

THE pH VALUE, AN IMPORTANT PARAMETER IN ANALYTICAL SEPARATION METHODS

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ABSTRACT

Owing to the fact that pH is one of the most important factors governing separations, its concept is more deeply investigated. It is shown that the true (or non-isothermal) temperature coefficient of the electrode potential of an electrode is an absolute physical quantity depending on the individual activity of the electrochemically active ionic species determining the electrode potential of an electrode. This temperature coefficient is experimentally measurable and a way is therefore given of obtaining the individual activity coefficient (and thus also the pH) of ionic species provided that the correction term arising from the ionic heats of transport is correctly evaluated. The first experimental results obtained show activity coefficients that agree within some units per cent with those theoretically calculated following the Debye-Hückel theory.

Many analytical processes in solution require as a necessary condition for the success of the qualitative identification or of the quantitative determination, that the pH of the medium be rigorously fixed, otherwise uncertainties or even important systematic errors may arise. Moreover, the pH is of great importance in a broader analytical sense for many other determinations, for example that of the stability constant of complexes.

The pH is considered an obvious and easily reproducible quantity and this is sometimes true from a purely operational point of view. But a deeper consideration of the real meaning of pH immediately shows that this opinion can no longer be supported. In fact, an unambiguous theoretical definition of pH must be based on the concept of the individual activity of the hydrogen ions, a quantity that up to now is thought to be experimentally inaccessible. Therefore an operational definition¹ of pH (not of the hydrogen ion activity) was adopted and is currently used. It is known that this operational definition is based on the potentiometry of particular galvanic cells using dilute solutions of some selected buffers. This approach is the best one at our disposal today, but in the case where the technique is applied to not too dilute solutions, using galvanic cells with two different electrolytes, i.e. where a considerable potential difference due to the electrolytic junction may occur, highly reliable and reproducible results can no longer be expected (± 1 mV $\approx \pm 0.015$ pH at 25°C). This difficulty is still more exaggerated in the case of non-aqueous solutions for which no operational correlation can be made with the aqueous solutions.

The problem is therefore precisely located in the knowledge of the activities

of individual ionic species. Were it possible to solve this problem, then it would be possible to apply the rigorous theoretical definition

$$\text{pH} = -\log a_{\text{H}^+} \quad (1)$$

which does not depend theoretically on the properties of the solvent. At the same time it would be possible to correlate the properties of aqueous and non-aqueous solutions. All problems connected with a precise knowledge of the pH in any solvent, including the analytical ones, would be soluble.

The problem of activities is older than half a century. In fact this concept was first introduced by G. N. Lewis² about 70 years ago. Since that time many attempts were made, all unsuccessful, to obtain the activity coefficients of individual ionic species; therefore any new attempt to solve this problem is considered with some suspicion. The reason for this unsatisfactory situation is perhaps given by the fact that it is not possible to separate physically pure ionic species: each one is always accompanied by one or more other ionic species carrying an equivalent amount of electric charge of opposite sign. Therefore any theoretical or experimental attempt to solve this problem needs the introduction of some hitherto undemonstrated hypotheses or of some more or less arbitrary reference points to obviate the difficulty of separating the pure ionic species. Until now none of these attempts has been made starting from a physically absolutely measurable quantity, thus giving results always vitiated by the introduced uncertainty. This produced an unclear and ambiguous situation from which the many difficulties and conventions concerning the ionic activities (and in the case being considered the quantity pH) derived.

However, a way of obtaining the activity coefficient of individual ionic species is perhaps possible. Let us consider the general Nernst equation

$$U_{\text{rel}} = U_{0,\text{rel}} + (R T/z F) \ln a_{\text{act}} \quad (2)$$

where a_{act} is the activity on the molality scale of the potential-determining ionic species[†]. This equation expressed in terms of absolute quantities should be written as follows

$$U_{\text{rel}} = U_{0,\text{abs}} - U_{0,\text{abs,H}} + (R T/z F) \ln a_{\text{act}} \quad (3)$$

It is known that the use of equation 3 is the consequence of the impossibility of obtaining absolute electrode potentials. Relative values are therefore currently utilized where conventionally the value 'zero' is arbitrarily attributed to the standard electrode potential of the hydrogen electrode and also the value 'zero' to its temperature coefficient, i.e. considering the value of the temperature coefficient of the standard electrode potential of the hydrogen electrode to be zero. *This second convention is completely wrong*, and thus the weakness of this convention appears in its full extent.

The true temperature coefficient, i.e. the so-called *non-isothermal* tempera-

[†] For simplicity the case that *only one* ionic species is active in determining the electrode potential of the electrode is considered. More complex equations must, of course, be used for more complex electrode reactions, without any change of the theoretical considerations.

AN IMPORTANT PARAMETER IN ANALYTICAL SEPARATION METHODS

ture coefficient (see below) of the general electrode considered in equation 3 is the temperature derivative of its electrode potential

$$(dU_{\text{rel}}/dT) = (dU_{0,\text{abs}}/dT) + (R/zF) \ln m_{\text{act}} + (R/zF) \ln \gamma_{\text{act}} + (R T/zF) (d \ln \gamma_{\text{act}}/dT)_m \quad (4)$$

In equation 4 the term $(dU_{0,\text{abs}}/dT)$ is omitted because the *true* temperature coefficient is considered, viz. only the increment of the electrode potential of the electrode investigated as a function of the temperature increment, independently of the behaviour of the reference electrode (the standard hydrogen electrode) held at constant temperature and therefore at constant electrode potential. The temperature derivative $dU_{0,\text{abs}}/dT$ is thus equal to zero.

Theoretically it is always possible to consider the absolute instead of the relative electrode potential, given by equation 5

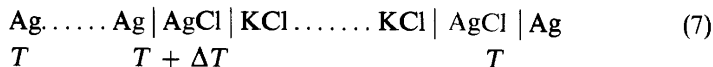
$$U_{\text{abs}} = U_{0,\text{abs}} + (R T/zF) \ln a_{\text{act}} \quad (5)$$

The temperature derivative of equation 5, i.e. the temperature coefficient of the absolute electrode potential is given by equation 6

$$(dU_{\text{abs}}/dT) = (dU_{0,\text{abs}}/dT) + (R/zF) \ln m_{\text{act}} + (R/zF) \ln \gamma_{\text{act}} + (R T/zF) (d \ln \gamma_{\text{act}}/dT)_m \quad (6)$$

The identity of the right hand terms of equations 4 and 6 is evident and it follows that the non-isothermal temperature coefficient of the relative electric (experimentally measurable) tension is identical with the temperature coefficient of the absolute electrode potential of the same electrode. This means that, even if the absolute electrode potential of an individual electrode cannot be obtained by direct measurement, or by computation, it is still possible to obtain its temperature coefficient *free* of any more or less arbitrary hypothesis or convention. In this way it can be experimentally verified that the temperature coefficient of the electrode potential of the standard hydrogen electrode is somewhat less than 1 mV/deg. C, not at all a negligible quantity, which clearly demonstrates how wrong is the second commonly adopted convention concerning the hydrogen electrode.

It can easily be shown that the non-isothermal temperature coefficient of the absolute electrode potential of an electrode can be experimentally obtained on the basis of an appropriate non-isothermal galvanic cell. For simplicity the following considerations will be applied to a practical example such as the cell given by scheme 7



The non-isothermal temperature coefficient of the electric tension of the Ag|AgCl|KCl electrode is the limit of the ratio of the measured electrode potential $N^{n,i}$ of galvanic cell 7 over the temperature difference ΔT for $\Delta T \rightarrow 0$

$$dU/dT = (U^{n,i}/\Delta T)_{\Delta T \rightarrow 0} \quad (8)$$

It can be determined experimentally that the value of the ratio ($U^{n,i}/\Delta T$) becomes constant with decreasing ΔT from a certain value of ΔT equal to about 10 deg. C. For $\Delta T \approx 10$ deg. C equation 9 therefore holds true

$$dU/dT = U^{n,i}/\Delta T \quad (9)$$

In galvanic cell 7 a number of contributions to the electrode potential must be considered and the complete equation for the experimental temperature coefficient as a measurable quantity is given³ by equation 10

$$\begin{aligned} (dU/dT)_{\text{exp}} = & \underbrace{(dU_0/dT)}_{\text{I}} + \underbrace{(R/zF) \ln m_{\text{Cl}^-}}_{\text{II}} + \underbrace{(R/zF) \ln \gamma_{\text{Cl}^-}}_{\text{III}} \\ & + \underbrace{(RT/zF) (d \ln \gamma_{\text{Cl}^-}/dT)_m}_{\text{IV}} + \underbrace{(dU/dT)_{\text{Ag}}}_{\text{V}} - \underbrace{(1/F T) \Sigma(t_i Q_i^*/z_i)}_{\text{VI}} \\ & - \underbrace{(1/F) (K^* \partial \mu_{\text{tot}}/\partial m - \partial \mu_{\text{Cl}^-}/\partial m) (dm/dT)_{\text{stat}}}_{\text{VII}} \\ & - \underbrace{(1/F) (\partial \mu/\partial m)_{\text{Cl}^-} (dm_{\text{Cl}^-}/dT)_{\text{stat}}}_{\text{VIII}} \end{aligned} \quad (10)$$

where the terms I, II, III and IV concern the electrode reaction and thus give the true temperature coefficient of the electrode potential of the $\text{Ag} | \text{AgCl} | \text{Cl}^-$ electrode, and the terms V, VI, VII and VIII are correction terms still to be considered in detail to ascertain whether and how much they influence the quantity investigated. Term V is due to the homogeneous electric tension developed within the metallic conductor (Ag) under the temperature gradient (Thomson effect) and is constant at a given temperature. The order of magnitude of this term is but a few $\mu\text{V}/\text{deg. C}$, i.e. of the same magnitude as the experimental error and can therefore be neglected. In any case, if required, it can be calculated on the basis of the data tabulated for the Thomson effect⁴. In the following this term will be omitted, considering it to be negligible or already included in the term $(dU/dT)_{\text{exp}}$. Term VI gives the homogeneous electrode potential, developed within the solution under the temperature gradient, arising from the existence of the ionic heats of transfer Q_i^* . It is the analogon of the Thomson effect for the electrolytic solution. In a solution submitted to a temperature gradient thermodiffusion produces, after a certain time, a stationary concentration difference between cold and warm half cells (Soret effect) originating another contribution of electrode potential like that of a concentration cell given by terms VII and VIII. In the absence of Soret effect, with strictly equal molalities in both half cells (i.e. at the initial state before thermodiffusion destroys the equality of molalities or when thermodiffusion is experimentally inhibited) terms VII and VIII disappear.

To obtain the true temperature coefficient of the electrode potential of the electrode from measurements on the thermogalvanic cell 7 in its initial state only term VI must still be evaluated. This evaluation will be discussed later on. For the time being it can be stated, at least as a working hypothesis, that term VI for the particular galvanic cell 7 can be evaluated. It can therefore be subtracted from equation 10 and no longer need be considered explicitly. Once the temperature coefficient of the $\text{Ag} | \text{AgCl} | \text{Cl}^-$ electrode is accurately known, it will be possible by appropriate combination of suitable electrode

pairs in isothermal galvanic cells at different temperatures to obtain the true temperature coefficient of the electrode potential of other electrodes⁵.

Let us reconsider equation 10 for galvanic cell 7 at the initial state, when terms VII and VIII are really equal to zero, further omitting explicitly terms V and VI either because they are negligible or because they may be evaluated and included in the term $(dU/dT)_{\text{exp}}$. Equation 10 can then be reduced to

$$(dU/dT)_{\text{exp, init.}} - (R/zF) \ln m_{\text{Cl}^-} = (dU_0/dT) + (R/zF) \ln \gamma_{\text{Cl}^-} + (R T/zF) (d \ln \gamma_{\text{Cl}^-}/dT)_m \quad (11)$$

The LHS of equation 11 consists of experimentally measurable quantities and tends to the limiting constant value (dU_0/dT) when the molality of the electrolyte tends to zero, because the activity coefficient tends to a constant value of one independently of the temperature. The last two terms of equation 11 therefore vanish by extrapolation of $m \rightarrow 0$ and the term (dU_0/dT) can be obtained from a series of measurements at decreasing molality.

Coming back to a finite molality, two measurements can be carried out at the same molality at two different mean temperatures T_1 and T_2 . The following equations then hold true:

$$(dU/dT)_{\text{exp, init. } T_1} - (R/zF) \ln m_{\text{Cl}^-} - (dU_0/dT)_{T_1} = (R/zF) \ln \gamma_{\text{Cl}^- T_1} + (R T/zF) (d \ln \gamma_{\text{Cl}^-}/dT)_{m, T_1} \quad (12)$$

$$(dU/dT)_{\text{exp, init. } T_2} - (R/zF) \ln m_{\text{Cl}^-} - (dU_0/dT)_{T_2} = (R/zF) \ln \gamma_{\text{Cl}^- T_2} + (R T_2/zF) (d \ln \gamma_{\text{Cl}^-}/dT)_{m, T_2} \quad (13)$$

By choosing the temperature interval $\langle T_1 - T_2 \rangle$ small enough so that the derivative $(d \ln \gamma_{\text{Cl}^-}/dT)_m$ can be considered constant within the interval the following equation 14 can be written

$$\ln \gamma_{\text{Cl}^- T_2} = \ln \gamma_{\text{Cl}^- T_1} + (d \ln \gamma_{\text{Cl}^-}/dT)_m \Delta T \quad (14)$$

where $\Delta T = T_2 - T_1$.

Substituting equation 14 into 13 and rearranging the system of equations 12 and 13 the relationships become:

$$(dU/dT)_{\text{exp, init. } T_1} - (R/zF) \ln m_{\text{Cl}^-} - (dU_0/dT)_{T_1} = (R/zF) \ln \gamma_{\text{Cl}^- T_1} + (R T/zF) (d \ln \gamma_{\text{Cl}^-}/dT)_m \quad (15)$$

$$(dU/dT)_{\text{exp, init. } T_2} - (R/zF) \ln m_{\text{Cl}^-} - (dU_0/dT)_{T_2} = (R/zF) \ln \gamma_{\text{Cl}^- T_1} + R(T_2 + \Delta T)/zF (d \ln \gamma_{\text{Cl}^-}/dT)_m \quad (16)$$

Equations 15 and 16 now constitute a system of two equations with only two unknowns and can be solved to give the roots $\ln \gamma_{\text{Cl}^- T_1}$ and $(d \ln \gamma_{\text{Cl}^-}/dT)_m$.

The magnitude of the temperature interval within which $(d \ln \gamma_{\text{Cl}^-}/dT)_m$ can be considered constant is not known *a priori*, it must be found experimentally by gradually narrowing it until the values of both roots of the system of equations 15 and 16 no longer change.

The evaluation of the correction term containing the individual ionic heats of transfer must now be discussed. The experimental data on the Soret effect provide the global heat of transfer of an electrolyte, in this case of KCl, which must be divided into two contributions, to fit equation 10. No rigorous thermodynamic criterion exists for this division but some criteria can be utilized to indicate which division is most probable. The first criterion states that any possible division must produce values of γ_{Cl^-} within the limits

$$1 > \gamma_{\text{Cl}^-} > \gamma_{\pm}^2 \quad (17)$$

Any division of $Q^*(\text{KCl})$ giving values of γ_{Cl^-} outside the limits indicated by equation 17 is not acceptable because it contradicts experience. The second criterion states that for sufficiently dilute solutions, for which the Debye-Hückel theory holds true, the correct division of $Q^*(\text{KCl})$ in $Q^*(\text{K}^+) + Q^*(\text{Cl}^-)$ must give values of γ_{Cl^-} in agreement with the calculated theoretical ones⁶. Finally, extending the investigation to the largest possible number of non-isothermal cells and electrolytes, the division of $Q^*(\text{KCl})$ utilized as the starting point to obtain the ionic Q^* values of any other ionic species must be such that no contradiction with experimental results arises. The uncertainty of the results will thus be reduced more and more until results with the same magnitude of uncertainty as the experimental error arise. Once the correct division of Q^* for KCl is known, appropriate combinations of electrolytes in thermocells and in Soret effect experiments will provide all other values of ionic Q^* s and γ s.

Work is in progress at present in my laboratory to test these ideas and perhaps the best way to conclude this article is to show some provisional results concerning the activity coefficients of Cl^- calculated following the concepts given above and using as a first approach the division of $Q^*(\text{KCl})$ into equal contributions by K^+ and Cl^- , i.e. $Q^*(\text{Cl}^-) = Q^*(\text{K}^+) = \frac{1}{2} Q^*(\text{KCl})$.

The reason for this choice is that K^+ and Cl^- have many physicochemical properties with practically the same numerical value: transference number, hydration, ionic dimensions etc. This partition has another particular advantage; the correction term VI of equation 10 in this case vanishes completely because the transference numbers of K^+ and Cl^- are equal also. The results are collected in *Table 1*.

Table 1. Ionic activity coefficients of Cl^- in KCl solutions

Molality	Ionic activity coefficients		
	Calculated		From non-isothermal measurements
	Debye-Hückel extended	Kielland ⁷	
0.001	0.965	0.975	0.999
0.002	0.952	0.964	0.992
0.005	0.927	0.945	0.990
0.01	0.902	0.925	0.986
0.02	0.870	0.899	0.982
0.05	0.817	0.851	0.973

AN IMPORTANT PARAMETER IN ANALYTICAL SEPARATION METHODS

The difference between experimental and calculated values is less than ten per cent up to 0.02 units of molality. These results, obtained with such a rough first approximation, are very promising and show that a more careful adjustment of the division and inclusion of the neglected correction term arising from the Thomson effect, refining the experimental technique (chiefly by obtaining highly reliable Q^* values from Soret effect measurements) and extending the experimental basis of research to as many electrolytes as possible will certainly improve these results.

I would consider my present work highly successful if this article stimulates some other colleagues to continue and to extend this research in both theoretical and experimental directions.

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