

Fig. 5.—Determination of combining ratio, n/m , for the zirconium-purpurin lake.

trations of lake, dye and zirconium remain at the equilibrium values for the alkaline medium. To test this explanation, the "equilibrium quotients" (Q = moles of lake divided by the product of moles uncombined zirconium and moles free alizarin) in Table III were calculated, $n/m = 1$ being assumed. The constancy of the Q 's, especially of those for the alizarin lake, makes the explanation seem reasonable.

In parallel experiments at different temperatures, lake formation from comparable amounts of zirconium and alizarin was found to be 67% complete at room temperature and 83% complete at 75°.

Summary

Spectrophotometric evidence indicates that the

TABLE III
EQUILIBRIUM QUOTIENTS AT ROOM TEMPERATURE

Moles dye added $\times 10^7$	Moles Zr added $\times 10^7$	Moles lake $\times 10^7$	Moles Zr uncombined $\times 10^7$	Moles dye uncombined $\times 10^7$	$Q \times 10^{-4}$
5.32	0.93	0.59	0.34	4.73	3.7
(Alizarin)	3.72	2.10	1.62	3.22	4.0
	4.65	2.37	2.28	2.95	3.5
	6.50	2.66	3.84	2.66	2.6
7.80	0.93	0.646	0.284	7.15	3.2
(Alizarin)	4.65	2.92	1.73	4.88	3.5
	9.30	5.32	3.98	2.48	5.4
	12.10	5.91	6.20	1.90	5.0
5.58	0.11	0.058	0.052	5.52	2.0
(Quin-alizarin)	0.55	0.397	0.153	5.18	5.0
	1.10	0.954	0.145	4.63	14.2
	2.20	1.65	0.055	3.93	7.6
	3.30	2.19	1.10	3.39	5.9
	4.40	2.61	1.79	2.97	4.9
	6.60	3.08	3.51	2.50	3.5
5.89	1.10	0.814	0.286	5.08	5.6
(Purpurin)	2.20	1.57	0.626	4.32	5.8
	4.40	2.65	1.75	3.24	4.7
	5.50	3.02	2.47	2.87	4.3
	7.70	4.13	3.57	1.76	6.6
	8.80	4.56	4.22	1.33	8.1

lakes formed by zirconium with each of the dyes, alizarin, purpurin and quinalizarin, are definite compounds, the two constituents being combined in equimolar amounts.

The spectrophotometric behavior, and the incomplete lake formation observed under some conditions, resemble closely experimental results obtained on the hafnium-alizarin lake. On this basis, it is logical to assign the three lakes studied here a chelate-ring formula analogous to that given the lake formed by hafnium and alizarin.

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The Partial Pressure of Hydrogen Chloride from Its Solutions in Aprotic Solvents: Comparison of Solubility and Infrared Absorption Studies¹

BY S. JAMES O'BRIEN² AND CECIL V. KING

Data were presented in previous papers³ which indicated that the entropy of solution of hydrogen chloride in aprotic solvents is related linearly to the shift produced by the various solvents in the position of the 3.46 μ absorption band as meas-

ured by Gordy and co-workers.⁴ In further work along these lines, measurements have been made at two or more temperatures of the partial pressure of hydrogen chloride above its solutions in four more aprotic solvents for which infrared absorption values are available. These determinations provide additional facts pertinent to the relationships between the entropy of solution of hydrogen chloride and the shift of its 3.46 μ absorption band. It is the purpose of this paper to

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(3) S. J. O'Brien, THIS JOURNAL, **63**, 2709 (1941); **64**, 951 (1942).

(4) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 99 (1939); W. Gordy, *ibid.*, **9**, 215 (1941).

report the new measurements which were made in phenetole, *n*-butyl phenyl ether, diphenyl ether and *m*-nitrotoluene and to consider them in connection with the relationship between the partial molal entropy of solution and the shift of the infrared absorption band of the solute.

Experimental

The apparatus and procedure used were the same as in the earlier work.^{3,5} The phenetole, *n*-butyl phenyl ether, diphenyl ether and *m*-nitrotoluene were all Eastman Kodak Co. products which were carefully dried and redistilled before using. The index of refraction, or in the case of *m*-nitrotoluene the melting point, was taken as the criterion of purity.

Results

As in the earlier studies, it was found that hydrogen chloride agreed with the law of Henry in the four solvents employed in the present work. The results of the partial pressure measurements are summarized in Table I.

TABLE I
HENRY LAW CONSTANTS AND THE MOLE FRACTION SOLUBILITY OF HYDROGEN CHLORIDE AT 1 ATM.

Solvent	Temp., °C.	Detns.	<i>k</i>	Dev. ±	<i>N</i>
Phenetole	25	6	1.02	0.04	0.107
Phenetole	20	2	0.90	.01	.120
Phenetole	10	2	0.70	.03	.151
<i>n</i> -Butyl phenyl ether	25	4	1.37	.05	.100
<i>n</i> -Butyl phenyl ether	20	4	1.21	.04	.110
Diphenyl ether	30	4	3.52	.01	.0442
Diphenyl ether	25	4	3.33	.07	.0494
<i>m</i> -Nitrotoluene	35	4	2.08	.04	.0614
<i>m</i> -Nitrotoluene	25 ^a	7	1.65	.05	.0768

^a Reported previously: S. J. O'Brien and C. L. Kenny, *THIS JOURNAL*, **62**, 1189 (1940).

In Table I, the first column gives the solvent; the second, the temperature at which the measurements were made; the third, the number of individual determinations; the fourth column gives the Henry law constant, *k*, in the form

$$k = p/m$$

where *p* is the partial pressure in atmospheres and *m* is the molal concentration of hydrogen chloride in the solution; the fifth column contains the average deviation from the mean of the individual Henry law constants; the last column gives the mole fraction solubility of hydrogen chloride at a partial pressure of 1 atmosphere calculated by means of the equation

$$N = 1/(1 + km_s)$$

N being the mole fraction solubility and *m_s* the number of moles of solvent in 1000 g.

Discussion

In the earlier work,³ it was found that the

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

change of mole fraction solubility of hydrogen chloride with temperature could be represented by an equation of the form

$$\log N = A/T + B \quad (1)$$

where *T* is the absolute temperature and *A* and *B* are constants which may be identified with the heat and entropy of solution.⁶ That is

$$A = \Delta H/2.303R \quad (2)$$

$$B = \Delta S/2.303R \quad (3)$$

where ΔH is the partial molal heat of solution of the solute, ΔS is the partial molal entropy of solution and *R* is the molar gas constant. The data presented above for phenetole solutions also fit an equation of this type, and it has been assumed that a similar relationship between the temperatures and the solubility of hydrogen chloride is valid in the other solvents. On this basis, the heats and entropies of solution were derived from the mole fraction solubilities given in Table I. These calculated thermodynamic values are shown in the second and third columns of Table II.

TABLE II
THE HEAT AND ENTROPY OF SOLUTION

Solvent	- ΔH , cal.	- ΔS , eq. 3, e. u.	- ΔS , eq. 4, e. u.
Phenetole	3950	17.6	17.7
<i>n</i> -Butyl phenyl ether	3780	17.2	17.3
Diphenyl ether	3800	18.9	19.0
<i>m</i> -Nitrotoluene	3900	18.8	18.7

The connection between the entropy of solution of hydrogen chloride and the shift of its 3.46 μ absorption band in solution, which was suggested by the data given in a prior paper,³ could be expressed by the linear equation

$$\Delta S = 10.0 \Delta \mu - 21.1 \quad (4)$$

in which ΔS is the partial molal entropy of solution of hydrogen chloride and $\Delta \mu$ is the shift of the infrared absorption band. The data reported in this paper are also in agreement with this equation. This is demonstrated in Table II where the last column contains entropy values calculated by means of equation (4) using the infrared absorption data of Gordy.⁴ All of the available data relative to this proportionality between the entropy of solution and the shift of the absorption band are summarized graphically in Fig. 1. The line drawn in this diagram is a plot of equation (4); the circles define values obtained from the experimental data as presented in this and the earlier papers.³ The agreement between the experimental points with equation (4) is quite good; the values assigned to the slope and intercept are adequate. This linear correlation of the shift of the infrared absorption band with the entropy of solution makes it evident that a good straight line connection is not to be expected between the shift of the infrared band

(6) Compare J. H. de Boer, *Chem. Weekblad*, **35**, 839 (1938), and V. A. Kireev, *Acta Physicochim. (U. R. S. S.)*, **13**, 531 (1940).

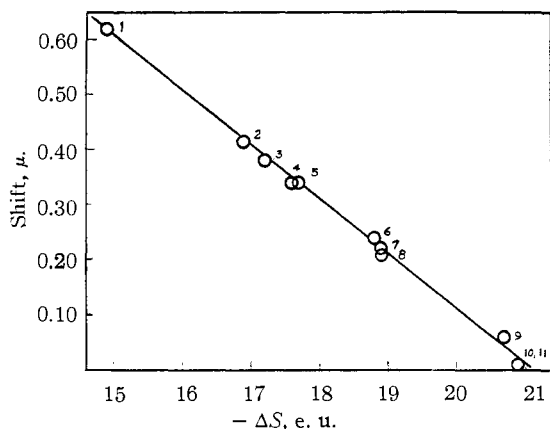


Fig. 1.—A plot of the shift of the 3.46μ absorption band of hydrogen chloride against its entropy of solution in: (1) diethyl ether, (2) β,β' -dichlorodiethyl ether, (3) *n*-butyl phenyl ether, (4) phenetole, (5) anisole, (6) *m*-nitrotoluene, (7) nitrobenzene, (8) diphenyl ether, (9) chlorobenzene, (10) bromobenzene and (11) benzene. The spectroscopic data are taken from the papers of Gordy⁴ except those for chlorobenzene and bromobenzene [W. West and P. Arthur, *J. Chem. Phys.*, **2**, 215 (1934)] and for benzene [E. K. Plyler and D. Williams, *Phys. Rev.*, **49**, 215 (1936)]. The entropy values not presented in Table II were taken from the earlier papers.³

and the deviation of hydrogen chloride from the law of Raoult.⁷ Differences in the heat of solution in the various solvents would lead to deviations from such a relationship. It is, of course, interesting that the increase in the partial molal entropy of the solute is greatest in the more basic solvents in which the infrared absorption band is shifted to the greatest extent.

Summary

1. The partial pressure of hydrogen chloride from its solutions in phenetole, *n*-butyl phenyl ether, diphenyl ether and *m*-nitrotoluene have been determined at two or more temperatures. From these data, the mole fraction solubilities at 1 atm., the partial molal heats and the partial molal entropies of solution of hydrogen chloride have been calculated.

2. A linear relationship between the entropy of solution and the shift of the 3.46μ absorption band of hydrogen chloride reported previously is further substantiated by a comparison of the calculated entropies of solution with the spectroscopic data available in the literature.

(7) Compare W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940).

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The Importance of Interatomic Spacing in Catalysis. A Correlation between Hydrogen Overvoltage on Metals and the Distance between Atoms¹

BY HENRY LEIDHEISER, JR.

Introduction

It is of great importance to the theories of surface phenomena to understand the importance of the distance between surface atoms in controlling the rates of reactions. A few studies indicate the importance of this distance in catalytic reactions.² Recent measurements of the hydrogen overvoltage offer a series of values which may be utilized to compare the relative catalytic activities of a number of metals under similar experimental conditions. Hydrogen overvoltage may be considered as a numerical value representing the ability relative to platinized platinum with which a material catalyzes the over-all reaction, $2\text{H}^+ + 2e = \text{H}_2(\text{gas})$, in an acid solution. The greater the numerical value of the hydrogen overvoltage,

the greater the difficulty with which the reaction occurs.

Correlations of the results of hydrogen overvoltage studies on different metals have been made previously with position in the periodic table, melting point, catalytic activity for the combination of hydrogen atoms, and thermionic work functions,³ but no one has pointed out the interesting correlation between hydrogen overvoltage and the distance between atoms in the surface.

Results

In Fig. 1 values for the hydrogen overvoltage at 10^{-3} amp./sq. cm. are plotted *versus* the distance of closest approach of atoms for all the body-centered cubic and face-centered cubic metals for which reliable values are available. The values for nickel, copper, molybdenum, tantalum and columbium were taken from Bokris,⁴ the values for lead, aluminum, silver, chromium (estimated from the value at 10^{-1} amp./sq. cm.), iron, tungsten, plati-

(1) This paper was written during the author's residence at the University of Virginia under a grant from the Research Corporation. Present address: Virginia Institute for Scientific Research, Richmond 20, Virginia.

(2) See for example: O. Beeck, *Revs. Modern Physics*, **17**, 61 (1945); J. Turkevich and R. K. Smith, *Nature*, **157**, 874 (1946); H. Leidheiser, Jr., and A. T. Gwathmey, *THIS JOURNAL*, **70**, 1200, 1206 (1948); H. Leidheiser, Jr., and R. Meelheim, *ibid.*, **71**, 1122 (1949).

(3) See J. O'M. Bokris, *Chem. Revs.*, **43**, 525 (1948), for a recent comprehensive discussion of the theories of hydrogen overvoltage and a critical evaluation of the data.

(4) J. O'M. Bokris, *Trans. Faraday Soc.*, **43**, 417 (1947).