563. *The Effect of Time and Temperature on Potentials Measured with the Glass Electrode.*

By H. IRVING and R. J. P. WILLIAMS.

Potentials of a glass electrode | buffer | Ag/AgCl system agree with those predicted by the Nernst equation when the temperature is raised progressively, but, on cooling, a hysteresis effect is observed. The implications in the determination of paH are discussed.

WHEN tested on different occasions with fresh portions of the same buffer (0·05M-potassium hydrogen phthalate in 0·5M-potassium chloride), values of $E_{\text{phthalate}}$ for the E.M.F., at 20°, of the cell

Ag/AgCl in 0·1M-HCl	⋮	Glass membrane	⋮	Buffer in 0·1M-KCl	‖	Ag/AgCl in 0·1M-KCl

showed random variations of as much as 4 mv. The same lack of reproducibility characterised similar measurements of E_{borate} with a borate buffer. That changes in the asymmetry potential of the glass electrode were responsible was established by measuring the E.M.F. first with a phthalate buffer and then, immediately after, at the same temperature with the borate buffer. The potential difference

$$\Delta E = E_{\text{phthalate}} - E_{\text{borate}} = (\boldsymbol{RT/F})\,(\text{paH}_{\text{borate}} - \text{paH}_{\text{phthalate}})$$

was now found to be constant to within a few tenths of a mv. on each occasion and its magnitude corresponded, within $\pm 0{\cdot}2$ mv., to the value calculated from the known activity exponents of the buffers and the theoretical value at 20° of the gradient $\boldsymbol{RT/F}$ of the plot of ΔE against paH. Similar experiments at other fixed temperatures confirmed that the difference ΔE between consecutive E.M.F. measurements on the above cell when made up at any time with any chosen pair of buffers was accurately reproducible although individual measurements on either buffer separately were subject to a more or less random drift.

A new series of measurements was next carried out as follows. The E.M.F. of the cell was measured as before at one fixed temperature with phthalate and borate buffers in succession. During two minutes the temperature was raised by 5° and, when thermal equilibrium had again been attained, the E.M.F. measurements were repeated on fresh portions of the same phthalate and borate buffers, previously brought to the desired temperature. Over the range 0—40° the plot of ΔE against T was effectively a straight line of slope 4×10^{-4} v./°c. But if measurements were continued with the two buffers at progressively lower temperatures the values of ΔE at any given temperature were not reproducible and did not correspond with those previously obtained : points for the " cooling " curve sometimes lay on the " heating " curve but more often above it. After some time " normal " values of ΔE were once again obtainable. A similar hysteresis effect could be duplicated by other glass electrodes and other pairs of buffer solutions.

If E_p and E_q are consecutive measurements at any fixed temperature of our cell with buffers of activity exponents $\mathrm{paH_p}$ and $\mathrm{paH_q}$ it is easy to see that the total variation of ΔE with temperature will be a function compounded of the temperature variation of the hydrogen-ion activity of each buffer, and of the multiplier $\boldsymbol{RT/F}$. Explicitly, by differentiating the above equation,

$$\begin{aligned}\partial\Delta E/\partial T &= (\boldsymbol{R}/\boldsymbol{F})(\mathrm{paH_q} - \mathrm{paH_p})_T + (\boldsymbol{RT}/\boldsymbol{F})(\partial\mathrm{paH_q}/\partial \mathrm{T}) - (\boldsymbol{RT}/\boldsymbol{F})(\partial\mathrm{paH_p}/\partial T)\\ &= \quad A \quad + \quad B \quad - \quad C\end{aligned}$$

Values for the gradients B and C for the borate and the phthalate buffer calculated by Hamer and Acree (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 215) and Manor, DeLollis, Lindvall, and Acree (*ibid.*, 1946, **36**, 543) appear in the third and fourth columns of the Table below, which includes calculated values of A. The agreement between the experimental and calculated values of $\partial\Delta E/\partial T$ is seen to be very satisfactory, the effective constancy of the slope being the result of a somewhat fortuitous compensation of three terms of comparable magnitude.

Similar measurements carried out with a phthalate and a phosphate buffer pair confirmed the previous results, a graph of almost constant slope $3{\cdot}1 \times 10^{-4}$ v./°c. being obtained with rising but not with falling temperatures. The agreement between the calculated and experimental values of $\partial\Delta E/\partial T$ shown in the second section of the Table is scarcely less satisfactory, considering the uncertainty which attaches to the long extrapolations involved in assessing the magnitudes of the terms B and C and the greater sensitivity of the hydrogen-ion activity of phosphate buffers to changes of temperature. In the corresponding measurements with three different hydrochloric acid–potassium chloride buffers no allowance has been made for the (unknown) variation of $\mathrm{paH_{HCl}}$ with temperature, but this must clearly be small. Automatic temperature compensation in most commercial pH-meters compensates only for variations in the term A, and the extent to which errors may be introduced by simultaneous variations due to the terms B and C can be inferred from the Table.

				$\partial\Delta E/\partial T \times 10^5$, v./°c.,	
T, °c.	*A*.	*B*.	*C*.	calc.	found.
Borate.					
20	+104·4	−62·8	+ 2·1	+40	+46
25	+103·5	−55·6	+ 8·3	+40	+40
30	+102·3	−51·7	+10·8	+40	+35
35	+101·3	−51·4	+12·2	+38	+36
40	+100·2	−43·5	+14·9	+42	+40
Phosphate.					
16	+56·98	−25·82	+ 1·6	+29·5	+34
20·5	+56·59	−20·97	+ 2·1	+33·5	+32
28·5	+56·94	−11·95	+ 9·3	+35·7	+29
32·0	+55·67	−10·9	+11·4	+33·4	+31
37·5	+55·22	− 6·2	+13·5	+35·5	+31
Hydrochloric acid (1).					
20	−44·5	—	+ 2·1	−47	−43
25	−44·6	—	+ 8·3	−53	−56
30	−44·8	—	+10·8	−55	−53
35	−45·0	—	+12·2	−57	−54
40	−45·2	—	+14·9	−60	−63
Hydrochloric acid (2).					
20	−25·3	—	+ 2·1	−27	−33
25	−25·4	—	+ 8·3	−34	−33
30	−25·5	—	+10·8	−36	−40
35	−25·7	—	+12·2	−38	−36
40	−25·9	—	+14·9	−41	−39
Hydrochloric acid (3).					
20	−6·2	—	+ 2·1	− 8·0	− 8·0
25	−6·3	—	+ 8·3	−15	−11
30	−6·5	—	+10·8	−17	−15
35	−6·6	—	+12·2	−19	−20
40	−6·9	—	+14·9	−22	−22

Measurements with a 0·05M-phthalate buffer of paH (25°) 3·932 alternated with those of buffers *Q* comprising respectively 0·05M-borate of paH (25°) 9·112, M/40-potassium dihydrogen phosphate with M/40-disodium hydrogen phosphate of paH (25°) 6·734, and hydrochloric acid buffers (1), (2), and (3) of paH (25°) 1·681, 2·654, and 3·614. All buffers were 0·1M. with respect to KCl. Columns *A*, *B*, and *C* give the gradients referred to in equation (1) in volts × 10⁵ per °c.

There is abundant evidence that the glass electrode can be relied upon for measurements at constant temperature (cf. Dole, " The Glass Electrode," J. Wiley & Sons, New York, 1941). The present work confirms this and shows, moreover, that it is equally reliable even when the temperature of measurement is varied moderately rapidly, provided always that (*a*) such measurements are made only with an increasing monotonic sequence of temperatures, and (*b*) the intercept of the linear plot of E.M.F. against paH (*i.e.*, the " constant " E_0 of the Nernst equation) is redetermined at each temperature by measurements with one or more buffers of known hydrogen-ion activity. Owing to the relatively large temperature gradient of the quinhydrone electrode (which is, moreover, opposite in sign to that of the Ag/AgCl electrode) glass electrodes containing this internal electrode are unsuitable for measurements of the type recorded above, for the plot of ΔE against T is strongly curved and hysteresis effects were more pronounced. A point of considerable practical importance is the limited degree of efficiency of silvering and chloridising of the internal reference electrodes of some commercial glass electrodes. After but two thermal cycles (20° to 40° and back), one Danish electrode failed completely, and individual electrodes of English manufacture were visibly affected after 50 cycles; others appeared unchanged after as many as 100 cycles.

INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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