.0, pC=0.0). Similarly, a line can be drawn representing the hydronium ion concentration as a function of pH. By definition
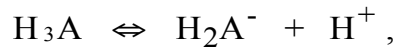
$$-\log[H^+] = pH, \text{ therefore}$$
$$\frac{\Delta\left(-\log[H^+]\right)}{\Delta pH} = 1$$

When the pH equals 0, the -log[H⁺] equals 0. This results in a line being drawn from (pH=0.0, pC=0.0) to (pH=14.0, pC=14.0).

The next line (or set of lines) normally drawn is the one representing the total concentration of acid or base, C_T. When pC-pH diagrams are drawn by hand, C_T is drawn as a straight horizontal line starting at pC_T on the y-axis. This line is actually a combination of two or more lines depending of the number of protons present in the acid. At each pK_a, two lines intersect, one with a slope of -1 and one with a slope of +1. For diprotic and triprotic systems, as one species line crosses a second line (or pK_a), the slope of the line shifts from -1 or +1 to -2 or +2, respectively. These lines represent the concentration of each chemical species. Three cases are given below, a triprotic system (the phosphate system), a diprotic system (the carbonate system), and a monoprotic system (a generic system).

For a triprotic system, the lines for each individual chemical species can be represented by

$$H_3A \Leftrightarrow H_2A^- + H^+ ,$$

where $K_1 = \dfrac{[H_2A^-][H^+]}{[H_3A]}$,

$$H_2A^- \Leftrightarrow HA^{-2} + H^+ ,$$

where $K_2 = \dfrac{[HA^{-2}][H^+]}{[H_2A]}$, and

$$HA^{-2} \Leftrightarrow A^{-3} + H^+ ,$$

where $K_3 = \dfrac{[HA^{-3}][H^+]}{[HA^{-2}]}$.

The total concentration of the acid or base, C_T, is a sum of all protonated and nonprotonated species, such that

$$C_T = H_3A + H_2A^- + HA^{-2} + A^{-3}$$

When the equilibrium expressions, given above, and the C_T equation are combined and solved for H_3A, H_2A^-, HA^{-2}, and A^{-3} in terms of C_T, $[H^+]$, and the equilibrium constants, four equations are obtained

$$[H_3A] = C_T \left(\frac{1}{1 + (K_1/[H^+]) + (K_1K_2/[H^+]^2) + (K_1K_2K_3/[H^+]^3)} \right),$$

$$[H_2A^-] = C_T \left(\frac{1}{([H^+]/K_1) + 1 + (K_2/[H^+]) + (K_2K_3/[H^+]^2)} \right),$$

$$[HA^{-2}] = C_T \left(\frac{1}{([H^+]^2/K_1K_2) + ([H^+]/K_2) + 1 + (K_3/[H^+])} \right), \text{ and}$$

$$[A^{-3}] = C_T \left(\frac{1}{([H^+]^3/K_1K_2K_3) + ([H^+]^2/K_2K_3) + ([H+]/K_3) + 1} \right).$$

If a pH dependent constant, α_H, is defined as

$$\alpha_H = \frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3} + 1,$$

the previous equations can be simplified to:

$$[H_3A] = \frac{C_T[H^+]^3}{K_1K_2K_3\alpha_H},$$

$$[H_2A^-] = \frac{C_T[H^+]^2}{K_2K_3\alpha_H},$$

$$[HA^{2-}] = \frac{C_T[H^+]}{K_3\alpha_H}, \text{ and}$$

$$[A^{3-}] = \frac{C_T}{\alpha_H}.$$

Several important points on the pC-pH diagram should be noted. The plot shown below for the triprotic system was made for a 0.001 M phosphate system. Note the lines representing the hydrogen and hydroxide ion concentrations that have a slope of +1 and -1, respectively. The system points, designated by "S", represent the pH where each chemical species adjacent to the "S" points, are at equal concentration. Note that this condition is met at each equilibrium constant (K_a) or using the negative log scale, at each pK_a value. For the phosphate system these values are $10^{-2.1}$ for K_1, $10^{-7.2}$ for K_2, and $10^{-12.3}$ for K_3. Note that at pH values less than pK_1, the system is dominated by the H_3PO_4 species; at pH values between pK_1 and pK_2 the system is dominated by the $H_2PO_4^-$ ion; at pH values between pK_2 and pK_3 the system is dominated by the HPO_4^{2-} ion; and at pH values above pK_3 the system is dominated by the PO_4^{3-} ion. Also note that as the line describing the concentration of a species reaches a pK_a value, the slope of the line changes from zero to +1 or -1. As this line crosses another chemical species line (at a new pK_a), the slope changes to +2 or -2.

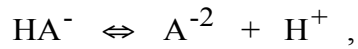## pC-pH Diagram for Triprotic System

pH

pC

H_3PO_4 $H_2PO_4^-$ HPO_4^{2-} PO_4^{3-}

S   S   S

OH^- H^+
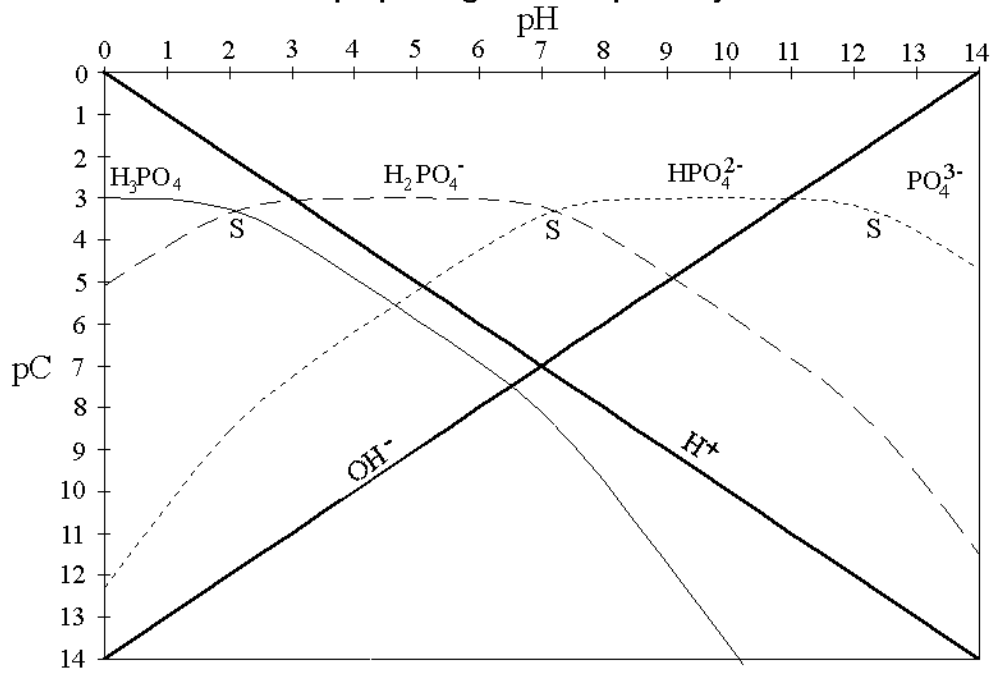
For the diprotic system, the equilibrium equations for H_2A, HA^-, and A^{-2} are:

$$H_2A \; \Leftrightarrow \; HA^- \; + \; H^+ \; ,$$

where $K_1 \; = \; \dfrac{[HA^-]\,[H^+]}{[H_2A]}$,

$$HA^- \; \Leftrightarrow \; A^{-2} \; + \; H^+ \; ,$$

where $K_2 \; = \; \dfrac{[A^{-2}]\,[H^+]}{[HA^-]}$.

When these equations are combined with the mass balance equation,

$$C_T \; = \; H_2A \; + \; HA^- + A^{-2} \; ,$$

and solved for H_2A, HA^-, and A^{-2} in terms of C_T, $[H^+]$, and the equilibrium constants, three equations are obtained

$$[H_2A] \; = \; C_T \left(\frac{1}{1 \; + \; (K_1 / [H^+]) \; + \; (K_1 K_2 / [H^+]^2)} \right) ,$$

$$[HA^-] \; = \; C_T \left(\frac{1}{([H^+] / K_1) \; + \; 1 \; + \; (K_2 / [H^+])} \right) , \text{ and}$$

$$[A^{-2}] \; = \; C_T \left(\frac{1}{([H^+]^2 / K_2 K_2) \; + \; ([H+] / K_2) \; + \; 1} \right) .$$

If a pH dependent constant, $\checkmark_H$, is defined as

$$\alpha_H \; = \; \frac{[H^+]^2}{K_1 K_2} \; + \; \frac{[H^+]}{K_2} \; + \; 1 \; ,$$

the previous equations for the diprotic system can be simplified to:

$$[H_2A] = \frac{C_T[H^+]^2}{K_1 K_2 \alpha_H} \quad ,$$

$$[HA^-] = \frac{C_T[H^+]}{K_2 \alpha_H} \quad , \text{ and}$$

$$[A^{-2}] = \frac{C_T}{\alpha_H} \quad .$$

For a monoprotic system, the governing equations are

$$[HA] = \frac{C_T [H^+]}{[H^+] + K_a} \quad \text{and}$$

$$[A^-] = \frac{C_T K_a}{[H^+] + K_a} \quad .$$

The utility of a pC-pH diagram is that all of the ion concentrations can be estimated at the same time for any given pH value. This computer simulation allows the user to select an acid system, enter the pK_a values, and draw the pC-pH diagram. After the diagram is drawn, the user can point the cursor at a given pH and the concentrations of each ion will be given. Additional discussions of pC-pH diagrams can be found in Langmuir (1997) and Snoeyink and Jenkins (1980).

References

Langmuir, D. Aqueous Environmental Geochemistry, Prentice Hall, New Jersey, 1997.

Snoeyink, V.L. and D. Jenkins. Water Chemistry, John Wiley & Sons, New York, 1980.