

**337.** *The Conductivity and  $p_{\text{H}}$  Values of Calcium Hydroxide Solutions at 25°.*

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Existing data on the conductivity of calcium hydroxide solutions at 25° show discrepancies. New data are given which confirm certain of the previously published results. Values of  $p_{\text{H}}$  for calcium hydroxide solutions at 25° are also given and compared with the only other available data, those of Flint and Wells at 30°.

THE solutions were prepared by igniting pure calcium carbonate (British Drug Houses, A.R.) at 1000° to constant weight, slaking the product in conductivity water ( $\kappa = 1 - 2 \times 10^{-6}$ ), and keeping the mixture with intermittent shaking for several days. The solution was decanted, and the extraction repeated several times to remove any alkali. The saturated solution was diluted in the conductivity cell or electrode vessel with conductivity water to the concentration required, the necessary precautions being taken to avoid contamination by atmospheric carbon dioxide. In most cases the calcium hydroxide content was estimated gravimetrically by precipitation as oxalate and ignition to carbonate at  $550^\circ \pm 20^\circ$ . This method has been used by the authors for some years, since it avoids the difficulties inherent in the weighing of calcium oxide (cf. Bassett, J., 1934, 1270; Willard and Boldyreff, *J. Amer. Chem. Soc.*, 1930, **52**, 1888). The estimation was carried out on 50 c.c. of the solution from the conductivity cell and, with this volume, the precision is not greater than 0.3% even with the more concentrated solutions. The use of larger bulk solutions from which the conductivity cell is filled, or the preparation of solutions from known weights of solid calcium oxide, is open to other objections.

The conductivity measurements were carried out at  $25^\circ \pm 0.1^\circ$  in hard-glass cells, a Cambridge reed hummer (frequency 1100 cycles) and a bridge made up of a Cambridge low-induction resistance box and inductionless ratio arms being used. The *E.M.F.* measurements at  $25^\circ \pm$



In order to determine  $E_x$  it is necessary to allot values to  $e_1$ ,  $e_2$ , and  $E_s$ . Flint and Wells (*Bur. Standards J. Res.*, 1933, **11**, 163), in determining the activities of calcium hydroxide solutions at 30° by measurements of the cell



calculated the value of  $e_1$  from the Henderson formulæ in the form :

$$e = \frac{RT}{F} \frac{(\Delta cf)_{\text{KCl}}(n_{\text{K}} - n_{\text{Cl}}) + (\Delta c)_{\text{Ca(OH)}_2}(n_{\text{OH}} - \frac{1}{2}n_{\text{Ca}})}{(\Delta cf)_{\text{KCl}} - (\Delta c)_{\text{Ca(OH)}_2}} \log \frac{(\Delta cf)_{\text{KCl}}}{(\Delta c)_{\text{Ca(OH)}_2}} \quad (1)$$

The value used for the transport number of the potassium ion (0.473) was that found in saturated solutions. Guggenheim and Schindler (*J. Physical Chem.*, 1934, **38**, 533), however, have recommended that, as most of the contribution to the diffusion potential comes from the more dilute end of the transition layer, the value  $n_{\text{K}} = 0.490$ , which is constant for potassium chloride solutions up to 0.5N, should be used. This gives values for the diffusion potential  $e_1$  only about one third of those calculated by Flint and Wells. For the present calculations the value  $n_{\text{K}} = 0.490$  has been used. The activity coefficient for  $\text{Ca(OH)}_2$  has been assumed unity, and  $n_{\text{Ca}} = 0.214$ , similarly to Flint and Wells. The data for potassium chloride used in the calculations were as follows :

	Sat. KCl.	N-KCl.	0.1N-KCl.		Sat. KCl.	N-KCl.	0.1N-KCl.
$\Lambda$ .....	95*	112	129.0	$n_{\text{K}}$ .....	0.49	0.49	0.49
$f$ .....	0.57	0.61	0.78	$c$ .....	4.18	1.0	0.1

\* Obtained by extrapolation of data up to 4N.

If the activity coefficient for potassium chloride is omitted from equation (1), the calculated diffusion potential  $\text{Ca(OH)}_2|\text{sat.KCl}$  becomes about 0.0005 volt more negative for the most dilute calcium hydroxide solution and 0.001 volt more negative for the most concentrated.

The value of  $E_s$  adopted for the 0.1N-calomel electrode was 0.3337 volt at 25° as recommended by Guggenheim and Schindler (*loc. cit.*). This is a different basis from that used by Flint and Wells, who took the value 0.2383 volt for the saturated calomel electrode at 30°.\* The value taken for the N-calomel electrode was 0.2799 volt, the potential difference between the N- and the 0.1N-calomel electrode being taken as 0.0528 volt and the diffusion potential  $\text{N-KCl}|0.1\text{N-KCl}$  calculated from formula (1) as 0.0010 volt.

The data obtained in the present investigation are in Table III.

TABLE III.

$p_H$  of Calcium Hydroxide Solutions.

CaO, g. per l.	CaO, g.-equiv. per l. (c).	Measured cell <i>E.M.F.</i>		$e_1$ .	$e_2$ .	$E_x$ .	$p_H$ .
		Against 0.1N-calomel.	Against N-calomel.				
0.064	0.00228	—	— 0.9480	— 0.0028	+ 0.0006	— 0.6659	11.27
0.065	0.00232	—	— 0.9490	— 0.0028	+ 0.0006	— 0.6669	11.28
0.122	0.00435	— 1.0165	—	— 0.0023	+ 0.0016	— 0.6821	11.54
0.164	0.00585	—	— 0.9705	— 0.0021	+ 0.0006	— 0.6891	11.66
0.271	0.00970	— 1.0365	—	— 0.0016	+ 0.0016	— 0.7028	11.89
0.462	0.0165	— 1.0482	—	— 0.0010	+ 0.0016	— 0.7151	12.10
0.680	0.0243	—	— 1.0065	— 0.0005	+ 0.0006	— 0.7267	12.29
0.710	0.0254	—	— 1.0076	— 0.0005	+ 0.0006	— 0.7279	12.31
0.975	0.0348	— 1.0670	—	+ 0.0001	+ 0.0016	— 0.7350	12.44
1.027	0.0367	—	— 1.0166	+ 0.0002	+ 0.0006	— 0.7375	12.47
1.160	0.0414	—	— 1.0195	+ 0.0005	+ 0.0006	— 0.7407	12.53

The  $p_H$  values shown in the last column of Table III would be altered by as much as 0.1 unit by the adoption of other values still commonly used for the 0.1N-calomel electrode and the various diffusion potentials.

The  $p_H$  values obtained by Wells at 30° are 0.17 unit below the present values at 25° at  $c = 0.003$ , and 0.20 unit lower in the solutions of highest concentration. This large

\* Derived from the value 0.3372 at 30° for the 0.1N-calomel electrode, 0.0942 for the potential difference directly measured between the 0.1N- and the saturated calomel electrode, and 0.0046 calculated diffusion potential using the value  $n_{\text{K}} = 0.473$ .

variation is due in part to the difference in the values adopted for the standard electrodes, which, as far as calculation can be made, affects the  $p_{\text{H}}$  by about 0.02, and to a larger extent to the different methods used for calculating the diffusion potentials. The use of the diffusion potential values adopted in the present work would raise the  $p_{\text{H}}$  values of Flint and Wells by about 0.1 unit at the lowest concentrations and 0.05 unit at the highest.

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