



Distribution of Species in Aquatic Systems

Environmental Chemistry, vanLoon & Duffy – Chapter 10

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Introduction

The species distribution or “speciation” for an element or compound depends on the nature of the chemical and also on the particular environmental conditions in which it is found.

It is often possible to calculate or predict the forms that will be present, assuming one has available the appropriate analytical data and the required thermodynamic constants.

For rigorous calculations, activities rather than concentrations should be used, but this requires knowledge of the total ionic composition of the solution (simplifying assumption that activity and concentration are equal may cause errors).

In many situations, the errors generated by neglecting activity coefficients are smaller than those arising from uncertainties in the analytical data available for multicomponent environmental materials.

Two calculation situations are encountered:

✓ Detailed individual calculations related to specific sets of conditions. For example, a calculation how to show what fraction of an acidic species is in protonated and what fraction is in deprotonated form at a given solution pH.

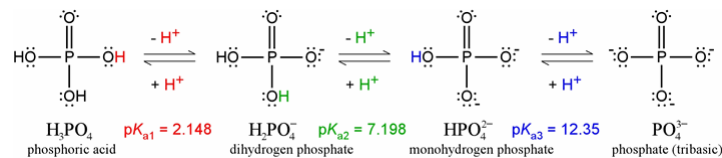
✓ Diagrams that show how species distributions can vary as conditions change. In the process of constructing such diagrams, methods for calculation individual situations become clear. There are many kinds of distribution diagrams. We will look into the construction of several types and we will examine how to interpret these and others.

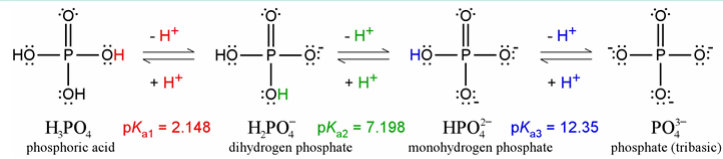


A single variable diagram is a plot of some measure of species concentration (y-axis) versus a particular variable like pH, redox status, or concentration of an important complexing ligand (x-axis).

A well known case, useful for describing the chemistry of species that exhibit acid-base behavior, is a plot of α (alpha), the fractional concentration, of individual species against pH.

A good example of this application is the phosphate system. Phosphorus exists in water almost exclusively as P(V) species, particularly in forms of orthophosphate.





The fraction $\alpha_{\text{H}_3\text{PO}_4}$ of undissociated H_3PO_4 in a solution containing phosphate species is

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_3\text{PO}_4]}{C_p}$$

where C_p = the total concentration of all four orthophosphate species.

For the other phosphate species, similar fractions are given by

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_2\text{PO}_4^-]}{C_p}$$

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{HPO}_4^{2-}]}{C_p}$$

$$\alpha_{\text{PO}_4^{3-}} = \frac{[\text{PO}_4^{3-}]}{C_p}$$

The three dissociation constants expressions can be arranged to give the concentration of each individual species in terms of $[\text{H}_3\text{PO}_4]$ and $[\text{H}_3\text{O}^+]$.

$$[\text{H}_2\text{PO}_4^-] = \frac{K_{a1} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]}$$

$$[\text{HPO}_4^{2-}] = \frac{K_{a1} \times K_{a2} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^2}$$

$$[\text{PO}_4^{3-}] = \frac{K_{a1} \times K_{a2} \times K_{a3} \times [\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^3}$$

$$C_p = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

$$= [\text{H}_3\text{PO}_4] \left(1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right)$$

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]} = \frac{[\text{H}_3\text{PO}_4]}{C_p} \quad (10.3)$$

From eqn 10.3

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{PO}_4] \left(1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3} \right)} \quad (10.11)$$

We then multiply the top and bottom of the right-hand side of the equation by $[\text{H}_3\text{O}^+]^3$

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}_3\text{O}^+]^3}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.12)$$

Using similar calculations, we find that

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_3\text{O}^+]^2 \times K_{a1}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.13)$$

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.14)$$

$$\alpha_{\text{PO}_4^{3-}} = \frac{K_{a1} \times K_{a2} \times K_{a3}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 \times K_{a1} + [\text{H}_3\text{O}^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.15)$$

Note that each of equations 10.12-10.15 can be used to calculate the fraction of an individual species in the phosphate system at a given pH. When the α values are plotted over a range of pH values, we have a distribution diagram.

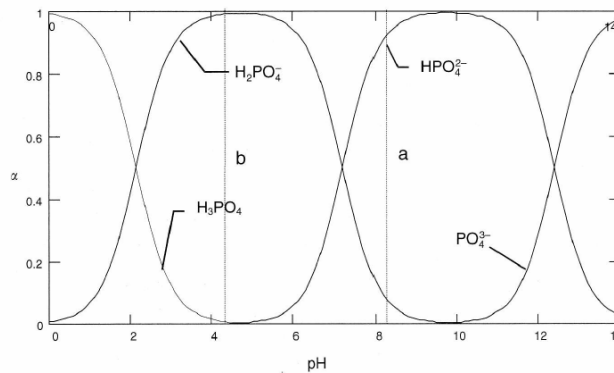


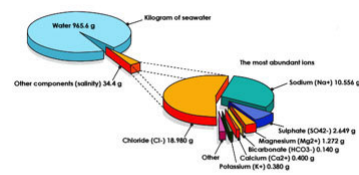
Fig. 10.1 Distribution of phosphorus species expressed as the fraction, α , as a function of aqueous solution pH.

In what was mentioned previously, no account was taken of the solution ionic strength.

Soil solution typically have an ionic strength of 0.002, which leads to an activity coefficient of about 0.95 for a singly charged ion.

Incorporating the activity coefficient into the calculation would make only a small difference and the correction would be even smaller for the lake water.

While assuming zero ionic strength in this situation leads to a small error, the error could be much larger for medium like sea water that contains a high ionic concentration.



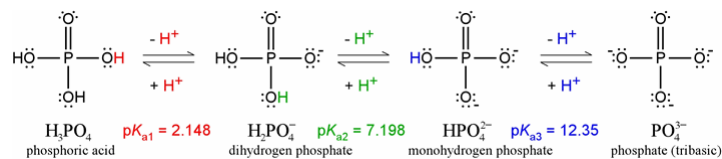
Chemical Composition of Sea Water

Apparent acid dissociation constants have been calculated for phosphoric acid in sea water:

$$K_{a1} = 2.4 \times 10^{-2} \quad pK_{a1} = 1.62$$

$$K_{a2} = 8.8 \times 10^{-7} \quad pK_{a2} = 6.06$$

$$K_{a3} = 1.4 \times 10^{-9} \quad pK_{a3} = 8.85$$



Zero ionic strength

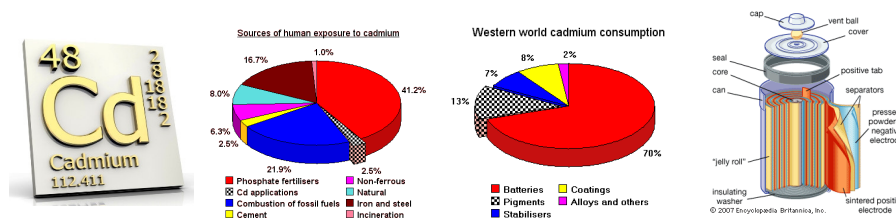
Table 10.1 Acid dissociation constants for phosphoric acid.

	K_a	pK_a
First dissociation	7.1×10^{-3}	2.15
Second dissociation	6.3×10^{-8}	7.20
Third dissociation	4.2×10^{-13}	12.38

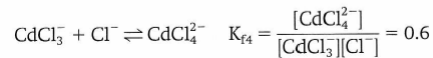
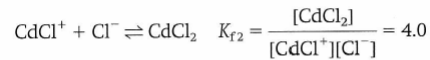
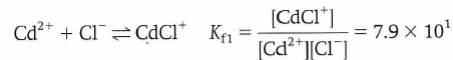
A second version of a single variable distribution diagram is a plot of the fractional concentration of a particular species versus a chosen variable, usually the concentration of an important ligand.

As an example, we will consider the distribution of aqueous cadmium chloro complexes as a function of chloride ion concentration.

in the absence of chloride or any other complexing ligand, cadmium exists in aqueous solution as an aquo complex, perhaps $\text{Cd}(\text{H}_2\text{O})_4^{2+}$.

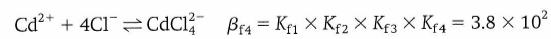
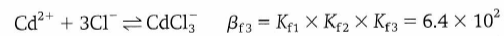
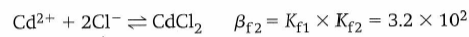


Chloride ion forms complexes with cadmium in a stepwise fashion, with the displacement of one water molecule each time a chloride is added.



The reactions may also be described using “overall” steps and the overall stability constants are symbolized as β_f .

$$\beta_{fn} = K_{f1} \times K_{f2} \times K_{f3} \times \dots \times K_{fn}$$



The total concentration of cadmium in an aqueous solution containing chloride is

$$C_{\text{Cd}} = [\text{Cd}^{2+}] + [\text{CdCl}^+] + [\text{CdCl}_2] + [\text{CdCl}_3^-] + [\text{CdCl}_4^{2-}]$$

$$\frac{C_{\text{Cd}}}{[\text{Cd}^{2+}]} = 1 + \frac{[\text{CdCl}^+]}{[\text{Cd}^{2+}]} + \frac{[\text{CdCl}_2]}{[\text{Cd}^{2+}]} + \frac{[\text{CdCl}_3^-]}{[\text{Cd}^{2+}]} + \frac{[\text{CdCl}_4^{2-}]}{[\text{Cd}^{2+}]}$$

Substituting the expressions for the β functions,

$$\frac{C_{\text{Cd}}}{[\text{Cd}^{2+}]} = 1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4$$

Rearranging eqn 10.27,

$$[\text{Cd}^{2+}] = \frac{C_{\text{Cd}}}{1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4}$$

Similarly, the concentrations of other cadmium chloro species are given by

$$[\text{CdCl}^+] = \frac{\beta_{f1}[\text{Cl}^-]C_{\text{Cd}}}{1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4}$$

$$[\text{CdCl}_2] = \frac{\beta_{f2}[\text{Cl}^-]^2 C_{\text{Cd}}}{1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4}$$

$$[\text{CdCl}_3^-] = \frac{\beta_{f3}[\text{Cl}^-]^3 C_{\text{Cd}}}{1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4}$$

$$[\text{CdCl}_4^{2-}] = \frac{\beta_{f4}[\text{Cl}^-]^4 C_{\text{Cd}}}{1 + \beta_{f1}[\text{Cl}^-] + \beta_{f2}[\text{Cl}^-]^2 + \beta_{f3}[\text{Cl}^-]^3 + \beta_{f4}[\text{Cl}^-]^4}$$

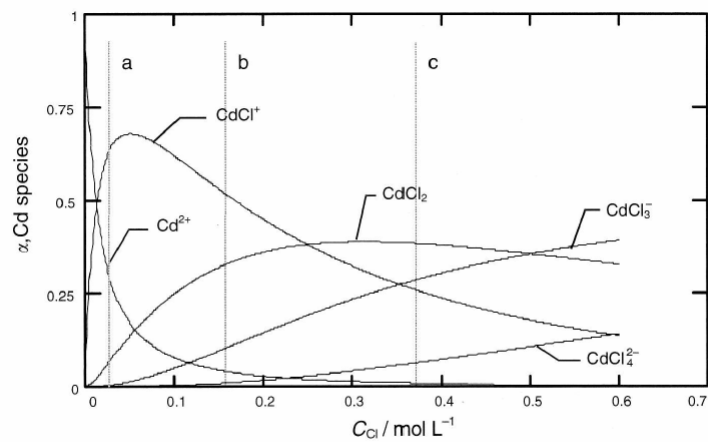


Fig. 10.2 Distribution of cadmium chloro complexes as a function of the concentration of chloride ion in water. The range of chloride concentrations is from zero to 0.56 mol L⁻¹; the latter value is the approximate concentration in sea water.

Figure 10.2 can be useful in several situations.

For example, we may use it to describe the changing cadmium species distribution in an estuary.

An estuary has been defined as “a semi-enclosed coastal body of water which has a free connection with the open sea and within which sea water is measurably diluted with fresh water derived from land drainage”.



A principal feature of any estuary is a regular variation from low to high in dissolved salt concentration as one moves from the inflowing river to the mouth where it opens out into the ocean.

In the vertical dimension salt concentration changes as well.

Usually, there is a steady but sometimes irregular increase in salt concentration with depth, in part due to the greater density of the high salt solution.

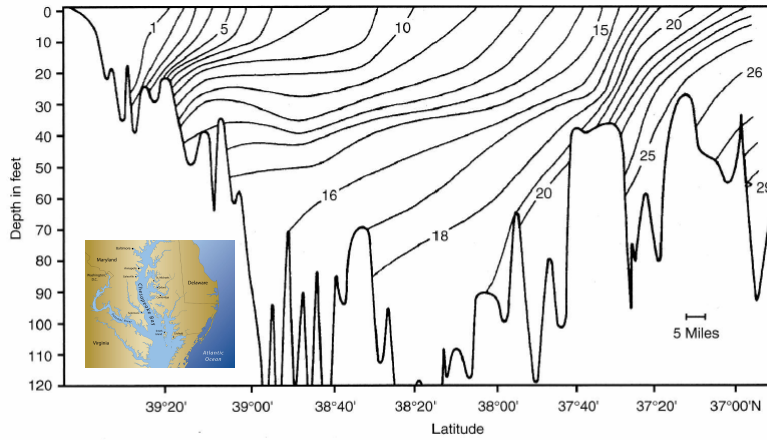


Fig. 10.3 Salinity contours for Chesapeake Bay in springtime. The left (west) side of the diagram is the inland part of the estuary and salinity approaches that of fresh water. The right (east) side is where the estuary opens out into the Atlantic Ocean (Schubel, J.R., *The estuarine environment*, American Geological Institute; 1971). Note also the increase in salinity with depth indicating that the fresh water from the river layers on to the surface of the saline matrix. Reprinted with permission.