[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Activity of Glycine in Aqueous Solutions of Potassium Chloride, from Electromotive Force Measurements

BY RICHARD M. ROBERTS[1] AND JOHN G. KIRKWOOD

Measurements of the electromotive force of concentration cells with transference, together with accurate transference data, have been successfully used for the determination of the activities of the chlorides of hydrogen,[2] sodium,[3] potassium,[4] and lanthanum[5] in aqueous solution. The purpose of the investigation to be described here was to test this method as a means of determining the activities of non-electrolytes in aqueous electrolyte solutions. Glycine is a non-electrolyte particularly suited for such a test, since in solutions of high dielectric constant it forms a dipolar ion of large electric moment, and the resulting interaction with ions present in the solution gives rise to a very considerable electrostatic contribution to the chemical potential.[6] Galvanic cells of the type indicated schematically below were accordingly chosen for study

$$\underset{}{\mathrm{Ag}\mid\mathrm{AgCl}}\mid \underset{\mathrm{I}}{\mathrm{KCl}(m_1)} \mid \underset{\mathrm{II}}{\mathrm{KCl}(m_1),\ \text{glycine}\ (m_2)} \mid \mathrm{AgCl}\mid\mathrm{Ag}$$

The liquid phases designated I and II both contained potassium chloride at the same molality, m_1, while II also contained glycine at the molality m_2. The phases I and II were separated by a liquid junction across which the composition changed in some continuous but unspecified manner from that of I to that of II.

The electromotive force, E, of the above cell (at constant temperature and pressure) is given by the relation

$$E = -\frac{2RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} t_+\,\mathrm{d}\ln(\gamma_\pm m_1) - RT\int_{\mathrm{I}}^{\mathrm{II}} t_2\,\mathrm{d}\ln(\gamma_2 m_2) \tag{1}$$

where F and R are the Faraday and gas constants, T is the absolute temperature, t_+ is the transference number of potassium ion, $\gamma_\pm$ is the mean ion activity coefficient of potassium chloride, and γ_2 is the activity coefficient of glycine. t_2, the mass transference number of glycine, is defined by the relation $J_2 = t_2 I$, where J_2 is the mass current (in moles/sq. cm./sec.) and I is the electrical current in amperes. The integration is to be taken from the value of the argument in I to its value in II. The inclusion of the last term in equation (1) is necessary since the electrochemical process in the liquid junction involves the transport of neutral solute as well as electrolyte.[7]

We now change the variable of integration to m_2, obtaining

$$E = -\frac{2RT}{F}\int_0^{m_2} t_+\left(\frac{\mathrm{d}\ln\gamma_\pm m_1}{\mathrm{d}m_2}\right)_P \mathrm{d}m_2 - RT\int_0^{m_2} t_2\left(\frac{\mathrm{d}\ln\gamma_2 m_2}{\mathrm{d}m_2}\right)_P \mathrm{d}m_2 \tag{2}$$

in which the derivative is taken along the path P of the line integration, the parametric equations of this path being $m_1 = f_1\,(x,t)$, $m_2 = f_2\,(x,\,t)$, where x is the distance along the transition layer between I and II and t is the time. The functions f_1 and f_2 are determined by the differential equations of diffusion and by the initial form of the transition layer. We note that we may write

$$\left(\frac{\mathrm{d}\ln\gamma_\pm m_1}{\mathrm{d}m_2}\right)_P = \left(\frac{\partial\ln\gamma_\pm}{\partial m_2}\right)_{T,p,m_1} + \left(\frac{\partial\ln\gamma_\pm m_1}{\partial m_1}\right)_{T,p,m_2}\left(\frac{\mathrm{d}m_1}{\mathrm{d}m_2}\right)_P \tag{3}$$

Now if m_1 is initially constant throughout the transition layer, then $(\mathrm{d}m_1/\mathrm{d}m_2)_P$ vanishes initially; and if coupled diffusion is small $(\mathrm{d}m_1/\mathrm{d}m_2)_P$ will remain substantially zero, and we may neglect the second term on the right side of equation (3). A similar argument with regard to $(\mathrm{d}\ln\gamma_2 m_2/\mathrm{d}m_2)_P$ enables us to rewrite equation (2) as

$$E = -\frac{2RT}{F}\int_0^{m_2} t_+\left(\frac{\partial\ln\gamma_\pm}{\partial m_2}\right)_{T,p,m_1}\mathrm{d}m_2 - RT\int_0^{m_2} t_2\left(\frac{\partial\ln\gamma_2 m_2}{\partial m_2}\right)_{T,p,m_1}\mathrm{d}m_2 \tag{4}$$

By a simple transformation equation (4) may be put in the following form, for constant T, p, and m_1

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(2) Shedlovsky and MacInnes, THIS JOURNAL, **58**, 1970 (1936).

(3) Brown and MacInnes, *ibid.*, **57**, 1356 (1935).

(4) Shedlovsky and MacInnes, *ibid.*, **59**, 503 (1937).

(5) Shedlovsky and MacInnes, *ibid.*, **61**, 200 (1939).

(6) Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).

(7) We are indebted to Professor Scatchard for emphasizing the necessity of including the last term of equation (1). Fortunately it turns out to be of negligible magnitude in the present case. It should not be assumed that this term can always be neglected. Properly, the analysis of the electromotive force data of such cells must be based on measurements of the transference number of the non-electrolyte as well as of the electrolyte. Measurements of the mass transference number of glycine in the presence of electrolytes are in progress in this Laboratory.

$$\ln\frac{\gamma_{\pm}}{\gamma_{\pm}{}^0} = -\frac{FE}{2RTt_+{}^0} + \frac{F}{2RTt_+{}^{02}}\int_0^E \Delta t_+ \,\mathrm{d}E - \frac{F}{2}$$
$$\int_0^{m_2} \frac{t_2}{t_+{}^0}\left(1 - \frac{\Delta t_+}{t_+{}^0}\right)\left[\frac{1}{m_2} + \left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{T.p.m_1}\right]\mathrm{d}m_2 \quad (5)$$

In equation (5) $\gamma_{\pm}{}^0$ is the mean ion activity coefficient of potassium chloride in the absence of glycine, and $1/t_+$ has been replaced by $\frac{1}{t_+{}^0}\left(1 - \frac{\Delta t_+}{t_+{}^0}\right)$, where $t_+{}^0$ is the transference number of potassium ion in the absence of glycine, and $\Delta t_+ = t_+ - t_+{}^0$.

The second and third terms on the right side of equation (5) are very small relative to the first term. Longsworth[8] has measured the transference number of potassium ion in solutions of potassium chloride and glycine at 25° by the moving boundary method, and has found $\Delta t_+ = -0.005\ m_2$. This information, together with the measurements of electromotive force about to be described, permits the calculation of the second term.

No experimental data on the transference of glycine are at present available, but a theoretical estimate of the contribution of the third term to $\ln(\gamma_{\pm}/\gamma_{\pm}{}^0)$ can be made. According to this theoretical calculation[9]

$$t_2 = -4 \times 10^{-9} m_2$$

Substituting this value for t_2, and replacing F and $t_+{}^0$ by their numerical values, leads to an estimate of $-4 \times 10^{-4}\ m_2 + 0(m_2^2)$ for the third term. This contribution to the coefficient of m_2 in the expression for $\ln(\gamma_{\pm}/\gamma_{\pm}{}^0)$ (*vide infra*, equation (7)) is only of the order of 0.2%, which is well within the experimental error of these measurements. We are therefore justified in neglecting the effect of the transport of glycine.

Omitting the third term on the right side of equation (5), and substituting Longsworth's value for Δt_+, we have

$$\ln\frac{\gamma_{\pm}}{\gamma_{\pm}{}^0} = -\frac{FE}{2RTt_+{}^0} - \frac{0.005\ F}{2RTt_+{}^{02}}\int_0^E m_2 \mathrm{d}E \quad (6)$$

The experimental plan adopted involved the measurement of E for a number of series of cells. m_1 was held constant throughout each series, and m_2 was allowed to vary stepwise. The values of $\ln(\gamma_{\pm}/\gamma_{\pm}{}^0)$ for each pair of concentrations (m_1, m_2) were then computed from equation (6).

Experimental Procedure

The solutions to be used as phases I and II of the cell were prepared in the following way. Approximately two liters of a solution of molality m_1 in potassium chloride was made up by weight. This solution was then divided into two portions, and the required amount of glycine was weighed into one portion; thus two solutions were obtained, one having a given molality m_2 in glycine, and both having the same molality m_1 in potassium chloride. All weighings were reduced to their values *in vacuo*.

An apparatus of the type described by Shedlovsky and MacInnes[2] was employed to prepare and contain the cell. Drs. Shedlovsky and MacInnes kindly lent us a replica of their apparatus for use in this work. Silver–silver chloride electrodes were deposited simultaneously *in situ* in this apparatus by methods already described.[2] Electrodes formed in this manner were tested by filling the apparatus throughout with approximately 0.05 N potassium chloride solution, and the difference of potential of the electrodes was measured; electrodes showing a potential difference greater than 0.01 mv. were not used.

After preparation of the electrodes, the Shedlovsky–MacInnes apparatus was rinsed four or five times and filled on each side with the appropriate solution. The denser of the two solutions (that containing glycine) was always used for making the liquid junction, thus avoiding downward streaming of the denser solution into the junction chamber and the consequent extensive mixing of the two solutions.

The cell A thus prepared was placed in an oil-bath and brought to a temperature of 25 ± 0.005°. After thermal equilibrium was reached (usually in about fifteen minutes), the electromotive force of the cell was measured at half-hour intervals for a period of four to six hours, using the 0.01 scale of a Leeds and Northrup Type K-2 potentiometer, and an Eppley standard cell of the unsaturated type, furnished with a certificate by its manufacturers and compared frequently with three similar cells. In the cells measured, the electrode on the side containing glycine was always found to be positive, therefore the electromotive forces of the cells when arranged as in the schematic diagram have been considered positive.

The electromotive forces of the cells studied were either found to remain constant during the period of observation (sometimes as long as twenty-four hours), or to decline at a rate of a few microvolts per hour from their initial and maximum value. In the latter case, an average of measurements during the first two hours was taken. After the completion of these observations, the apparatus was removed from the thermostat and emptied, and the remainder of the previously prepared solutions was used to rinse and fill the cell again, this time reversing the positions of the two solutions in the apparatus. The electromotive force of the cell made up in this manner was then determined. The mean value of this measurement and the previous one was taken as the true electromotive force of the cell, since the asymmetry due to the potential difference of the silver–silver chloride electrodes has been thus eliminated. The difference between these two measurements was never greater than twice the potential difference of the electrodes (determined directly, as previously described, after each pair of measurements), a result to be expected if the electromotive force of the cell were reproducible. Solutions were made up and used on the same day in a pair of measurements, to avoid error due to possible fermentation of glycine.

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(8) Privately communicated by Dr. L. G. Longsworth.

(9) The theory of transport of non-electrolytes by Mr. Arthur Squires of this Laboratory, to be published soon.

The potassium chloride used in preparing the solutions was purified as follows: the best obtainable grade of salt was precipitated from aqueous solution by hydrogen chloride gas, then recrystallized twice from conductivity water, and finally fused in air in a platinum crucible and cast into sticks in a platinum boat. That the fusion did not produce hydrolysis was shown by the fact that solutions of samples of the fused salt in conductivity water had the same *p*H (determined with a glass electrode) as the water itself.

Ammonia-free glycine manufactured by Eastman Kodak Company was purified by two recrystallizations from 50% alcohol–water solution, and dried in an oven at 80–90° for ten to twelve hours.

Water used in preparing the solutions was obtained from a Barnstead conductivity water still.

The solutions covered by this investigation were fairly concentrated, and it was therefore thought unnecessary to sweep the solutions free of carbon dioxide and prepare the cell in the absence of air.

Results

The electromotive forces of seventy-eight cells with different pairs of values (m_1, m_2) were measured in the manner just described. The results of these measurements are displayed in the first three columns of Table I. The fourth column shows the values of $-\ln(\gamma_{\pm}/\gamma_{\pm}^0)$ of equation (6). Values of t_+^0 (corresponding to the various values of m_1) used in equation (6) were taken from Longsworth.[10] The integral in equation (6) was

TABLE I

THE ELECTROMOTIVE FORCES OF THE CONCENTRATION CELLS: Ag | AgCl | KCl (m_1) | KCl (m_1), GLYCINE (m_2) | AgCl | Ag AT 25°, AND THE COMPUTED VALUES OF $-\ln(\gamma_{\pm}/\gamma_{\pm}^0)$, FOR EACH PAIR ($m_1$, m_2)

Moles of KCl per 1000 g. H₂O. *in vacuo*, m_1	Moles of glycine per 1000 g. H₂O. *in vacuo*, m_2	E. m. f., mv., E	$-\ln \frac{\gamma_{\pm}}{\gamma_{\pm}^0}$
0.050343	0.051114	0.200	0.007949
.050023	.10430	.399	.01586
.050294	.15097	.567	.02255
.050610	.20227	.755	.03003
.052391	.25500	.923	.03672
.049919	.30511	1.104	.04393
.049762	.35163	1.276	.05079
.049828	.40294	1.423	.05666
.050815	.46110	1.588	.06324
.049775	.51202	1.756	.06995
.075353	.052899	0.182	.007235
.078715	.16712	.562	.02236
.079994	.25870	.863	.03434
.10017	.048732	.159	.006321
.099651	.097771	.316	.01257
.10023	.15427	.492	.01957
.10049	.19769	.627	.02494
.10024	.25763	.810	.03223
.099061	.29499	.914	.03638
.10087	.35048	1.078	.04292
.10036	.40215	1.212	.04827
.10081	.46129	1.380	.05497
.099684	.50787	1.494	.05952
.15839	.052087	0.146	.005806
.14991	.099579	.295	.01174
.15481	.16031	.453	.01803
.14996	.20916	.597	.02376
.15753	.25652	.711	.02831
.14980	.30228	.845	.03365
.15145	.36006	.984	.03919
.14982	.39732	1.089	.04338
.15288	.47775	1.257	.05009
.15023	.50449	1.346	.05365
.20056	.049888	0.134	.005331
.19987	.10189	.274	.01090
.20002	.14972	.394	.01568
.20059	.20649	.532	.02118
.19979	.25137	.656	.02613
.20278	.30991	.770	.03067
.20010	.34807	.875	.03486
.19920	.40123	.990	.03946
.20069	.45494	1.119	.04461
.19800	.50876	1.229	.04901
.25935	.050690	0.123	.004895
.24936	.10301	.255	.01020
.26032	.15355	.366	.01457
.24934	.19813	.481	.01916
.25626	.25415	.602	.02398
.24978	.29860	.702	.02797
.25221	.35915	.823	.03280
.24987	.40145	.917	.03655
.25803	.46554	1.027	.04095
.24930	.50904	1.143	.04559
.29926	.10773	0.246	.009794
.29881	.21791	.486	.01936
.29997	.30826	.675	.02690
.29846	.41470	.893	.03561
.30120	.51163	1.066	.04253
.36077	.052465	0.108	.004300
.36658	.15456	.324	.01291
.35770	.25582	.513	.02044
.36086	.36379	.723	.02883
.35780	.45364	.892	.03559
.39819	.10082	.208	.008284
.40032	.21103	.419	.01670
.39784	.31864	.619	.02468
.40022	.41698	.790	.03151
.39704	.52143	.964	.03847
.46935	.051446	.095	.003784
.47277	.16066	.309	.01231
.45898	.25902	.478	.01906
.45610	.35922	.646	.02577
.45666	.46034	.805	.03213
.49929	.10411	.193	.007690
.49931	.20866	.374	.01491
.49908	.31235	.544	.02170
.49925	.41601	.709	.02829
.49893	.49480	.832	.03322

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[10] Longsworth, THIS JOURNAL, 54, 2741 (1932).

evaluated graphically. A plot of m_2 against E for a given series of cells proved very nearly linear; in consequence the integral was computed by obtaining the area under the broken-line plot joining the points. In no case was the contribution of the integral to ln $(\gamma_\pm/\gamma_\pm^0)$ greater than 0.2% hence one may assume with confidence that the errors introduced by the lack of complete constancy of m_1 in a given series (an experimental difficulty), and by the method of evaluating the integral, are negligible.

In order to present the data of Table I in analytical form it was assumed that ln $(\gamma_\pm/\gamma_\pm^0)$ may be represented by a power series expansion in $m_1^{1/2}$ and m_2, in which the contribution of all but the four most important terms is neglected. The following polynomial accordingly was used to represent the data

$$\ln \frac{\gamma_\pm}{\gamma_\pm^0} = \frac{Am_2}{2} + Bm_1^{1/2}\, m_2 + Cm_2^2 + Dm_1m_2 \quad (7)$$

in which A, B, C, D are constants.

Using the data of Table I, the coefficients of equation (9) were determined by the method of least squares. It was found that

$$\ln \frac{\gamma_\pm}{\gamma_\pm^0} = -0.2059m_2 + 0.2824m_1^{1/2}m_2 + 0.02474m_2^2 - 0.1446m_1m_2 \quad (8)$$

The conditions of integrability of the differential of the Gibbs free energy require that

$$2\left(\frac{\partial \ln \gamma_\pm}{\partial m_2}\right)_{T,p,m_1} = \left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{T,p,m_2} \quad (9)$$

Equations (7) and (9) together give

$$\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{T,p,m_2} = A + 2Bm_1^{1/2} + 4Cm_2 + 2Dm_1 \quad (10)$$

In order to obtain an expression for ln γ_2 at low concentrations of glycine, we take $m_2 = 0$ in equation (10), and integrate with respect to m_1, with the result

$$\ln \gamma_2 = Am_1 + Dm_1^2 + \frac{4}{3}Bm_1^{3/2} \quad (11)$$

Substituting in equation (11) the numerical values of the coefficients A, D, and B found previously, we have

$$\ln \gamma_2 = -0.4119m_1 - 0.1446m_1^2 + 0.3765m_1^{3/2}, \text{ or}$$
$$\log \gamma_2 = -0.1789m_1 - 0.06278m_1^2 + 0.1635m_1^{3/2} \quad (12)$$

$A/2.303$, the coefficient of m_1 in the second of these two equations, will hereafter be referred to as A'.

Discussion

The limiting slope of log γ_2, A', is of some interest, since the dipole moment of the glycine dipolar ion can be calculated from this coefficient. Using a spherical model of the glycine dipolar ion, Kirkwood[11] has obtained a theoretical expression for A'. Replacing the universal constants by their numerical values for water at 25° this expression is

$$A' = -5.48 \times 10^{-3}\mu^2/a + 4.66 \times 10^{-3}V_2/a \times \alpha(\rho) \quad (13)$$

where μ is the dipole moment of the dipolar ion in Debye units and V_2 is the partial molal volume of the dipolar ion component. $a = b + r$, where b is the radius of the dipolar ion, and r is the radius of the real ion; $\alpha(\rho)$, where $\rho = b/a$, is a tabulated function.[11] a, b, r are in Å. The first term on the right side of equation (13) arises from ion-dipole interaction, and represents "salting-in." The second term, representing "salting-out," arises from the repulsion between the real ion and its image distribution in the cavity created by the dipolar ion in the solvent. Taking $V_2 = 57$ cc.,[12] $b = 2.82$ Å.,[12] $r = 1.38$ Å. (the arithmetic mean of the radii of the potassium and chloride ions), and substituting the value $A' = -0.18$ obtained from our data, the dipole moment of glycine is found to be 14.4 Debye units. This is slightly lower than the value, 15 Debye units, calculated from structural considerations for the $^+NH_3$-CH_2COO^- ion in which the terminal groups carry residual charges +e and −e.

No experimental determinations of A' for glycine and potassium chloride by other methods are available for comparison with our data. However, glycine and sodium chloride have been studied by Joseph[13] by measurements of the electromotive force of cells without transference, and by Scatchard and Prentiss,[14] by freezing point methods. They obtained a value of −0.24 for A'. A somewhat higher value of this coefficient in the case of sodium chloride than in that of potassium chloride is to be expected because of the smaller positive ion, and thus smaller value of a in equation (13). The experimental method used here will undoubtedly prove useful in the study of the interaction of other non-electrolytes, such as proteins, with electrolytes.

Summary

Measurements of electromotive force at 25° were made on seventy-eight concentration cells

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[11] Kirkwood, *Chem. Rev.*, **24**, 233 (1939), equation (12).

[12] Cohn, McMeekin, Ferry and Blanchard, *J. Phys. Chem.*, **43**, 169 (1939).

[13] Joseph, *J. Biol. Chem.*, **111**, 479, 489 (1935).

[14] Scatchard and Prentiss, THIS JOURNAL, **56**, 2314 (1934).

with transference, of the type

Ag | AgCl | KCl (m_1) | KCl (m_1), glycine (m_2) | AgCl | Ag

The molalities of potassium chloride and glycine, m_1 and m_2, were varied over a range from 0.05 to 0.50. These measurements were used along with accurate transference data to calculate log γ_2 at low glycine concentration, where γ_2 is the activity coefficient of glycine. It was found that at low m_2

$$\log \gamma_2 = -0.1789m_1 - 0.06278m_1^2 + 0.1635m_1^{3/2}$$

From the limiting slope of log γ_2, −0.1789, the dipole moment of the glycine dipolar ion was calculated to be 14.4 Debye units.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Rate and Equilibrium Studies on the Thermal Reaction of Hydrogen and Iodine[1]

BY ALFRED H. TAYLOR, JR.,[2] AND R. H. CRIST

The well-established homogeneous and bimolecular character of the thermal reaction between the hydrogen isotopes and iodine allows theoretical calculations to be made with some certainty. Experimentally the reaction has been studied in the classical researches of Bodenstein[3] and others, and is generally considered to be one of the most carefully investigated gaseous reactions to be found in the literature. A critical review of the kinetics has been given by Kassel.[4]

From the calculated free energy function and the equilibrium constant of Bodenstein[3] for the dissociation of hydrogen iodide, Murphy[5] obtained the free energy as a function of temperature. However, when Murphy plotted log K *vs.* $1/T$ as derived from his free energy values, the slope was quite different from the best straight line through all the available experimental data. The same calculation has been made for deuterium iodide by Blagg and Murphy,[6] but since the heat of reaction at absolute zero was not available, it was calculated from the equation

$$^{2}\Delta E_0^0 = {}^{1}\Delta E_0^0 + \left(\frac{1}{2} E_{0\mathrm{D}_2}{}^0 - E_{0\mathrm{DI}}{}^0 - \frac{1}{2} E_{0\mathrm{H}_2}{}^0 + E_{0\mathrm{HI}}{}^0\right) \quad (1)$$

where ${}^{1}\Delta E_0^0$ and ${}^{2}\Delta E_0^0$, respectively, refer to the reactions

$$\mathrm{HI} \longrightarrow \tfrac{1}{2}\mathrm{H}_2 + \tfrac{1}{2}\mathrm{I}_2 \quad (2)$$

$$\mathrm{DI} \longrightarrow \tfrac{1}{2}\mathrm{D}_2 + \tfrac{1}{2}\mathrm{I}_2 \quad (3)$$

and the other terms are the zero point energies of the molecules indicated.

Wheeler, Topley and Eyring[7] have calculated the ratio of the rates of the reaction between the halogens and hydrogen and deuterium, from potential energy surfaces. For the ratio of the rates of formation of hydrogen and deuterium iodides, these authors have given the values 2.6, 2.34, and 2.26 at 575, 700, and 781°K., respectively. This may be compared with the experimental work of Blagg and Murphy[6] on the reverse reaction by making use of the equilibrium constants, that for hydrogen iodide being taken from Bodenstein, and that for deuterium iodide from the calculation of Blagg and Murphy. Thus

$$\frac{k_{1\mathrm{HI}}}{k_{1\mathrm{DI}}} = \frac{k_{2\mathrm{HI}}}{k_{2\mathrm{DI}}}\frac{K_{\mathrm{DI}}}{K_{\mathrm{HI}}} = 1.53 \times 1.23 = 1.88\ (700°\mathrm{K.}) \quad (4)$$

Geib and Lendle[8] determined the ratio of the rates of the combination reactions directly and found the value of 2.45 at 700°K. This is higher but closer to the theoretical value than that of Blagg and Murphy. However, the experimental error of Geib and Lendle is uncertain since they followed the course of their reaction by measuring the extinction coefficient of iodine by a photometric method. Large corrections were found to be necessary on their calibration curves mainly due to their use of white light and their precision is therefore considered low.

The discrepancies between the experimentally determined values and those calculated from theory make desirable a careful redetermination of the equilibrium constant for the hydrogen iodide reaction, as well as a new comparison of the kinetic reactions. The equilibrium constant

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(3) Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899). "Habilitationsschrift," Heidelberg, 11–36, W. Engelmann, Leipzig, 1899.

(4) Kassel, "Kinetics of Homogeneous Gas Reaction," The Chemical Catalog Co., New York, N. Y., 1932.

(5) Murphy, *J. Chem. Phys.*, **4**, 344 (1936).

(6) Blagg and Murphy, *ibid.*, **4**, 631 (1936).

(7) Wheeler, Topley and Eyring, *ibid.*, **4**, 178 (1936).

(8) Geib and Lendle, *Z. physik. Chem.*, **B32**, 463–470 (1936).