pH MEASUREMENT AND CONTROL

The acidity or alkalinity of solutions is indicated by a pH value which it is important to control in many chemical and biotechnical processes, especially in water and wastewater treatment. The significance of pH in industrial processes lies in the fact that many phenomena, such as flotation, precipitation, and coagulation, occur in a certain pH range. The inhibition of corrosion is another application of pH control. In industrial applications of biotechnology, such as fermentation, the pH is an essential factor in the growth process.

The neutrality of pure water is an important factor in human life. Municipal water is kept slightly alkaline (about pH 8) to avoid corrosion. The quality of wastewater has a significant influence on environmental water ecology. Changes in the acidity of water influences, for instance, the solubility of compounds and the growth of flora and fauna. The acceptable pH range of wastewater is usually pH 6 to pH 9. An important pH control application is the preparation of wastewater flowing through a sewer system to chemical or biological purification plants. Chemical purification occurs best at a pH of 5.5 in aluminum sulphate precipitation and at a value of 9 in ferrosulfate precipitation. Fast pH changes are unacceptable in wastes flowing in an active sludge purification plant because of the bacteria death risk. For these reasons reliable measurement and good control of pH are very important aspects of a wide range of systems.

GENERAL PROPERTIES OF LIQUIDS

Liquid phase systems consist of a solvent and dissolved components. The most common solvent is water, the properties of which are well known. Most chemical constants related to pH are connected with systems where water is the solvent.

When solid compounds are introduced into water, there is an upper limit of how much substance can be dissolved, called the solubility. When the solvent contains the maximum amount of dissolved component or more (the solid phase contains the excess component), the solution is saturated.

The concentration [.] of a solution is defined as the amount of dissolved substance per the amount of solvent. Concentration is usually given in moles per liter (sometimes moles per cubic foot, grams per liter, mass or volumetric percentages, etc.).

Compounds that form ionic bonds dissolve into ions in water. A typical example is the dissolution of table salt, sodium chloride:

$$\mathrm{NaCl} \Leftrightarrow \mathrm{Na}^+ + \mathrm{Cl}^- \tag{1}$$

Many physical and chemical phenomena are related to the activity {.} of a given ion. In dilute solutions activity coincides with concentration, but in more concentrated solutions there can be significant differences. In the literature the activity is sometimes called the efficient concentration. The relationship between concentration and activity of a substance i is often assumed to be the following:

$$\{i\} = f_i \cdot [i] \tag{2}$$

The activity coefficient f is assumed to be 1.0 in very dilute solutions. For somewhat more concentrated solutions the activity coefficient can be estimated with the help of ionic strength. For very concentrated solutions calculating f becomes rather complicated.

There are many excellent books in the field of ionic equilibrium and pH systems. The notations used in this article are close to those of Butler (1) and Bates (2). These books are also recommended for a more detailed treatment of the subject.

Chemical Reactions

Most chemical reactions are reversible. There are always two reactions taking place simultaneously, an advancing reaction and a reverse reaction. Consider the general reaction

$$a\mathrm{A} + b\mathrm{B} \Leftrightarrow c\mathrm{C} + d\mathrm{D} \tag{3}$$

A reversible reaction consists of an advancing reaction $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$ and a reverse reaction $c\mathrm{C} + d\mathrm{D} \rightarrow a\mathrm{A} + b\mathrm{B}$.

A reaction that takes place in a single step is called a unit reaction. For unit reactions the rate of reaction depends on the activities of the participating components. For an advancing reaction the rate of reaction is given by the following:

$$r_1 = k_1 \cdot \{\mathrm{A}\}^a \cdot \{\mathrm{B}\}^b \tag{4}$$

Correspondingly for the reverse reaction

$$r_{-1} = k_{-1} \cdot \{\mathrm{C}\}^c \cdot \{\mathrm{D}\}^d \tag{5}$$

The reaction rate constants k_1 and k_{-1} are strongly dependent on temperature. In some cases the relationship can be described by the well-known Arrhenius equation.

At equilibrium the reaction rates of the advancing and the reverse reactions are the same ($r_1 = r_{-1}$), and the overall reaction does not go in either direction:

$$k_1 \cdot \{\mathrm{A}\}^a \cdot \{\mathrm{B}\}^b = k_{-1} \cdot \{\mathrm{C}\}^c \cdot \{\mathrm{D}\}^d \tag{6}$$

The ratio of the reaction rate constants is called the equilibrium constant K.

$$\frac{k_1}{k_{-1}} = \frac{\{\mathrm{C}\}^c \cdot \{\mathrm{D}\}^d}{\{\mathrm{A}\}^a \cdot \{\mathrm{B}\}^b} = K \tag{7}$$

A large value of the equilibrium constant indicates that the overall reaction (3) tends to go to the right toward the reaction products, and a small value that the overall reaction tends to go to the left toward the source materials. Similarly to reaction rate constants, the equilibrium constant also depends on temperature.

Acids and Bases

Acids contain hydrogen that is released under certain conditions. Acids are monoprotic or polyprotic (diprotic, triprotic, etc.) depending on the number of hydrogen ions H^+ that

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they can donate. The hydrogen ion H^+ forms different compounds with the water molecule, but usually in acid-base systems all of the hydrogen ion combinations (e.g., H_3O^+, $H_9O^+{}_4$) are symbolized by a simple hydrogen ion H^+ or an oxonium ion H_3O^+:

$$HA + H_2O \Leftrightarrow A^- + H_3O^+ \qquad \text{(monoprotic acid)} \tag{8}$$

$$H_3A + 3H_2O \Leftrightarrow A^{3-} + 3H_3O^+ \qquad \text{(triprotic acid)} \tag{9}$$

Acids are generally symbolized with letter A and bases with letter B. Polyprotic acids donate hydrogen ions in several stages, and therefore the latter reaction (9) can be separated into three unit reactions:

$$\begin{cases} H_3A + H_2O \Leftrightarrow H_2A^- + H_3O^+ \\ H_2A^- + H_2O \Leftrightarrow HA^{2-} + H_3O^+ \\ HA^{2-} + H_2O \Leftrightarrow A^{3-} + H_3O^+ \end{cases} \tag{10}$$

Bases accept hydrogen ions and similarly to acids they are also called monoprotic or polyprotic:

$$B + H_2O \Leftrightarrow HB^+ + OH^- \tag{11}$$

The hydrogen ion is actually a proton and therefore in the literature acids are defined as proton donors and bases as proton acceptors. Every acid HA has a corresponding base A^-, and together they form an acid-base pair. A substance that either accepts or donates a proton is called an ampholyte. The most important ampholyte is water (as can be seen from all of the previous examples).

Acid-Base Constants. Equilibrium constants can also be written for acids and bases. For monoprotic acids that react as in Eq. (8), the equilibrium constant is defined as follows:

$$K = \frac{\{A^-\} \cdot \{H_3O^+\}}{\{HA\} \cdot \{H_2O\}} \tag{12}$$

The reaction takes place in an aqueous solution and the activity (and the concentration) of water can be considered a constant and is combined with the equilibrium constant:

$$K_a = K \cdot \{H_2O\} = \frac{\{A^-\} \cdot \{H_3O^+\}}{\{HA\}} \tag{13}$$

The modified equilibrium constant is called the acid constant. For bases a corresponding base constant is developed. For reaction in Eq. (11) the base constant is given by the relationship

$$K_b = \frac{\{HB^+\} \cdot \{OH^-\}}{\{B\}} \tag{14}$$

Polyprotic acids and bases have equilibrium constants for each dissociation step. The acid constants of a triprotic acid that reacts by the reaction mechanism Eq. (10) are as follows:

$$K_{a1} = \frac{\{H_2A^-\} \cdot \{H_3O^+\}}{\{H_3A\}}, K_{a2} = \frac{\{HA^{2-}\} \cdot \{H_3O^+\}}{\{H_2A^-\}}, \\ K_{a3} = \frac{\{A^{3-}\} \cdot \{H_3O^+\}}{\{HA^{2-}\}} \tag{15}$$

Acid and base constants describe the strengths of acids and bases. A large acid constant indicates a strong acid that donates practically all of its protons. Weak acids have a small acid constant, and only some of the protons that could be released are actually donated.

The equilibria of weak acids and bases can be moved to either side of the reaction by adding or removing reaction products or source materials. A typical method of removing reaction products is neutralizing a solution by adding bases to acids and vice versa. Neutralization is treated in more detail in the next section.

Neutralization. The oxonium ion H_3O^+ (hydrogen ion H^+) and the hydroxide ion OH^- neutralize each other and produce water:

$$H_3O^+ + OH^- \Leftrightarrow 2H_2O \tag{16}$$

Consider an example where sodium hydroxide and hydrochloric acid are mixed together:

$$NaOH + HCl \Leftrightarrow Na^+ + Cl^- + H_2O \tag{17b}$$

The overall reaction is as follows:

$$NaOH + HCl \Leftrightarrow Na^+ + Cl^- + H_2O \tag{17b}$$

Mixing equal amounts of sodium hydroxide and hydrochloric acid yields table salt and water.

Ionic Product of Water. The neutralization reaction in Eq. (16) is also reversible. The reverse reaction is called autoprotolyzation of water:

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \qquad K = \frac{\{H_3O^+\} \cdot \{OH^-\}}{\{H_2O\}^2} \tag{18}$$

The equilibrium constant is modified similarly to the acid and base constants:

$$K_w = K \cdot \{H_2O\}^2 = \{H_3O^+\} \cdot \{OH^-\} \tag{19}$$

The modified equilibrium constant is called the ionic product of water [at 25°C $K_w = 1.0 \cdot 10^{-14}$ $(\text{mol/L})^2$].

The Definition of pH. In acidic solutions there are more oxonium ions than hydroxide ions, and vice versa in alkaline solutions. If the system is neutral, there are equal amounts of both ions. The previous section stated that the product of oxonium and hydroxide ion activities (efficient concentrations) is constant.

$$\begin{array}{ll} \{H_3O^+\} > \{OH^-\} & \text{acidic} \\ \{H_3O^+\} = \{OH^-\} = \sqrt{K_w} = 1.0 \cdot 10^{-7}, \text{(at 25°C)} & \text{neutral} \\ \{H_3O^+\} < \{OH^-\} & \text{alkaline} \end{array}$$

For practical reasons the logarithmic scale is more appealing (ten-base logarithm $\log_{10}$ is marked with lg). pH is defined as

$$\mathrm{pH} = -\log_{10}\{\mathrm{H_3O^+}\} = -\mathrm{lg}\{\mathrm{H_3O^+}\} \tag{20}$$

At 25°C the neutrality of a solution is given as follows:

$\mathrm{pH} < 7$	acidic
$\mathrm{pH} = -\mathrm{lg}10^{-7} = 7$	neutral
$\mathrm{pH} > 7$	alkaline

The pH usually varies between 1 and 14, but higher or lower values are also possible.

Weak acids and bases have equal amounts of dissociated and undissociated forms when the oxonium ion activity is equal to the acid or base constant, as can be seen from Eqs. (13)–(15). There are important practical phenomena when this happens (such as maximum buffering, explained in the next section) and therefore the pH which enables that is significant. Often the equilibrium constants K_a and K_b are given in $\mathrm{p}K_a$ and $\mathrm{p}K_b$ values whose definitions are identical to Eq. (22):

$$\mathrm{p}K_a = -\mathrm{lg}K_a, \mathrm{p}K_b = -\mathrm{lg}K_b \tag{21}$$

$\mathrm{p}K_a$ and $\mathrm{p}K_b$ values indicate directly important pH ranges that have practical significance.

Buffer Solutions. In many practical situations the pH should be close to an optimal value. This is typically the case for biochemical processes. The solution should be insensitive to small additions of acids or bases and, if this applies, the solution is called a buffered solution. Many natural systems contain buffers (e.g., blood) but buffers can also be produced artificially from weak acids and bases and their salts.

A typical buffer solution is produced from acetic acid (*HAc*) and sodium acetate (*NaAc*). The resulting solution contains both acetic acid and acetic ion ($\mathrm{Ac^-}$). The reaction is as follows:

$$\mathrm{HAc} + \mathrm{H_2O} \Leftrightarrow \mathrm{Ac^-} + \mathrm{H_3O^+} \tag{22}$$

If acid is added, the free hydrogen ion (oxonium ion) reacts with excess acetic ion to form undissociated acetic acid (reverse reaction). The pH is not significantly affected until the buffer solution runs out of acetic ions. Correspondingly, if base is added, the free hydroxide ions react with hydrogen ions to form water. The acetic acid ionizes more (advancing reaction) to satisfy the equilibrium condition. The pH changes only a little until the buffer solution runs out of undissociated acetic acid. The buffer solution can be considered a reservoir of ions that are released when needed in the reaction.

The efficiency of a buffer solution is described by the buffer index β defined as follows:

$$\beta = \frac{\mathrm{d[B]}}{\mathrm{dpH}} = -\frac{\mathrm{d[A]}}{\mathrm{dpH}} \tag{23}$$

The differential change in the concentration of a strong base B versus the differential change in the pH (or negative differential change in the concentration of a strong acid A vs. the differential change in the pH) corresponds to the reverse of the titration curve's slope. In Fig. 1, the buffering index of the acetic buffer solution described earlier is presented as a function of pH. The maximum buffering is reached at pH = $\mathrm{p}K_a$ = 4.75. The curve (buffer solution) is compared to the corresponding curve of a solution (no buffering) that contains only water and strong acids and bases.

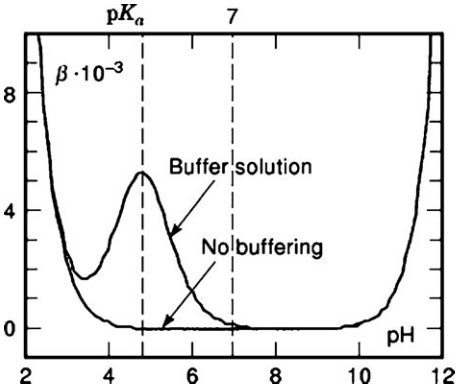

Figure 1. The buffer index of acetic acid solution.

Gibbs Free Energy

Deep understanding of the chemical equilibrium can be achieved only by thermodynamics, but that is beyond the scope of this article. The elementary principles rely on the Gibbs free energy defined by the relationship

$$G = H - TS \tag{24}$$

where H is the enthalpy, T is the absolute temperature, and S is the entropy. Any free system is autonomously moving toward small values of G, and it does not stop until it has reached the minimum Gibbs free energy, that is equilibrium.

The practical significance of this fundamental truth is the fact that many parameters and constants related to Gibbs free energy are tabulated or easily calculated enabling the calculation of equilibrium constants in changing situations, such as varying temperatures.

The free energy of any substance X is calculated as follows:

$$G_x = G_x^0 + RT\ln\{X\} \tag{25}$$

where $G^0{}_\mathrm{X}$ is the standard free energy and R is the gas constant. For Eq. (3) $a\mathrm{A} + b\mathrm{B} \Leftrightarrow c\mathrm{C} + d\mathrm{D}$ the change in Gibbs free energy is given by

$$\Delta G = cG_\mathrm{C} + dG_\mathrm{D} - aG_\mathrm{A} - bG_\mathrm{B} = G^0 + RT\ln\frac{\{\mathrm{C}\}^c\{\mathrm{D}\}^d}{\{\mathrm{A}\}^a\{\mathrm{B}\}^b} \tag{26}$$

ΔG is called the reaction work (work done by the chemical reaction).

Chemical Energy and Electrical Energy

Chemical energy is transformed into electrical energy in a galvanic element consisting of two electrodes in contact with liquid. If a metallic element is introduced into an ion-

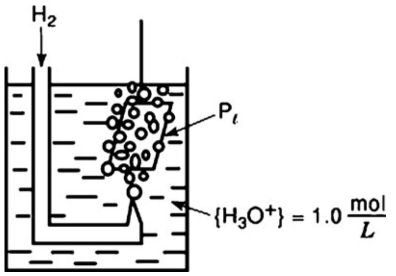

Figure 2. Standard hydrogen electrode.

ized salt solution containing the same metal ion, there is an equilibrium. The electrons and metal ions remain in different phases close to each other creating an electrical potential.

The potential of the galvanic element is a direct measure of the cell work and correspondingly also of the change in the free energy. The free energy change is calculated as follows:

$$\Delta G = -nFE \tag{27}$$

where n is the number of electrons transferred in the cell reaction, F is the Faraday constant, and E is the cell potential. By combining Eqs. (29) and (30), Nernst's equation results:

$$E = E^0 - \frac{RT}{nF}\ln\frac{\{C^c\}\{D\}^d}{\{A\}^a\{B\}^b} \tag{28}$$

where the standard potential E^0 of the cell is defined as follows:

$$E^0 = -\frac{G^0}{nF} \tag{29}$$

The standard potential of any electrode is determined by combining it with a reference electrode in a galvanic cell. The standard hydrogen electrode (shown in Fig. 2) is arbitrarily chosen as a general reference electrode with a zero potential. The standard hydrogen electrode consists of a platinum plate that is constantly saturated with hydrogen by a continuous hydrogen gas stream.

The standard potentials of electrodes measured against a standard hydrogen electrode are found in numerous tables.

PERMEABLE GLASS ELECTRODE

Permeable Glass Membrane

The most common pH measuring electrode is the glass electrode. Around 1906 Cremer found that some types of glass gave a potential difference whose magnitude depends on the acidity of the liquid in which the glass is immersed (3). Later Haber and Klemensiewics proved that this potential difference, within a fixed pH range, follows Nernst's potential in the same way as the hydrogen electrode (4).

Corning Glass Works Inc. developed a well known glass material called Corning 015 consisting of 72.2 mol% SiO_2, 6.4 mol% CaO and 21.4 mol% Na_2O. This glass can be used for pH measurement in the range from 0 to 9. After that glasses containing LiO_2, Cs_2O, BaO, and La_2O_3 were developed. With these glasses more alkaline pH values could be measured.

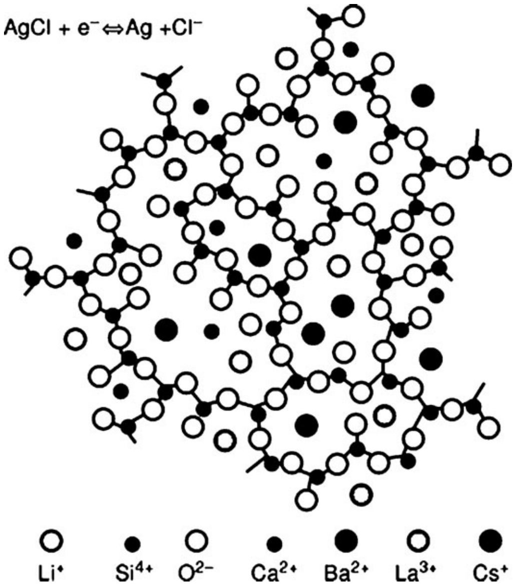

Figure 3. The texture of pH glass.

Glass can be considered an "undercooled" electrolyte consisting of an irregular SiO_2 structure containing other components which move in the interspaces. These components give the membrane an electron balance; see Fig. 3. When immersed in aqueous solution, glasses exchange the metal ions in the glass with the H^+ ions in the solution. As a result of this reaction a "gel layer" is developed on the surface of the glass membrane. This gel layer is the equivalent of the metal ion layer in Nernst's theory and therefore is essential for the operation of the glass electrode. After one or two days the electrode reaches an equilibrium, and the resulting gel layer has a thickness between 10 nm and 100 nm. This mechanism depends on several factors, such as the composition of the glass and the temperature at which the glass is immersed. Many theories have been developed on the subject of gel layer formation (2).

The electrical potential with the glass electrode is generated by a method somewhat different from that with metal electrodes. In glass electrodes only the ions change location not the electrons.

Construction of the Glass Electrode

The construction scheme of the glass electrode is shown in Fig. 4. The electrode consists of a glass tube, into which a bulb-shaped membrane of a specific pH glass is welded. The electrode is filled with a buffer solution containing Cl^- ions. Usually the pH of this electrolyte is 7. An inner electrode, constructed of a metal pin covered by its sparingly soluble salt, is connected to the output cable of the electrode. The inner electrode is immersed in the electrolyte containing anions of the salt.

A typical inner electrode is the silver–silver chloride electrode, in which AgCl salt covers the Ag pin. When the electrolyte contains Cl^- ions, the following electrode reac-

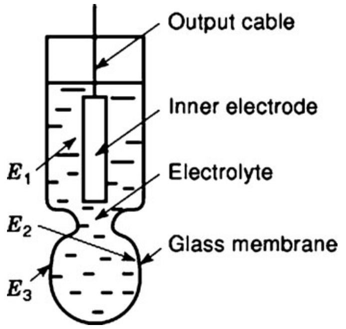

Figure 4. The construction scheme of the glass electrode.

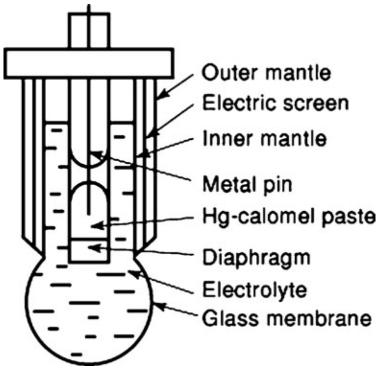

Figure 5. The construction of the glass electrode.

tion occurs:

$$\mathrm{AgCl} + e^- \Leftrightarrow \mathrm{Ag} + \mathrm{Cl}^- \tag{30}$$

A potential difference between the inner electrode pin and the electrolyte is formed as a redox reaction Eq. (33); see Fig. 4. The potential difference is calculated from Nernst's equation.

Another common inner electrode is the calomel electrode in which the output cable has a galvanic connection with mercury, which is in contact with mercury chloride (Hg_2Cl_2). This compound is known as calomel. The electrode reaction is as follows:

$$\mathrm{Hg_2Cl_2} + 2e^- \Leftrightarrow 2\mathrm{Hg} + 2\mathrm{Cl}^- \tag{31}$$

The potential difference between the inner electrode and the electrolyte is calculated from Nernst's equation. A thallium amalgam–thallium inner electrode is used especially when the temperature of the process liquid to be measured is high. In the electrode thallium amalgam is in contact with thallium chloride.

As mentioned earlier the pH-sensitive membrane is produced from special glass. Its thickness is usually 50 μm to 200 μm, but in measuring very aggressive solutions it can even be 1 mm. After immersion in water, the glass electrode can measure the process solution. A potential difference between the process liquid and the glass surface is created, and this difference is a function of the activity of H_3O^+ ions and thus also a function of the pH. Figure 5 shows the structure of a typical glass electrode with a calomel inner electrode.

As shown in Fig. 4, the following three potential differences (electromotive forces) are created in the glass electrode:

- E_1 between the inner electrode and the electrolyte
- E_2 between the inner surface of the glass electrode and the electrolyte
- E_3 between the outer surface of the glass electrode and the liquid to be measured

As mentioned earlier E_1 is a constant potential difference. The potential difference E_3 is the significant indicator of the pH. Nernst's equation holds quite well:

$$E_3 = E_0 + (RT/F)\ln\{\mathrm{H_3O^+}\}_{\mathrm{OUTER}} \tag{32}$$

where E_0 is constant at a specific temperature and $\{H_3O^+\}_{\mathrm{OUTER}}$ is the activity of the H_3O^+ ions in the process liquid. A pH-sensitive gel layer is also developed on the inner surface of the glass membrane. The potential difference E_2 also obeys Nernst's equation:

$$E_2 = E_0 + (RT/F)\ln\{\mathrm{H_3O^+}\}_{\mathrm{INNER}} \tag{33}$$

where $\{H_3O^+\}_{\mathrm{INNER}}$ is the activity of the H_3O^+ ions in the electrolyte inside the electrode. Because the electrolyte is a buffer solution, the potential difference E_2 is constant. At constant temperature only E_3 is a variable, and it changes when the H_3O^+ content changes in the measured process liquid. By noting that $\ln\{H_3O^+\} = \ln 10\ \lg\{H_3O^+\}$ and $\mathrm{pH} = -\lg\{H_3O^+\}$, Eq. (35) can be rewritten as

$$E_3 = E_0 - (RT\ln 10/F)\mathrm{pH}_{\mathrm{OUTER}} \tag{34}$$

m

and Eq. (36) as

$$E_2 = E_0 - (RT\ln 10/F)\mathrm{pH}_{\mathrm{INNER}} \tag{35}$$

The total potential in the output cable of the electrode is given by

$$E_M = E_1 - E_2 + E_3 \tag{36}$$

Now Eq. (39) can be rewritten as

$$E_M = E_{M0} - (RT\ln 10/F)\mathrm{pH}_{\mathrm{OUTER}} \tag{37}$$

where

$$E_{M0} = E_1 + (RT(\ln 10)/F)\mathrm{pH}_{\mathrm{INNER}} \tag{38}$$

Equation (40) shows that the potential of the glass electrode is a function of the pH and the temperature. If the glass electrode potential obeys Eq. (40), it is said to be ideal.

Resistance of the Glass Membrane

The definition of pH requires the potential difference of the measuring and the reference electrodes. If it is measured with a semiconductor converter, a small electric current is created through the electrodes. The current penetrates the pH-sensitive membrane whose resistance is quite high (about 10 MΩ to 500 MΩ at room temperature) and varies as a function of temperature. For instance, the resistance of a membrane produced from Corning 015 glass is about 200 MΩ at room temperature and 1000 MΩ at 10°C.

The high resistance of the glass electrode causes practical problems in constructing measuring circuits. Different kinds of glasses are developed for different measurement conditions. The important considerations are the acidity and temperature ranges of the liquids to be measured. The resistance of the glass membrane, however, should be as small as possible in all cases.

The Asymmetry Potential

The reason for the asymmetry potential is the difference in the behavior of the outer and inner surfaces of the glass membrane. If the inside and outside liquids are identical and there are identical electrodes on both sides, a potential difference still exists between the electrodes. This is called the asymmetry potential. It is only a few millivolts, but it changes slowly during aging of the electrode. Following are the reasons for the asymmetry potential:

- Different strains in the inner and outer surfaces of the electrode
- During production thermal effects decrease the cation content in the outer surface of the membrane and that is why the penetration of water differs on different sides of the membrane
- The outer surface is vulnerable to mechanical and chemical effects
- Fouling of the membrane

Alkaline and Acidic Errors

The pH measurement error in strong alkaline liquids is called the alkaline error or sometimes the sodium error. In alkaline solutions above pH 9, other monovalent cations, such as Na^+ and Li^+ influence the electrode potential causing measured values too low. Alkaline error increases with high temperatures. Nowadays special electrodes with a small alkaline error are available. They are well suited for measurements in strong alkaline conditions.

In very concentrated acid solutions the output voltage does not completely obey Nernst's law. Tests show that the gel layer absorbs acid molecules and consequently that the hydrogen ion concentration (and activity) increases, resulting an increase in pH. Acid error is significant only at very low pH values, and it is relatively small compared to the alkaline error. Acid error does not depend very much on temperature.

REFERENCE ELECTRODE

Purpose

pH measurement requires both a measuring electrode and a reference electrode, which gives the reference potential against which the potential of the measuring electrode is compared. The reference potential has to remain constant when the properties of the process liquid change. On the other hand, the reference electrode builds a galvanic contact from the process liquid to the pH converter.

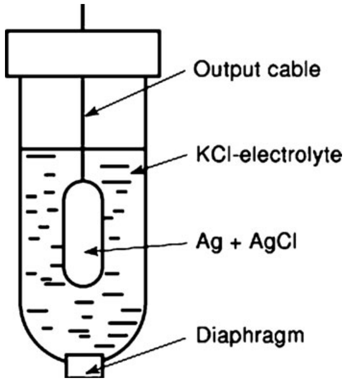

Figure 6. The structure of the Ag–AgCl reference electrode.

Silver–Silver Chloride (Ag–AgCl) Electrode

This electrode is named after its inner electrode. The inner electrode has the same structure as the corresponding measuring electrode, that is silver coated with silver chloride, and it is immersed in a KCl solution. The structure of the electrode is shown in Fig. 6. Galvanic contact is created through a diaphragm in the glass mantle of the reference electrode. The diaphragm is produced from ceramics, Teflon, or different kinds of fibers. The KCl solution flows very slowly through the diaphragm, and that is why care must be taken to ensure that there is always enough KCl solution. The pressure inside the electrode has to overcome the pressure of the process liquid at all times. Otherwise the flow through the diaphragm changes direction, and the electrode becomes poisoned.

The concentration of the KCl solution decreases in the diaphragm, and a diffusion potential exists. This potential disturbs the measurement, and its value must be minimized. KCl solution has been chosen as the electrolyte for the particular reason that the sizes and thus the mobilities of K^+ and Cl^- ions are almost equal, and thus the diffusion potential is very small. The usual electrolytes are 1 molal, 3 to 3.5 molal or saturated KCl solutions.

Calomel Electrode

Another commonly used reference electrode is the calomel electrode, also named after its inner electrode. Figure 7 shows two different calomel electrode constructions. Again the inner electrode is immersed in KCl solution. In the construction of Fig. 7(a) the body of the inner electrode consists of a closed glass tube with mercury at the bottom. A platinum pin connected to the output cable is immersed in mercury, which is further connected to a paste prepared from mercury, calomel, and KCl. The electric contact with the KCl solution is realized with a diaphragm on the side of the inner glass tube. Figure 7(b) shows another construction. An amalgamated platinum pin is in contact with Hg-calomel paste, and the electric connection is realized with a diaphragm. In both cases calomel and mercury make up the electrode. The potential difference is the same as in the calomel measuring electrode.

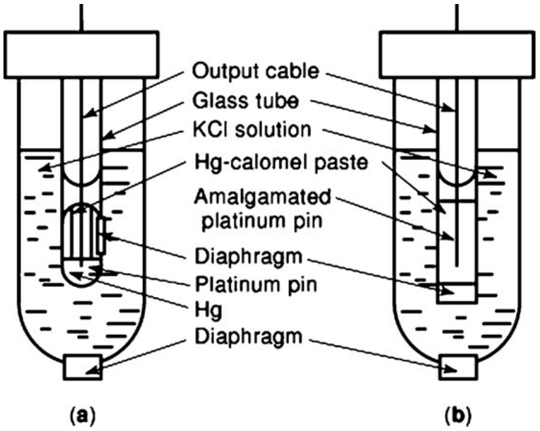

Figure 7. Constructions of the calomel reference electrode.

Thallium–Thallium Chloride (Tl-TlCl) Electrode

The Ag–AgCl electrode operates up to temperatures of 100°C and the calomel electrode up to 80 °C. The Tl–TlCl-electrode can be used for higher temperatures. It measures pH up to 135 °C or even 150 °C. The construction of the electrode is analogous to the other reference electrodes. The potential difference is created according to the following reaction:

$$TlCl + e^- \Leftrightarrow Tl + Cl^- \quad (39)$$

Special Constructions

A steady flow of KCl solution out of the electrode is essential. The amount of the flow can be decreased by adding a gel to the KCl solution (5–7). Another technique is to impregnate the KCl solution into a piece of wood (5). Both techniques decrease the possibility of electrode poisoning.

If the process liquid includes compounds which react with the KCl solution, an additional chamber can be constructed between the KCl chamber and the process liquid. It is connected by a diaphragm in both directions and filled with a special electrolyte (6). There is also another approach to avoid KCl-reactions, a nonpermeable reference electrode [SOLPHET^{TM} (26)]. In drossy circumstances the diaphragm must be constructed large enough to assure good functioning. In very drossy circumstances the diaphragm can be replaced by a capillary flow tube (6, 8). Then the consumption of KCl solution is increased, but the fouling effect is avoided. One manufacturer produces a special electrode which controls the pressure of the KCl solution chamber with a bellows connected to the pressure of the process liquid. The elasticity of the bellows maintains the KCl solution chamber at a slightly higher pressure than the process pressure thus avoiding fouling of the diaphragm. Pressures below atmosphere are also possible (6).

COMBINED ELECTRODE CONSTRUCTION

As an alternative to the normal configuration with separated glass and reference electrodes, a system may be used that combines both electrodes into one unit. With this construction the high-ohmic glass electrode is screened by the electrolyte of the reference electrode, and the metal screen can be omitted. The advantage of the combined electrode is the ease of maintenance and the ability to measure pH in very small quantities of liquid. The construction of the joints into the pressurized flow tubes is also simpler. A major disadvantage is that because of the construction of the electrode it is not possible to provide the selection of glass types for many applications. Figure 8 shows the construction of a combined electrode.

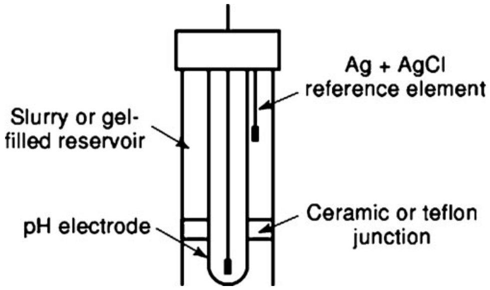

Figure 8. A combined electrode structure.

MEASUREMENT OF THE PH

The Measurement Circuit

The measurement circuit includes the measuring electrode, the reference electrode, and the signal converter (Fig. 9). The electrodes constitute the voltage source, and if the measurement signal is a standard signal, say 4 mA to 20 mA, the converter is a pH transmitter. The following potential differences exist:

- E_3 between the outer surface of the glass electrode and the process liquid
- E_2 between the inner surface of the glass electrode and the electrolyte
- E_1 between the inner electrode of the glass electrode and the electrolyte
- E_4 between the inner electrode of the reference electrode and the electrolyte
- E_5 the diffusion potential of the reference electrode

An electric circuit shown in Fig. 10 is created in the measurement system. The source voltage of the system is the sum of all of the potential differences:

$$E_S = E_1 - E_2 + E_3 - E_4 - E_5 \quad (40)$$

Usually the inner electrodes and the Cl^--ion activities in the electrolytes of both electrodes are identical, and thus $E_1 = E_4$. In usual constructions E_5 is so small that it can be neglected and thus

$$E_S = E_3 - E_2 \quad (41)$$

The membrane resistance R_L is 10 MΩ to 1000 MΩ, and the resistances R_R and R_N are much smaller and therefore are neglected. The isolation resistance R_E between the connecting cables must be very large. If the decrease of the isolation resistance caused by moisture can be avoided, its value can be assumed insignificant in the circuit. With these assumptions the voltage in the input cables obeys the following equation:

$$U_T = [R_T/(R_L + R_T)]E_S \tag{42}$$

Because the value of the voltage U_T should be as equal as possible to E_S, the input resistance R_T must be very large, about 1 TΩ to 10 TΩ.

The Effect of Temperature

By substituting Eqs. (37) and (38) in Eq. (44), the following form is obtained:

$$\begin{aligned} E_S &= [(RT \ln 10)/F](\mathrm{pH_{INNER}} - \mathrm{pH_{OUTER}}) \\ &= k(\mathrm{pH_{INNER}} - \mathrm{pH_{OUTER}}) \end{aligned} \tag{43}$$

The electrolyte of the measuring electrode is a buffer solution, and thus $\mathrm{pH_{INNER}}$ is a constant with a usual value of 7. The coefficient k in Eq. (46) is a function of the absolute temperature T. When the temperature is constant, Eq. (46) defines a straight line with a negative slope. The values of the coefficient k as a function of temperature are listed in Table 1. Figure 11 shows the source voltage as a function of temperature for $\mathrm{pH_{INNER}} = 7$. The lines intersect at the so-called isopotential point. Ideally this should be $E_S = 0$, $\mathrm{pH_{INNER}} = 7$ per Eq. (46). In a real situation with existing electrodes, the isopotential voltage differs from zero as shown in Fig. 11. The pH of the intersection point can also differ from 7. The following conditions affect the isopotential voltage:

Table 1. Values of the Coefficient k

t (°C)	k (mV/pH-unit)
0	54.20
25	59.16
50	64.12
75	69.08
100	74.04

Small differences between the inner electrodes
The asymmetry potential of the glass electrode
The diffusion potential of the reference electrode
Fouling of the glass membrane

The temperature dependence of the electrodes can be compensated for by using a Pt 100 or a thermistor immersed in the process liquid. The sensor reads the temperature, and based on this information the signal converter compensates. The temperature sensor can be a third electrode in the conventional assembly, or it can be integrated into the same body as the two other electrodes in a combined electrode.

A more serious problem is caused by the temperature dependence of the pH of the process liquid to be measured. That cannot be compensated for easily because the effect is a function of the liquid composition which is why it is usually omitted.

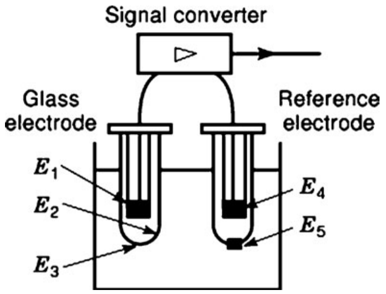

Figure 9. $E_S = f(\mathrm{pH_{OUTER}})$ of the real electrodes at different temperatures.

Signal Converter

The special properties of the pH measurement circuit establish some requirements for the signal converter or the transmitter, for example high input impedance, temperature compensation, and elimination of electrode ageing. Cheaper transmitters are realized by the analogue technique and the more sophisticated by the microprocessor technique. In both cases high input impedance is easy to realize by semiconductor techniques. Besides the temperature dependence the isopotential voltage must be compensated for. Automatic temperature compensation is included in almost all applications, and only in laboratory devices is compensation realized with a potentiometer. The output signal of the transmitter is usually 0.4 mA to 20 mA in industrial applications. If personal computers are used in on-line control applications, a voltage output signal can also be used, for example 0.1 V to 5 V or 0.2 V to 10 V.

The microprocessor technique improves functioning of the transmitters in many ways:

The measurement scale can be changed during continuous use
Advanced diagnostics are available
The hold function of the signal works during maintenance
Better possibilities for temperature compensation
Improved measurement accuracy
Digital signal transfer is possible

Diagnostics can include the functions of both the transmitters and the electrodes. By measuring the resistance of the glass membrane, the resistance of the reference electrode, the change of the isopotential voltage, and some other properties, conclusions can be drawn as to whether the electrodes are broken, fouled, aged, or not immersed in the process liquid (6–10). In special cases when the composition of the process liquid is accurately known, the change of the pH of the liquid as a function of the temperature can also be compensated for. This is the case, for example, in alkaline turbine water including one base and demineralized water (6).

Special Developments

If the process liquid is very drossy or contains glass etching substances (e.g., hydrofluoric acid, HF), an antimony measuring electrode can be used. When the antimony electrode is immersed in the process liquid, a potential is created which obeys Nernst's law. The applicable pH range is only from 2 to 9, but antimony electrode measurement is much faster than that of a glass electrode. A typical time constant (response time from 0 to 63% of the change) in glass electrode measurement is about 5 s. The antimony electrode is easy to clean because of its metallic structure.

To avoid the nonideal features of the conventional measurement-reference electrode pair, a differential pH measurement method was developed (11). This method uses two identical glass electrodes. One of these electrodes measures the process liquid, and the other is immersed in a buffer solution connected to the process liquid via a salt bridge. A metallic reference electrode is also immersed in the process liquid. The resulting source voltage is the difference between these two measuring electrode source voltages and the same reference potential, and thus the actual reference potential is suppressed. Thus fouling of the reference electrode and the small leakage currents in the liquid caused by the inaccuracy of isolation between the reference electrode and the liquid ground are avoided.

One manufacturer has developed sensors using semiconductor technology. The product is an ion-sensitive field effect transistor (*ISFET*). A conventional reference electrode can be used. The response time of this electrode is about 1 s. The system is small and maintenance is easier than for the glass electrode (7).

Another manufacturer has developed a combined enamel electrode consisting of an enamel measuring electrode and an enamel Na-selective electrode, used as the reference electrode. With this electrode the pH of a dough or paper mass can be measured up to 14% consistency (12). There is also a nonpermeable combined electrode for masses with very low water content [SOLPHET™ (26)].

A technique which may be important in the future is optical glass fiber measurement. The color of light shows the pH. The fiber optic sensor can measure the resulting mean value from a large region not only pointwise. This technique is not yet ready for reliable pH measurement, but it is used in a moisture alarm for concrete structures.

An interesting approach to industrial pH measurement was developed by Ville Voipio (27). The novel instrument he developed is based on measuring color changes of pH sensitive dye molecules which are trapped in a thin porous glass membrane. The main advantage of the dye measurement is the strong measurement signal, as there are no noisy low-level electrochemical signals to be measured.

PRACTICAL PH MEASUREMENT

Calibration of pH Measurement

Calibration is done with standard buffer solutions. Two or three different buffer solutions are needed. A buffer having a pH near 7 is always used because at that value the theoretical voltage is about zero. When the measurement range is acidic, a buffer solution with a pH near 4 is used. On the alkaline side, a buffer with a pH near 10 is needed. Alternatively all three buffers are used. The buffer and the process liquid sample must be at the same temperature. The sensors must be rinsed with ion-exchanged water between immersions in the different buffers. The zero potential point is set with buffer 7, and the slope of the line is tuned with the other buffers. Specific electrical calibrators are sometimes used, but they do not take into account the individual differences of the electrodes.

The ionic strength affects the movement of ions in the diaphragm and, thus, the reference potential and pH-value to be measured. For this reason the ionic strength of the buffer solutions should be on the same level as in the sample to be measured. The buffer solutions are usually commercially available in two ionic strengths. The effect of the ionic strength can also appear in the growth of the activity coefficients. Thus liquids having the same hydrogen ion concentration can have different pH-measurement results. The most common buffer solutions with different ionic strengths are presented in Ref. 2.

Practical Definition of pH

Practical definition of pH compares the measured value of the process sample with that of the buffer solution. When these voltages are denoted as E_{S} and E_{SB}, the definition is constructed by using Eq. (43):

$$pH_{\mathrm{OUTER}} = pH_{\mathrm{BUFFEROUTER}} - F(E_S - E_{SB})/(RT \ln 10) \quad (44)$$

Installation, Use, and Maintenance of Electrodes

In an industrial environment electrodes must be protected against breakage with robust mounting chambers. The most common types, the immersing chamber and the bypass flow chamber, are shown in Fig. 12. The combined electrode assembly shown in Fig. 13 is often used in the pulp and paper industry. In this case the pulp flowing in the pipes can have even 15% consistency. In this case measurement is possible in the thin liquid film formed on the tube wall. In abrasive circumstances an automated sample system must be used. The system automatically takes a sample, measures the pH, ejects the sample, washes the electrodes, and takes a new sample. In the mounting grounding the process liquid is important. In mountings made of steel no problems exist. Otherwise a special ground electrode is often used.

Cleaning is important in industrial measurement. It can be automated to function periodically but in more demanding situations manual maintenance is also needed. The following automated cleaning methods are used:

Mechanical spherical brushing of the sensor head
Water spraying periodically
Chemical spraying periodically
Ultrasonic washing
Small ceramic particles in a cage around the sensor head

The electrodes can be washed manually with different chemicals depending on the cause of fouling. Sterilization can be done chemically or physically with hot steam if needed. The form of the sensor head is important in fouling. A flat sensor head is suitable for measuring the pH of thick samples in pipes. Other sensor head profiles are useful for other reasons. For example, it is possible to measure very small liquid samples with a spherical sensor head.

The reference electrode consumes KCl solution, and additional solution must be added periodically. Microprocessor-based transmitters with diagnostics help in planning sensor maintenance. When the glass electrode is not used in measurement, it is usually kept in a buffer with pH 4. If it is stored dry, it must be soaked in distilled or ion-exchanged water for at least 24 hours before use.

PH MODELING

pH value is a significant factor in many chemical and biological phenomena. At the same time it is considered a basic measurement in industry and it can be measured online whereas many other important measures are still performed off-line. There are many different approaches to pH modeling for better understanding of chemical systems. pH models are divided into static and dynamic models. Modeling methods can be theoretical or experimental. A more detailed treatment of pH modeling can be found in (28).

Static Modeling

A static model is obtained when a system has reached equilibrium and does not change further with time. Acid–base unit reactions can be considered instantaneous, and therefore static modeling is a very natural approach. Static models include titration curves and distribution diagrams. Experimental static models are often basic tools for product quality control and process state indicators. Experimental methods have been used for both qualitative and quantitative analysis.

Titration Curves. Titration curves are traditional pH models. They describe the pH as a function of the difference in the acid-base content. Experimental titration curves usually present the pH as a function of added acid or base volume. Titration curve pH vs. added reagent volume V_A depend on the sample volume, whereas pH vs. added reagent concentration [HA]–[B] does not. The only difference is in scaling. The shape of the titration curve is determined by the participating chemical components. A group of typical titration curves is shown in Fig. 14 where mixtures of acetic acid (HAc), ammonia (NH_3), and water are treated with strong acids and bases. The solutions containing HAc have a titration bump at the pK_a of acetic acid, the solutions containing NH_3 have a titration bump at the pK_b of ammonia, and pure water shows a typical strong acid, strong base titration curve. Polyprotic acids donate more than one hydrogen ion, and the titration curves have correspondingly more than one step as in Fig. 15 which shows the titration curve for phosphoric acid (H_3PO_4).

Theoretical titration curves can be calculated from equilibrium constants and the total concentrations of acids and bases. An experimental curve, on the other hand, requires only a sample. Theoretical titration curves can be generated from the electroneutrality equation (also known as the charge balance equation). The electroneutrality equation takes into account all of the charged ions of the solution. The solution has no overall charge, and therefore the sum of all individual charges must be zero:

$$\sum_n \pm z_n \cdot [x z_{n\pm}] = 0 \tag{45}$$

$z_{n\pm}$ is the charge of an individual ion. Ions are usually divided into the components of water (oxonium and hydroxide ions), the components of strong acids (H_zA) and bases (B), and the components of weak acids (H_za) and bases (b):

$$\begin{aligned}[H_3O] - [OH^-] + \sum_n z_n[H_{z_n} B z_{n+}] - \sum_n z_n[A z_{n-}] \\ + \sum_n z_n[H_{z_n} b z_{n+}] - \sum_n z_n[a z_{n-}] = 0\end{aligned} \tag{46}$$

The titration curve shows the relationship between pH (a function of oxonium ion activity) and acid/base concentration. Strong acids and bases dissociate completely, so their ion concentrations are also total concentrations. Weak components dissociate only partially, so their ion concentrations have to be calculated from equilibrium constants. Each weak acid or base ion concentration can be replaced in Eq. (49) by a function of oxonium, hydroxide, and total ion concentrations calculated from equilibrium equations, such as Eqs. (13)–(15). Then the hydroxide ion concentration is replaced by a function of the oxonium ion concentration and the ionic product of water in accordance with Eq. (20).

After all this manipulation Eq. (49) contains only total acid and base concentrations and oxonium ion concentration (from which the pH is calculated by Eq. (22)). A more detailed modeling procedure is given in Ylén and Jutila (13).

Distribution Diagrams. Distribution diagrams give more information than titration curves. They are generated for specific compounds, and they describe the distribution of different forms of a compound as a function of pH. Figure 16 shows the distribution diagram of pure phosphoric acid (H_3PO_4) solution, and Fig. 17 shows the same diagram on a logarithmic scale.

Distribution diagrams are generated from the total balance of a compound. Consider phosphoric acid

$$[P]_{TOT} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \tag{47}$$

Each concentration in Eq. (50) is replaced by a function of equilibrium constants, oxonium ion concentrations, and total phosphoric concentrations. The distribution for component X is defined as follows:

$$\alpha_i = \frac{[X_i]}{[X]_{TOT}} \tag{48}$$

Distribution diagrams are useful for evaluating optimal pH ranges for specific reactions, such as separation processes. In separation processes a distribution diagram is often made for different phases of the compound. Figure 18 shows the distribution of calcium in solid and liquid phases of a calcium carbonate solution. A similar distribution diagram could be constructed for carbonate in the

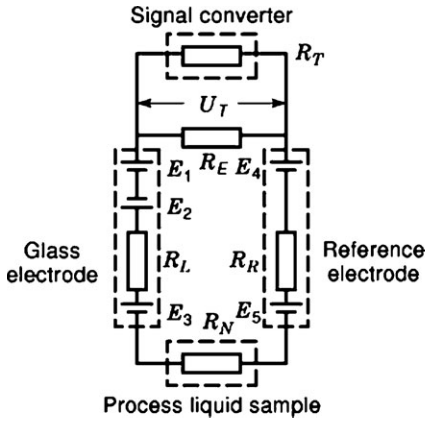

Figure 10. The solid–aqueous distribution diagram of $CaCO_3$.

same solution. That would be a three-phase diagram (carbon dioxide in the gas phase, calcium carbonate in the solid phase and all carbonates in the liquid phase, consisting of dissolved carbon dioxide, carbonic acid, hydrocarbonate ions, calcium bicarbonate ions, and carbonate ions).

Distribution diagrams for reactions with different compounds do not usually reach a maximum value of one for each fraction. In Fig. 18 the maximum value of the $CaCO_3$ fraction is determined by the ratio of the total calcium concentration and the total carbonate concentration. There is more calcium than carbonate and thus the carbonate runs out and some of the calcium is left in the liquid phase.

Dynamic Modeling

Dynamic modeling is fundamentally more difficult than static modeling. Static modeling concentrates only on the equilibrium state where the system does not change with time. In dynamic modeling the behavior of the pH and related phenomena are considered as functions of time.

Dynamic pH systems can be divided into two categories, systems where chemical phenomena are significantly faster than flow and mixing phenomena and systems where this is not the case. These categories are treated in more detail in the following sections.

Separate Dynamics for Chemical Reactions and Flow Phenomena. In this simple case the reaction kinetics are much faster than the flow dynamics and can be treated separately. At every instant the chemical reaction takes place instantaneously, and therefore it can be treated as a static nonlinearity. The static models presented in earlier chapters can easily be embedded into flow dynamics. The simplest models are obtained when the weak acid and base component concentrations are constant throughout the system and only the strong acid or base concentrations change. If this applies, the shape of the titration curve does not change. Only the position on the curve changes. In this case the acid–base concentration difference is driven by flow dynamics, and the output is filtered by the titration curve that is presented as pH versus acid–base concentration difference.

The dynamic model is somewhat more complicated if weak components also change. In this case the titration curve of the system can also change arbitrarily and no fixed nonlinearity can be used. The pH value has to be iterated at each step. Two widely used methods are iteration of the aqueous solution's electroneutralitity equation or minimization of the Gibbs energy function. Both methods require that each participating chemical component is driven by flow dynamics before the iteration is performed to find the pH.

Interconnected Chemical and Flow Dynamics. Models become even more difficult when chemical kinetics and flow dynamics have approximately the same timescale. In these cases the two phenomena cannot be separated, and the models have to be treated simultaneously. Systems requiring this kind of model are typically multiphase processes or they have slow side reactions that bring the overall chemical reaction rate up to the same level as the flow dynamics.

PH CONTROL APPLICATIONS

Difficulties With pH Control

Difficulties can arise in pH control from the quality of the process liquid or the reagent, the dimensioning of the reactor, pH electrode problems, or because the process liquid has rapid and wide variations in quality and quantity.

Calcium hydroxide [$Ca(OH)_2$] is a cheap chemical, so it is widely used in neutralization as a base reagent. Because its solubility is quite low, 1.16 g/L at 25 °C, sufficiently large continuous flow reactors are needed to complete the neutralization reactions before the flow reaches the output point of the reactor. The dominating time constant in a stirred tank reactor must be at least 15 min. Calcium hydroxide is supplied to the reactor as a lime slurry, for example 10% by weight. The preparation of the lime slurry calls for large equipment investment. When very large amounts of base are needed, solid lime, quicklime CaO, or even limestone ($CaCO_3$) can be used as the reagent. In these cases the accuracy of the supplying devices limits the quality of pH control (14). If process liquids including sulfuric acid (H_2SO_4) are neutralized with lime, precipitation of calcium sulfate may cause problems. Sodium hydroxide (NaOH) is an easy-to-handle base, but it is four times as expensive as lime. Sulfuric acid is widely used as an acid reagent. Its use is inhibited by the maximum allowed concentration of sulfates (in wastewater, about 300 to 400 mg/L). The cheapest source of acid reagent, carbon dioxide (CO_2), is flue gas. Its use in the neutralizing alkaline wastes is limited by the high cost of the equipment needed.

When the process liquid is either acidic or alkaline, both acid and base reagents are needed for neutralization. This requires additional investment in supply devices. When acidic and alkaline waste amounts alternate, it is often beneficial to construct an assembly vessel before the neutralization reactor for maximal self-neutralization and to avoid using two reagents; see Fig. 19.

In many basic scientific papers, the large sensitivity of the pH-process is said to be the main problem in the pH-control (15). This is based on the simplest model of the pH-process—the strong acid–strong base model in dilute water solutions. In this theoretical case no buffering com-

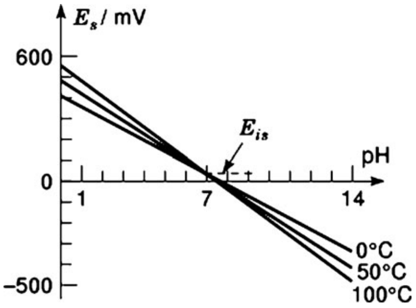

Figure 11. A wastewater neutralization plant in a dairy.

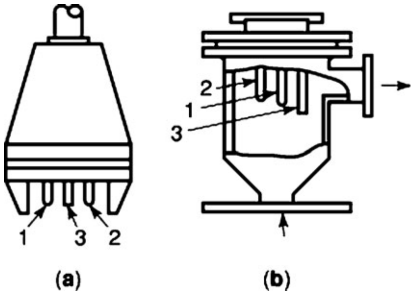

Figure 12. A neutralization reactor with a holding tank and recycle.

ponents exist, and the very high demand of the rangeability of the reagent supply devices is connected to the enormous sensitivity. When reactors with good mixing include a dead time of 5% to 10% of the dominant time constant and the accuracy of the reagent supply devices is limited while the pH-sensor has a small time constant, the whole task seems impossible. However, the situation is never quite so difficult.

For instance, the alkalinisation of turbine water consists of adding strong base to demineralized water. There is always soluted carbon dioxide present, which decreases the demand of reagent addition accuracy considerably. In this case, the pH step is 3 units from ca. 5 to 8. Because of the buffering, the dosage accuracy demand is much less than three decades. In almost every practical control task many additional buffering salts are present, and many decades of the accuracy demand are left away.

In practical sensitive pH-processes, the S-shape of the titration curve is still quite strong, and the sensitivity is high near the neutral point. However, in most cases the high frequency oscillation around the setpoint (usually the neutral point) in the pH-control is less dangerous than long period offsets far from the setpoint. For this reason the authors have the opinion that the main difficulty from the algorithmic point of view is the nonlinear dependence of the pH-value on the reagent amount. In practice, two parallel reagent supply devices are enough to meet the largest demands of the rangeability in the control of the most sensitive pH-processes.

pH Control in Stirred Tank Reactors

Different Algorithm Types. The difficulty of controlling neutralization processes in continuous-flow, stirred, tank reactors arises from two basic features: the nonlinearity of the process and the changes in this nonlinearity based on the buffering effects caused by varying species. Poor pH control can be improved by adding mixing capacity in series with the neutralization reactor, thus attenuating oscillations that exceed allowable limits. When the process flow is very large, this method is very expensive; see Fig. 20.

If the process sample titration curves are not steep and do not vary in shape (large but constant buffering), the usual PID-feedback can be used for pH control. Even on–off control or ratio control using the throughput flow may be adequate. If the titration curves are quite nonlinear but do not vary much in shape (small but constant buffering), a fixed nonlinear reshaping element in the feedback PID-control can be used. Feedforward control based on a fixed titration curve shape can also be combined with feedback control. When the titration curve shapes change significantly, adaptive controls strategies that take into consideration changes in the process gain on-line give the best results.

Constant Parameter Algorithms. Based on electroneutrality, it can be shown that when the concentrations of weak (buffering) components are constant and only concentrations of the strong component change, all of the titration curves (pH vs. strong reagent concentration) have the same shape. When the concentration of the strong reagent is very high compared to the other concentrations, the pH titration curves versus the reagent flow also have similar shapes. These kinds of titration curves can be used in the constructing the feedback or feedforward-feedback control. Construction of the feedforward control is presented in Fig. 21(a) and 21(b). The amount of acid reagent with different values of input pH, pH_1, pH_2, and pH_3, can be read from the horizontal axis. The quantity $\mathrm{pH}_{\mathrm{ref}}$ is the set point value of the pH. Now the reagent demand Q_{C} can be calculated as $Q_{\mathrm{C}}/Q_{\mathrm{P}} = f_1(\mathrm{pH}_{\mathrm{ref}}) - f_1(\mathrm{pH}_{\mathrm{input}})$. The process liquid flow Q_{P} can change and thus the feedforward control action Q_{CFF} obeys the following equation:

$$Q_{CFF} = [f_1(pH_{\mathrm{REF}}) - f_1(pH_{\mathrm{INPUT}})]Q_P \tag{49}$$

The function f_1 (the titration curve shape in Fig. 21(b)) is easy to realize with a microprocessor by defining a suitable number of points and using interpolation. In constructing the feedback, the same titration curve shape can be used (Fig. 22). If the process flow Q_{P} changes markedly the feedback PID-algorithm can be flow-adaptive:

$$\begin{aligned} Q_{\mathrm{CFB}} = {} & \frac{Q_P(k)}{Q_{\mathrm{PNM}}} K_P \left[e(k) + \frac{T_D Q_{\mathrm{PNM}}}{Q_P(k)} \cdot \frac{e(k) - e(k-1)}{\Delta T} \right] \\ & + \sum_{i=1}^{k} \frac{K_P Q_P^2(i)}{T_I Q_{\mathrm{PNM}}^2} e(i) \Delta T \end{aligned} \tag{50}$$

where K_{P}, T_{I}, and T_{D} are the tuning parameters of the PID-controller, Q_{PNM} is the operating point value of the process flow (the point at which the controller has been tuned), and $Q_{\mathrm{P}}(k)$ is the instantaneous value of the process flow. If the feedforward and feedback algorithms are connected, the final control is given by $Q_{\mathrm{C}} = Q_{\mathrm{CFF}} + Q_{\mathrm{CFB}}$. If the input pH value cannot be measured, the operating point value can be added to this position PID-algorithm. The final control law is given by $Q_{\mathrm{C}} = Q_{\mathrm{CFB}} + Q_{\mathrm{P}}(k)Q_{\mathrm{CFBNM}}/Q_{\mathrm{PNM}}$, where Q_{CFBNM} is the operating point value of the feedback control Q_{CFB}.

The suitable size for the time constant of the mixing reactor with soluble reagents is about 0.5 min to 3 min. Only in cases of constantly highly buffered process liquids can the neutralization reactor consist of the chamber of an efficient pump or static mixer.

Adaptive Algorithms. When shape of the titration curve changes significantly, feedforward control is not very effective, and consequently adaptive algorithms are needed. Analysis of the past trajectory is the basis for the adaptive feedback control method developed by Welfonder et al. (16). The method is realized with a minicomputer, and it has been tested in an actual wastewater treatment plant. Foxboro Inc. has presented a commercially available adaptive unit controller Exact (17) that also examines the past trajectory (during a waiting period) whether it is oscillating or overdamped. If needed, a new PID-tuning (using a specific tuning algorithm) is used after each waiting period. A narrow deadband around the reference pH value avoids adaptation to noise. This controller has been widely used in pH control, but it is suited only to systems with continuous pH measurement. Subsequently, other instrument manufacturers have made their own versions of this type of controller.

Another adaptive method that does not include any modeling knowledge was developed by Kurz (18). In this method the adaptation mechanism tries to manipulate the gain of the PID-controller so that the measured pH approaches the reference value along a reference trajectory. This method has been applied in industrial wastewater treatment plants.

The commercially available ASEA Novatune controller has also been applied to pH control. Its function is based on identifying a nonphysical time-series model, and it uses the self-tuning control principle (19). Another method which does not include an exact model is the self-organizing fuzzy controller. It has two fuzzy logic hierarchies. The higher hierarchy adapts the ordinary lower level fuzzy controller to meet changing process conditions. This control method has been applied to the control of an ammonia gas scrubber (13). The self-organizing Kohonen map has also been successfully applied to pH control (20). On the other hand, neural back-propagation algorithms do not apply as well to adaptive pH control.

Kaesser has developed an adaptive feedback control algorithm based on an approximate process model. In his method the slope of the titration curve is estimated and used in tuning the feedback PI-control loop (21). This method has also been applied in neutralizing industrial wastewater. Gustafsson and Waller (22) and Jutila and Visala (23) used more complex physicochemical models closer to practical processes. In these papers model knowledge was also included in designing adaptive control algorithms. The variables to be identified were concentrations of reaction invariants or hypothetical species, and with this knowledge it was possible to construct an instantaneous titration curve and to linearize the PID-control loop. These algorithms were tested by simulation and laboratory-scale pilot plants.

Lee et al. constructed an algorithm including the physicochemical model of one weak acid. Both the dissociation constant and the concentration of this weak acid were identified and used in the linearizing the control. Only simulation tests were made with a process model differing slightly from the identification model (24). The model reference approach of the pH control made by Pajunen includes a Wiener model (25). Simulation and pilot plant control results are presented in that paper. Many simulation articles have been published, in which advanced control concepts are developed for simple, precisely known processes. Problems may occur in real-life application of such methods, because an accurate model is included in the control algorithm. Model predictive algorithms may turn out to be an interesting choice for pH control, but there are still few actual applications.

Tracking Control

The control of batch fermenters in producing enzymes is a good example of tracking control of pH. Both the growth of the biomass and the production of the enzyme can be controlled with the pH and temperature. It has been shown that keeping these factors constant lowers production compared to the case where these factors change based on optimizing certain growth and production models.

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