

3. The adsorption of oxygen on the catalyst has been determined at constant pressure.

4. The adsorption and desorption of carbon monoxide has been studied at pressures of 150 mm. and 15 mm., respectively.

5. The catalytic efficiency for high temperature oxidation of carbon monoxide has been determined for amorphous, crystallized, reduced and oxidized samples of the catalyst.

6. It has been suggested that adsorption on the catalyst occurs in the following three steps:⁴

nearly instantaneous adsorption with activation energies of 3–6 kcal./mole; solid solution of the adsorbed gas; penetration of the dissolved gas into the interior of the catalyst.

7. It has been suggested further that catalysis takes place in three states. These follow each other with rising temperature in the order: "gas phase," "solution phase," "phase of chemical binding."

This work will be continued on other chromites.

BALTIMORE, MD.

RECEIVED JULY 19, 1940

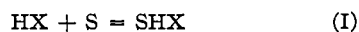
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CREIGHTON UNIVERSITY]

The Partial Pressure of Hydrogen Bromide from its Solutions in Some Aprotic Solvents at 25°

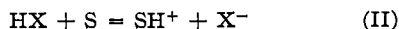
BY S. JAMES O'BRIEN AND EDWARD G. BOBALEK¹

Measurements of the partial pressure of hydrogen chloride from its solutions in various solvents have given evidence of an acid-base reaction in many solvents that are generally considered as aprotic, and in some cases have intimated the chelation and association of the solvent molecules.² It seemed of interest to determine how closely the conclusions derived for hydrogen chloride solutions parallel those for hydrogen bromide solutions.

In hydrogen chloride solutions where a reaction between solute and solvent seemed likely, the data were interpreted in terms of a reaction of the type^{2a}



or of the type



in which S represents the solvent; SHX, an unionized acid-solvent complex; and SH⁺, a solvated proton. In either case the extent of the reaction is dependent, at least, on the strengths of the acid and the solvent base.³ These factors are, then, included in the equilibrium constant for the reaction, and a comparison of the constants for two different acids in various solvents should show to what degree the reactions depend upon acidity and basicity alone. A method of

deriving equilibrium constants for reactions such as (I) and (II) from vapor pressure data was outlined in the first paper of this series.^{1a} In order to evaluate constants for hydrogen bromide to compare with those obtained for hydrogen chloride, measurements have been made of the partial pressure of hydrogen bromide from its solutions in benzene, toluene, and the ortho and meta isomers of nitrotoluene. These data and, in addition, measurements of the partial pressure of hydrogen chloride from toluene solutions, are reported in this paper.

Experimental

The apparatus and method were again the same as those employed in the previous work.^{2c,4}

The benzene and toluene were of good quality. They had been stored over sodium and were distilled in an all-Pyrex apparatus before using. The nitrotoluenes were redistilled after standing over calcium oxide. Some physical constants of the liquids so treated are as follows: benzene, m. p. 5.48°; toluene, n_D^{20} 1.4959; *o*-nitrotoluene, n_D^{20} 1.5453; *m*-nitrotoluene, m. p. 15.35°, n_D^{20} 1.5460.

Hydrogen bromide was prepared by the action of bromine on tetralin in an all-Pyrex apparatus. It was led through two long tubes, one containing red phosphorus and the other phosphorus pentoxide, before being introduced into the liquids.

Results

The results of the experiments are given in Table I. The first column of each section gives the molality of the hydrogen halide; the second its vapor pressure in mm. of mercury; and the third the Henry law constant, $k = p/m$, in atm.

(4) J. Saylor, *THIS JOURNAL*, **59**, 1712 (1937).

(1) Present address: Chemistry Department, University of Indiana, Bloomington, Indiana.

(2) (a) S. J. O'Brien, C. L. Kenny and R. A. Zuercher, *THIS JOURNAL*, **61**, 2504 (1939); (b) S. J. O'Brien and C. L. Kenny, *ibid.*, **62**, 1189 (1940); (c) S. J. O'Brien and J. B. Byrne, *ibid.*, **62**, 2063 (1940).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, especially pp. 251-262.

per mole per 1000 g. of solvent. The mean values of the constants and the deviations were obtained by the method explained in an earlier paper.^{2b}

The hydrogen bromide data are also shown graphically in Fig. 1, in which the logarithm of the pressure is plotted against the mole fraction (N_2) of the acid. In obtaining the theoretical line, the fugacity of hydrogen bromide was taken as 18.3 atm. This value was calculated following the same procedure employed for hydrogen chloride,^{2a} using the data in "International Critical Tables"⁵ for the vapor pressure, and assuming that the deviation of hydrogen bromide from the ideal gas law is the same⁶ at 25° as it is at 0°.

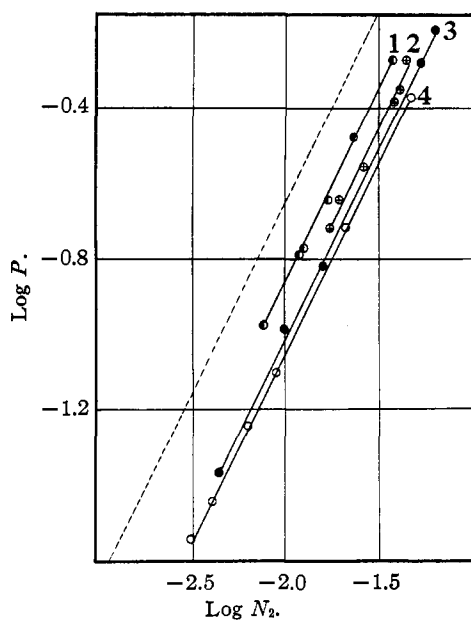


Fig. 1.—The partial pressure of hydrogen bromide from its solutions in (1) benzene, (2) toluene, (3) *m*-nitrotoluene and (4) *o*-nitrotoluene. The broken line represents the law of Raoult.

Discussion

The data presented above show that hydrogen bromide solutions are like hydrogen chloride solutions in that the law of Henry is followed, and in that there is a negative deviation from the law of Raoult. There is, however, a difference in the behavior of the two acids in these solvents which is evident from a consideration of the Henry law constants summarized in the second and third columns of Table II. It is seen that, in general, the molal solubility (*i. e.*, $1/k$ for 1 atm.) of

(5) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. III, p. 228.

(6) E. Moles, *Compt. rend.*, **162**, 94, 686 (1916).

TABLE I

THE PARTIAL PRESSURE OF HYDROGEN HALIDES AT 25°					
<i>m</i>	<i>p</i> , mm.	<i>k</i>	<i>m</i>	<i>p</i> , mm.	<i>k</i>
I. Hydrogen Chloride from Toluene			III. Hydrogen Bromide from Toluene		
0.137	214	2.05	0.477	358	0.99
.119	190	2.11	.446	335	.97
.0762	120	2.07	.407	299	.97
.0468	73.3	2.06	.286	210	.97
.0465	73.9	2.09	.194	171	1.15
.0167	25.7	2.02	.185	146	1.03
.0153	25.1	2.16	Mean 0.99 = 0.03		
Mean 2.09 = 0.03			IV. Hydrogen Bromide from <i>o</i> -Nitrotoluene		
II. Hydrogen Bromide from Benzene			0.323	333	1.35
0.477	429	1.18	.147	147	1.31
.302	233	1.02	.0632	60.5	1.26
.226	170	0.99	.0450	43.9	1.28
.167	128	1.01	.0300	28.6	1.25
.162	125	1.01	.0226	22.0	1.27
.097	83.3	1.13	Mean 1.32 = 0.04		
Mean 1.03 = 0.06			V. Hydrogen Bromide from <i>m</i> -Nitrotoluene		
			0.449	493	1.45
			.374	402	1.42
			.112	116	1.36
			.0688	73.5	1.41
			.0315	32.2	1.35
			Mean 1.42 = 0.04		

hydrogen bromide is greater than that of hydrogen chloride, but that the order of solubilities in the four solvents studied is reversed. That hydrogen bromide is less soluble in the nitrotoluenes than in the hydrocarbons is surprising, and the fact that it is more soluble in the ortho compound than in the meta compound throws doubt on the conclusion drawn previously^{2b} (pp. 1190–1191) concerning the apparent discrepancy between the basicities of the nitro compounds as determined by vapor pressure and infrared absorption studies.⁷ Except for the reversal of the order

TABLE II

Solvent	$k(\text{HCl})$	$k(\text{HBr})$	$K_a(\text{HCl})$	$K_a(\text{HBr})$	$\frac{K_a(\text{HCl})}{K_a(\text{HBr})}$
Benzene	2.04 ^a	1.03	0.16	0.33	0.49
Toluene	2.09	.99	.37	.71	.52
<i>o</i> -Nitrotoluene	1.77 ^b	1.32	1.35	.94	1.44
<i>m</i> -Nitrotoluene	1.65 ^b	1.42	1.53	.80	1.91
	$k_1(\text{HCl})$	$k_1(\text{HBr})$	$K_d(\text{HCl})$	$K_d(\text{HBr})$	$\frac{K_d(\text{HCl})}{K_d(\text{HBr})}$
Water	0.000664 ^c	0.000383 ^d	1.23×10^8	2.20×10^8	0.0056

^a Ref. 1a, ^b Ref. 1b, ^c G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., p. 337, ^d *ibid.*, p. 519.

(7) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939).

in the nitrotoluenes, the mole fraction solubilities of hydrogen bromide in these solvents are in the same sequence as that of hydrogen chloride as demonstrated by the figure.

Equilibrium constants of the acid-solvent reactions are listed in the fourth and fifth columns of Table II. It was assumed that equation (I) represents the reactions which occur in the organic solvents for which the equilibrium constant is given by the equation^{2a} (p. 2506)

$$K_a = (f_0 - km_a)/km_a \quad (1)$$

in which f_0 is the fugacity of the hydrogen halide, k is the Henry law constant, and m_s is the number of moles of monomer in 1000 g. of solvent. Data for water have also been included in the table.^{8,9} In solvents like water, the reaction is taken to be as represented by equation (II), for which the equilibrium constant takes the form

$$K_d = f_0/m_s k_1^2 \quad (2)$$

where k_1 is the constant in the equation,⁹ $p^{1/2} = k_1 \gamma m$. The ratios of the hydrogen chloride to the hydrogen bromide constants are given in the last column of Table II. If the acid-solvent reaction depended only upon acidity and basicity this ratio should represent the relative strengths of the two acids and should remain constant in all solvents. While the strengths of the two acids are in the same order in water and hydrocarbon solutions as that derived by other methods,¹⁰ it is reversed in the nitrotoluenes,¹¹ and, quantitatively, it is evident that the apparent relative strengths change considerably as the type of solvent varies. In the hydrocarbons, hydrogen bromide is about twice as strong as hydrogen chloride; in the nitro compounds, hydrogen chloride is the stronger by more than one and one-half times; in water, the hydrogen bromide is again the stronger, by more than 100 times.

No doubt this is to be expected, for it is not likely that the reactions are in all cases as simple as those represented by equations (I) and (II), especially when the varying tendencies of solvents toward association are taken into consideration. Solvent association in the above reactions would be comparable with indicator association in re-

actions between acids and an indicator base, the effect of which has been demonstrated.¹² There is evidence that the association in different solvents is changed in different ways by a solute,^{2a,2b} and it may also be that different solvents affect differently the association in any one solvent. Such a possibility might provide at least a partial explanation for the reversal in the order of acidities of the hydrogen halides in the nitrotoluene solutions. Moreover, if the distinction between *proton-donor* and *electron-acceptor* acidities, suggested by the contribution of Bartlett and Dauben,¹³ is real, the adaptation of this distinction to reactions (I) and (II) seems to be reasonable, and would be a further explanation for the differences in acid strengths encountered. Accordingly, reaction (I) is to be considered as an acid-base reaction involving electron-acceptor acidity; reaction (II) as one involving proton-donor acidity. Such a differentiation is, perhaps, one of degree rather than of kind, for it must still be the acid and basic strengths of the reactants which determine whether reaction (I) or (II) is to be followed, not the magnitude of the dielectric constant of the medium, judging by the electrical conductivity,¹⁴ the infrared absorption⁷ and the vapor pressure relationship^{2a} of hydrogen chloride solutions in nitrobenzene with its relatively high dielectric constant. Indeed, it seems more probable that if the combined effects of acidity and basicity are great enough, reaction (II) will occur (complicated in solvents of low dielectric constant by ion-pair formation, etc.) regardless of the size of the dielectric constant of the medium; if the respective acid and basic strengths of the substances are not great enough, the reaction will proceed only to the stage indicated by equation (I). The implication is, then, that even when other medium effects, association, etc., are taken into consideration, the two kinds of acidity may not be comparable, any more than the acidities of acids of different charge type are comparable. Thus generalizations concerning acid and basic strengths may be further limited³ (pp. 256-259) to groups of solvents in which the acid-solvent reactions are of nearly the same type, or to acid-base reactions in which the type of reaction is not greatly

(8) S. J. Bates and H. D. Kirschman, *THIS JOURNAL*, **41**, 1991 (1919).

(9) Lewis and Randall, *loc. cit.*, pp. 329-330.

(10) A. Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923); Hantzsch and W. Voigt, *Ber.*, **62B**, 975 (1929); see, however, J. N. Brønsted and R. P. Bell, *THIS JOURNAL*, **53**, 2478 (1931).

(11) See Hantzsch, *Ber.*, **59B**, 1096 (1926), for a reversal in the order of the catalytic action of the hydrogen halides in the saponification of esters.

(12) V. K. LaMer and H. C. Downes, *THIS JOURNAL*, **55**, 1840 (1933).

(13) P. D. Bartlett and H. J. Dauben, Jr., *ibid.*, **62**, 1339 (1940).

(14) D. M. Murray-Rust, H. J. Hadow and H. Hartley, *J. Chem. Soc.*, 215 (1931).

changed by varying the medium, which appears to be approximately true in some acid-indicator base reactions.^{12,15}

Acknowledgment.—The sincere thanks of the authors are due to Dr. C. L. Kenny for his support of this work, and to Mr. E. E. Velehradsky for his assistance in making the hydrogen chloride-toluene measurements.

Summary

Measurements are reported of the partial pressure of hydrogen chloride from its toluene solutions over the concentration range 0.015–0.137 molal, and of hydrogen bromide from its solutions in benzene, toluene, *o*-nitrotoluene and

(15) See, *e. g.*, L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **54**, 2721 (1932); D. C. Griffiths, *J. Chem. Soc.*, 812 (1938).

m-nitrotoluene over the concentration ranges 0.097–0.447, 0.185–0.447, 0.023–0.323 and 0.032–0.449 molal, respectively. The law of Henry is followed in all these solutions, but there is a negative deviation of the hydrogen halide from the law of Raoult. The molal solubilities of hydrogen bromide are greater than those of hydrogen chloride in the solvents considered.

Equilibrium constants for the hydrogen bromide-solvent reactions in the above mentioned solvents and in water are calculated and compared with those of hydrogen chloride-solvent reactions. The apparent relative acidity of the two acids is different in the various types of solvents, and the relative order of acid strengths is reversed in the nitrotoluenes.

OMAHA, NEBRASKA

RECEIVED AUGUST 31, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Heat of Neutralization of Sodium Hydroxide with Hydrochloric Acid

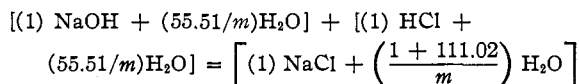
BY GERSON KEGELES

Introduction.—Lewis and Randall first undertook the task of tabulating the thermodynamic functions of the elements and their compounds with the ultimate purpose of combining these functions in order to obtain the properties of reactions in which these substances are involved. Their method is equally applicable to reactions in solution, provided the necessary thermodynamic data are known. In the case of solutions of electrolytes, the thermodynamic properties vary extensively with the concentration, and until recently data have been lacking for large concentration ranges. Calorimetric measurements for sodium chloride solutions by Wüst and Lange,¹ Robinson,² and Gulbransen and Robinson,³ and extended thermodynamic studies of hydrochloric acid solutions by Åkerlöf and Teare,⁴ and of sodium hydroxide by Åkerlöf and Kegeles,⁵ now make it possible to determine the heat of neutralization of sodium hydroxide with hydrochloric acid through 16 molal acid and base at 25°. The results obtained from these separate data

- (1) Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).
- (2) Robinson, *THIS JOURNAL*, **54**, 1311 (1932); see also Young and Vogel, *ibid.*, **54**, 3030 (1932).
- (3) Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934); see also Young and Machin, *ibid.*, **58**, 2254 (1936).
- (4) Åkerlöf and Teare, *ibid.*, **59**, 1855 (1937); see also Harned and Ehlers, *ibid.*, **55**, 2179 (1933), for lower concentrations.
- (5) Åkerlöf and Kegeles, *ibid.*, **62**, 620 (1940); see also Harned and Hecker, *ibid.*, **55**, 4838 (1933), for lower concentrations.

agree very well in the lower concentration range with direct calorimetric measurements reported by Richards and co-workers.⁶ The heat of neutralization is found to reach very high values at the highest concentrations treated.

Method of Calculation.—The reaction between acid and base of molality *m* may be expressed as follows



In terms of *m*, the molality of the resulting sodium chloride is $m' = 55.51m/(111.02 + m)$. The corresponding molal heat of reaction is given by the expression⁷

$$\Delta H = [\bar{H}_2(m' \text{NaCl}) + 55.51/m' \bar{H}_1(m' \text{NaCl})] - [\bar{H}_2(m \text{NaOH}) + 55.51/m \bar{H}_1(m \text{NaOH})] - [\bar{H}_2(m \text{HCl}) + 55.51/m \bar{H}_1(m \text{HCl})]$$

Upon making the substitutions $\bar{H}_2 = \bar{H}_2^0 + \bar{L}_2$, and $\bar{H}_1 = \bar{H}_1^0 + \bar{L}_1$, and rearranging, the expression becomes

$$\Delta H = \Delta H^0 + [\bar{L}_2(m' \text{NaCl}) - \bar{L}_2(m \text{NaOH}) - \bar{L}_2(m \text{HCl})] + (55.51/m)[(m/m')\bar{L}_1(m' \text{NaCl}) - \bar{L}_1(m \text{NaOH}) - \bar{L}_1(m \text{HCl})] \quad (1)$$

(6) Richards and Rowe, *ibid.*, **44**, 684 (1922); Richards and Hall, *ibid.*, **51**, 731 (1929).

(7) The nomenclature of Lewis and Randall ("Thermodynamics") is used here.