جامعة الانبار

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اسم المادة باللغة العربية: **الكيمياء التحليلية**

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

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عنوان المحاضرة باللغة العربية: منحنيات التسحيح لانظمة الحوامض والقواعد

عنوان المحاضرة باللغة الإنكليزية : **Titration Curves for Complex Acid-Base Systems**

6.1 Introduction

Complex systems are defined as solutions made up of:

(1) two acids or two bases of different strength.

(2) an acid or a base that has two or more acidic or basic functional groups.

(3) an amphiprotic substance, which is capable of acting as both an acid and a base.

Polyfunctional acids and bases play important roles in many chemical and biological systems. The human body contains a complicated system of buffers within cells and within bodily fluids, such as human blood. The pH of human blood is controlled to be within the range of 7.35 to 7.45 primarily by the carbonic acid/bicarbonate buffer system.

6.2 Mixture of Strong and Weak Acids or Strong and weak Bases

It is possible to determine each of the components in a mixture containing a strong acid and a weak acid (or a strong base and a weak base) provided that the concentrations of the two are the same order of magnitude and that the dissociation constant for the weak acid or base is somewhat less than about 10^{-4}. To demonstrate that this statement is true, let us show how a titration curve can be constructed for a solution containing roughly equal concentrations of HCl and HA, where HA is a weak acid with dissociation constant of 10^{-4}.

When the amount of base added is equivalent to the amount of hydrochloric acid originally present, the solution is identical in all respects to one prepared by dissolving appropriate quantities of the weak acid and sodium chloride in a suitable volume of water. The sodium chloride, however, has no effect on the pH (neglecting the influence of increased ionic strength); thus, the reminder of the titration curve is identical to that for a dilute solution of HA.

The shape of the curve for a mixture of weak and strong acids, and hence the information obtainable from it, depends in large measure on the strength of the weak acid. Figure 6-1 depicts the pH change that occurs during the titration of mixtures containing hydrochloric acid and several weak acids.

Note that the rise in pH at the first equivalence point is small or essentially nonexistent when the weak acid has a relatively large dissociation constant (curve *A* and *B*). For titrations such as these, only the total number of millimoles of weak and strong acid can be determined accurately. Conversely, when the weak acid has a very small dissociation constant, only the strong acid content can be determined. For weak acids of intermediate strength (K_a somewhat less than 10^{-4} but greater than 10^{-8}), there are usually two useful end points.

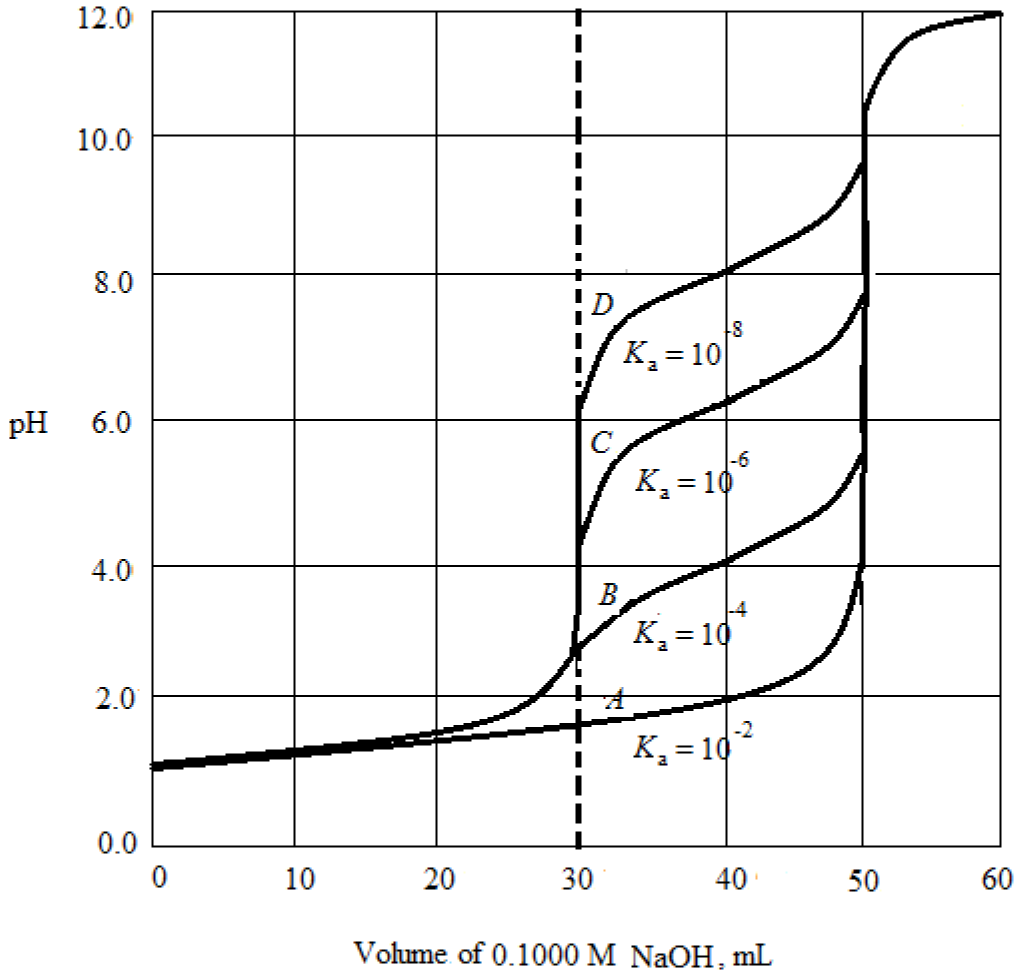

Figure 6-1 Curves for the Titration of Strong Acid/Weak Acid Mixtures with 0.1000 M NaOH. Each titration is on 25.00 mL of a solution that is 0.1200 M in HCl and 0.0800 M in HA.

Determination of the amount of each component in a mixture that contains a strong base and a weak base is also possible, subject to the constraints just described for the strong acid/weak acid system. The computation of a curve for such a titration is analogous to that for a mixture of acids.

6.3 Polyfunctional Acids and Bases

Several species are encountered in analytical chemistry that have two or more acidic functional groups. Generally, the two groups differ in strength and, as a consequence, exhibit two or more end points in a neutralization titration.

**** The phosphoric acid system***

Phosphoric acid is a typical polyfunctional acid. In aqueous solution, it undergoes the following three dissociation reactions:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \quad K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3}$$

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+ \quad K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$= 6.32 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+ \quad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$= 4.5 \times 10^{-13}$$

With this acid, as with other polyprotic acids, $K_{a1} > K_{a2} > K_{a3}$.

When we add two adjacent stepwise equilibria, we multiply the two equilibrium constant to obtain the equilibrium constant for the resulting overall reaction. Thus, for the first two dissociation equilibria for H_3PO_4, we write:

$$K_{a1}K_{a2} = \frac{[H_3O^+]^2[HPO_4^{2-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} = 4.49 \times 10^{-10}$$

Similarly, for the reaction:

$$H_3PO_4 \rightleftharpoons 3H_3O^+ + PO_4^{3-}$$

we may write:

$$K_{a1}K_{a2}K_{a3} = \frac{[H_3O^+]^3[PO_4^{3-}]}{[H_3PO_4]}$$

$$= 7.11 \times 10^{-3} \times 6.32 \times 10^{-8} \times 4.5 \times 10^{-13} = 2.0 \times 10^{-22}$$

**** The carbon dioxide carbonic acid system***

When carbon dioxide is dissolved in water, a dibasic acid system is formed by the following reaction:

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad K_{hyd} = \frac{[H_2CO_3]}{[CO_{2(aq)}]} = 2.8 \times 10^{-3}$$

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \quad K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.5 \times 10^{-4}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \quad K_2 = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

The first reaction describes the hydration of aqueous CO_2 to form carbonic acid. Note that the magnitude of K_{hyd} indicates that the concentration of $CO_{2(aq)}$ is much larger than the concentration of H_2CO_3 (that is, $[H_2CO_3]$ is only about 0.3% that of $[CO_{2(aq)}]$. Thus, a more useful way of discussing the acidity of solutions of carbon dioxide is to combine the first and the second equations to give:

$$CO_{2(aq)} + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^- \qquad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[CO_{2(aq)}]}$$

$$= 2.8 \times 10^{-3} \times 1.5 \times 10^{-4}$$

$$= 4.2 \times 10^{-7}$$

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-} \qquad K_{a2} = 4.69 \times 10^{-11}$$

6.4 Titration Curves for Polyfunctional Acids

Compounds with two or more acid functional groups yield multiple end points in a titration provided that the functional groups differ sufficiently in strength as acids.

Figure 6-2 shows the titration curve for diprotic acid H_2A with dissociation constant of $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$.

We can calculate each equivalence point for reaction like this.

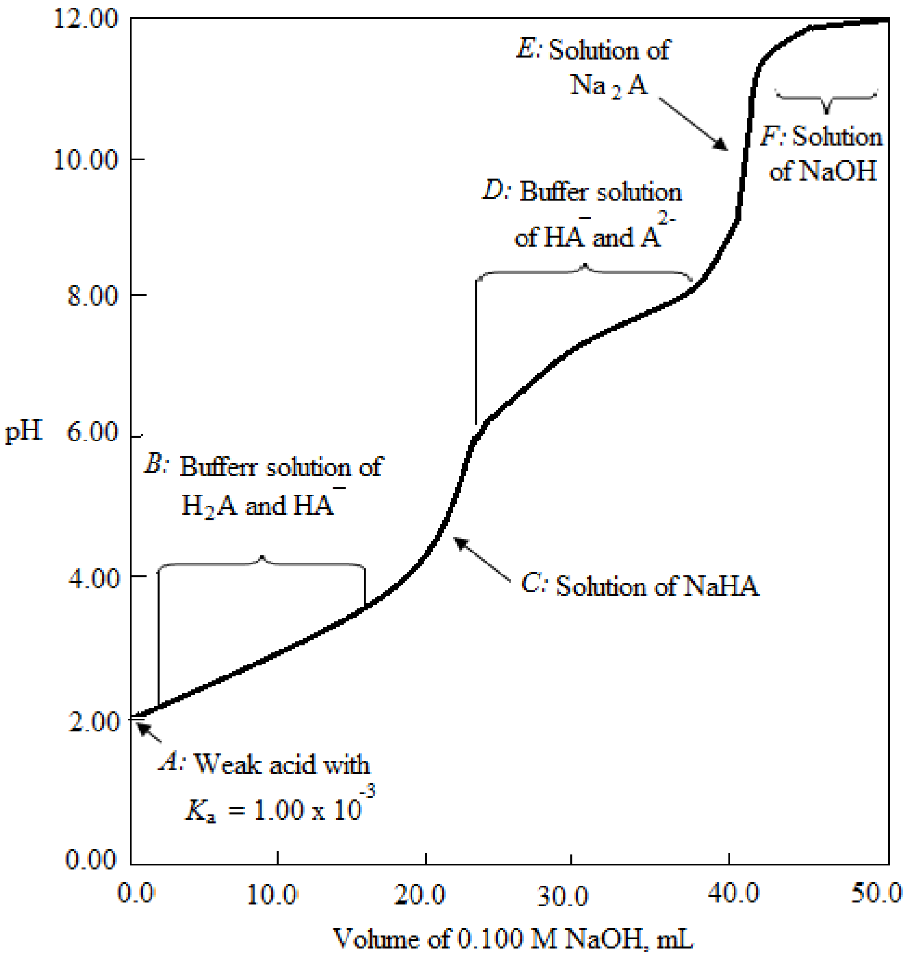

Figure 6-2 Titration of 20.00 mL of 0.1000 M H_2A with 0.1000 M NaOH. For H_2A, $K_{a1} = 1.00 \times 10^{-3}$ and $K_{a2} = 1.00 \times 10^{-7}$. The method of pH calculation is shown for several points regions on the titration curve.