

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

ION ACTIVITIES IN HOMOGENEOUS CATALYSIS. THE FORMATION OF PARACHLORO-ACETANILIDE FROM ACETYLCHLORO-AMINO-BENZENE

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Introduction

The catalytic effect of specific ions on the velocities of certain reactions, in liquid systems, has been the subject of much investigation. The velocity of hydrolysis of esters and the inversion of sucrose are accelerated by the presence of either the hydrogen or the hydroxyl ion. Benzaldehyde is converted to benzoin by the catalytic influence of the cyanide ion. Hydrogen peroxide decomposes into water and oxygen upon the introduction of the iodine ion. Acetyl-chloro-amino-benzene is converted to *p*-chloro-acetanilide by the simultaneous presence of the hydrogen and chlorine ions.

It was early noticed that, in very dilute solutions, the velocities of such reactions were proportional to the concentrations of the catalyzing ions, as computed from conductivity ratios, a relation which would be predicted by the classic dissociation theory. As the concentration of the catalyzing ion increases, however, this proportionality no longer holds. The velocity increases more rapidly than would be expected from conductivity measurements. To explain this discrepancy the "Dual Theory" of catalysis was advanced by Senter,² Acree³ and others. This theory attributed a catalytic effect not only to the ion in question, but also to the undissociated molecule.

As against, or as supplementing, the theory of the undissociated molecule, it has been proposed that the activities of the ions are the determining factors.

Arrhenius⁴ found that the increase in cane sugar and ester hydrolysis by neutral salt addition could not be calculated from the calculated change in the hydrogen-ion concentration. He suggested that the velocity constant should be proportional to the osmotic pressure of the ions. Acree⁵ and his collaborators attempted to introduce hydrogen-electrode measurements for obtaining the hydrogen-ion activities necessary in the calculation

¹ Presented to the Graduate School of the University of Pennsylvania by Harry Seltz in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Senter, *J. Chem. Soc.*, **91**, 467 (1907).

³ Acree, *Am. Chem. J.*, **37**, 410 (1906); *ibid.*, **38**, 258 (1907).

⁴ Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

⁵ Acree, *et al.*, *Am. Chem. J.*, **43-46**.

of ester hydrolysis, etc. G. N. Lewis⁶ defined and indicated the importance of the activity function in chemical equilibrium calculations, thus putting the thermodynamic theory of concentrated solutions on a basis which was at the same time exact and simple. Harned⁷ suggested that the ion activities as defined by G. N. Lewis must play an important role in homogeneous catalysis, and later⁸ attempted to apply the theory to neutral salt catalysis.

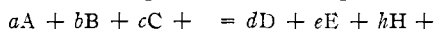
That the activity theory, in cases where the reaction depends on successive states of equilibria and no other factor, is a thermodynamic necessity may be seen from the following considerations. The thermodynamic criterion for equilibrium in any system at constant pressure and temperature, where only mechanical work is done, is that the change in free energy, F , is zero. Thus

$$[dF]_{P,T} = 0 \quad (1)$$

The activity of any ionic or molecular species of a system is related to the partial molal free energy by the equation⁶

$$\bar{F} = RT \ln a + i \quad (2)$$

where \bar{F} is the partial molal free energy, and i is a constant. This is a convenient way of defining "a" as pointed out by Brönsted.⁹ Using Equation 1 and Definition 2, it is a simple matter to show in general for a chemical reaction at constant pressure and temperature such as



that

$$\frac{a_D^d a_E^e a_H^h}{a_A^a a_B^b a_C^c} = K \quad (3)$$

where K is an equilibrium constant.¹⁰

The mass-action law is the special case of this more general law in dilute systems. If this equilibrium is considered to be a dynamic one, the opposing velocities being equal, it follows that the velocities in the two directions will be given by

$$\left. \begin{aligned} v_1 &= k_1 a_A^a a_B^b a_C^c \\ v_2 &= k_2 a_D^d a_E^e a_H^h \end{aligned} \right\} \quad (4)$$

Such considerations lead directly to the idea that the proportionality of reaction velocities in homogeneous catalysis is not to the concentrations of such ions but to their activities.

According to all kinetic theories of reaction velocities, all actual velocities must be proportional to the concentration of the substances entering into

⁶ Lewis, *Proc. Am. Acad. Arts Sci.*, **37**, 49 (1901); **43**, 259 (1907); *THIS JOURNAL*, **35**, 1 (1913), etc.

⁷ Harned, *THIS JOURNAL*, **37**, 2460 (1915).

⁸ Harned, *ibid.*, **40**, 1462 (1918).

⁹ Brönsted, *ibid.*, **42**, 761 (1920).

¹⁰ Proof is given by Lewis, Ref. 6.

the reaction, or in other words, the number of collisions in unit time. As a consequence of this and Equation 4, the activity of a species will be related to its concentration through the number of collisions. Since, in many cases, it has been shown that the activity of an ionic species must differ considerably from its concentration, only approaching it in infinite dilution, it may be stated that the power of an ion to accelerate a reaction or its reactivity may be changed by varying the environment at constant pressure and temperature, without changing the ion concentration.

The best evidence up to this time for the activity theory is that of Jones and W. C. McC. Lewis¹¹ who studied the inversion of sucrose by sulfuric acid, from the view point of the activity of the catalyzing hydrogen ion. They calculated this activity, in the presence of various concentrations of sucrose, from electromotive force measurements of the cells, $\text{H}_2 | \text{H}_2\text{-SO}_4(C) \text{ Sucrose } (c_1) | \text{Sat. KCl} | \text{HgCl} | \text{Hg}$. They found that the reaction could be explained on the basis of the hydrogen-ion activity, providing the water displacement effect be taken into consideration. They obtained good agreement for k_{bi} from the relation

$$k_{bi} = \frac{k_{uni}}{[\text{H}_2\text{O}] \times a_{\text{H}}}$$

in which k_{bi} is the true bimolecular velocity constant at any temperature, k_{uni} the observed unimolecular constant, (H_2O) the concentration of the water, and a_{H} the activity of the hydrogen ion. A criticism which may be made of this work is the fact that the calculation of the hydrogen-ion activities from the cell indicated above, requires the elimination of the liquid junction potential by a saturated potassium chloride solution. Furthermore, in this reaction the water molecule enters into the stoichiometrical equation, introducing a complicating factor.

More recently, Åkerlof¹² has carried out an extensive investigation of the hydrolysis of ethyl acetate by acids in the presence of neutral salts, with corresponding measurements of hydrogen-ion activities. The introduction of neutral salts complicates the problem considerably, and although good evidence was obtained, the problem remains unsolved. In this case also, liquid junction potentials, although small, may interfere.

It is the purpose of this paper to attempt to establish the activity relation free from any such complicating influences as those mentioned above. A reaction apparently ideal in this respect is the conversion of acetyl-chloro-amino-benzene to *p*-chloro-acetanilide, catalyzed by hydrochloric acid. This reaction was first studied in aqueous solution, from a dynamic standpoint, by Rivett.¹³ He determined the velocity constants of the conversion at 25° for concentrations of hydrochloric acid

¹¹ Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920).

¹² Åkerlof, *Z. physik. Chem.*, **98**, 260 (1921).

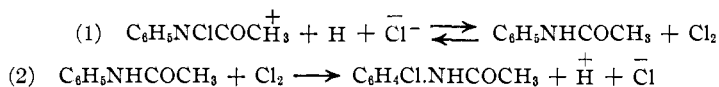
¹³ Rivett, *ibid.*, **82**, 201 (1913).

varying from 0.1 to 1.0 M . This reaction is catalyzed by the simultaneous presence of the hydrogen and chlorine ions but, as shown by Rivett, the velocity is not proportional to the product of the concentrations of these ions, as calculated from conductivity measurements, the deviation being over 30% in the range studied.

This reaction is particularly adaptable to study from the activity standpoint. Since both the hydrogen and chlorine ions enter into the catalysis, it should be the product of the activities of these ions which determines the velocity at any temperature. The activity product of hydrochloric acid can be calculated, as shown below, from electromotive-force measurements of the cells, $H_2|HCl_{(c)}|HgCl|Hg$, with thermodynamic accuracy, and without any errors caused by liquid-junction potential difficulties. The reaction under consideration, also, appears to be free from complications brought about by having the water molecule take part.

The Reaction, Acetyl-chloro-amino-benzene \longrightarrow *p*-Chloro-acetanilide

According to the investigations of Orton and Jones,¹⁴ this reaction probably takes place in two steps.



They have shown that, in carbon tetrachloride solutions, with anilides which do not chlorinate, the reaction $ArNCl.Ac + HCl \longrightarrow ArNHAc + Cl_2$ is quantitative. (The chlorine was determined by the aspiration method.)

Reaction 1 above, is a measurably slow reaction, while Reaction 2 is very rapid, so that the system approximates a continuous series of successive equilibria, with the concentration of the hydrochloric acid remaining practically constant.

Thus, if Reactions 1 and 2 express correctly the mechanism, then from the above considerations and Equation 4, it can readily be shown that the velocity should be proportional to the product of the activities of the acetyl-chloro-amino-benzene, the hydrogen ion and the chlorine ion, or $v = Ka_A \times a_H \times a_{Cl}$ in which a_A is the activity of the chloro-amine. Since the concentration of the hydrochloric acid remains constant, during the course of the reaction, $a_H \times a_{Cl}$ is also constant, and we can write, $v = ka_A$. If the activity coefficient of the chloro-amine is proportional to its concentration throughout the reaction, then k should correspond to a first order reaction constant. Since the concentration of the compound does not exceed 0.02 M in any experiment, such an assumption is justified, and the reaction will be monomolecular. The value of k should be given by the equa-

¹⁴ Orton and Jones, Rept. Brit. Assoc. Adv. Sci. p. 85, 1910.

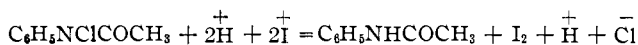
tion, $k = K_T a_H \times a_{Cl}$, where K_T is constant at any given temperature, or $K_T = \frac{k}{a_H \times a_{Cl}}$.

Experimental

The values of the unimolecular velocity constant k , for the reaction acetyl-chloro-amino-benzene to *p*-chloro-acetanilide, have been determined at 17.65°, 25.00° and 35.00°, for concentrations of hydrochloric acid from 0.1 to 1.0 *M*; all concentrations were in mols per 1000 g. of water. The acetyl-chloro-amino-benzene was prepared by the method of Slosson¹⁵ and was purified by recrystallization. The hydrochloric acid used throughout was made by diluting constant-boiling acid, and its concentration was checked by gravimetric analysis.

The procedure was similar to that used by Rivett. A hot saturated aqueous solution of the compound was prepared, and after standing for some hours, was filtered. A weighed quantity of this solution was cooled slightly below the temperature at which the reaction was to be carried out, and a sufficient weight of the standardized acid added to bring the concentration to the required molality. It is important to note that a considerable rise in temperature, amounting to a degree in some cases, may take place upon mixing. The temperature was always adjusted before a zero reading was taken. The thermostat was regulated to $\pm 0.02^\circ$. A careful regulation of the temperature is essential, since a change of 0.1° causes a change of about 2% in the velocity constant.

The course of the reaction was followed by removing 25 cc. of the solution in a pipet, at definite time intervals, and introducing it into a solution of potassium iodide. The following reaction takes place.



The *p*-chloro-acetanilide does not react with the iodide. The free iodine liberated was titrated with a dilute (0.015 *M*) solution of sodium thio-sulfate, using starch as an indicator. The value of k was calculated from the usual first order equation,

$$k = \frac{1}{t} \log \frac{A_0}{A_1}$$

in which A_0 is the zero titer and A_1 the titer after "*t*" minutes. Readings were taken at such time intervals that 6 to 10 titers could be made before the reaction reached the half-way point. These time intervals, naturally, varied greatly, depending on the temperature and concentration of acid. At 18° for 0.1 *M* acid, readings were taken every 2 hours; while at 35°, for 1.0 *M* acid, it was necessary to make them every 30 seconds.

In Table I are given the final mean values of k for each concentration

¹⁵ Slosson, *Ber.*, **28**, 3265 (1895).

of acid; the maximum variation in a series was $\pm 1\%$. The concentration of acid (C) is given in mols per 1000 g. of water.

TABLE I
OBSERVED VELOCITY CONSTANTS¹³

C.	17.65°	25.00°	35.00°
	k	k	k
0.1	0.0002160	0.000467	0.001500
0.2	0.000781	0.001718	0.00562
0.3	0.001710	0.003756	0.01200
0.4	0.003040	0.00666	0.02070
0.5	0.00472	0.01040	0.03254
0.6	0.00694	0.01505	0.0473
0.7	0.00952	0.02104	0.0645
0.8	0.01276	0.02800	0.0868
0.9	0.01660	0.0366	0.1126
1.0	...	0.0465	0.1431

The Activity Values

The free energy decrease ($-\Delta F$), for a solution of hydrochloric acid in going from a concentration C_1 to C_2 can be determined by measurements of the electromotive force of the cells, $H_2|HCl_{(C)}|HgCl|Hg$, at concentrations C_1 and C_2 . The difference in electromotive forces at these two concentrations, multiplied by the faraday, gives the free energy of transfer of one mol of hydrochloric acid directly in joules.

Ellis¹⁷ has accurately determined these free energy changes for hydrochloric acid at 18°, 25° and 35°, over a large range of concentrations.

From the equation

$$(-\Delta F) = RT \ln \frac{a_{HCl}}{a'_H a'_Cl}$$

the ratio of the products of the ion activities can be calculated. Calling F_H and F_{Cl} the activity coefficients of the hydrogen and chlorine ions, respectively, then $F_H C \times F_{Cl} C = a_H \times a_{Cl}$, in which C is the concentration of the acid. The value $\sqrt{F_H \times F_{Cl}}$ denoted by F_a' is the activity coefficient of the acid.

Ellis assumes that this activity coefficient for hydrochloric acid equals the conductance ratio at 0.001 M , a value at this concentration of 0.985. He calculates from this the values of the activity coefficients for the higher concentrations.

The activity coefficients used in this paper were not taken directly from a plot of Ellis's data, but were calculated by a method suggested by Harned¹⁸ from the equation, $\log F_a' = \alpha' C - \beta' C^m$, in which α' , β' and m' are constants at any temperature, and C is the concentration of the acid.

¹⁶ The data by Rivett (Ref. 13) at 25° were determined on a volume normal basis, at odd concentrations. When corrected to weight molal they correspond fairly well to the values given above.

¹⁷ Ellis, *THIS JOURNAL*, **38**, 737 (1916); **39**, 2532 (1916).

¹⁸ Harned, *ibid.*, **44**, 252 (1922).

The values of these constants were determined graphically to give the best mean values of Ellis's results.¹⁹

Discussion of Results

The values of k (Table I) at each temperature, increased rapidly with the increase in concentration of hydrochloric acid. As a first approximation it was noticed that these velocity constants were roughly proportional to the square of the concentration of the acid. An examination of the value of k/C^2 (Table II) shows, however, a pronounced minimum for each temperature, at 0.5 M acid. Col. 4, Table II, shows the corresponding values

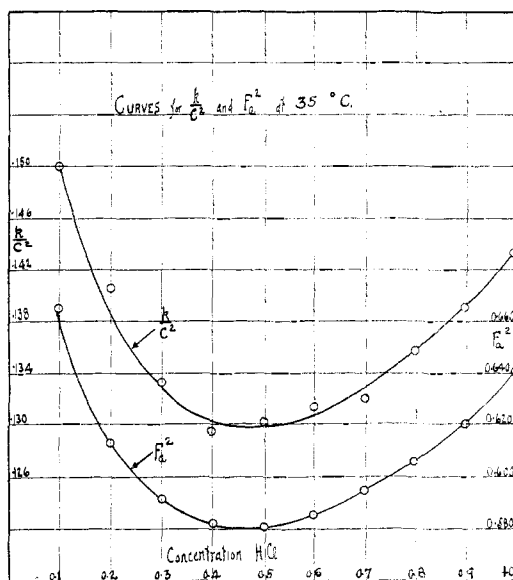


Fig. 1.

of the activity coefficients, calculated as described above. It is immediately apparent that the minima for these values occur at precisely the same concentration, namely 0.5 M . This point is well illustrated by the curve (Fig. 1) in which the values of $(F_a')^2$ are plotted against concentration of acid. The form of the curve is similar to that of k/C^2 with a perfect coincidence of the minima.

In Col. 6 are given the final values of $k/(F_a' C)^2$. The constancy of these figures, at each temperature, over the entire range of concentration, is well within the limit of experimental error.

¹⁹ The constants determined for the above equation are,

T	α'	β'	m'
18°	0.200	0.285	0.455
25°	0.200	0.286	0.434
35°	0.180	0.277	0.414

Since, by definition of F_a' , $(F_a' \times C)^2 = a_H \times a_{Cl}$ the relation $K_T = \frac{k}{a_H \times a_{Cl}}$ is without any question substantiated. This conclusion

TABLE II
Temp. 17.65°

(1)	(2)	(3)	(4)	(5)	(6)
C.	k	$\frac{k}{C^2}$	F_a'	$(F_a')^2$	$\frac{k}{(F_a' C)^2}$
0.1	0.0002160	0.02160	0.832	0.692	0.0314
0.2	0.000781	0.01953	0.800	0.640	0.0311
0.3	0.001710	0.01900	0.785	0.617	0.0308
0.4	0.003040	0.01900	0.781	0.610	0.0313
0.5	0.00472	0.01888	0.780	0.608	0.0311
0.6	0.00694	0.01928	0.783	0.614	0.0314
0.7	0.00952	0.01940	0.790	0.624	0.0313
0.8	0.01276	0.01990	0.799	0.639	0.0314
0.9	0.01660	0.02050	0.810	0.655	0.0310

Mean 0.0312

Temp. 25.00°

0.1	0.000467	0.0467	0.822	0.676	0.0692
0.2	0.001718	0.0430	0.790	0.623	0.0690
0.3	0.003756	0.04175	0.777	0.604	0.0691
0.4	0.00666	0.0416	0.773	0.598	0.0695
0.5	0.01040	0.0416	0.773	0.598	0.0695
0.6	0.01505	0.0418	0.778	0.605	0.0692
0.7	0.02104	0.04295	0.785	0.616	0.0697
0.8	0.02800	0.0438	0.795	0.632	0.0693
0.9	0.03660	0.0448	0.807	0.651	0.0694
1.0	0.0465	0.0465	0.820	0.672	0.0692

Mean 0.0693

Temp. 35.00°

0.1	0.001500	0.1500	0.815	0.664	0.226
0.2	0.00562	0.1405	0.783	0.613	0.229
0.3	0.01200	0.1333	0.769	0.591	0.226
0.4	0.02070	0.1294	0.763	0.582	0.223
0.5	0.03254	0.1302	0.762	0.581	0.224
0.6	0.0473	0.1315	0.765	0.585	0.225
0.7	0.0645	0.1317	0.771	0.594	0.222
0.8	0.0868	0.1358	0.779	0.606	0.224
0.9	0.1126	0.1390	0.788	0.620	0.224
1.0	0.1431	0.1431	0.800	0.640	0.224

Mean 0.224

is particularly significant in this case, when we consider that these results are based entirely on accurate thermodynamic activity data, without complications due to liquid junction potentials, and without any assumptions as to individual ion activities.

The Temperature Coefficient

With the development of the radiation hypothesis of reaction velocity, it is of considerable importance to obtain the temperature coefficients

of reaction velocity constants. The temperature coefficient should be expressed by an equation of the form

$$\frac{d \ln K_T}{dT} = \frac{E_c}{RT^2} \quad (6)$$

where E_c may be called the critical increment. According to the rule of Arrhenius E_c is a constant. It is not necessary to mention the various meanings attached to E_c by different authors,²⁰ but it is of some value to point out that in this case the rule of Arrhenius is not valid over the short range of temperature. The plot of $\ln K_T$ against $1/T$ is not a straight line but has considerable curvature, showing that E_c varies considerably with the temperature. Integration of (6) between temperature limits T_1 and T_2 , assuming that E_c is constant, gives

$$E_c = \frac{4.571 T_1 T_2}{T_1 - T_2} \log \frac{K_{T_1}}{K_{T_2}}$$

whence E_c is found to be 1.356×10^5 cal. between 25° and 35° , and 1.196×10^5 cal. between 17.65° and 25° . This is sufficient to show that the rule of Arrhenius does not hold.

The Neutral Salt Effect

From measurements of the electromotive forces of cells of the type $H_2 | HCl(0.1 M) + MeCl(c) | HgCl | Hg$, it is possible to obtain the product of the activities of the hydrogen and chlorine ions in acid salt mixtures exactly, without any difficulties arising from liquid junction potentials. Exact measurements of these cells have been made by Harned²¹ so that the required thermodynamic data are available for applying the activity theory to the velocity of conversion of acetyl-chloro-amino-benzene to *p*-chloro-acetanilide. Velocity measurements on this reaction have been made, using hydrochloric acid-sodium chloride mixtures, and hydrochloric acid-potassium chloride mixtures which show that the relation

$K_T = \frac{k}{a_H \times a_{Cl}}$ which holds so beautifully for hydrochloric acid alone fails

to hold in the presence of the neutral salts. K_T instead of remaining constant, decreases considerably with increasing salt concentration. This study will be the subject of a future communication.

Summary

1. It has been derived, from thermodynamic considerations, that, in reactions in liquid systems catalyzed by specific ions, it is the activities of such ions which determine the velocity of the reaction at any temperature when the catalysis depends on successive states of equilibria.

²⁰ W. C. McC. Lewis "System of Physical Chemistry," Longmans, Green and Co., Perrin, *Ann. Phys.*, [9] **11**, 5 (1919). Tolman, *THIS JOURNAL*, **42**, 2506 (1920); and others.

²¹ Harned, *THIS JOURNAL*, **38**, 1986 (1916); **42**, 1808 (1920).

2. The velocity constants of the reaction acetyl-chloro-amino-benzene to *p*-chloro-acetanilide, catalyzed by hydrochloric acid, have been determined at 17.65°, 25° and 35° for concentrations of acid from 0.1 to 1.0 *M*.

3. It has been shown that these velocity constants at each temperature are proportional to the product of the activities of the hydrogen and chlorine ions of the catalyzing acid.

4. As far as we are aware, this is the first case in which homogeneous catalysis may be calculated with exactness over a wide concentration range and in concentrated solutions, without uncertainties arising in liquid junction potentials.

5. The temperature coefficient has been considered and the critical increment has been roughly calculated and shown to vary considerably with rise in temperature.

6. The relation $K_T = \frac{k}{a_H a_{Cl}}$ which holds exactly for solutions of hydrochloric acid alone, fails to hold when acid-salt mixtures are used as catalysts.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE]

THE ELECTROMETRIC TITRATION OF URANIUM WITH POTASSIUM PERMANGANATE AND POTASSIUM DICHROMATE

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When an acid solution of uranium is treated with a reducing agent such as zinc, the product of the reduction is a mixture of tetravalent uranium with smaller and varying amounts of the trivalent form. Although potassium permanganate solution may be used to oxidize either form to the hexavalent state and since the velocity constant of the oxidation of the lowest form is much greater than that of the tetravalent, it becomes advisable for the volumetric determination of uranium to either have all of it in the tetravalent state or to determine, in the case of a mixture, the ratio of the two. McCoy and Bunzel¹ found that when a reduced solution of uranium was filtered and allowed to come in contact with the atmosphere it contained nearly all of the uranium in the tetravalent form, the velocity constant for the oxidation of the trivalent to the tetravalent being very large compared with that for the oxidation of the latter. Such a solution could be titrated with potassium permanganate.

In this investigation we have accomplished three things: first, we have measured the amount of trivalent uranium in solution by oxidizing it to tetravalent uranium both with potassium permanganate in sulfuric

¹ McCoy and Bunzel, *THIS JOURNAL*, **31**, 367 (1909).