Figure 2 shows the percentage of original pantothenate and thiamin remaining at each *p*H studied. The maximum shift in *p*H during autoclaving was 0.2 unit. The point at which the two curves cross, *p*H 4.6, represents the condition under which destruction of the two compounds is equally rapid. In other experiments using somewhat different conditions some variation in the slope of the curves and in the point at which they cross has been noted. In general, however, the latter point falls in the *p*H range 4.5–4.8.

That stability of thiamin is favored by acid conditions has been known for some time.[3,4] More recently the thermal decomposition of thiamin was shown to be a first order reaction at a number of different acidities.[5] Reports have since appeared that the type of buffer used has a large effect on the rate of this decomposition at different acidities.[6,7]

In contrast to this, stability of pantothenate has been shown to be largely independent of the presence or type of buffer at *p*H 3.7–4. Other studies, however, have confirmed the earlier indications that buffer substances cause significant increases in the rate of destruction in the *p*H range 4–7. The positive effect of nicotinamide or phosphate in hydrolysis of pantothenate is most apparent in the range in which pantothenate is normally most stable, *i. e.*, *p*H 5–7.

Destruction of thiamine appears from the facts at hand to be considerably more complicated than that of pantothenate. Rate of hydrolysis of pantothenate is chiefly a function of *p*H, but may be catalyzed by the presence of electrolytes. Destruction of thiamin, however, appears to be subject to many influences other than *p*H and may even be inhibited by presence of certain compounds.

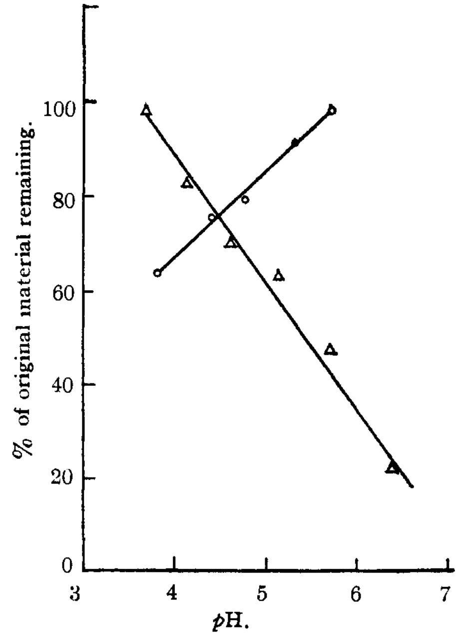

Fig. 2.—Relative rates of destruction of calcium pantothenate and thiamin hydrochloride in acid solution: ○, 1% solution of calcium pantothenate; △, 0.1% solution of thiamin hydrochloride. All solutions were run in an autoclave at 15 lb. pressure for fifteen minutes.

Summary

Hydrolysis of pantothenate in acid solution follows a first order relation with respect to pantothenate concentration.

The activation energy of the reaction has been measured to be 19,000 cal., corresponding to an increment per 10° of 2.6.

The contrasting effect of acidity on rate of hydrolysis of thiamin and pantothenate has been studied and discussed.

NO. CHICAGO, ILLINOIS RECEIVED NOVEMBER 8, 1943

(3) H. C. Sherman and G. W. Burton, *J. Biol. Chem.*, **70**, 639 (1926).

(4) B. C. Guha and J. C. Drummond, *Biochem. J.*, **23**, 880 (1929).

(5) A. Watanabe, *J. Pharm. Soc. Japan*, **59**, 52 (1939).

(6) B. W. Beadle, D. A. Greenwood and H. R. Kraybill, *J. Biol. Chem.*, **149**, 339 (1943).

(7) F. C. McIntire and D. V. Frost, Abstracts 106th meeting Amer. Chem. Soc., Pittsburgh, Sept. 1943, p. 63.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Solubility of Aluminum Bromide in *n*-Butane

BY JULIUS D. HELDMAN[1] AND CARL D. THURMOND

Aluminum bromide exists as the dimer in the crystal, in the molten salt, in solution in non-basic solvents, and in the vapor phase over a wide range of conditions. Although it forms highly polar double salts and complexes with organic bases, it would be expected to show normal solubility characteristics in non-polar, inert solvents, of which the paraffin hydrocarbons are good examples.

It has been shown that pure, dry aluminum bromide exerts no catalytic influence on the butanes[2] or *n*-heptane,[3] even though in the presence of a "promoter" (a hydrogen halide or substance capable of producing hydrogen bromide by reaction with the salt) aluminum bromide acts as a catalyst for paraffin conversions, notably isomerization.[2,3,4]

The stability of *n*-butane in dry aluminum

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[1] National Research Fellow in Chemistry, 1942–1943.

(2) Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943).

(3) Sensel, Dissertation, Western Reserve University, Cleveland, Ohio, 1938.

(4) See Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, N. Y., 1942, Chapter 1 and Tables, pp. 218, *et seq.*

bromide makes possible a phase study of the binary system. Solubility measurements are here reported, and their relation to molecular structure and other aluminum bromide systems is discussed.

Experimental

The hydrocarbon employed was Phillips pure *n*-butane of better than 99% purity, sulfur 0.005 wt. % or less, free of unsaturates.

The preparation of the aluminum bromide and method of obtaining sealed solution sample tubes were essentially those described by Leighton and Heldman.[2]

The sample tubes were heated in either a water or glycerol bath with shaking until the last crystal had disappeared. All solutions were clear and colorless. The rate of heating near the solution temperature was never greater than 0.2° per min. Temperatures were read on one of two calibrated 0.1° thermometers, with ranges 0–50° and 50–100°. Solution temperatures were reproducible to 0.3° and usually to 0.2°.

The method of transfer of aluminum bromide into the sample tubes usually produced large crystals which dissolved in the *n*-butane very slowly. Therefore, before measurement of the solution temperature, the sample tubes were heated until all the bromide had dissolved and then quickly cooled, with shaking. A mass of finely-divided crystals resulted. These crystals dissolved so readily upon subsequent heating that presumably there was equilibrium between the solid and liquid phases at all times.

Because of the high vapor pressures of *n*-butane at the temperatures measured, the vapor volume in each sample tube at the solution temperature was estimated, in order to apply a correction. The lack of uniformity in tube size and therefore vapor volume arises from the fact that the vacuum distillation of the aluminum bromide into the many tubes sealed to the manifolds used is not easily controllable; consequently some larger tubes received less of a bromide charge than some of the smaller ones. For the same reason, the spacing of the experimental points is somewhat fortuitous, and the rather frequent close duplication of composition inherent in the sampling method.

Samples were analyzed by weighing the sealed tube and contents, freezing in liquid air and either heating the tip to suck in the glass and reaming out the opening or merely breaking open the tube, washing out the contents, and weighing the glass parts. The aluminum bromide was calculated by difference from the tare of the glass and the known weight of *n*-butane introduced.

The butane from one tube, which had been brought to its solution temperature of 67.0° twice and then purposely set aside to stand at room temperature for fifteen days, was analyzed in a dew pressure apparatus and found to be over 98% *n*-butane. Considerable isomerization would be expected if traces of water or hydrogen bromide had been present.[2,5]

Results

In Table I are given the solution temperatures and composition of the mixtures examined. The moles of aluminum bromide are calculated on the basis of the formula Al_2Br_6. The actual moles of *n*-butane in the liquid phase have been calculated by subtracting from the total butane charge the estimated moles of vapor. This quantity was approximated using the vapor pressure of *n*-butane at the solution temperature[6] and the estimated vapor volume, assuming both the perfect gas equation and Raoult's law to be valid for the system. Neither of the assumptions hold strictly, but the former can introduce no important error. The deviation from Raoult's law could have been estimated from the solubility curve and a second-order approximation of the vapor pressure made, but this procedure is not justified by the accuracy of the results.

The internal consistency of the results points to an accuracy of about 1 or 2% in determining the composition of the mixtures. If we arbitrarily fix the maximum error arising in calculating the moles of liquid *n*-butane on the above assumptions as one-fourth of the estimated moles of *n*-butane vapor, the accuracy of the calculated moles of liquid *n*-butane is usually 0.25 to 2%, and, in a few cases, 3 to 5%. The possible error in mole fraction derived from this arbitrary basis is, in general greater than the scattering of the experimental points indicates, except for the

TABLE I

SOLUTION TEMPERATURES OF ALUMINUM BROMIDE–*n*-BUTANE MIXTURES

t, °C.	Est. vapor vol., cc.	Est. moles n-C_4H_{10} in vapor × 10^4	Moles liq. n-C_4H_{10} × 10^2	Moles Al_2Br_6 × 10^2	Mole fraction Al_2Br_6
	A. $2.50_3 \times 10^{-2}$ moles n-C_4H_{10} added				
28.3	2	$2._1$	2.48_2	0.131	0.0501
32.2	2	$2._3$	2.48_0	.161	.0609
38.8	2	$2._6$	2.47_7	.238	.0874
39.2	2	$2._6$	2.47_7	.243	.0893
46.7	2	$3._0$	2.47_3	.364	.128
48.6	2	$3._2$	2.47_1	.400	.139
	B. $2.13_4 \times 10^{-2}$ moles n-C_4H_{10} added				
53.4	1	$1._7$	2.11_7	0.475	0.183
	C. $1.06_7 \times 10^{-2}$ moles n-C_4H_{10} added				
43.2	3	$4._2$	1.02_5	0.124	0.108
48.7	3	$4._8$	1.01_9	.172	.144
51.4	2	$3._3$	1.03_4	.203	.164
57.6	2	$3._3$	1.03_4	.312	.232
64.1	2	$3._3$	1.03_4	.494	.323
67.0[a]	2	$3._3$	1.03_4	.599	.367
67.8	2	$3._3$	1.03_4	.653	.387
71.1	3	$5._0$	1.01_7	.770	.431
71.7	7	$11._3$	0.95_4	.830	.465
72.7	5	$8._0$	$.98_7$	.841	.460
74.1	9	$14._7$	$.92_0$	.902	.495
77.2	2	$2._8$	1.03_9	1.367	.568
79.8	10	$13._3$	0.93_4	1.373	.595
80.9	2	$2._6$	1.04_1	1.838	.639
81.4	7	$9._1$	0.97_6	1.635	.628
82.5	9	$11._7$	0.95_0	1.674	.638
84.3	1	$1._1$	1.05_6	3.333	.759
86.3	7	$5._8$	1.00_9	3.200	.761
89.9	3	$1._9$	1.04_8	5.10	.830
	D. No n-C_4H_{10} added				
97.5					1.000

[a] Set aside for fifteen days after measurements and analyzed; *vide supra*.

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(5) Montgomery, McAteer and Franke, THIS JOURNAL, **59**, 1768 (1937); papers presented before the Petroleum Division of the American Chemical Society, Part I, Baltimore meeting, April 3-7, 1939, p. M-1.

(6) Sage, Webster and Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

measurement at 84.3°, which is not consistent with the rest and is presumably in error in some way.

Although it would have been desirable to obtain measurements at even greater concentrations of aluminum bromide than the highest reported here, the techniques employed do not lend themselves to the handling of the larger amounts of bromide necessary.

Discussion

The usual plot of the logarithm of the solubility expressed in mole fraction of aluminum bromide (as Al_2Br_6) *vs.* the reciprocal of the absolute temperature is shown in Fig. 1. All of the points, with the single exception noted, fall close to a smooth curve of the reverse S type commonly encountered when the solvent and solute have different internal pressures.[7]

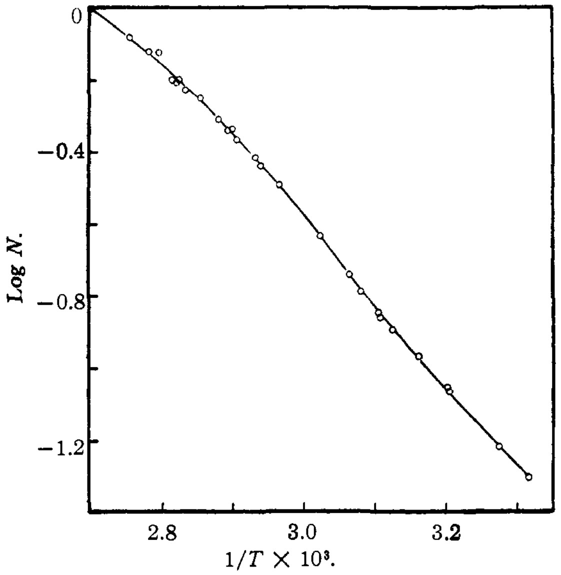

Fig. 1.—Solubility of aluminum bromide in *n*-butane (N = mole fraction Al_2Br_6).

Kendall, Crittenden and Miller[8] and Kaveler and Monroe[9] have reported a phase change in aluminum bromide just above 70° on the basis of solubility measurements. In the present case there is no change in slope of the solubility curve near 70°, nor was any change in aluminum bromide at that temperature visually observed, even with very slow heating and cooling. Kendall, *et al.*,[8a] and Crittenden[8b] claim to have authenticated the existence of two crystalline modifications of aluminum bromide by "thermal analysis" of the pure salt. No cooling curve data were presented, however. We have taken several cooling curves with pure aluminum bromide and have found them noteworthy only in the check on the melting (freezing) point obtained with the thermocouple and with the thermometer in the solubility work. Otherwise the cooling curves are completely regular. Also, the specific heat[10] and volume[11] of solid aluminum bromide are apparently smooth monotonic functions of the temperature.

Furthermore, the solubility curves from which Kendall, Crittenden and Miller, and Kaveler and Monroe, infer a phase change in aluminum bromide show no discontinuities near 70°, nor has Isbekow,[12] who has reported thermal analyses of some of the same systems, found any irregularities near 70°. Indeed, a re-plot of their data in terms of log N *vs.* $1/T$, Fig. 2, clearly shows that there is no necessity for assuming two modifications of aluminum bromide. One of the systems on which Kendall, Crittenden and Miller base their conclusions, PBr_3–Al_2Br_6, actually shows a small decrease in negative slope starting near 70°, and the internal consistency of the data for any of the systems is not great enough to justify postulating a discontinuity. It should be noted that the carbon tetrabromide used by Isbekow melted 1.9° higher than that of Kendall, *et al.*, whereas his arsenic tribromide melted 0.8° lower.

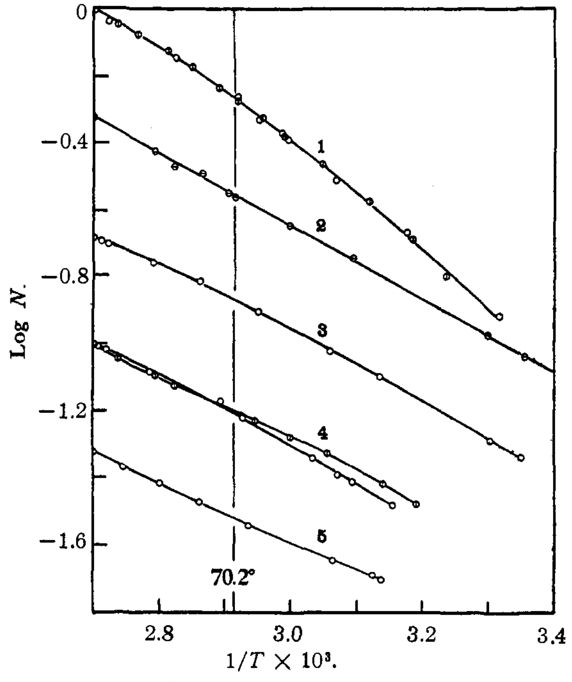

Fig. 2.—Solubility of aluminum bromide in various solvents (N = mole fraction Al_2Br_6): Curve 1, $AsBr_3$; 2, CS_2, add $^1/_3$ to log N; 3, $SnBr_4$, add $^2/_3$ to log N; 4, CBr_4, add 1 to log N; 5, PBr_3, add $1^1/_3$ to log N; ○, Kendall, Crittenden and Miller; ⊖, Kaveler and Monroe; ⦶, Isbekow.

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(7) Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Corporation, New York, N. Y., 1936, p. 170.

(8) (a) Kendall, Crittenden, and Miller, THIS JOURNAL, **45**, 963 (1923); (b) Crittenden, Dissertation, Columbia University, New York, 1922.

(9) Kaveler and Monroe, THIS JOURNAL, **50**, 2421 (1928).

(10) Fischer, *Z. anorg. allgem. Chem.*, **200**, 332 (1931).

(11) Klemm, Tilk and Muellenheim, *ibid.*, **176**, 11 (1928).

(12) Isbekow, *ibid.*, **143**, 80 (1925).

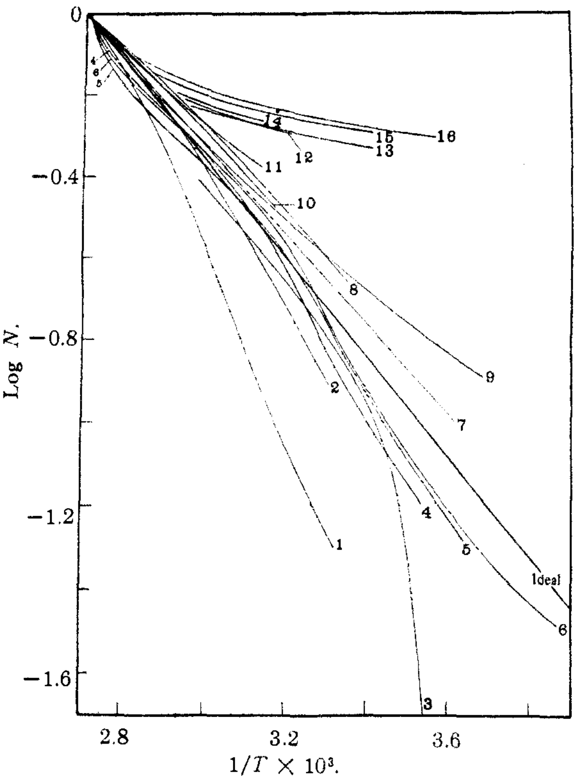

Fig. 3.—Smoothed curves of solubility of aluminum bromide in various solvents (N = mole fraction Al_2Br_6). Curves for benzene derivatives, except toluene and *p*-xylene, are arbitrarily terminated for clarity near the convergence point: 1, *n*-C_4H_{10}; 2, $AsBr_3$; 3, C_6H_6[13f]; 4, *p*-$C_6H_4(CH_3)_2$; 5, C_6H_6[13a]; 6, $C_6H_5CH_3$; 7, CS_2; 8, $SnBr_4$; 9, $C_2H_4Br_2$; 10, CBr_4; 11, PBr_3; 12, $(C_6H_5)_2CO$; 13, $C_6H_5NO_2$; 14, *p*-$BrC_6H_4NO_2$; 15, *p*-$ClC_6H_4NO_2$; 16, C_6H_5COCl.

In Fig. 3 are drawn smoothed curves from various sources[13] showing the solubility of aluminum bromide in various solvents and also the ideal solubility derived from the heat of fusion, 5.5 kcal. per mole (for the dimer),[14] using the van't Hoff isochore

$$\log N = \frac{-Lf}{4.58}\left(\frac{1}{T} - \frac{1}{Tm}\right) \qquad (1)$$

It is of interest to note that in many cases where the actual solubility is greater than the ideal, there is evidence of either compound formation or solvation of the aluminum bromide. The compounds with nitrobenzene and its derivatives are well known.[13d,15]

Benzene and its analogs give curves that are particularly interesting and somewhat puzzling, being of the unreversed S type, which is extremely uncommon in solubility work. The molecular state of aluminum bromide in benzene is that of the monomer (probably $AlBr_3 \cdot C_6H_6$) in very dilute solution and essentially the dimer at ordinary concentrations.[13f,16] The reported existence of an unstable solid compound $AlBr_3 \cdot C_6H_6$[13f] and the lack of agreement between the solubility data of Menschutkin and Plotnikow and Gratsianskiĭ indicate that the curvature may be due to non-equilibrium conditions with respect to the solid phase in Menschutkin's work.

The deep color of concentrated solutions of aluminum bromide in carbon disulfide leads us to believe that here solvation is increasing solubility over the expected values.

It is apparent that difference of internal pressure between the two components, which is usually an important factor in predicting solubility relationships,[17] is of little value in most cases involving aluminum bromide because in even very weakly basic solvents its strongly acid character produces chemical effects far overshadowing the relatively small constitutive effects of structure.

The increase in solubility over ideal in carbon tetrabromide, ethylene dibromide, phosphorus tribromide and tin tetrabromide may be explained either on the basis of simple solvation or chemical interaction to form a complex in solution. The lability of aliphatically bound halogen in the presence of aluminum bromide has led many workers to postulate compounds of the type $RAlBr_3X$.[18] Aluminum bromide is monomeric in ethyl bromide solution.[19,20] The phase diagram for the system Al_2Br_6–PBr_3 has not been fully determined,[3] and an isolable compound may exist.

In the case of *n*-butane, in which the solubility of aluminum bromide is much less than the ideal, a calculation based on the equation given by Hildebrand[21]

$$RT \ln \gamma_1 = V_1\left(\frac{N_2V_2}{N_1V_1 + N_2V_2}\right)^2\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \qquad (2)$$

is of interest. We can estimate the energy of vaporization of aluminum bromide at 25° from the heat of vaporization at the boiling point, 12.0 kcal. per mole at 255°, and ΔC_p of vaporization =

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(13) (a) Reference 8, arsenic tribromide, phosphorus tribromide, tin tetrabromide, carbon tetrabromide; (b) Reference 9, carbon disulfide; (c) Reference 12, arsenic tribromide, carbon tetrabromide; (d) Menschutkin, *Chem. Zentr.*, **14**, 164 (1910), nitrobenzene, benzophenone, benzoyl chloride, *p*-chloronitrobenzene, *p*-bromonitrobenzene, ethylene bromide; (e) *ibid.*, **14**, 167 (1910), benzene, toluene, *p*-xylene; (f) Plotnikow and Gratsianskiĭ, *Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R.*, **5**, 213 (1939), benzene.

(14) The data of Kablukow [*C. A.*, **3**, 870 (1909)] lead to the value 5.58 kcal; two determinations by Fischer[10] give values of 5.1_2 and 5.5_8 kcal. The weighted average is here taken as 5.5 kcal. Any value between 5 and 6 kcal. will not affect the qualitative conclusions to be drawn.

(15) Mezheniĭ and Turov, *Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R.*, **5**, 98 (in English) (1938).

(16) (a) Plotnikow, Sheka and Yankelewich, *ibid.*, **4**, 382 (in German) (1938); (b) Ulich, *Z. physik. Chem.*, Bodenstein Festband, 423 (1931); (c) Ulich and Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

(17) See reference 7, Chapters III, V, VI.

(18) See for example Brejevna, Roginsky and Schilinsky, *Acta Physicochim. U. R. S. S.*, **6**, 744 (1937); **7**, 201 (1938).

(19) (a) Konowaloff and Plotnikow, quoted in Walden, "Molecular-grossen von elektrolyten," T. Steinkopff, Dresden, 1923, p.207.

(20) Wertyporoch, *Ber.*, **64B**, 1361 (1931).

(21) Ref. 7, p. 73

-18 cal. per deg. mole,[22] giving the heat of vaporization at 25° as 16.14 kcal. per mole. Subtraction of RT leaves the energy of vaporization, 15.55 kcal. per mole. It must be emphasized at the outset, however, that the uncertainty in ΔC_p leaves a margin of about 1.5 kcal. per mole in ΔE, which will be reflected in the calculation based on equation (2).

From the density of solid aluminum bromide at 25°, 3.01, and the coefficient of cubical expansion, 2.83×10^{-4},[11] the molal volume at 100° is calculated as 181 cc. At that temperature, the molal volume of the liquid is 203 cc.[23] Assuming the same percentage increase in volumes on melting the solid at 25 and 100°, we find the molal volume of molten aluminum bromide at 25° to be 198 cc. The possible error in this value can be at most 10 cc. and will not affect the conclusions to be drawn.

Hildebrand lists the required constants for *n*-butane,[24] the energy of vaporization and molal volume at 25° being 4.44 kcal. per mole and 102.0 cc., respectively.

The value of $\ln \gamma$ calculated from equation (2) on the above bases is 1.4, which is to be compared with the observed value of 1.3, taken as the ratio of the ideal to the observed (extrapolated 3°) solubility. The agreement is quite good and could be made perfect by a slight lowering of $-\Delta C_p$ of vaporization of aluminum bromide. We conclude that solutions of aluminum bromide in *n*-butane are quite regular in the Hildebrand sense.[25]

The system Al_2Br_6–$AsBr_3$ is apparently normal. There is good evidence for the lack of compound formation.[26]

We have throughout written aluminum bromide as the dimer Al_2Br_6. It seems to us that this is logical in view of our knowledge of its molecular state when no chemical reaction has occurred. To write it as $AlBr_3$ would be analogous to using the formula I for liquid iodine or iodine in solution. The fact that in both cases a reaction with certain solvents may occur renders it even more important to compare such solutions with others on the basis of the ideal solution, in which Al_2Br_6 (or I_2) is certainly the true molecular formula.

Summary

The solubility of aluminum bromide in *n*-butane has been measured from 28.3° to the melting point of the salt, 97.5°.

There appears to be no convincing evidence for a phase transformation in aluminum bromide near 70°, as has been reported by other workers.

The difference between the actual and ideal solubility of aluminum bromide in *n*-butane is predicted by Hildebrand's equation relating solubility to internal pressure differences. The system is regular in the Hildebrand sense.

The solubility relationships of aluminum bromide in other solvents have been briefly discussed.

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[22] Fischer and Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 1 (1932). The value of $-\Delta C_p$ is surprisingly large.

[23] Biltz and Voight, *ibid.*, **126**, 39 (1923).

[24] Hildebrand, ref. 7, p. 104.

[25] Other effects, such as deviations from random mixing in solution [Rushbrooke, *Proc. Roy. Soc.* (London), **166A**, 294 (1938); Kirkwood, *J. Phys. Chem.*, **43**, 97 (1939)], and a size effect due to dimerization of the solute, which can be applied in this case [Fowler and Rushbrooke, *Trans. Faraday Soc.*, **33**, 1272 (1937)], are quite small in comparison to the Hildebrand term for regular solutions.

[26] Yankelewich and Sheka, *Mem. Inst. Chem. Acad. Sci. Ukrain. S. S. R.*, **5**, 81 (in English) (1938).

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 2, 1943

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Acid-Base Studies in Gaseous Systems. I. Precise Dissociation Measurements

BY HERBERT C. BROWN,[1] MODDIE D. TAYLOR AND MELVIN GERSTEIN

The rarity of simple reversible organic reactions has always been a major difficulty in the development of rational chemical theories. Because of this scarcity, the effects of structure and of substituents upon chemical behavior have been investigated largely by means of competitive reactions and reaction rate studies. Work with irreversible systems and the interpretation of the results thus obtained, however, involve great difficulties and uncertainties. Although much ingenuity has been displayed in overcoming such obstacles, and although modern physical methods for examining molecular structure have been of great service, simple reversible reactions, were they available, would still play an important role in the further development of organic chemical theory.

The reversible dissociation of addition compounds in the vapor phase has been the object of several studies in recent years.[2] These dissociations of the type $B{:}A$[3] $\rightarrow B{:} + A$ are simple reversible reactions are representative of a large class, the study of which should yield much valuable information. In studies of such dissociations, it is possible to make quantitative measurements from

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[1] Present address: Department of Chemistry, Wayne University, Detroit, Mich.

[2] (a) Schlesinger, Flodin and Burg, THIS JOURNAL, **61**, 1078 (1939); (b) Davidson and Brown, *ibid.*, **64**, 316 (1942); (c) Brown and Adams, *ibid.*, **64**, 2557 (1942); (d) Laubengayer and Finlay, *ibid.*, **65**, 887 (1943).

[3] The formula of the addition compound is frequently written $B^{+}{:}^{-}A$ in order to indicate the formal charges on the bonding atoms. Since there is no evident advantage in this more complex symbolism, the simpler version will be here employed.