

een computed, and the absolute activity coefficients approximately estimated.

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## THE TRANSFERENCE NUMBERS OF HYDROCHLORIC ACID IN SOLUTIONS OF ETHYL ALCOHOL

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In the preceding contribution on the activity coefficient of hydrochloric acid in solutions of ethyl alcohol<sup>1</sup> measurements of cells are given from which it is possible to compute the electromotive forces of the cells,  $\text{Ag} | \text{AgCl} | \text{HCl} (m_2) | \text{H}_2 | \text{HCl} (m_1) | \text{AgCl} | \text{Ag}$ , which are without liquid junctions. From these measurements and those of the cells,  $\text{Ag} | \text{AgCl} | \text{ICl} (m_2) | \text{HCl} (m_1) | \text{AgCl} | \text{Ag}$ , with liquid junctions, it is possible to compute by an exact thermodynamic method the transference numbers of the ions of the acid. The present investigation contains the results of measurements of these cells with liquid junctions in alcohol and 50 mole per cent. alcohol-water mixtures at 25° and the calculation of the transference numbers.

The preparation of materials and the methods employed in making up the solutions have been carefully described in the preceding article.

The cell consisted of two parts, one containing a 1mm. capillary and the other a cup into which the capillary could be fitted and held in place by means of a rubber stopper. The part containing the capillary always contained the same solution (0.01 *M* hydrochloric acid) which was compared with solutions of different concentrations contained in the other half of the cell. In making a measurement, each half of the cell was filled with its solution and the silver electrodes, washed six times with the proper solution, were inserted in the electrode compartments. Before being connected, each part of the cell was allowed to remain at room temperature, about 25°, for one hour, so that equilibrium between the electrode and solution was obtained. The connections were then made, a liquid junction was established by mixing the solutions from each part in the cup, and the cell placed in the thermostat. The stopcocks leading to the electrode chambers were kept closed for half to three-quarters of an hour until the cells attained the temperature of the bath. After opening the cocks, readings of the electromotive forces were taken every quarter to half an hour until at least six were obtained, a mean of which constituted a measurement of the cell. Both solutions were renewed for every measurement.

<sup>1</sup> THIS JOURNAL, 47, 82 (1925).

The experimental data are contained in Table I. Solutions A of the alcohol series were made by diluting one analyzed solution; Solutions B and C by diluting others. All measurements obtained are included. The results of the alcohol-water cells are contained in the fifth column. The series denotation in the first column refers only to alcohol cells. All concentrations are expressed in moles per 1000 g. of solvent.

TABLE I  
MEASUREMENTS AT 25° OF THE CELLS Ag | AgCl | HCl ( $m_2$ ) | HCl (0.01) | AgCl | Ag

Series	Solvent: Alcohol		Solvent: 50 mole % alcohol-water	
	$m_2$	$E$	$m_2$	$E$
C	0.002	-0.0440	0.001	-0.0742
C	.005	-.0169	.002	-.0534
..	.01	.0000	.005	-.0223
A	.02	.0204	.01	.0000
A	.05	.0439	.02	.0227
A	.100	.0614	.05	.0503
A	.200	.0766	.1	.0737
A	.500	.1004	.2	.0945
A	.750	.1122	1.	.1534
B	1.699	.1272	1.5	.1719
B	3.335	.1419	2.	.1876

In order to obtain the best values of the transference numbers from the measurements of the cells with and without liquid junctions, the method employed by MacInnes and Beattie<sup>2</sup> has been followed. The fundamental equations for the electromotive forces of cells of types under consideration with and without liquid junctions may be written

$$dE_t = 2n_c \frac{RT}{F} d \ln a_{\pm} \quad (1)$$

$$\text{and} \quad dE = \frac{2RT}{F} d \ln a_{\pm} \quad (2)$$

respectively, where " $a_{\pm}$ " is the square root of the ion-activity product.  $E_t$  and  $E$  are the electromotive forces which are summed up in reference to any chosen values. Thus, the 0.02  $M$  value referred to the 0.002  $M$  value of the alcohol series would be 0.0644.

If values of  $E$  be plotted as the ordinates and the logarithms of the corresponding mean activities as abscissas, a straight line with a slope equal to  $\frac{dE}{d \log a}$  or  $\frac{2RT}{F}$  is necessarily obtained. Numerically, this value equals 0.1183 when common logarithms are employed. Likewise, for values of  $E_t$ , a curve is obtained having the slope equal to  $\frac{dE_t}{d \log a}$  or  $\frac{2RT}{F} n_c$ , which is a variable, since  $n_c$  is a variable. The transference number of the cation at any activity and hence at any concentration is therefore the ratio of these slopes at corresponding points.

<sup>2</sup> MacInnes and Beattie, THIS JOURNAL, 42, 1117 (1920).

To obtain the slope of the curve with transference, an empirical equation of the form  $E_t = a + b(\log A) + c(\log A)^2$ , where  $A$  is the activity of the electrolyte multiplied by  $10^4$  and  $a$ ,  $b$  and  $c$ , are constants, has been employed. The values of the constants were determined by the method of least squares from the values of  $\log(a \times 10^4)$  or  $\log A$ , computed from Table IV of the preceding article and the values of  $E_t$  in Table I.

From the alcohol series, it was found that  $E_t$ , referred to 0.002  $M$  acid, is given<sup>3</sup> by

$$E_t = -0.11085 + 0.09629(\log A) - 0.003772(\log A)^2 \quad (3)$$

whence the slope of the curve is given by

$$\frac{dE_T}{d \log A} = 0.09629 - 0.007544(\log A) \quad (4)$$

and  $n_c$  by

$$n_c = \frac{\frac{dE_T}{d \log A}}{\frac{dE}{d \log A}} = \frac{\frac{dE_T}{d \log A}}{0.1183} = 0.81395 - 0.063777(\log A) \quad (5)$$

In the case of the 50 mole per cent. water-alcohol series,  $E_t$  referred to the 0.001  $M$  acid is given<sup>4</sup> by

$$E_t = -0.08850 + 0.08989(\log A) - 0.000764(\log A)^2 \quad (6)$$

and

$$n_c = 0.7598 - 0.01292(\log A) \quad (7)$$

In Table II are given the values of  $n_c$  at round concentrations (moles per 1000 g. of solvent) computed by Equations 5 and 7.

TABLE II

CATION TRANSFERENCE NUMBER OF HYDROCHLORIC ACID IN ALCOHOL AND 50 MOLE PER CENT. ALCOHOL-WATER MIXTURES AT 25°

$m$ .....	0.001	0.002	0.005	0.01	0.02	0.05			
Solvent—Alcohol, $n_c$ .....	.753	.738	.718	.702	.687	.669			
Solvent—50 mole % Alcohol-Water; $n_c$	.747	.744	.740	.736	.733	.728			
$m$ .....	0.1	0.2	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Solvent—Alcohol; $n_c$ .....	.654	.641	.626	0.610	0.602	0.595	0.589	0.584	0.580
Solvent—50 mole % Alcohol-Water; $n_c$	.725	.722	.717	.713	.710	.707	.706	...	...

Lapworth and Partington<sup>5</sup> obtained 0.63 for the mean cation transference number between 0.0731 and 1.114  $N$  alcohol solutions, which value is in good agreement with the above.

<sup>3</sup> The mean deviation, positive and negative, of the observed results from those computed by this equation was 1.6% of the total electromotive force. The sum of the positive and negative values of course equalled zero.

<sup>4</sup> The mean deviation, positive and negative, in this series from those computed by this equation was 0.5% of the total electromotive force. Therefore, it would seem that reproducibility of the electromotive forces of this kind becomes more difficult as the solvent contains more alcohol.

<sup>5</sup> Lapworth and Partington, *J. Chem. Soc.*, 99, 1417 (1911).

### Summary

1. Measurements of the cells Ag | AgCl | HCl ( $m_2$ ) | HCl ( $m_1$ ) | AgCl | Ag at 25° with alcohol and 50 mole per cent. alcohol-water mixtures have been presented.

2. By the method employed by MacInnes and Beattie the cation transference numbers in these solutions have been calculated.

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## LUMINESCENCE OF GRIGNARD COMPOUNDS: SPECTRA AND BRIGHTNESS

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In a previous article,<sup>1</sup> the authors reported the results of a rather extended investigation of the luminescence of compounds of the type RMgX, where R is an organic radical and X a halogen. The effect of several factors on the color and on the brightness of the luminescence was discussed. It was shown that, in order to obtain light from these compounds in ether solution, on oxidation with oxygen, it is necessary for the magnesium to be attached directly to an unsaturated carbon atom in R.

It is the purpose of the present article to record observations of a few new compounds, to describe work on the spectra of the luminescence, and to give the results of an attempt to secure quantitative measurements of the brightness of the chemiluminescence.

### Extension of Previous Investigations

One of the factors discussed in the previous article referred to, is the nature of the oxidizing agent used. It was shown that while benzene triozonide had been reported as giving some light, the only other oxidizing agent of any importance is oxygen, which is much more effective than anything else tried. Certain organic peroxides, however, are found to give some light. The writers are indebted to Professor Henry Gilman of the University of Iowa for the information that benzoyl peroxide, ethyl peroxide, and diacetone peroxide, give light. Tests show, however, at least with benzoyl peroxide, that the light so obtained is faint compared with that from oxygen. The tests were made on such representative compounds as  $C_6H_5MgBr$ ,  $p\text{-}BrC_6H_4MgBr$  and  $p\text{-}ClC_6H_4MgBr$ .

The question of obtaining light from compounds containing other metals than magnesium was also discussed in the article referred to. Zinc compounds were shown not to be luminescent and mercury compounds were also so reported. The work on the mercury compounds has been

<sup>1</sup> Dufford, Calvert and Nightingale, THIS JOURNAL, 45, 2058 (1923).