pH-metry

Operational definition of pH: The utility of pH as a measure of the acidity and alkalinity of aqueous media, the wide availability of commercial glass electrodes, and the relatively recent proliferation of inexpensive solid state pH-meters have made the potentiometric measurement of pH perhaps the most common analytical technique in all of science. It is thus extremely important that pH be defined in a manner that is duplicated at various times and in various laboratories through out the world. To meet this requirement, it is necessary to define pH in operational terms- that is, by the way the measurement is made. Only then will the pH measured by one worker be the same as that by another.

$$E_{cell} = (E_{ind} - E_{ref}) + E_j \rightarrow (1)$$

For a cation X^{n+}, at 25°C, the Nernst equation: $E_{ind} = L + (0.059/n)\log a_x \rightarrow (2)$

where L is a constant and a_x is the activity of the cation. For metallic indicator electrodes, L is ordinarily the standard electrode potential; for membrane electrodes, L is the summation of several constants, including the time-dependent asymmetry potential of uncertain magnitude.

Substitution of equation (2) to equation (1)yields with rearrangement,

$$px = -\log a_x = -\{E_{cell} - (E_j - E_{ref} + L)\}/0.059/n \rightarrow (3)$$

The constant terms in parentheses can be combined to give a new constant K.

$$px = -\log a_x = -(E_{cell} - K)/0.059/n \rightarrow (4)$$

For an anion A^{n-}, the sign of equation (4) is reversed:

$$pA = (E_{cell} - K)/0.059/n = n(E_{cell} - K)/0.059 \rightarrow (5)$$

All direct potentiometric methods are based upon equation (4) and (5).

Let us consider, for example, the glass/calomel system. When these electrodes are immersed in a standard buffer, equation (4) applies and we can write:

$$pH_S = -(E_S - K)/0.059 \rightarrow (6)$$

where E_S is the cell potential when the electrodes are immersed in the buffer. Similarly, if the cell potential is E_U when the electrodes are immersed in a solution of unknown pH, we have,

$$pH_U = -(E_U - K)/0.059 \rightarrow (7)$$

By subtracting the first equation from the second and solving for pH_U, we find:

$$pH_U = pH_S - (E_U - E_S)/0.059 \rightarrow (8)$$