zation of menthyl α-phenylacetoacetate.

2. The results show that enolization takes place through some intermediate step. In this step nearly two-thirds of the racemization occurs, only one-third involving actual transformation to the enol.

3. Alternative explanations are offered, one involving loss of configuration in an intermediate anion, the other reversible formation of a small amount of open-chain enol followed by a slower accumulation of chelated enol.

DURHAM, N. H. RECEIVED JULY 7, 1936

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. II. Hydrochloric Acid at 25°

BY THEODORE SHEDLOVSKY AND DUNCAN A. MACINNES

In the first article of this series[1] it was shown that the activity coefficients, f, of chlorides in aqueous solution could be obtained from the potentials, E_t, of galvanic cells of the type

Ag; AgCl, MCl (C_1): MCl (C_2), AgCl; Ag (A)

with aid of the relation

$$E_t = \frac{2RT}{F}\int_{C_1}^{C_2} t \ \mathrm{d} \log Cf \qquad (1)$$

in which t is the transference number of the positive ion constituent, M, C is the concentration, and the other terms have their customary significance.[2]

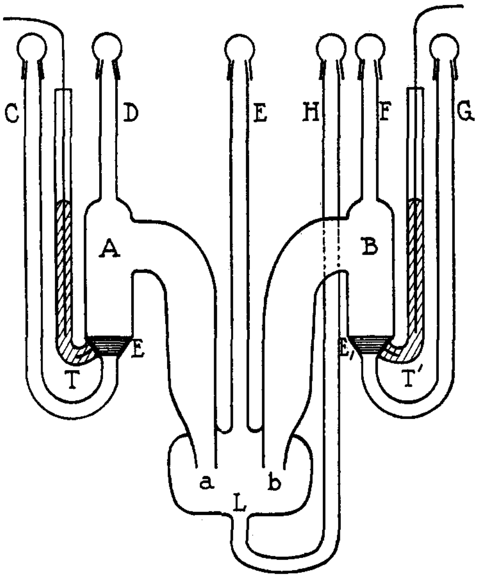

Fig. 1.

However, cells of type A contain a liquid junction and, until the present researches, have not been used to obtain activity coefficients. It was therefore decided to include hydrochloric acid in the series of measurements since the activity coefficients of that substance have been determined, with considerable accuracy, by various workers, using concentration cells without liquid junction of the form

Ag; AgCl, HCl (C_1); H_2 (Pt) —
(Pt) H_2; HCl (C_2), AgCl; Ag (B)

Since cells of type B do not involve amalgam electrodes, with their attendant experimental difficulties, this case affords the most favorable comparison of the methods involving cells with and without liquid junction.

This paper will therefore deal with the determination of the potentials of the cell

Ag; AgCl, HCl (C_1): HCl (C_2), AgCl; Ag (C)

in which C_2 varied from about 0.003 to 0.08 N, and C_1 was 0.1 N. The results have afforded a test of the Debye-Hückel relations connecting the activity coefficients of aqueous solutions of hydrochloric acid with the concentration.

Apparatus and Experimental Procedure

Although the principle involved is the same as that utilized in the work of Brown and MacInnes[1] decided changes have been made in the apparatus used. The new cell is shown diagrammatically in Fig. 1. Instead of forming the silver–silver chloride electrodes on wire, as in the previous work, hollow truncated cones of platinum foil, indicated at E and E′, are used. The outer surfaces of these cones are sealed into the glass, contact being made with the mercury in tubes T and T′. The chief advantage of electrodes of this design is that they are completely protected from mechanical disturbance of their active surfaces. This we have found to be essential if the reproducibility is to reach 0.01 mv. or better. The electrodes are plated with silver and chloridized electrolytically, using the precautions suggested by Brown.[3] It is also found desirable to wash the plated silver with

---

[1] Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).

[2] For a derivation of equation (1) see MacInnes and Brown, *Chem. Rev.*, **18**, 335 (1936).

[3] Brown, THIS JOURNAL, **56**, 646 (1934).

strong ammonia, followed by water, before chloridizing. This assures the removal of the last possible traces of silver cyanide. In filling the cell it is first turned upside down. Solution is run into half-cell A, for instance, through either tube C or D (from a flask of the type shown in Fig. 3 of the article by Brown and MacInnes[1]), and out of the other tube or tube E. Several thorough rinsings are given, after which the half-cell is filled to the point a. The half-cell B is then filled in a similar manner with the second solution. The apparatus is then turned from its inverted to its normal position. A liquid junction is next made at a or b by flowing the heavier of the two solutions through tube H and filling the connecting vessel L. Unless pendent drops are present at a and b air bubbles form that rise through the connecting tubes and mix the solutions. Such pendent drops may be readily formed if necessary by a momentary lifting of an appropriate ground glass cap. The apparatus is next placed in an oil thermostat regulating to ±0.002° and readings of the potential are available as soon as the cell has reached its final temperature. These readings remain constant, within a few microvolts, for many hours. This constancy is due to the fact that the only important source of variation of potential is a change of composition of the solution in immediate contact with the electrodes, such as could be brought about by diffusion or convection. An advantage of this apparatus and procedure over that of Brown and MacInnes is that by avoiding the sliding contact in making the liquid junctions a source of contamination from the grease is avoided.

There is usually a slight difference of potential (of the order of 0.01 mv.) between the electrodes E and E′ which may be corrected for in two ways. In the first place, this potential is measured directly by placing the same chloride solution in both halves of the apparatus. In addition measurements with each pair of solutions are made which are duplicates but with the positions of the solutions reversed. Since the design of the apparatus is symmetrical this is possible. The difference between the potentials of these duplicate determinations should be twice the directly measured difference of potential of the electrodes. This was true within a few microvolts for all the measurements described in this paper.

The potential measurements were made with a calibrated type K potentiometer. The potential standard consisted of five Eppley saturated Weston standard cells kept at 25° in the thermostat. The standard cells were calibrated by the Bureau of Standards.

Results and Discussion

The results of all the measurements are given in columns 1 and 2 of Table I. The solutions of the concentrations given in moles per liter at 25° were prepared by weight from constant boiling acid[4] and their compositions were checked by conductance measurements.[5] As indicated, one of two solutions in the cell was always 0.1 N hydrochloric acid. The water used had a conductance of $2 \pm 1 \times 10^{-7}\ \Omega^{-1}$. Since the greater part of this conductance was due to traces of carbon dioxide the effective conductance of the solvent in the acid solutions was less than this value, and the correction (discussed in the previous paper) for solvent impurities is therefore negligible even at the lowest concentrations.

The method for obtaining the change Δf of the activity coefficient with the concentration from the e. m. f. data, using equation (1), is given in the previous paper.[1] The necessary transference numbers, given in column 3 of the table, are interpolated from the work of Longsworth.[6] The resulting values of $-\Delta \log f$ relative to 0.1 N are given in the fourth column. To obtain activity coefficients f from these data use may be made, as in the earlier paper, of a plot, Fig. 2, of $(\Delta \log f - \alpha\sqrt{C})$ against $(A - \Delta \log f)\sqrt{C}$ in which α is the constant (0.5056 at 25°) of the Debye–Hückel equation

$$-\log f = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) \qquad (2)$$

The constant (A), which is the logarithm of the activity coefficient of the reference 0.1 N hydrochloric acid solution, must be obtained by a short series of approximations in which the value of A chosen finally agrees with the intercept of the plot. The slope of the straight portion of the curve for the lower concentrations yields the constant β of equation (2). The plot yields a value of $A = -0.0973$ from which the activity coefficients f (observed) in column 5 of Table I were obtained from the relation

$$\log f = A - \Delta \log f \qquad (3)$$

The constant β has a value of 1.847, corresponding to a distance of closest approach of 5.62 Å. for the ions. With this value of β equation (2) represents the data up to about 0.04 normal, as is shown in column 6 of the table. Agreement throughout the whole concentration range measured can be obtained, however, with the aid of the Hückel equation

$$-\log f = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) - DC \qquad (4)$$

As is also the case with sodium chloride[1] it is necessary to shift the value of β in order to fit this equation to the results. The computed values of f, using equation (4) and the constants $\beta = 1.5274$ and $D = 0.105$, are given in the last column of the table. These computed values agree with the "observed" values in column 5 throughout the range of the measurements.

---

(4) Foulk and Hollingsworth, THIS JOURNAL, **45**, 1220 (1923).

(5) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(6) Longsworth, *ibid.*, **54**, 2741 (1932).

TABLE I

THE POTENTIALS OF THE CONCENTRATION CELL: Ag: AgCl, HCl (0.1 *N*): HCl (C_2), AgCl; Ag AT 25°, AND THE COMPUTATION OF THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

Concn. moles per liter at 25°, C_2	E. m. f., mv.	Trans. no., t_H	Log activity coeff. ratio $-\Delta \log f$	Activity coefficients		
				f, obsd.	*f*, computed equation (2)	*f*, computed equation (4)
0.0034468	136.264	0.8234	0.07065	0.9405	0.9402	0.9400
.0052590	118.815	.8239	.06486	.9280	.9283	.9280
.010017	92.529	.8251	.05453	.9062	.9063	.9061
.010029	92.480	.8251	.05450	.9061	.9063	.9060
.019914	64.730	.8266	.04068	.8778	.8777	.8778
.020037	64.464	.8266	.04072	.8778	.8775	.8775
.020132	64.282	.8266	.04051	.8774	.8773	.8773
.040492	36.214	.8286	.02372	.8441	.8430	.8442
.059826	20.600	.8297	.01344	.8244	.8219	.8246
.078076	9.948	.8306	.00630	.8110	.8070	.8113
.1000	0	.8314	0	.7993	.7926	.7993

The most extensive study of cells without liquid junction involving hydrochloric acid has been made by Harned and Ehlers.[7] From their critical summary of their work they have obtained potentials at round molalities from which e. m. f. values of cells of type B may be computed, making allowance for the difference in the concentration scales used in our work and theirs. These results are also plotted in Fig. 2, using the *A* value given above. It will be seen that there is substantial agreement in the results from the cells with and without liquid junction. Less complete agreement, though probably within the limits of error of the available data, is found with the earlier critical summary of results from cells without liquid junction by Scatchard.[8] Carmody[9] gives his results on cells without liquid junctions only to 0.1 mv. and a plot of his figures indicates errors greater than that amount. However, if allowance is made for this rather large experimental error there is substantial agreement between his results and ours. The deviation produced by an error of 0.1 mv. is shown in the figure.

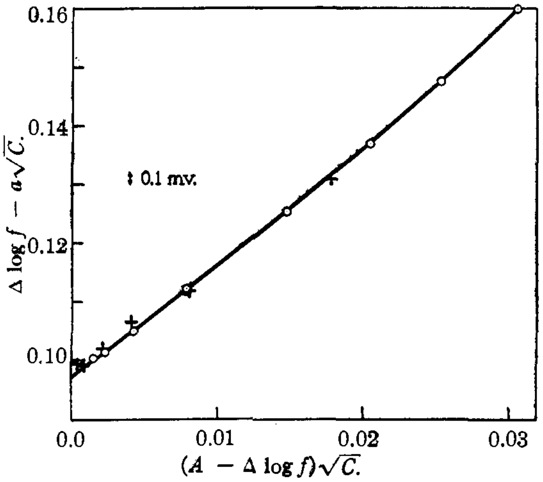

Fig. 2.—O, Shedlovsky and MacInnes; +, Harned and Ehlers.

Summary

Accurate measurements of hydrochloric acid concentration cells, with liquid junction, have been obtained, from which activity coefficients of the ions of the acid have been computed. The results are shown to be in close agreement with those obtained using cells without liquid junctions. The activity coefficients have been found to follow the Debye–Hückel theory with a "distance of closest approach" of 5.62 Å., up to about 0.04 *N*. Accurate agreement with the Hückel equation is observed throughout the concentration range of 0.003 to 0.1 *N*.

NEW YORK, N. Y. RECEIVED JULY 10, 1936

---

[7] Harned and Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933); **55**, 2179 (1933).

[8] Scatchard, *ibid.*, **47**, 641 (1925).

[9] Carmody, *ibid.*, **54**, 188 (1932).