

CHAPTER 3

ACID-BASE EQUILIBRIA IN WATER

HISTORICAL OVERVIEW

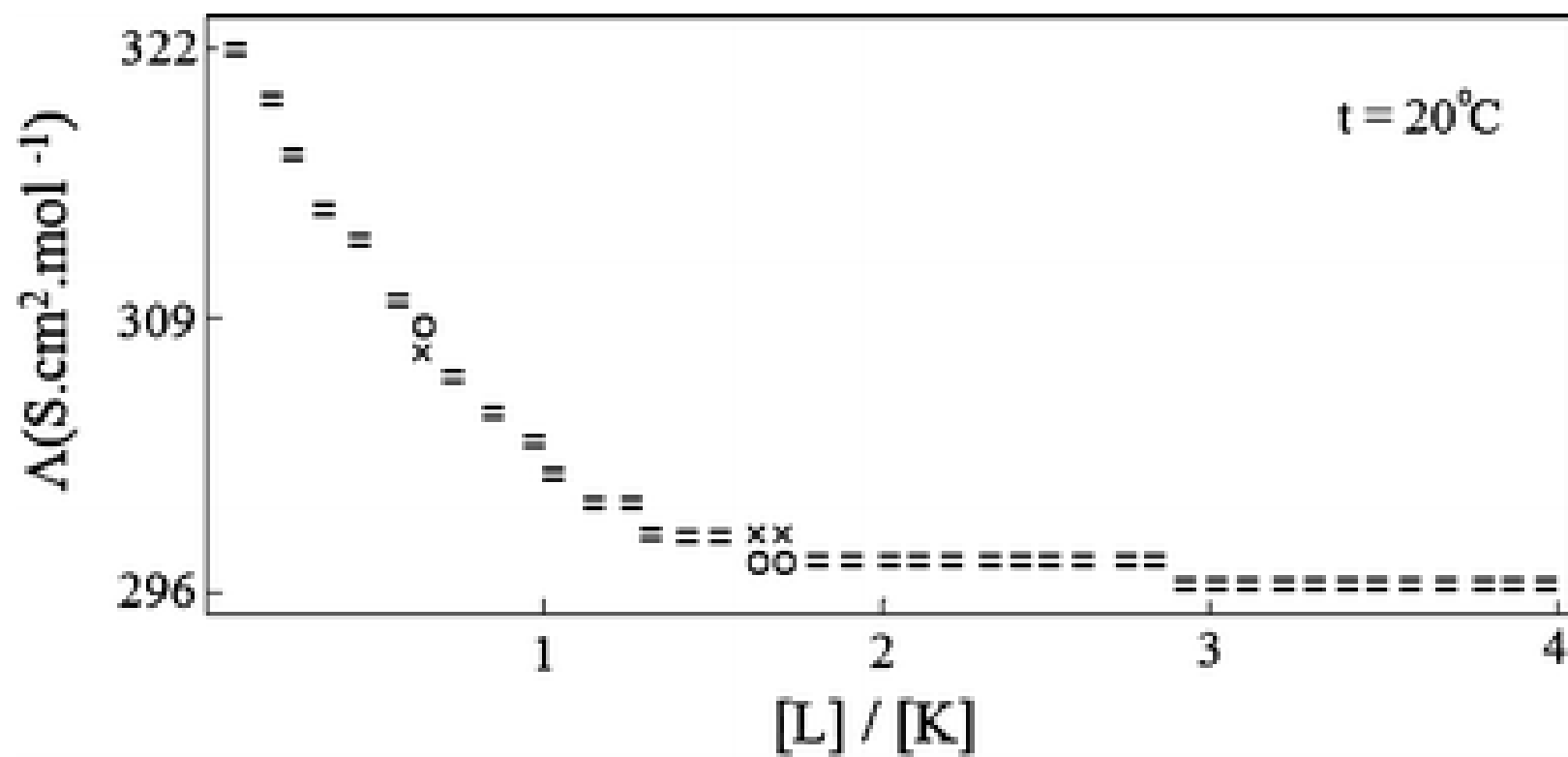
- ◉ Acids and bases were defined and described by early chemists, including Boyle,
- ◉ Lavoisier,
- ◉ Davy,
- ◉ Berzelius,
- ◉ Liebig, Arrhenius.
- ◉ At the present time, depending on
- ◉ objectives, one of two definitions of acids and bases is likely to be accepted.
- ◉ Arrhenius
- ◉ Brønsted and Lowry
- ◉ **Lewis**
- ◉ **Solvent System**

SOLVENT SYSTEM DEFENITION



METHODS OF DEALING WITH EQUILIBRIA

- ① 1. The equilibrium concentrations of species can be calculated without simplifying assumptions. (Mass Balance, Charge Balance) KINFIT, FORTRAN, MINI-QUAD, HYPER-QUAD,...



METHODS OF DEALING WITH EQUILIBRIA

- ◎ 2. The behavior of equilibrium systems can often be visualized and clarified through one of several graphical approaches.

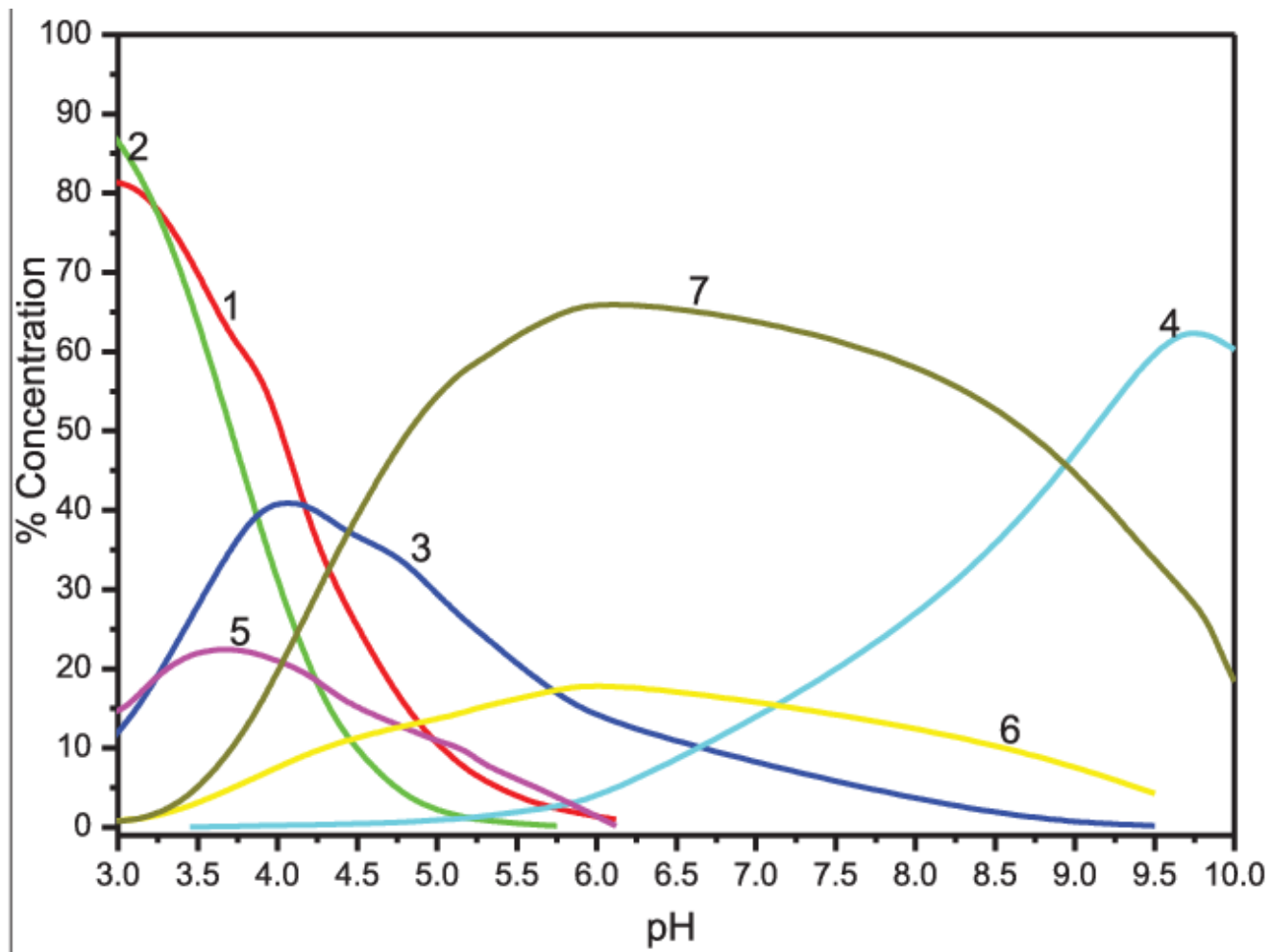
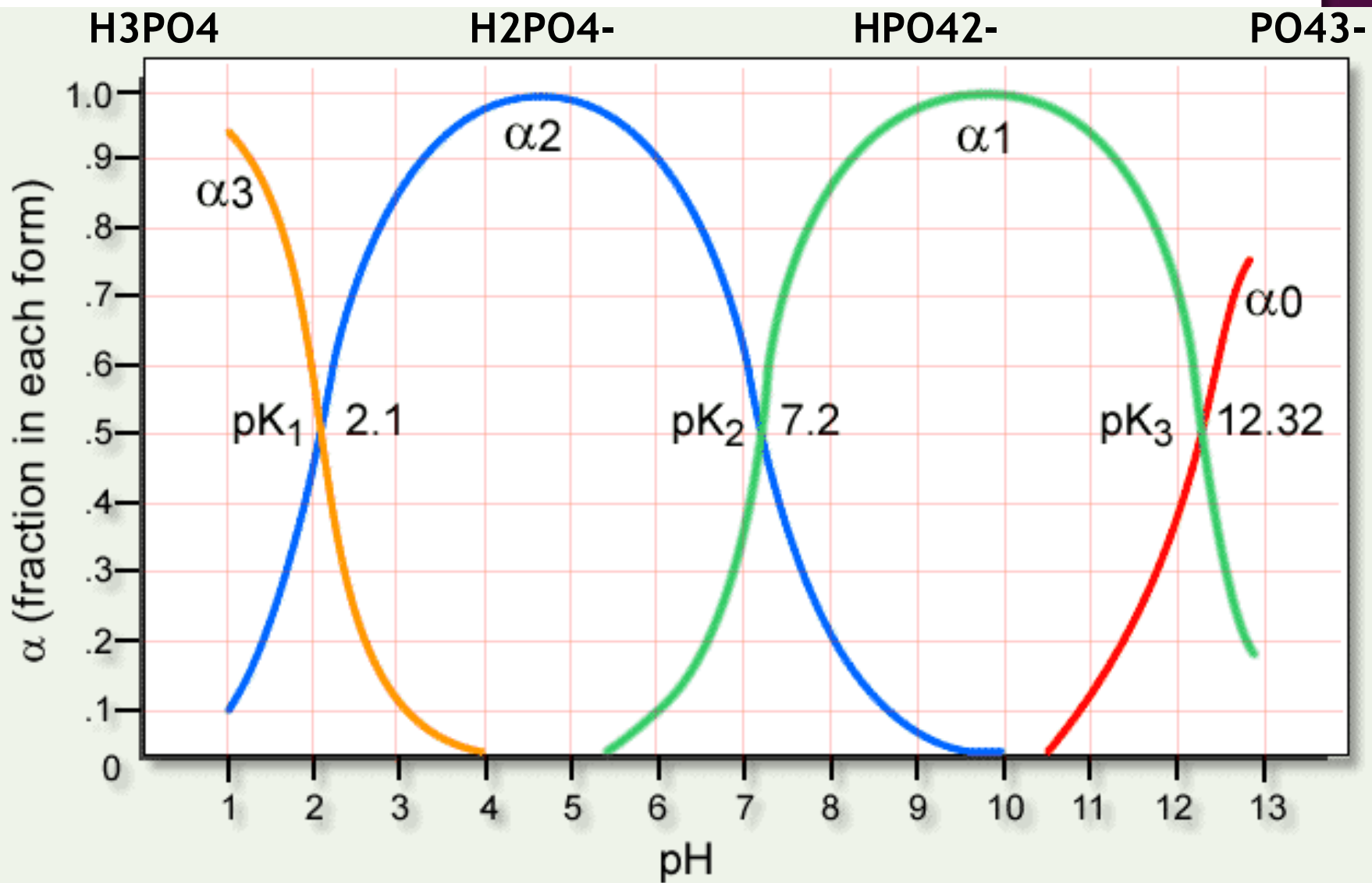
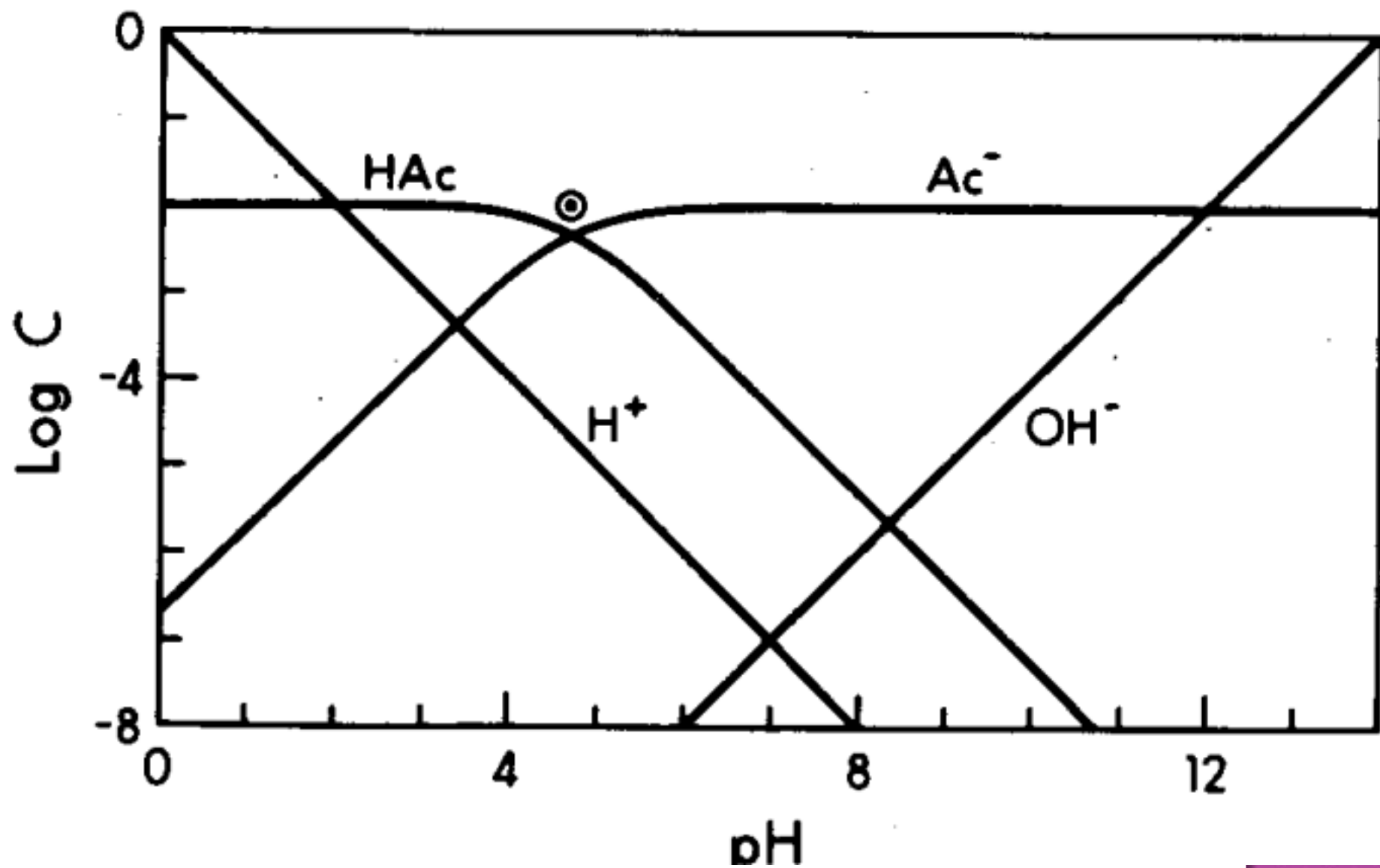
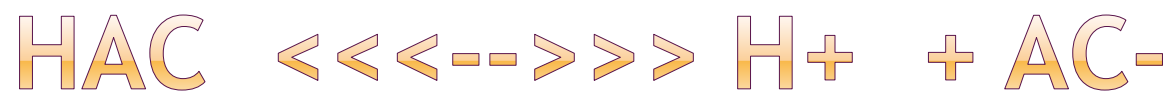


Fig. 3: Species distribution curve of 1:1:1 Cu(II)L₁L₂ ternary complex



Fractional composition diagram (distribution curves)
for the phosphoric acid (H₃PO₄) system.



is initial concentration. Figure 3-1 illustrates a logarithmic diagram for aqueous $10^{-2} M$ acetic acid ($pK_a = 4.7$). Such a diagram is constructed⁷ by first selecting two axes, one for pH from 0 to pK_w and the other for $\log C$ corresponding to a change of several orders of magnitude of C . Lines of slope ± 1 are drawn for hydrogen ion and hydroxyl ion corresponding to $\log [OH^-] = pH - pK_w$. Next, the system point at $pH = 4.7$ and $\log C_0 = -2$ is located. A line of slope 0 and downward lines of $+1$ and -1 are drawn with origins at the system point. Finally, a point 0.3 unit below the system point is located, and the linear parts of each species are joined with short curves passing through this point. The value 0.3 (or $\log 2$) arises from the fact that at $pH = pK_a$ the value of $\log [CH_3COOH] = \log [CH_3COO^-] = \log (C_0/2) = \log C_0 - \log 2$.

METHODS OF DEALING WITH EQUILIBRIA

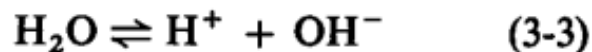
- ③ 3. A third approach, the use of judgment or chemical intuition to introduce simplifying approximations at early stages in the equilibrium calculation.

3-2 EQUILIBRIUM IN PURE WATER

The autoionization of water can be represented by



or conventionally by



with the understanding that the symbol H^+ represents the *hydrated proton*, which is written in the most general way as $(\text{H}_2\text{O})_n\text{H}^+$. From (3-2) the ionization constant K_i of water in terms of activities is

$$K_i = \frac{a_{\text{H}_3\text{O}^+} a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}^2} \quad (3-4)$$

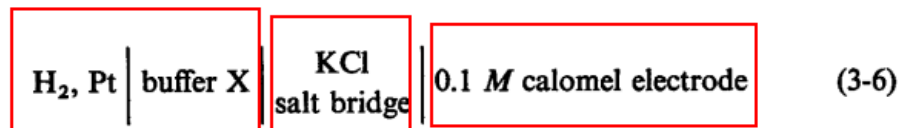
The usual standard state for water as solvent (Section 2-2) is defined as pure water having unit activity. Hence the equilibrium constant is generally written as the ion activity product of water:

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} \quad (3-5)$$

$$p[H] = -\log [H^+] \quad pH = pa_H = -\log a_{H^+}$$

3-3 DEFINITION OF THE pH SCALE

The negative logarithm of hydrogen ion *concentration* was defined by Sørensen¹² as the pH.† Sørensen did not actually measure hydrogen ion concentrations, but something more nearly related to activities. He measured the emf of galvanic cells such as



and attempted to eliminate the liquid-junction, or diffusion, potentials by an extrapolation procedure developed by Bjerrum.¹⁴ At the time of Sørensen's original work the difference in cell emf of two such cells with different hydrogen ion concentrations was assumed to be a measure of the ratio of hydrogen ion concentrations in the solutions, according to the Nernst equation:

$pH = -\log a_H$ in dilute solution

$$E_1 - E_2 = \frac{RT}{F} \ln \frac{[H^+]_2}{[H^+]_1} \quad (3-7)$$

To establish a pH scale, Sørensen chose a dilute hydrochloric acid solution for a standard. He took the concentration of hydrogen ions in such a solution to be given by αC , where C is the concentration of hydrochloric acid and α is a *degree of dissociation* determined from conductance measurements. His procedure had drawbacks: first, there is evidence that the extrapolation procedure does not actually reduce the liquid-junction potential of Cell (3-6) to zero; second, the hydrochloric acid is completely dissociated (dissociation constant about 1.6×10^6),¹⁵ and therefore the concentration of H^+ is C rather than a somewhat smaller quantity.

The Sørensen pH unit, often designated psH , is neither the negative logarithm of concentration pC_H nor the activity of hydrogen ion pa_H . It does, however, closely resemble modern "operational" pH scales.

When the concept of thermodynamic activity became established, Sørensen and Linderstrøm-Lang¹⁶ defined the term pa_H as the negative logarithm of hydrogen ion activity. Thus

$$pa_H = -\log a_{H^+} = -\log [H^+] \gamma_{H^+} \quad (3-8)$$



In a more general way, HA can be written HA^n , where the charge n may be an integer with a positive, negative, or zero value. The conjugate base is then A^{n-1} . Similarly, for a base designated B the conjugate acid would be BH^+ .

For the ionization of water,



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If C_{HA} and C_{A^-} are the analytical concentrations of HA and A^- , and if $[\text{HA}]$ and $[\text{A}^-]$ are the equilibrium concentrations, the relations

$$[\text{HA}] = C_{\text{HA}} - ([\text{H}^+] - [\text{OH}^-]) \quad (3-14)$$

and

$$[\text{A}^-] = C_{\text{A}^-} + ([\text{H}^+] - [\text{OH}^-]) \quad (3-15)$$

result because the analytical concentration of HA is diminished by the amount of hydrogen ion produced in Reaction (3-12), which in turn is the total hydrogen ion concentration minus the hydroxyl ion concentration.

The equilibrium constant K_{eq} of (3-12) in terms of concentration is

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad (3-16)$$

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where K_a is by definition the acid-dissociation constant, or ionization constant, of the acid HA. Solving for hydrogen ion concentration gives

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} = K_a \frac{C_{\text{HA}} - [\text{H}^+] + [\text{OH}^-]}{C_{\text{A}^-} + [\text{H}^+] - [\text{OH}^-]} \quad (3-17)$$

This is the general equation that may be used, in conjunction with Equations (3-11) to (3-16), to calculate hydrogen ion concentrations in various situations that involve a single acid-base system in water. To illustrate, we consider several examples.

STRONG ACID

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Solution of strong acid

A strong acid, by definition, is one for which (3-11) is complete to the right, so that $[HA]$ is essentially zero. From (3-14)

$$[H^+] = C(HCl) = 0.1 M \quad 10^{-8} M \rightarrow [H^+] = C_{HA} + [OH^-] \quad (3-18)$$

The total concentration of hydrogen ion is that from the strong acid plus that from the water (equal to $[OH^-]$). Unless the solution is extremely dilute ($C_{HA} < 10^{-6} M$), the second term may be neglected. Consider, for example, $C_{HA} = 10^{-6} M$. As a first approximation $[H^+] = 10^{-6} M$, and therefore $[OH^-] = 10^{-14}/10^{-6} = 10^{-8} M$; this represents only a 1% correction on the first approximation.