

oxide is reduced to cuprous oxide and it follows that cupric oxide is a relatively poor catalyst for the foregoing reaction. Cuprous oxide, on the other hand, seems to be a very good catalyst and is therefore only slightly reduced when only an equivalent quantity of potassium is used. The ease of reduction of bismuth trioxide and silver oxide precludes the possibility of their exerting any appreciable catalytic effect. Germanic oxide exhibits no marked catalytic effect toward the reaction between potassium and ammonia.

The formation of insoluble or soluble intermetallic compounds of potassium (by the interaction of potassium and the metal liberated from the oxide in the reduction reaction) might have been anticipated, particularly in the case of bismuth.² Such reactions were suppressed by the utilization of only that quantity of potassium

required for the removal of oxygen, and by the fact that the velocity of the reduction reaction proved to be much greater than that of intermetallic compound formation.

Summary

1. A study of the action of liquid ammonia solutions of potassium on certain metal oxides has shown that: (a) cupric oxide is largely reduced to cuprous oxide; (b) cuprous oxide is reduced to elemental copper to a slight extent; (c) silver oxide and bismuth trioxide are reduced quantitatively to the corresponding elemental metals; and (d) germanic oxide is not reduced.

2. Germanic oxide is not acted upon by a liquid ammonia solution of potassium amide at room temperature.

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RECEIVED JUNE 19, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CREIGHTON UNIVERSITY]

The Partial Pressure of Hydrogen Chloride from its Solutions in Ethylene Glycol and Other Solvents at 25°

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It has been pointed out by Rodebush and Ewart² that the measurement of the partial pressure of a volatile acid solute provides a means of estimating the extent of the acid-solvent base reaction. More recently, Zellhoefer and co-workers³ have shown that measurements of the solubility of halogenated hydrocarbons at various pressures in a number of solvents may be interpreted in terms of a solute-solvent reaction, involving the formation of a hydrogen bond, and in terms of the association of the medium. It would seem, then, that a similar study employing a solute like hydrogen chloride, which is at the end opposite to that of the halogenated hydrocarbons, on the scale of hydrogen activity, should be interesting from this point of view. Data of this kind for hydrogen chloride solutions, however, are quite limited. With the exception of a few measurements of the solubility at pressures of about one atmosphere the only direct measurements of the partial pres-

sure of hydrogen chloride from its solutions recorded in the literature are those from water at 25°,⁴ glacial acetic acid at the same temperature,² and benzene at 30°.⁵ Additional information of this kind is also indirectly available for benzene and nitrobenzene solutions at 25° from distribution studies.⁶ It is believed that further studies of this kind would be worth while.

Since the work of Zellhoefer and co-workers^{3b,3c} shows the solubility of monofluorodichloromethane to be less in ethylene glycol than in nitrobenzene and in acetic acid, while it is to be expected that the solubility of hydrogen chloride in ethylene glycol is greater than that in either of these two solvents, considering the high solubility of hydrogen chloride in alcohols in general, it was decided to make a study of the partial pressure of hydrogen chloride from its ethylene glycol solutions in order to provide concrete evidence concerning this point. It is the purpose of this paper, then, to report the results obtained in this study, and to discuss the available data in terms of the acid-solvent base reaction.

(1) Taken in part from a thesis submitted by R. A. Zuercher to the graduate school of The Creighton University in partial fulfillment of the requirements for the M. S. degree, June, 1939.

(2) Rodebush and Ewart, *THIS JOURNAL*, **54**, 419 (1932).

(3) (a) Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937); (b) Zellhoefer, Copley and Marvel, *THIS JOURNAL*, **60**, 1337 (1938); (c) *ibid.*, p. 2666; (d) *ibid.*, p. 2714. See also Copley and Holley, *ibid.*, **61**, 1599 (1939), on similar work with acetylenic compounds.

(4) Randall and Young, *ibid.*, **50**, 1001 (1928).

(5) Saylor, *ibid.*, **59**, 1712 (1937).

(6) Wynne-Jones, *J. Chem. Soc.*, 1064 (1930).

Experimental

Apparatus and Method.—Since the apparatus and method are almost identical with those employed by Saylor,⁵ details will not be given here. However, preliminary experiments were performed using solutions of known vapor pressures which showed that the solution-vapor equilibria were established within twenty-four hours. Consequently, the time allowed for the glycol solutions to come to equilibrium with their vapor was approximately two days instead of the longer periods suggested by Saylor.

The constant temperature bath was regulated at 25.00 ± 0.02°.

Materials.—The ethylene glycol used was an Eastman Kodak Co. product of good grade. It was not purified further since the method employed is not of sufficient accuracy to give results that would be seriously affected by the traces of impurities present.

The hydrogen chloride was generated in an all-glass apparatus using C. P. grade potassium chloride and sulfuric acid. It was passed through a drying tower of phosphorus pentoxide before being introduced into the ethylene glycol.

Results

The results obtained are given in Table I in which the first column contains the molalities of the solutions, the second the partial pressure of hydrogen chloride from the solutions and the third, values for the quantity,⁷ $k'\gamma$, which will be considered below.

TABLE I

THE PARTIAL VAPOR PRESSURE OF HYDROGEN CHLORIDE FROM ETHYLENE GLYCOL SOLUTIONS AT 25°

<i>m</i>	<i>p</i> , atm.	$k'\gamma$
1.33	0.0008	0.0212
2.27	.0025	.0220
2.45	.0032	.0231
2.72	.0046	.0250
3.02	.0074	.0285
3.07	.0075	.0282
3.11	.0086	.0298
3.13	.0079	.0284
4.66	.0357	.0406
6.57	.135	.0558
6.63	.139	.0562
6.92	.172	.0598
8.78	.424	.0742

A logarithmic plot of the data in Table I, together with those for water, acetic acid, benzene and nitrobenzene solutions, is given in Fig. 1. The data for water solutions were taken from those given by Randall and Young⁴; that for glacial acetic acid solutions from the investigation of Rodebush and Ewart²; and those for the benzene and nitrobenzene solutions are direct measurements of

(7) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 329-330, 337.

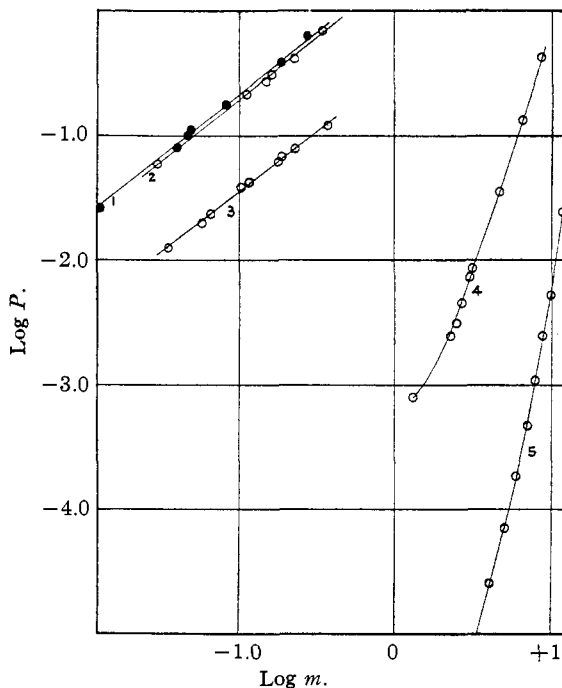


Fig. 1.—The partial pressure of hydrogen chloride from solutions in (1) benzene, (2) nitrobenzene, (3) acetic acid, (4) ethylene glycol, (5) water.

the hydrogen chloride pressure above the solutions at 25°, which were taken from unpublished studies made in this Laboratory.^{8,9} Since these seem to be the only direct measurements made in these solvents at 25°, some representative data are also given in Tables II and III.

TABLE II

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS BENZENE SOLUTIONS AT 25°

<i>m</i>	<i>p</i> , atm.	<i>m</i>	<i>p</i> , atm.
0.273	0.601	0.048	0.111
.191	.391	.047	.100
.112	.211	.040	.078
.096	.197	.014	.026

TABLE III

THE PARTIAL PRESSURE OF HYDROGEN CHLORIDE FROM ITS NITROBENZENE SOLUTIONS AT 25°

<i>m</i>	<i>p</i> , atm.	<i>m</i>	<i>p</i> , atm.
0.338	0.689	0.161	0.312
.323	.636	.146	.278
.319	.654	.110	.213
.225	.428	.030	.059

Discussion

From Fig. 1 it is evident that hydrogen chloride solutions in the solvents considered, fall into two groups. In one, which includes benzene, nitro-

(8) Schmelzle, Master's Thesis, The Creighton University, 1938.
 (9) Westfall, Master's Thesis, The Creighton University, 1938.

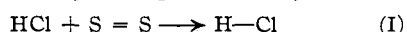
benzene, and acetic acid, its solubility is low, and the law of Henry in the form

$$p = km \quad (1)$$

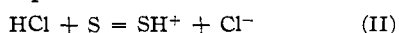
is followed.¹⁰ In the second, which includes water and ethylene glycol solutions, its solubility is high, and the law of Henry, in the form of equation (1), does not hold, but, as is customary for aqueous solutions, the data can be treated in terms of the law of Henry (or a law similar to it) in the form⁷

$$p^{1/2} = k'\gamma m \quad (2)$$

It seems logical to consider this possible treatment of the data in terms of two forms of the law of Henry, as an indication of two different acid-solvent reactions. Equation (1) corresponds to a reaction which may be represented by



where S represents the solvent and $\text{S} \longrightarrow \text{H}-\text{Cl}$ is written to indicate the formation of a hydrogen bond with some atom in the solvent. Equation (2) would correspond to the reaction



where SH^+ represents the solvated proton.

Also, the extent to which these acid-base reactions proceed may be determined, if it can be assumed that the unreacted molecular hydrogen chloride in the solutions corresponds to the law of Raoult⁶ (p. 1070)

$$f = f_0 N_u \quad (3)$$

where f is the fugacity of the hydrogen chloride in solution, f_0 is the fugacity of pure liquid hydrogen chloride, and N_u is the mole fraction of unreacted hydrogen chloride. First, however, it should be pointed out that since reaction (I) takes place to some extent, equation (1) should be written

$$p = k(m_u + m_r) \quad (4)$$

where m_u represents the molality of unreacted hydrogen chloride, m_r , reacted hydrogen chloride, and

$$m = m_u + m_r \quad (5)$$

Equation (2), of course, could be written in a similar manner, but since the molality of unreacted solute is negligible in comparison with that which has reacted, in all the cases so far considered which fit into this group, it is only necessary to set

$$m = m_r \quad (6)$$

in order to follow through in equation (2) the notation adopted in equation (4).

(10) Compare Heston and Hall, *THIS JOURNAL*, **56**, 1462 (1934).

The equilibrium constant of the reaction represented by (I) is given by

$$K_a = a_r/a_u \quad (7)$$

where the a 's refer to activities and the subscripts have the same significance as in the previous equations. Using equation (3) and setting $p = f$, it is found that¹¹

$$m_u = m_s p / f_0 \quad (8)$$

where m_s is the number of moles of solvent in 1000 g. Assuming that activities are equal to molalities in this case, and making use of equations (4), (5) and (8), equation (7) becomes

$$K_a = (f_0 - km_s) / km_s \quad (9)$$

In like manner, making use of equations (2), (6) and (8), and assuming that the activity coefficients of unreacted hydrogen chloride are equal to unity, the equilibrium constant for reaction (II) becomes

$$K_d = f_0 / m_s k'^2 \quad (10)$$

In Table IV are given values of these constants for hydrogen chloride solutions in benzene, nitrobenzene, acetic acid, glycol and water. In obtaining these constants, the value of $f_0 = 30.3$ atm. at 25° was calculated from the vapor pressure of liquid hydrogen chloride, interpolated from the data in "International Critical Tables,"¹² using the approximate method of Lewis and Randall⁷ (pp. 197-199), and assuming that the deviation of hydrogen chloride from the perfect gas law at 25° is the same as that indicated by the work of Gray and Burt¹³ at 0°; the Henry's law constants given in the second column of this table were obtained from the same data used in constructing Fig. 1, for benzene, nitrobenzene, and acetic acid; that for water is from Lewis and Randall⁷; that for glycol was obtained by extrapolating a plot of m against $k'\gamma$ (Table I) to $m = 0$, where, as in the case of aqueous solutions, it is assumed that $\gamma = 1$. The

TABLE IV
EQUILIBRIUM CONSTANTS FOR THE HYDROGEN CHLORIDE
SOLVENT BASE REACTIONS AT 25°

Solvent	k	K_a
Benzene	2.04	0.16
Nitrobenzene	1.98	0.88
Acetic acid	0.347	4.25
	k'	K_d
Ethylene glycol	0.02	4.68×10^3
Water	0.000664	1.23×10^8

(11) The denominator of equation (8) is, of course, $f_0 - p$, but p is neglected since in most cases it is small in comparison with f_0 . In the more concentrated solutions of hydrogen chloride, however, this simplification introduces an error of about 3%.

(12) "International Critical Tables," Vol. III, p. 228.

(13) Gray and Burt, *J. Chem. Soc.*, **95**, 1633 (1908).

partial pressure data could not be carried to low enough concentrations by the method employed to make the extrapolation with any great degree of certainty, but the curve was well enough defined so that the value given should be of the correct order of magnitude and may be accepted tentatively until activity data at lower concentrations are available.

The values for K_a and K_d given in this table indicate the relative basicities of the solvents, and the method of their derivation seems to be additional confirmation of the opinion that the basicity of a solvent is determined by the strength of the hydrogen bond formed with some atom in the solvent molecule acting as an electron donor.¹⁴ When the bond formed is weak, the hydrogen chloride remains in the solution in the form of hydrogen bond compound, although the bond distance between the proton and the negative constituent of the acid is increased, as indicated by infrared absorption studies^{14d} (p. 224). In solvents forming such bonds, the solubility of hydrogen chloride is low. When the bond formed is relatively strong, the bond between the proton and the negative constituent is so weakened that more or less complete ionization takes place, and when this occurs the solubility of hydrogen chloride is high.

While the formation of a complex between benzene and hydrogen chloride is indicated in Table IV, it should be pointed out that the magnitude of the deviation from the law of Raoult, which leads to the value given for K_a , may be of the same order as the uncertainty involved in the calculation of f_0 . In other words, it is not possible to conclude definitely from this work that reaction (I) takes place in this case, although such a process might serve as the explanation for the increased dielectric polarization of hydrogen chloride in benzene solutions,¹⁵ and the apparent slight shift toward longer wave lengths of the vibrational band occurring in the infrared spectra of hydrogen chloride at 3.46μ .¹⁶ In addition,

(14) (a) Gordy, *J. Chem. Phys.*, **7**, 93 (1939); (b) Gordy and Martin, *ibid.*, **7**, 99 (1939); (c) Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2528 (1938); (d) Rodebush and Buswell, *J. Phys. Chem.*, **43**, 219 (1939).

(15) Fairbrother, *J. Chem. Soc.*, **44** (1932).

(16) Plyler and Williams, *Phys. Rev.*, **49**, 215 (1936); Williams, *ibid.*, **49**, 719 (1936).

Hantzsch¹⁷ has considered such a possibility as the explanation for the catalytic action of hydrogen chloride in toluene solutions on the decomposition of diazoacetic acid ester.

The results obtained in this study of ethylene glycol solutions also definitely establish the inverted order of solubility of hydrogen chloride in nitrobenzene, acetic acid and glycol, compared to the solubility of monofluorodichloromethane. This appears to be an indication that the solute itself is an important factor in determining the basicity of the solvent, insofar as it may affect the hydrogen bonding between the molecules of the solvent. The solubility of hydrogen chloride in ethylene glycol is greater than expected from the law of Raoult, while that of monofluorodichloromethane is less. That this is due to a reduction in the amount of association of the glycol in the presence of hydrogen chloride seems quite likely, since the converse case of reduction of hydrogen bonding of solutes in the presence of other solutes that have a strong tendency to form hydrogen bonds, is fairly well established.¹⁸ However, further studies are in progress in this Laboratory and since these may give additional information concerning this point, further discussion will be postponed until the results of these investigations can be given.

Summary

1. The partial vapor pressure of hydrogen chloride from its solutions in ethylene glycol at 25° , over the concentration range, 1.33 to 8.78 *m*, has been measured. Also, data from unpublished studies on the partial pressure of hydrogen chloride from benzene and nitrobenzene solutions at 25° are included.

2. The available data on the partial pressure of hydrogen chloride from solutions in various solvents have been considered in terms of two different acid-base reactions. A method of calculating the equilibrium constants for these reactions has been given.

3. The importance of hydrogen bonding, and the nature of the solute, in determining the basicity of the solvent is indicated.

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RECEIVED JUNE 19, 1939

(17) Hantzsch, *Ber.*, **58B**, 630 (1925).

(18) Lassettre, *Chem. Rev.*, **20**, 274-278 (1937); Barger, *J. Chem. Soc.*, **87**, 1042 (1905).