tivation energy of the dissolution process. This is significant in itself; if one goes farther, however, and accepts the Einstein equation for the diffusion coefficient

$$D = K'(T/\eta)$$

where

$$K' = R/N6\pi r,\ \eta = \text{viscosity},\ T = \text{temperature}$$

as applicable to the process under consideration, and assumes that the dissolution process is diffusion controlled, then

$$k_1 = KD = k''(T/\eta)$$

or

$$\log k_1 = \log (T/\eta) + C$$

It follows, therefore, that a plot of log k_1 *vs.* log (T/η) should give a straight line of slope 1.0. Figure 6 shows good agreement with this prediction. It should be noted that Van Name[9] was able to treat the dissolution of cadmium in iodine in an analogous manner.

In order for K and K'', in the above equation, to be a true constant the effective thickness of the diffusion layer must remain the same over the entire temperature (viscosity) range. King[10] has shown, by a consideration of convection currents next to a solid interface, that this is a valid assumption provided density changes are not large.

[9] R. G. Van Name, *Am. S. Sci.*, [4] **43**, 449 (1917).

[10] C. V. King, *J. Am. Chem. Soc.*, **57**, 828 (1935).

PHASE RULE STUDIES IN ANHYDROUS ALUMINUM BROMIDE

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Pure, anhydrous aluminum bromide freezes at 97.5°. No phase transformation was found in solid aluminum bromide near 70°. Mixtures of bromine and aluminum bromide form only a simple eutectic system; this is also true of mixtures of bromoform with aluminum bromide and of bromobenzene with aluminum bromide. Pure ethyl bromide forms a 1:1 complex with aluminum bromide. Several other saturated aliphatic bromides, other than ethyl bromide, were found to evolve hydrogen bromide readily when mixed with aluminum bromide. Benzyl bromide and triphenylbromomethane form a stable system with aluminum bromide only in high mole fractions of aluminum bromide.

Because of the current interest in the mechanism of reactions catalyzed by anhydrous aluminum halides, we became interested in investigating compound formation in binary systems composed of aluminum bromide and bromine and bromine derivatives of various types of hydrocarbons. Thermal analyses of the systems $AlBr_3$–C_2H_5Br, $AlBr_3$–C_6H_5Br, $AlBr_3$–$CHBr_3$ and $AlBr_3$–Br_2 are reported herein.

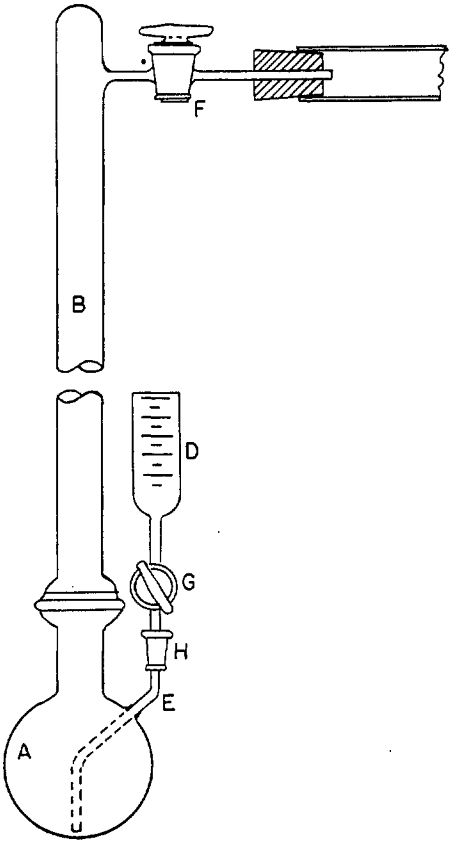

Fig. 1.—For the preparation for $AlBr_3$.

Experimental

Materials.—Aluminum bromide was prepared by the addition of redistilled bromine to aluminum pellets in a round bottom flask fitted with a reflux column (Fig. 1). After the reaction rate had decreased, the aluminum bromide was refluxed in the column until all the bromine had reacted. The column was then exchanged for a stillhead (Fig. 2) and pure, white aluminum bromide (m.p. 97.5°) was distilled into a reaction tube.

The bromine (Coleman and Bell) was purified by distillation; the middle fraction was used. The purified sample had a boiling point of 59.0° and a freezing point of −7.5°.

The bromoform was an Eastman Kodak Company sample with a boiling point of 149.0° and a freezing point of 7.0°.

The ethyl bromide was a Coleman and Bell, C.P. grade with a boiling point of 38.0° and a freezing point of −188.0°. It was purified by redistillation and recrystallization in various stages of this research.

The bromobenzene was an Eastman Kodak Company sample which was purified by redistillation and the middle fraction boiling at 156.0° was collected for use. The freezing point was −30.0°.

Procedure.—The systems were studied by the freezing point method. The freezing points were determined by means of cooling curves recorded by a Leeds and Northrup Micromax recorder. The iron–constantan thermocouple was calibrated, over the range of temperatures covered in this research, at the melting points of the following carefully purified substances: carbon tetrachloride, chloroform, ethyl acetate, toluene, mercury, water, *p*-toluidine and tin. It was also calibrated with a standard mercury thermometer calibrated at the National Bureau of Standards.

Samples were prepared for thermal analysis by first distilling the aluminum bromide into the reaction tube (S, Fig.

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[1] Mound Laboratory, Monsanto Chemical Co., Miamisburg, Ohio.

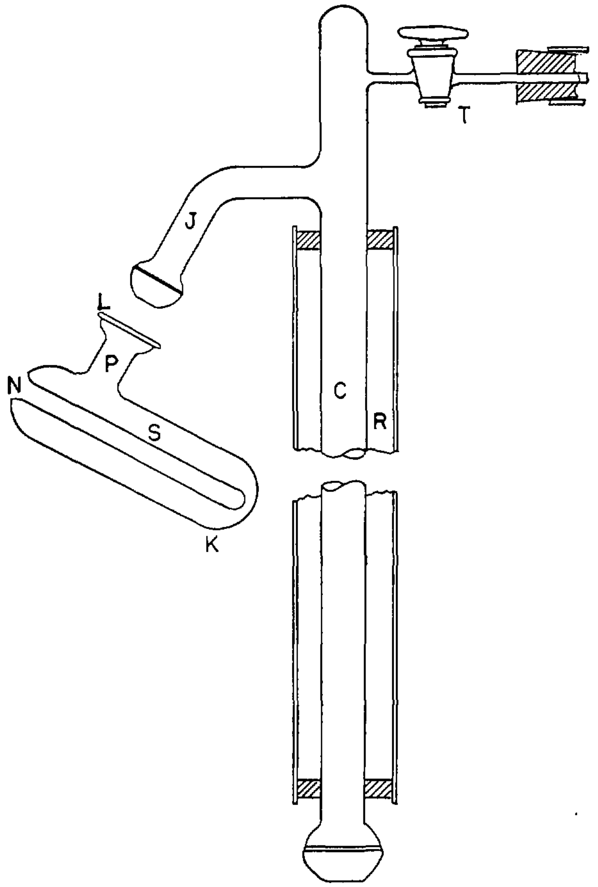

Fig. 2.—For the distillation of $AlBr_3$ into sample flask.

2) and weighing it. To this a sufficient amount of the second component was then added to give the mixture which was desired for analysis. This mixture was then heated until a completely homogeneous melt was obtained. The system was protected from atmospheric moisture by means of a drying train containing barium oxide and phosphorus oxide (P_4O_{10}). The calibrated thermocouple was inserted into a glass well (N in Fig. 2) which extended into the reaction tube in such a manner that it made intimate contact with the molten mixture. In practically all cases, 20 to 40 g. of material was used for each determination and the material was agitated continuously. Cooling curves were obtained over the entire range of compositions for each system studied. The data are believed to be accurate to ± 1.0°. All points were determined two or more times.

Results and Discussion

The freezing point–composition diagrams for the five systems studied in this research are given in Figs. 3, 4, 5 and 6.

The carefully purified anhydrous aluminum bromide gave a freezing point of 97.5°. We found no phase transformation in solid aluminum bromide near 70°, as reported by Kendall, Crittenden and Miller.[2] Our conclusions are in accord with those of Heldman and Thurmond[3] who claim there is no convincing evidence of a phase transformation in aluminum bromide near 70°.

The aluminum bromide–bromine system has a eutectic at −18.0 ± 0.5° but forms no compound.

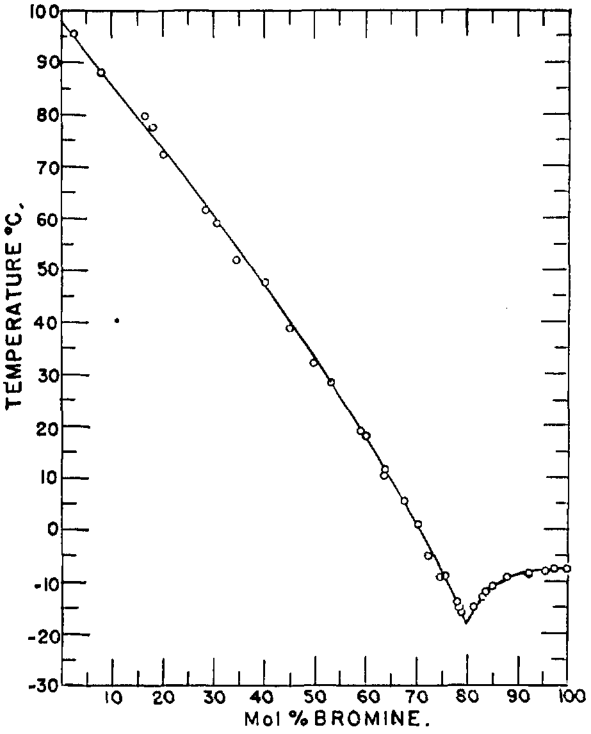

Fig. 3.—The bromine–aluminum bromide system.

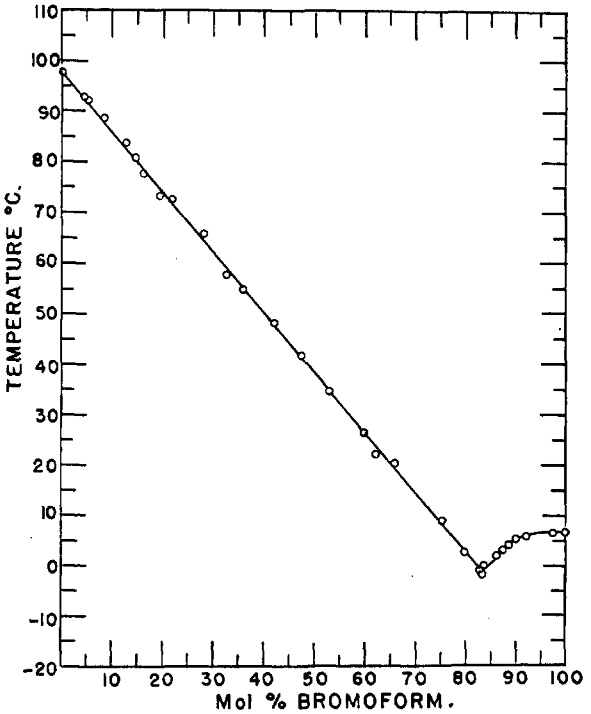

Fig. 4.—The bromoform–aluminum bromide system.

The aluminum bromide–bromoform system has a eutectic at −3.5 ± 0.5 and forms no compound. This is consistent with the conclusion of Ishekov[4] who found no compound formation with carbon tetrabromide and of Kablukov and Khanov[5] who found no compound formation with dibromomethane. No data have been determined for methyl bromide because of its low boiling point.

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[2] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Am. Chem. Soc.*, **45**, 963 (1923).

[3] J. D. Heldman and C. D. Thurmond, *ibid.*, **66**, 427 (1944).

[4] V. A. Ishekov, *J. Russ. Phys. Chem. Soc.*, **45**, 1792-8 (1913).

[5] I. Kablukov and A. S. Khanov, *ibid.*, **41**, 1755-62 (1909).

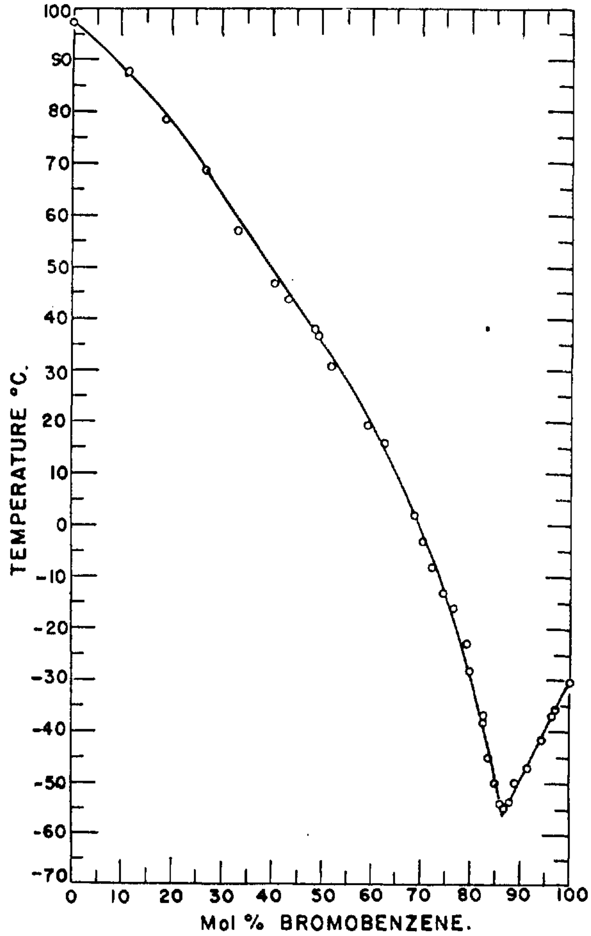

Fig. 5.—The bromobenzene–aluminum bromide system.

The aluminum bromide–bromobenzene system has a eutectic at −56.0 ± 0.5° and forms no compound. This casts some doubt on the interpretation of Wohl and Wertyporoch[6] of their electrical conductivity data on this system in which they assumed the formation of a complex.

The aluminum bromide–ethyl bromide system has eutectics at −68.5 and −132° and forms a compound having the empirical formula $AlBr_3 \cdot C_2H_5Br$. Considerable difficulty was encountered in obtaining this compound because of decomposition of the products with evolution of hydrogen bromide. Careful purification of the ethyl bromide by redistillation and recrystallization removed an impurity which seemed to catalyze the decomposition of the ethyl bromide. Recent evidence for the existence of a 1:1 compound of aluminum bromide–ethyl bromide has been obtained recently by Sheka and Sheka[7] from dielectric constant data.

Attempts to study the aluminum bromide–butyl bromide system led to decomposition of the alkyl halide. When liquid *n*-butyl bromide was added to solid aluminum bromide, hydrogen bromide was split from the *n*-butyl bromide and the resulting gaseous butene-1 immediately added to the aluminum bromide, forming the scarlet, liquid addition complex. The liquid addition complex, $C_4H_8 \cdot AlBr_3$, between aluminum bromide and butene-1 was isolated and analyzed quantitatively. This liquid complex is quite stable at room temperature in a closed system free of moisture. Conversely, direct addition of an olefin, hexene-1, to aluminum bromide resulted in the formation of a high molecular weight hydrocarbon and a mixture of by-products. The lower the temperature maintained during the addition, the greater the yield of hydrocarbon that was obtained.

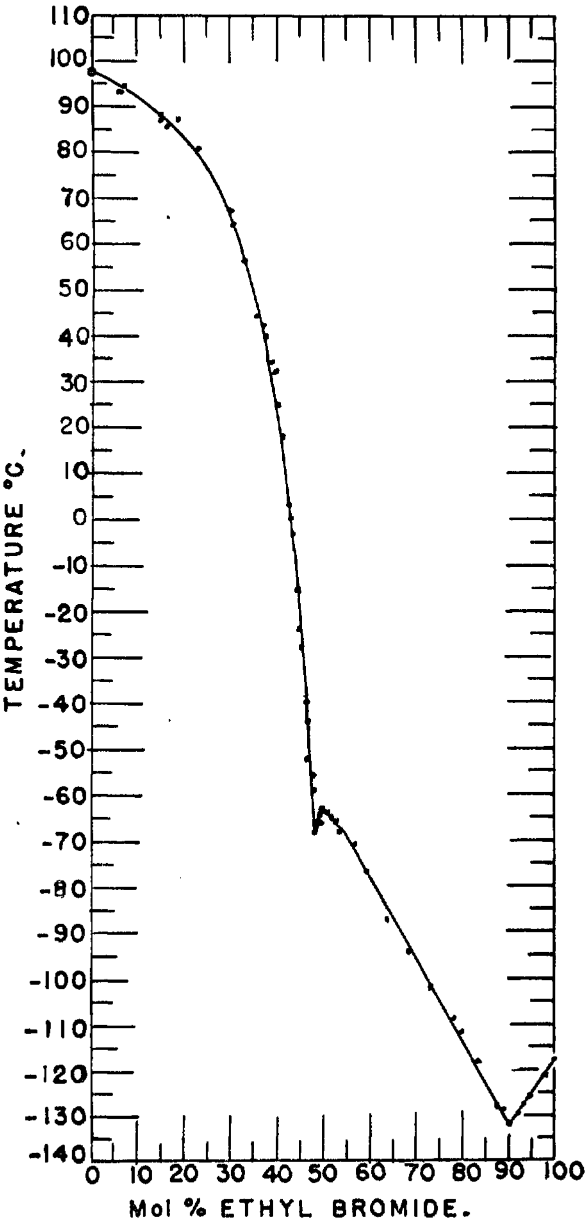

Fig. 6.—The ethyl bromide–aluminum bromide system.

Other bromide-bearing organic compounds were also investigated. Hydrogen bromide evolution was also noted when normal propyl and isopropyl bromides were added to aluminum bromide. Allyl bromide and vinyl bromide reacted violently with the aluminum bromide. The system triphenylbromomethane–aluminum bromide was stable to concentrations of 85 mole % of aluminum bromide.

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(6) E. Wohl and E. Wertyporoch, *Ber.*, **64B**, 1357 (1931).

(7) I. A. Sheka and Z. A. Sheka, *Doklady Akad. Nauk S.S.S.R.*, **73**, 739 (1950).

Above 15 mole % of the triphenylbromobenzene decomposition occurred as was indicated by irreproducibility of the freezing points. The benzyl bromide–aluminum bromide system was stable up to 34 mole % of benzyl bromide. Evidence of a eutectic was observed at 34.5 mole %. All mixtures above this value decomposed with evolution of copious quantities of gas.

THE SORPTION OF AMINES BY SILICA GELS[1]

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Received August 20, 1951

Sorption isotherms of primary aliphatic amines and a few related compounds have been determined on silica gels, mostly at 25°. On one sample of silica (gel B) the lower amines (ethylamine, *n*-propylamine and ethylenediamine) show small but definite hysteresis loops whereas the higher amines (*t*-butylamine, *n*-amylamine, *n*-hexylamine and *n*-heptylamine) show no loop. On the other sample (gel D) all show large loops which, however, decrease in size as the molecular diameter (σ) increases. The point of hysteresis inception in all systems corresponds to a pore radius (calculated from the Kelvin equation) between 2σ and 3σ. The saturation volumes are roughly constant as required by Gurvitsch's rule. The monolayer capacities correspond to the covering of a constant surface area, the number of moles adsorbed being inversely proportional to σ^2. The gradual decrease in the size of the hysteresis loop as σ increases, and its ultimate disappearance on gel B, together with the location of the point of hysteresis inception, are in agreement with the predictions of the open-pore theory, which appears to offer a more satisfactory explanation of the experimental data than the rival "ink-bottle" theory.

A systematic examination of the sorption isotherms of the aliphatic alcohols on silica gel[2,3] failed to reveal any marked decrease in the size of the hysteresis loop as the size of the adsorbed molecule increased, but later it was observed[4,5] that triethylamine gave a hysteresis loop much smaller than those found with the alcohols. This suggested that an investigation of the aliphatic amines might be of interest since these compounds are considerably more volatile than the corresponding alcohols and it is therefore possible to examine a wider range of molecular size. The open pore theory of sorption hysteresis[6] predicts that the loop should become smaller as the adsorbed molecule increases in diameter. This prediction has been confirmed in the present work, where it is shown that on one sample of silica gel the lower amines (ethylamine, *n*-propylamine and ethylenediamine) show definite loops whereas the higher amines (*t*-butylamine and *n*-amylamine upwards) show no loop. On other samples of silica gel and on ferric oxide gel[7] all these amines show large hysteresis loops similar to those reported by Bartell and Dobay[8] on a silica gel prepared by hydrolysis of silicon tetrachloride.

Experimental

The substance here designated "silica gel B2" is a commercial sample similar to, but not identical with, the "gel B" used in the earlier work with alcohols and triethylamine. After evacuation to constant weight at an activation temperature of 150° it lost a further 1% of water on ignition. Another commercial sample "silica gel D" was examined, which had a residual water content of 2.3% after evacuation at 200°. The experimental technique was similar to that used previously,[2] with minor modifications which, together with the methods used for purification of the amines, are described elsewhere.[7] Data for ethylamine were obtained by a modification of the method of Goldmann and Polanyi,[9] which unfortunately enabled only desorption points to be determined.

Isotherms for water and ethyl alcohol were first determined for comparison with corresponding data obtained previously on other gels.[2] The following substances were investigated on both gel B2 and gel D: ethylamine, ethylenediamine, *n*-propyl-, *n*-butyl-, *n*-amyl-, *n*-hexyl- and *n*-heptylamine, *t*-butylamine (Me_3CNH_2), cyclohexylamine and pyridine. An oxygen isotherm was also determined at 90.3°K. in order to obtain surface areas by the B.E.T. method.

Results

Gel B2.—These results are illustrated in Figs. 1–3 which show all the isotherms obtained, except those for water and *n*-butylamine. The water curve is similar to that reported on gel B by Broad and Foster[10] and shows a large hysteresis loop. The results obtained with *n*-butylamine were not reproducible but indicate the presence of a hysteresis loop. There seems to be some specific interaction between the amine and this particular gel since the volume adsorbed at saturation is abnormally high. Figures 1–3 show definite hysteresis loops with oxygen, ethyl alcohol, *n*-propylamine and ethylenediamine. It is reasonable to suppose that a loop would also have been detected with ethylamine had it been possible to determine the adsorption curve. The largest molecule to show a definite reproducible loop is *n*-propylamine; no loop is found with any of the straight chain amines above *n*-butyl or with *t*-butylamine, pyridine or cyclohexylamine.

Another feature of interest is that as the loop disappears, the linear middle portion of the isotherm becomes more prominent (*e.g.*, with *n*-amylamine and *t*-butylamine), but this linear region in turn diminishes and has practically vanished when *n*-heptylamine is reached. There is a perceptible flattening in the middle of the pyridine isotherm but cyclohexylamine gives a normal B.E.T. type 1 isotherm which follows the Langmuir equation over the entire range.

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(1) Based on a thesis presented by Marjorie J. Brown for the degree of Ph.D. in the University of London, 1950.

(2) A. G. Foster, *Proc. Roy. Soc.* (*London*), **A146**, 129 (1934).

(3) A. G. Foster, *ibid.*, **A150**, 77 (1935).

(4) D. W. Broad, Ph.D. Thesis, London, 1938.

(5) A. G. Foster, THIS JOURNAL, **55**, 638 (1951).

(6) A. G. Foster, *Trans. Faraday Soc.*, **28**, 645 (1932).

(7) M. J. Brown and A. G. Foster, *J. Chem. Soc.*, Feb., 1952.

(8) F. E. Bartell and D. G. Dobay, *J. Am. Chem. Soc.*, **72**, 4388 (1950).

(9) F. Goldmann and M. Polanyi, *Z. physik. Chem.*, **132**, 321 (1928).

(10) D. W. Broad and A. G. Foster, *J. Chem. Soc.*, 372 (1945).