

Discussion on the Measurement of Solution pH Quantity

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Abstract: This paper discuss the reason why it is impossible to adopt strict thermodynamic treatment and accurately measure the quantity of solution pH. Taking three batteries as an example, the principle, hypothetical conditions and ionic strength of the method of measuring electromotive force are described in detail. At the same time, the quantitative data of the experiment about pH are given as evidence, and the rationalization error analysis is proposed.

Keywords: Determination of pH; Single ion activity; Stand buffer solution; Debye-Huckel limit formula; Ionic strength;

1. Introduction

During a kinetic study in acetate buffers, we observed that the measured pH values were always a little lower than the ones expected, based on calculations. The explanation was the complex relation between the pH meter reading and the activity of hydrogen ions.

$$\alpha_{H^+} = [H^+]y_{H^+} \quad (1)$$

where $[H^+]$ is concentration, and y_{H^+} is the activity efficient on the molar scale.

A brief recall of the theory will clarify the problem. Chemical equilibrium and electromotive forces of cells depend on activities, not concentrations. So the original definition of pH by Sorensen was subsequently modified to

$$pH = -\log \alpha_{H^+} \quad (2)$$

Electrolyte solution contains positive and negative ions, and there is interaction between ions. It belongs to non-ideal solution system [1]. Therefore, in the thermodynamic formulas related to the number of electrolyte ions, ionic activity should be used instead of concentration. However, since the activity of a single ion can not be measured, the average value of the activity coefficient of an ion can be obtained by the relevant experimental methods. This is only a notional definition because a single ion activity is immeasurable. Experiments only give mean activities efficient. For example, in HCl solution we can measure but not the individual values y_{H^+} and y_{Cl^-} .

$$[H^+][Cl^-]y_{\pm} = (y_{H^+}y_{Cl^-})^{1/2} \quad (3)$$

The left-hand side of the following equation can be known exactly, but the two terms on the right-hand side cannot be separated without a non-thermodynamic as-

sumption. This is why the practical pH scale is based on standard reference solutions.

$$-\log 10y_{\pm}^2 + [H^+] = pH - \log 10y_{Cl^-} \quad (4)$$

The procedure used to obtain the pH of these solutions (pH(S)) illustrates the problem.

2. Standard Buffer Solution

Consider the following cell without a liquid junction.

Pt|H₂(p[⊖]) | Buffer solution, KCl (Saturated solution) || AgCl(s) | Ag(s)

Its potential is given by

$$E = E^{\ominus} - RT \ln 10 / F \times \log(\alpha_{H^+} + \alpha_{Cl^-}) \quad (5)$$

Rearranging, we get

$$\log(\alpha_{H^+} + \alpha_{Cl^-}) = (E - E^{\ominus})F / RT \ln 10 + \log[Cl^-] \quad (6)$$

From the measured E and the standard potential E^{\ominus} , $\log(\alpha_{H^+} + \alpha_{Cl^-})$ is obtained. This quantity is measured for several values of $[Cl^-]$, plotted against $[Cl^-]$ and extrapolated to $[Cl^-] = 0$, giving $(\log(\alpha_{H^+} + \alpha_{Cl^-}))_0$. Because y_{Cl^-} depends on all the ions in the solution, $(y_{Cl^-})_0$ is not equal to 1. Here non-thermodynamic assumption must be introduced: the Bates-Guggenheim convention.

$$\log y_{Cl^-} = -A|I|^{1/2} / 1 + 1.5|I|^{1/2} \quad (7)$$

where A is the Debye-Huckel limiting slope, and I is the ionic strength ($I < 0.1$). The pH scale is then defined by the following equation for some standard buffers.

$$pH(S) = (\log(\alpha_{H^+} + \alpha_{Cl^-}))_0 + (-\log y_{Cl^-})_0 \quad (8)$$

It is clear that the value with pH is repeatable and stable for the standard buffer solution, the buffer capacity is strong and easy to prepare, and the ionic strength of the

solution I less than 0.1. Obviously, pH(S) is close to log α_{H^+} only if we can use eq (7), and the meaning of the pH on this scale is only operational.

Through the above discussion, it can be seen that the calibration of pH value of standard buffer solution is not entirely determined by experiment [1]. When calculating γ_{Cl^-} with Debye-Shocker limit formula, a non-thermodynamic hypothesis is introduced. The rationality of the hypothesis is verified. When the concentration of solution is lower, the calculated γ_{Cl^-} values by Debye-Shocker limit formula are in good agreement with the experimental values, which shows that the limit formula is credible and the results obtained are reasonable. However, the Debye-Shocker Limit Formula is applicable to solutions with I < 0.1, so it is impossible to use battery a to measure the pH value in practice as calibrated standard buffer solution .

3. Determination and Discussion of pH Value of Calibrated Solution

Usually, pH values are measured with the following cell calomel electrode |KC(2.0M)| solution| glass electrode (b).

This cell is calibrated with a pH of standard buffers. Because the saturated potassium chloride solution contained in the saturated calomel electrode acts as a salt bridge and the pH value of the standard solution is close to that of the solution measured, the potential of the battery during the two measurements is very small and can be approximately equal, and the pH is calculated by (9).

$$pH(X) = Ph(S) + [E(S) - E(X)] \times F / RT \ln 10 \quad (9)$$

where S denotes the standard and X the test solution. The value so obtained is correct only if the liquid junction potential is the same with both solutions.

If the ionic strength of the solution is more than 0.1, the error of γ_{Cl^-} value calculated by Debye-Shocker limit formula will be larger, and the error of pH value obtained by formula (9) will be larger, but such measurement can also meet the practical demand to a certain extent.

It is generally admitted that the difference between the liquid junction potentials is small and reproducible because it is determined by the high KCl concentration and is quasi-independent of the composition of the measured solution [3]. this is only true with a carefully designed liquid junctions when the ionic strengths of the standard and the test solution are not too different. Use of a cell without liquid junction does not prevent the problem due to the effect of ionic strength. For example, if we use cell and eq (9), we must know the activity coefficient of the Cl^- . However, we must remember that activity coefficients are affected by all the ionic constituents of the solution. Tabulated values for pure salts are of little help for

real mixtures, and eq (9) is only valid for low ionic strengths. Even the pH of the stand solution cannot be obtained exactly using eq (9) for cell because the activities of chloride ions should be the same in the test and the standard solutions [4].

4. Determination and Discussion of pH Value of Acetic Acid Buffer Solution

We have measured the pH of a series of acetate buffers at 25 °C with a glass electrode (Tacussel TG100) and a calomel reference electrode (Tacussel TR100). The system was calibrated with Merck Titrisol buffers of pH 4 and 7 using a bracketing procedure. The slope of the electrode was near the Nernst slope. For each series of measurements we took the same concentrations of NaAc and HAc but different amounts of NaNO₃ to vary the ionic strength. Some results are given in the table, where a, s, and i are the numbers of mol/L of added HAc , NaAc , and NaNO₃ . The measured values pH mes decrease when the NaNO₃ concentration increases. Let's compare this observed effect with the expected effect of the ionic strength.

Table 1. Effect of the ionic strength on pH

a×10 ³	s×10 ³	i	pH mes	pH cal	ΔpH
2.04	0.5	0	4.11	4.13	0.02
2.04	0.5	0.12	4.02	4.08	0.06
2.04	0.5	0.23	4.00	4.10	0.10
2.04	0.5	0.44	4.00	4.11	0.11
1.02	0.5	0.23	4.30	4.31	0.01
1.02	2.00	0	4.89	4.94	0.05
1.02	2.00	0.23	4.77	4.88	0.11
1.02	2.00	0.12	4.67	4.74	0.07
1.02	2.00	0.44	4.65	4.78	0.13

The H⁺ concentration can be calculated exactly resolving the following three equations by an iterative method if the apparent dissociation constant K_a is known.

$$\alpha = [H^+] + [HAc] \quad (10)$$

$$\alpha + s = [Ac^-] + [Ac] \quad (11)$$

$$[H^+] + [Ac^-] = K\alpha [HAc] \quad (12)$$

The thermodynamic value of the dissociation constant is well-known, but we need the apparent value K_a.

$$K_a^\ominus = \alpha_{H^+} \alpha_{Ac^-} / \alpha_{HA} = 1.754 \times 10^{-5} (25^\circ C)$$

$$K\alpha = K^\ominus \alpha_{HAc} / \gamma_{H^+} \gamma_{Ac^-}$$

In order to simplify the calculation, we choose the semi-empirical constant D and take $K\alpha = K^\ominus \alpha / \gamma D^2$

$$-\log \gamma D = 0.51 \times I / 2 + I / 2 - DI \quad (13)$$

We take D = 0.18 and I ≤ 0.5M M. The calculated values (pH cal) in the table 1 are obtained by resolving eqs (10)–(12).

Values of ΔpH are reproducible and independent of the pH . They are always positive and increase with I . There could be two reasons for this variation: pH_{cal} is only an approximation of $-\log\alpha\text{H}^+$; pH_{mes} depends on the residual liquid junction potential. We have noted that a 50% decrease of D gives only a decrease of 0.02 unit of pH_{cal} if $I = 0.27$. Thus, we conclude that the differences between pH_{cal} and pH_{mes} are mainly (but not only) due to the residual liquid junction potential. The usual assumption that the liquid junction potential is constant is thus a rough approximation even for moderate ionic strength. This potential depends on the kind and shape of the junction, and free-diffusion junctions give better results. However, in the common practice we use commercial junctions of this last kind, and the error may be large. For moderate ionic strength, we see that the error may be larger than 0.1 unit even when the measurements are reproducible [5].

5. Conclusion

Much meaningful work has been done to study the calculation of pH . Most of these works give the exact value of $-\log[\text{H}^+]$ by means of mathematical calculation. It is important to realize that $-\log\alpha\text{H}^+$ cannot be calculated exactly because γH^+ cannot be calculated exactly. Also, the liquid junction potential is not always negligible. In the common practice we cannot hope to get differences between calculated and measured pH values less than 0.02, and we should not be surprised if they are much

larger. A second conclusion arises from the start of this paper. Consider a reaction in solution of rate order n with respect to $[\text{H}^+]$. For the kinetic constant k , a simple error calculation gives

$$dk/k = 2.3n d\log[\text{H}^+] \quad (14)$$

If we use pH values instead of $\log[\text{H}^+]$, then the kinetic constant includes a conventional activity efficient. It is conventional because the pH scale is conventional. Also, an error of 0.05 unit of pH gives an error on k of 11.5% if $n = 1$ and 23% if $n = 2$. It is much more difficult than usually realized to measure kinetic constants for acidity-dependent reactions.

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