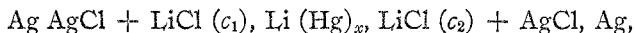


data agree roughly with the early data of Kuschel,<sup>1</sup> as quoted in a compilation by Kohlrausch and Holborn.<sup>2</sup> Their results, however, vary widely from the later and far more accurate transference measurements by Jahn, Bein and Washburn.<sup>3</sup>

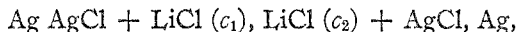
Recently, Allmand and Polack<sup>4</sup> have published the results of measurements on cells of the type: Hg, HgCl + NaCl, Na(Hg)<sub>x</sub>. Their work can only be regarded as preliminary, especially for the more dilute solutions, since no attempt was made to keep oxygen out of their solutions.

### 8. Summary.

The electromotive forces of cells without liquid junction



in which the concentrations  $C_1$  and  $C_2$  varied between 3.0 and 0.001 *N* have been measured at 25°, and the activities of the ions of the salt have been computed. With the aid of measurements on cells with liquid junction



the transference numbers of the ions have been obtained. Since these numbers, for lithium chloride, change rapidly with the concentration, a method has been devised by which the numbers can be computed from the electromotive force measurements and expressed as a function of the ion activity. The value of the transference number at any given concentration, within the range studied, can thus be obtained.

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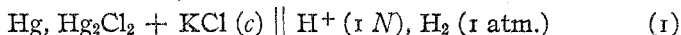
[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 126.]

## THE ACTIVITY COEFFICIENT OF NORMAL POTASSIUM CHLORIDE SOLUTION AND THE POTENTIAL OF THE NORMAL CALOMEL ELECTRODE.

BY JAMES A. BEATTIE.

Received March 12, 1920.

Since the normal hydrogen electrode and the normal calomel electrode are both used as standards in electromotive force calculations, it is desirable to know accurately the potential difference between them. The electromotive force of the system



is given by the equation

<sup>1</sup> *Wied. Ann.*, **13**, 289 (1881). Kuschel used diaphragms of gold beaters skin so his results were probably seriously influenced by electroendosmosis.

<sup>2</sup> "Leitvermögen der Electrolyte." The determinations were not made by Kohlrausch and Holborn, as stated by Phelps and Mortimer.

<sup>3</sup> *Loc. cit.*, see p. 1126.

<sup>4</sup> *J. Chem. Soc.*, **115**, 1020 (1919).

$$E = \bar{E} + \frac{RT}{F} \log c\alpha \quad (2)$$

where  $\bar{E}$  is the specific electrode potential of the calomel electrode, *i. e.*, its potential when the activity of the chloride ion is unity, and  $c\alpha$  is the activity of that ion in a  $c$  normal solution. It will be noted that the potential of the hydrogen electrode is assumed to be zero. If the activity of the chloride ion in a one normal potassium chloride solution is used in Equation 2, the value of  $E$  calculated is the potential of the normal calomel electrode in terms of the normal hydrogen electrode.

From their own measurements Noyes and Ellis<sup>1</sup> calculate  $\bar{E}$ , the specific electrode potential of the calomel electrode, to be  $-0.2700$  volt at  $25^\circ$ . Using a value of the chloride ion activity in  $N$  potassium chloride extrapolated from MacInnes and Parker's<sup>2</sup> results (which extend only to  $0.5$  molal), they find  $-0.2824$  volt as the value for the potential difference between the normal calomel and normal hydrogen electrodes. Lewis, Brighton and Sebastian,<sup>3</sup> by a different method, arrive at  $-0.2828$  volt for this potential, but their "normal electrode" includes the liquid junction potential between  $0.1$  and  $1.0 N$  potassium chloride solutions. The effect of this junction will be considered later.

Since the apparatus measuring the potentials of concentration cells without liquid junction, described in the article immediately preceding this, was in operation, I undertook, at the suggestion of Dr. A. A. Noyes, the direct determination of the activity ratio between  $1.0$  and  $0.1$  molal<sup>4</sup> potassium chloride solutions, to provide the necessary data for the calculation of the ion activity of a  $N$  potassium chloride solution.

The procedure was the same as that in the preceding article except that the solutions and amalgam were made up by the methods described by MacInnes and Parker.

TABLE I.

The E. M. F. of KCl Concentration Cells, without Transference, at  $25^\circ$ .  
 Ag, AgCl + KCl, K(Hg)<sub>x</sub> — K(Hg)<sub>x</sub>KCl + AgCl, Ag.

			E. M. F.
$1.0 m$	$0.004$	$0.1 m$	$-0.10650$
$1.0 m$	$0.004$	$0.1 m$	$-0.10660$

Using the equation  $E = \frac{2RT}{F} \log \frac{c_1\alpha_1}{c_2\alpha_2}$  and substituting  $-0.10655$  for  $E$  gives  $0.7956$  for the activity ratio of  $1.0$  to  $0.1$  molal potassium chloride. This value, together with those of MacInnes and Parker, and Harned<sup>5</sup>

<sup>1</sup> THIS JOURNAL, 39, 2532 (1917).

<sup>2</sup> *Ibid.*, 37, 1445 (1915).

<sup>3</sup> *Ibid.*, 39, 2258 (1917).

<sup>4</sup> In this article "normal" will be used to denote a solution containing one equivalent of solute in 1000 cc. of solution at the temperature under consideration, and "molal" to denote a solution consisting of one mol of solute in 1000 grams of water.

<sup>5</sup> THIS JOURNAL, 38, 1986 (1916).

were used to obtain the table of activities for potassium chloride given in an article by Noyes and MacInnes.<sup>1</sup> It must be remembered that it is the activity of the *chloride ion* that must be used in Equation 2. However, I will assume, following MacInnes,<sup>2</sup> that the activities of the 2 ions of potassium chloride are the same.

From the density of a 1 *N* potassium chloride solution, which is given as 1.0428 in "Landolt-Börnstein Tabellen," its *molal* concentration is found to be 1.0328, and the corresponding activity obtained from a plot of the values given by Noyes and MacInnes (against logarithms of concentration) is 0.592.

The potential of the normal calomel electrode then becomes, by Equation 2,

$$E = -0.2700 + 0.5915 \log 0.592 \times 1.0328,$$

or -0.2826 volt. This, of course, assumes the correctness of Noyes and Ellis' value for the specific electrode potential.

The calculation of the liquid junction potential of 0.1 to 1.0 *N* potassium chloride can be made by the formula of MacInnes,<sup>3</sup>  $E_l = E_i (1 - 1/2n)$ , where  $E_l$  is the liquid junction potential,  $E_i$  the electromotive force of the corresponding concentration cell with transference and  $n$  the cation transference number. Lewis and Sebastian,<sup>4</sup> and Harned<sup>5</sup> have both measured  $E_i$  for 0.1 to 1.0 *N* potassium chloride solutions; the former give 0.5290, and the latter 0.5287. Using the value 0.5290 and the transference number 0.496, from Table II below, the liquid junction potential is found to be +0.0004 volt which added to Lewis, Sebastian and Brighton's value (-0.2828) gives -0.2824 for the potential difference between the normal hydrogen and normal calomel electrodes.

The transference number of the potassium ion in a 1.0 to 0.1 molal potassium chloride solution is the ratio of the e. m. f. of the cell with liquid junction (-0.5290) to that without liquid junction (-0.10655) which equals 0.496. It can be shown that this is the transference number in a 0.3162 molal solution, *i. e.*, the geometrical mean of 1.0 and 0.1. Table II gives a résumé of the transference numbers of the potassium ion in potassium chloride solutions obtained from this work and that of MacInnes and Parker.

Since the transference number is practically constant over the entire range of concentration, it is not necessary to use the method of computation given in the previous article.

<sup>1</sup> THIS JOURNAL, 42, 239 (1920).

<sup>2</sup> *Ibid.*, 41, 1086 (1919).

<sup>3</sup> *Ibid.*, 37, 2301 (1915).

<sup>4</sup> *Ibid.*, 39, 2245 (1917).

<sup>5</sup> *Loc. cit.*

TABLE II.

The Transference Number of Potassium Ion in Potassium Chloride Solutions at 25°.

Concentration range.	Mean concentration.	Transference number.
1.0 - 0.1	0.3162	0.496
0.5 - 0.05	0.1581	0.498
0.1 - 0.01	0.03162	0.496
0.05 - 0.005	0.01581	0.494

**Summary.**

The work of MacInnes and Parker on the activity values and transference numbers of potassium chloride solutions is extended to one molal concentration.

The potential of the normal calomel electrode is calculated to be  $-0.2826$  volt, agreeing quite well with Lewis, Sebastian and Brighton's value ( $-0.2824$  volt), when corrected for the liquid junction potential between 0.1 and 1.0 *N* potassium chloride solutions.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY.]

**PRESSURE MEASUREMENTS OF CORROSIVE GASES. THE VAPOR PRESSURE OF NITROGEN PENTOXIDE.<sup>1</sup>**

BY FARRINGTON DANIELS AND ARTHUR C. BRIGHT.

Received March 20, 1920.

Pressure measurements of the higher oxides of nitrogen and nitric acid are difficult because these substances attack materials on which the chemist usually relies, including rubber tubing, mercury and stopcock grease. Since such measurements are necessary for the proper study of nitrogen fixation processes, an apparatus made entirely of glass has been devised which is capable of measuring gas pressures conveniently and accurately over a wide range of conditions. With it the vapor pressure of nitrogen pentoxide has been determined. Further related researches are also in progress.

**Description of the Apparatus.**

The vapor pressure apparatus in its final form is shown in Fig. 1. Its unique feature consists of the glass diaphragm, movement of which makes or breaks an electrical circuit and permits balancing of an air pressure against the unknown pressure. The air pressure is read directly on a mercury manometer as shown.

The method of making the glass diaphragm is shown in Fig. 2. A small bulb of glass, with a thin end, is blown as shown in the first illustration. This is flattened by plunging the end into a flame, momentarily, while rotating. A little practice is necessary to judge properly the ex-

<sup>1</sup> Published by permission of Mr. George J. Roberts, special Assistant to the Chief of Ordnance, U. S. A. and Dr. Mellow Whitney, Chief, Bureau of Soils.