

### Summary

1. The photochemical decompositions of methylamine and ethylamine have been studied. Gaseous products, mainly hydrogen, methane, ethane and nitrogen and a non-volatile liquid of uncertain composition are obtained.

2. A relatively fast photoreaction between methylamine and oxygen has been observed.

3. The photodecomposition of amines is a process of low quantum yield.

4. The photodecomposition of amines induces the polymerization of ethylene. The ratio of polymerized ethylene to amine decomposed is 6-8 at temperatures of 200° and upward in contrast to ammonia, with which this ratio obtains at room temperatures.

5. The reaction rates are independent of the ethylene concentration over a range of 2-25 cm. and also independent of the amine concentration for complete light absorption.

6. Ethane appears to inhibit the normal photodecomposition of ammonia. At the same time some polymerization of the hydrocarbon occurs.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN ALUMINUM CHLORIDE SOLUTIONS

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The cells



containing hydrochloric acid at 0.05 *M* concentration and varying amounts of aluminum chloride, and hydrochloric acid and aluminum chloride mixtures at both constant total molality and constant total ionic strength have been measured at 25°. These results supplement previous work with similar cells containing the acid in univalent and biunivalent halide solutions.<sup>1</sup>

### Experimental Results

The measurements were obtained with the usual type of cell without the employment of vacuum technique. At the concentrations of acid employed, any hydrolysis of the aluminum chloride solutions was sufficiently suppressed as to have no noticeable effect. The concentrated solution of aluminum chloride was prepared from the repurified salt, and its strength determined by analysis of the chlorine content. All other

<sup>1</sup> A bibliography of the earlier results may be found in Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1930, 2d ed., Vol. I, p. 801.

solutions were made from this by weighing suitable amounts of the ingredients. Table I, Section (1), gives the results for the cells containing 0.05 *M* acid and varying chloride concentrations. Section (2) contains the measurements at a constant total molality of 0.5 *M*, and Section (3) the values at 1 $\mu$  constant total ionic strength.

TABLE I  
ELECTROMOTIVE FORCES OF CELLS  
 $H_2 | HCl (m_1), AlCl_3 (m_2) | AgCl | Ag, \text{ at } 25^\circ$   
(1)

Constant Acid-Varying Salt ( $m_1 = 0.05 M$ )					
$m_2$	<i>E</i>	$\gamma$	$m_2$	<i>E</i>	$\gamma$
0.0	0.38626	(0.829)	0.15	0.33526	0.708
.005	.38085	.808	.2	.32799	.715
.0075	.37868	.798	.25	.31911	.766
.0101	.37686	.786	.3	.31589	.747
.01	.37688	.788	.4	.30570	.796
.02	.37036	.762	.45	.30096	.824
.03	.36506	.749	.6	.28821	.919
.05	.35743	.727	.8	.27156	1.104
.07	.35163	.713	1.0	.25597	1.400
.1	.34447	.707	2.0	.18281	3.95

(2)

Constant Total Molality of 0.5				
$m_1$	$m_2$	<i>E</i>	$\gamma$	
0.05	0.45	0.30096	0.680	
.1	.4	.28585	.691	
.2	.3	.27424	.717	
.25	.25	.27156	.725	
.3	.2	.27076	.742	
.35	.15	.26991	.744	
.45	.05	.27116	.747	
.5	.0	.30238	(.757) <sup>a</sup>	

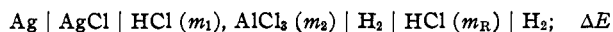
(3)

Constant Total Ionic Strength of 1 $\mu$				
$m_1$	$m_2$	<i>E</i>	$\gamma(\text{obs.})$	$\gamma(\text{calcd.})$
0.05	0.1583	....	0.709 <sup>b</sup>	0.712
.1	.15	0.31450	.719	.717
.15	.1417	.30220	.726	.722
.2	.1333	.29356	.728	.727
.25	.125	.28656	.731	.732
.3	.1167	.28015	.741	.737
.4	.1	.27032	.749	.748
.5	.0833	.26207	.759	.758
.6	.0667	.25511	.769	.769
.7	.05	.24877	.782	.780
.9	.0167	.23808	.803	.802
1.0	.0000	.23361	(.810) <sup>a</sup>	.813

<sup>a</sup> Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

<sup>b</sup> Obtained from graph of data in Section (1).

In the last column of all three sections are given the activity coefficients computed from the cell



by the equation

$$\Delta E = 0.1183 \log \frac{\gamma}{\gamma_R} + 0.05915 \log \frac{m_1(m_1 + 3m_2)}{m_R^2} \quad (1)$$

where  $\gamma$  is the activity coefficient in the salt solution and  $\gamma_R$  that in the reference solution of pure hydrochloric acid.  $\gamma_R$  was taken to be 0.829 at 0.05 *M* hydrochloric acid.<sup>2</sup>

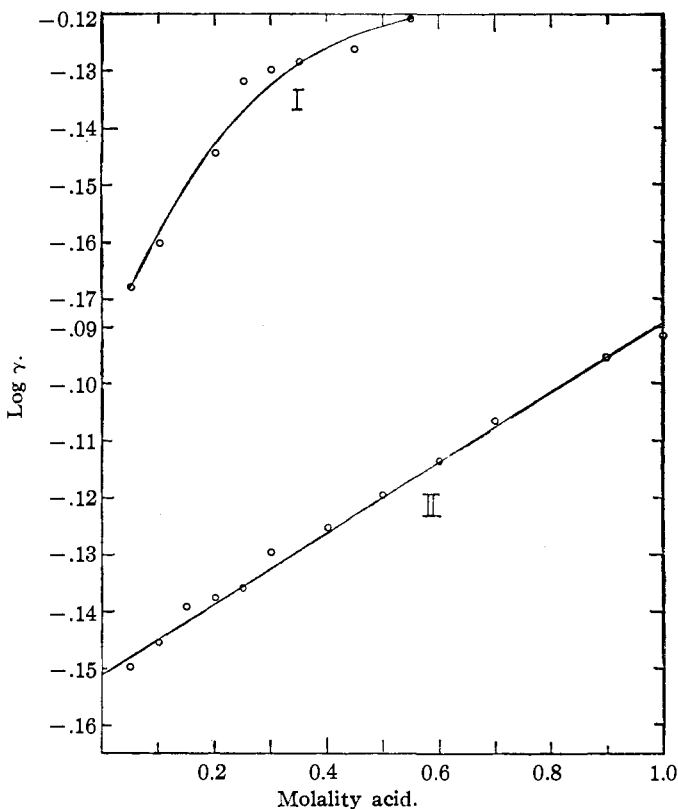


Fig. 1.—I,  $\text{Log } \gamma$ - $m_1$  plot at a constant total molality of 0.5. II,  $\text{Log } \gamma$ - $m_1$  plot at  $1\mu$  constant ionic strength.

### Discussion

The activity coefficient of the acid in aluminum chloride solutions varies with the ionic strength in a manner similar to its behavior in alkali chloride solutions, and shows the characteristic minimum. Indeed, the results

<sup>2</sup> Randall and Young, *THIS JOURNAL*, 50, 989 (1928).

are almost numerically identical with the activity coefficient of the acid in potassium chloride solutions.

By the data in Table I, Sections (2) and (3), we may test the equation

$$\log \gamma = \log \gamma_0 + \alpha m_1 \quad (2)$$

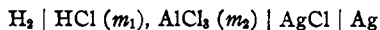
which has been shown to be valid for solutions containing hydrochloric acid in uniunivalent chloride solutions at constant total molality or ionic strength.  $\gamma$  is the activity coefficient of the acid,  $m_1$  its molality, and  $\gamma_0$  its activity coefficient in the acid-free salt solution. In Fig. 1, the upper curve represents the plot of  $\log \gamma$  against  $m_1$  at constant 0.5 total molality constructed from the results in Table I, Section (2). A pronounced curvature is obtained. The lower curve is the plot of  $\log \gamma - m_1$  at a constant total ionic strength of  $1\mu$ , and is a straight line expressed by the equation

$$\log \gamma = \bar{1}.8495 + 0.0605 m_1$$

In the last column of Table I, Section (3), are given the values of  $\gamma$  computed by this equation. Since a difference of 0.07 mv. causes an error of one in the third place of activity coefficient in this region, the agreement between calculated and observed results is good. The maximum error is at 0.15  $m_1$  and corresponds to 0.27 mv.

### Summary

#### 1. Measurements of cells



have been made at 25°.

2. The results at constant ionic strength of  $1\mu$  verify the law of the linear variation of  $\log \gamma$  and may be expressed by the equation

$$\log \gamma = \bar{1}.8495 + 0.0605 m_1$$

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