LIV. A p_H CHART.

BY GEORGE HOWARD BELL AND
ALEXANDER ROBERT CRAIG PATERSON.

From the Institute of Physiology, the University, Glasgow.

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THIS chart¹ was originally constructed to facilitate calculations on the measurement of p_H by the hydrogen electrode method. It gives, graphically, the solution to the equation

$$p_H = \frac{\text{E.M.F. of chain } (V) - \text{E.M.F. of calomel cell } (v)}{0.000198322 T} \quad \dots\dots(1),$$

or, more generally,

$$p_H = \frac{E}{2.303 \frac{RT}{F}} \quad \dots\dots(2),$$

from p_H 1.5 to 12.0 over the usual laboratory range of temperature, *viz.* 18° to 25°.

This graph has been found to be more convenient than tables such as those of Schmidt and Hoagland [1919], and of more general application than the graph of McClendon [1916].

APPLICATIONS.

(1) *Hydrogen electrode.* From the potential of the chain as found on the potentiometer subtract the E.M.F. (corrected for temperature) of the calomel cell in use. Find this value, designated $V - v$, on the upper edge of one of the sections of the chart, and from it carry a line downwards parallel to the sloping lines till the required temperature line (marked in °C. at the end of each section) is met. From the point of intersection drop a vertical to the lower edge which is marked off in p_H units. It should be possible to read the results to 0.01 p_H unit.

(2) *Glass electrode.* The preceding remarks apply particularly to the hydrogen electrode but it will be remembered that equation (2) is of common occurrence in p_H formulae. The formula for a glass electrode of a character suitable for p_H determinations is

$$E = 2.303 \frac{RT}{F} (p_{H_1} - p_{H_2}) + E_g \quad \dots\dots(3),$$

where E is the potential measured across the membrane, and E_g is the potential when the solutions on either side of the membrane are the same, *i.e.* when $p_{H_1} = p_{H_2}$.

¹ The chart is here reproduced upon a scale which is approximately two-thirds of the original.

From (3)

$$p_{\text{H}_1} - p_{\text{H}_2} = \frac{E - E_q}{2.303 \frac{RT}{F}} \quad \dots\dots(4),$$

which is of the same form as equation (2). The value of $p_{\text{H}_1} - p_{\text{H}_2}$ can therefore be obtained from the graph. p_{H_2} (a standard buffer solution of known p_{H} is used) added to this gives then the value of p_{H_1} .

(3) *The quinhydrone electrode.* The graph is also applicable to this case. In the following chain

Au/quinhydrone sol. of known p_{H} /sat. KCl/sat. calomel cell,

$$p_{\text{H}} = \frac{E_a + e_q}{2.303 \frac{RT}{F}},$$

or
$$2.303 \frac{RT}{F} p_{\text{H}} = E_a + e_q,$$

where E_a is the E.M.F. of the chain, and e_q is a constant.

By using the graph in the opposite direction to that given under "hydrogen electrode" above, one can find a voltage V corresponding to the known p_{H} . Since the graph gives

$$V = 2.303 \frac{RT}{F} p_{\text{H}},$$

then
$$V = E_a + e_q \text{ or } e_q = V - E_a.$$

Now in the following chain of E.M.F. E_x

Au/quinhydrone sol. of unknown p_{H} /sat. KCl/sat. calomel cell,

$$p_{\text{H}} = \frac{E_x + e_q}{2.303 \frac{RT}{F}}.$$

E_x is observed and e_q has been found above. By using their sum in the graph the p_{H} may be read off directly.

It may not be out of place here to make some remarks on the subject of the accuracy of the measurements as illustrated by this graph.

If p_{H} readings to ± 0.01 unit are required it is interesting to note the effect of the temperature. At p_{H} 2-3 it is necessary to know the temperature of the hydrogen half-cell only to the nearest degree. At p_{H} 6.5, 0.01 p_{H} unit corresponds to 0.43° . At p_{H} 10.5, 0.01 p_{H} unit corresponds to 0.27° , and therefore the temperature of the hydrogen half-cell must be known to 0.27° . The increase in the significance of T is shown on the graph by the greater angle that the sloping lines make with the vertical lines as the p_{H} figure increases.

It is customary in ordinary laboratory practice to neglect the effect of barometric pressure. The equation of the hydrogen electrode including the barometric correction, E_{bar} , is

$$p_{\text{H}} = \frac{E_0 + E_{\text{bar}} - E_{\text{cal}}}{0.000198322 T},$$

Chart to Solve $p_H = \frac{V-v}{0.00019832 T}$

where E_0 = observed potential; E_{cal} = potential of calomel electrode. Clark [1928] gives these figures:

At pressure 740 mm. Hg, 20° , $E_{\text{bar}} = + 0.64$ millivolt.

At pressure 780 mm. Hg, 20° , $E_{\text{bar}} = - 0.04$ millivolt.

From the graph it will be seen that $0.01 p_{\text{H}}$ unit is approximately equivalent to 0.5 millivolt. It is obvious that if p_{H} numbers correct to ± 0.01 are required it will be necessary in some experiments to allow for variations in barometric pressure.

It may be objected that this nomogram does not perform the subtraction $V - v$. The slide-rule of D. T. Harris and the nomogram of Grant [1930], which do perform this subtraction, do not claim to be readable, like the present chart, to $0.01 p_{\text{H}}$. On the other hand, where this degree of accuracy is not required, these devices may be more convenient.

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