475. *The System Benzene–Hydrogen Bromide–Aluminium Bromide. Part I.*

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There is no interaction between hydrogen bromide and aluminium bromide in the absence of benzene, whereas aluminium bromide alone forms an ideal solution of Al_2Br_6 molecules in benzene. The ternary system HBr–Al_2Br_6–C_6H_6, on the other hand, shows a profound interaction of its components. Two liquid phases are formed in thermodynamic equilibrium with solid Al_2Br_6 (if present) and gaseous hydrogen bromide. The upper liquid phase is weakly ionised, the lower " red oil " phase strongly ionised. The two liquid phases do not vary greatly in composition or conductivity with increase in pressure of hydrogen bromide, the composition of the lower phase being very approximately Al_2Br_6,HBr,$6C_6H_6$. This phase probably has more of the character of a " molecular coacervate " than that of a compound. With increase in hydrogen bromide pressure or decrease in temperature, in the absence of solid Al_2Br_6, the lower phase grows at the expense of the upper. There is no evidence for the formation of $HAlBr_4$, even in the presence of benzene. The nature of the ions and their organisation in the red oil are being further studied.

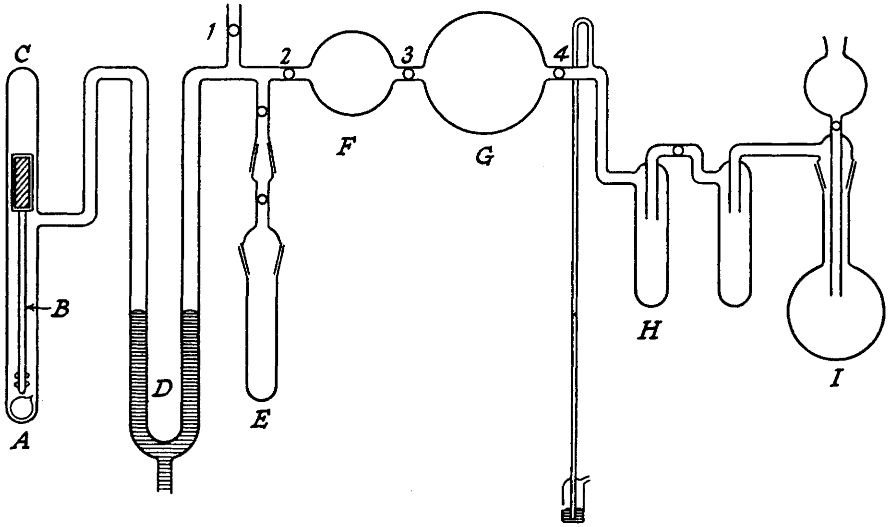
Freezing-point (Ulich, *Z. physikal. Chem., A, Bodenstein Festband,* 1931, p. 423) and solubility data (Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287) establish that aluminium bromide–benzene constitute an ideal solution of Al_2Br_6 molecules. Further evidence is the additivity of molar refractivities (Korshak, Lebedev, and Fedoseev, *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 575; *Chem. Abs.* 1948, **42**, 1217). A tendency to form C_6H_6,$AlBr_3$ is shown by a dissociation into monomer at high dilution (mole fraction $<0{\cdot}001$) and by the formation of a solid phase of this composition in equilibrium with solution below 37° (for refs. see Eley and King, *loc. cit.*). In this paper we extend these studies to the ternary system hydrogen bromide–aluminium bromide–benzene. In the first place we have shown that there is no tendency to form $HAlBr_4$ from the two pure components, under what are probably the most favourable conditions. The same conclusion for hydrogen chloride and aluminium chloride was recently reached by Brown and Pearsall (*J. Amer. Chem. Soc.*, 1951, **73**, 4681) and by Richardson and Benson (*ibid.*, p. 5096). Fontana and Herold (*ibid.*, 1948, **70**, 2883) found no appreciable interaction between hydrogen bromide and aluminium bromide in *n*-butane or *n*-hexane. In fact, the presence of aluminium bromide slightly decreased the solubility of hydrogen bromide in these solvents. The situation is quite different with benzene as solvent, as was first shown by Gustavson (*Ber.*, 1878, **11**, 2151; *J.*, 1879, **36**, 308, and subsequent references). This author reported the formation of orange oils, with formulæ such as Al_2Br_6,$6C_6H_6$, in the presence of hydrogen bromide. Menschutkin (*J. Phys. Chem. Soc., Russia*, 1909, **41**, 1089; *Chem. Zentr.*, 1910, **14**, 167) emphasised that hydrogen halide or moisture must be present to form the orange oil, which separated as a second liquid phase with a composition varying somewhat with temperature. His view that there was not formed a compound of definite composition agrees with that advanced here. Norris and Ingraham (*J. Amer. Chem. Soc.*, 1940, **62**, 1298) found hydrogen halide essential for complex formation, and isolated crystalline complexes with the alkylated benzenes. In a brief reference to benzene, they note the formation of an easily dissociable complex of variable composition, approximating to Al_2Br_6,$6C_6H_6$ plus a little HBr, but no crystals were obtained. Wohl and Wertyporoch (*Ber.*, 1931, **64**, 1357) have investigated the electrical conductivity in this system. Thus in taking up the study of the system benzene–aluminium bromide we have been concerned to extend this work, using modern high-vacuum technique. The system would seem to have several advantages over xylene–hydrogen chloride–aluminium chloride, for which Dilke, Eley, and Perry (*Research*, 1949, **2**, 538) obtained rather indefinite results.

EXPERIMENTAL

Apparatus.—The experiments involved the breaking of an ampoule containing aluminium bromide in the presence of the other components, introduced into the system in known amounts. In the first instance vapour-pressure measurements were made with a mercury manometer. Later, measurements were made of electrical conductivity. The basic vacuum system used is shown in Fig. 1.

Aluminium bromide was prepared and introduced into sealed fragile ampoules as described previously (Eley and King, *loc. cit.*). An ampoule was placed in the bottom of reaction vessel *A*, the stirrer-breaker *B* carefully inserted, and the reaction vessel sealed off at *C*. The top of the stirrer-breaker *B* contained a sealed-in piece of soft iron, so that it could be magnetically operated in the usual way. The mercury U-tube *D* served both as a cut-off and a manometer for measuring the pressure of the contents of the reaction vessel. Chemical attack of hydrogen bromide on the mercury was negligible. Benzene was kept over phosphoric oxide in tube *E*. A definite amount could be distilled into the reaction vessel by cooling the latter in liquid air. The whole system could be evacuated to 10^{-6} mm. Hg through tap 1. Known amounts of hydrogen bromide could be admitted *via* taps 4, 3, and 2, and the calibrated volumes *G* and *F*. Liquid hydrogen bromide was stored in the trap *H*, cooled in a solid carbon dioxide–methanol slurry. It was introduced into bulbs *F* and *G* at its equilibrium vapour pressure. It was necessary to allow adequate time for the liquid hydrogen bromide to reach its equilibrium vapour pressure. A bulb-full of hydrogen bromide could then be transferred to the reaction vessel *A* by cooling the latter in liquid air. All pressure measurements in a given series were carried out at a constant reaction vessel volume, the mercury in *D* always being raised to a fixed point on the left-hand limb. The volume was calibrated from the pressure developed by a known amount of hydrogen bromide admitted to the evacuated reaction vessel, containing only the stirrer and the sealed ampoule of aluminium bromide. A water-bath was used to keep the vessel *A* at 15° ± 0·1°, and for purposes of calculation the rest of the tubing was assumed to be at 20°.

FIG. 1.



Materials.—Benzene and aluminium bromide were prepared and purified as described earlier (Eley and King, *loc. cit.*).

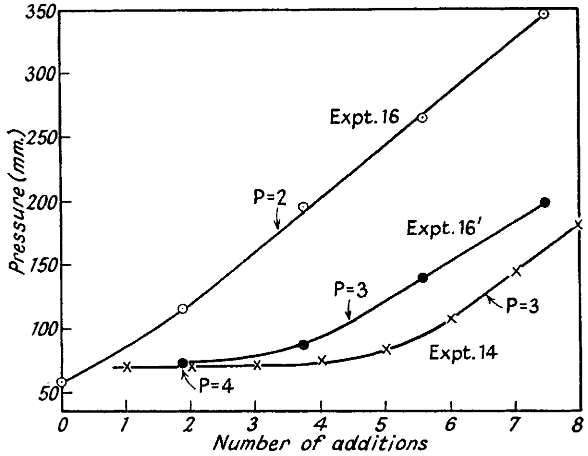
Hydrogen bromide was prepared by hydrolysis of phosphorus tribromide *in vacuo* in vessel *I*. The hydrogen bromide was frozen out in the first trap in liquid air, evacuated, and then purified by several distillations from a trap cooled in solid carbon dioxide–methanol to one cooled in liquid air. The residue was discarded each time. The hydrogen bromide was then stored in *H*, cooled with solid carbon dioxide–methanol. Its vapour pressure was 402 mm. at −78°, in agreement with the value in International Critical Tables.

Analysis.—Aluminium was determined gravimetrically, by using 8-hydroxyquinoline, bromide volumetrically with silver nitrate (eosin as indicator), and benzene by difference.

Hydrogen Bromide–Aluminium Bromide.—Two experiments were made in which hydrogen bromide was condensed on to 1 g. of aluminium bromide at −78°. In the first instance, successive doses were admitted from bulb *G*, each corresponding to 1·411 g. and, in the second, successive doses from bulb *F*, each corresponding to 0·1096 g. In all cases the vapour pressure remained at the value of 402 mm. characteristic of the pure hydrogen bromide. There was no visual evidence of solution, and the hydrogen bromide at the end could be distilled off, leaving the aluminium bromide unchanged. It is concluded that an $HAlBr_4$ complex is not formed even under conditions of temperature which would be expected to be especially favourable for its formation. There was no evidence either for interaction between solid Al_2Br_6 and gaseous hydrogen bromide at room temperature.

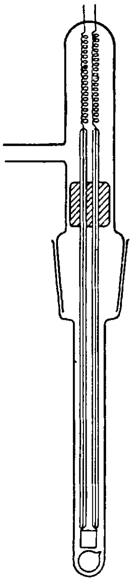
Hydrogen Bromide–Aluminium Bromide–Benzene.—A number of experiments were made in which doses of hydrogen bromide were admitted to (*a*) pure benzene and (*b*) benzene plus aluminium bromide, and pressure measurements were taken. In the first case the amount dissolved was calculated from known pressures and volumes, and it was found that Henry's law was obeyed, the slope of the curve relating pressure to the amount of gas in solution corresponding to $1{\cdot}4 \times 10^{-4}$ g. of hydrogen bromide per g. of benzene per mm. Hg pressure of hydrogen bromide at 15°. This is in reasonable agreement with previous workers. Expt. 16 ($P = 2$) in Fig. 2 shows the type of behaviour observed as a plot of pressure against number of additions of hydrogen bromide admitted. The initial pressure for zero dosage is the vapour pressure of benzene. The slight initial curvature of the graph at low pressures is to be attributed to lack of attainment of complete solution equilibrium. Several experiments of type (*b*) were made with a small $Al_2Br_6 : C_6H_6$ ratio, where all the aluminium bromide was initially in solution. Expt. 16′ ($P = 3$) in Fig. 2 is an example of this, with 2·667 g. of benzene and 2·01 g. of aluminium bromide. Other experiments were made with an excess of aluminium bromide so that solid Al_2Br_6 phase was present, Expt. 14 being an example, with 1·355 g. of benzene and 2·193 g. of aluminium bromide.

FIG. 2. *Relation between the pressure and the number o, additions (each* 13·3 *c.c. at N.T.P.) of hydrogen bromide.*



P = *the number of phases present.*

FIG. 3. *Conductivity cell.*



The general phenomena observed on addition of hydrogen bromide to a solution of aluminium bromide in benzene, in the absence of solid aluminium bromide, are as follows. The solution first becomes yellow, and when a certain pressure of hydrogen bromide is exceeded the solution separates into two phases.* The upper phase is a clear yellow, while the lower

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* The value of the pressure depends on the concentration of aluminium bromide. In a saturated solution, with solid aluminium bromide present, it is 18 mm. at 15° and 44 mm. at 22·5°.

phase is a clear orange-red. As more hydrogen bromide is added the lower layer increases in volume at the expense of the upper. The effect is reversible in that pumping off the gas leads to a decrease in volume of the lower layer and an increase in volume of the upper layer. Continued pumping leads to complete removal of all hydrogen bromide and benzene in agreement with Norris and Ingraham (*loc. cit.*). The aluminium bromide left is slightly discoloured by impurity to an extent depending on the age of the red oil. A number of analyses were carried out on the lower layer under various conditions of formation, hydrogen bromide pressure, etc., the extreme values for analysis being: Al, 3·6—6·6; Br, 48·3—55·8; C_6H_6, 49·1—37·6% (Calc. for $Al_2Br_6,HBr,6C_6H_6$: Al, 5·0; Br, 51·7; C_6H_6, 43·2%).

A typical figure for analysis of the top layer is Al, 0·46; Br, 9·44; C_6H_6, 90·1%. This corresponds to a dilute solution of aluminium bromide in benzene–hydrogen bromide, where the Br concentration is close to that expected from the Henry-law constant for pure benzene, namely, Br 5·2% (the experimental Br concentration in excess of that in the dissolved aluminium bromide is 5·37%).

Electrical conductivity. The electrical conductivity of the system was determined in the conductivity cell shown in Fig. 3, with a Cambridge conductivity bridge, down to 3×10^{-5} mho, and below this with standard resistors in conjunction with a valve voltmeter. The cell was attached in place of the previous reaction vessel to the vacuum system shown in Fig. 1. It was designed so that the electrode system could be raised and lowered magnetically, so as to take the conductivity successively of both the upper and the lower layer, and so that the system could be stirred to afford equilibrium with the gas phase. The measurements were made at 15°±0·1°. All substances were introduced and manipulated after initial evacuation of the system with rigid exclusion of air and water vapour. The cell constant was 0·9.

The specific conductivity of a solution of 3·375 g. of aluminium bromide in 5·672 g. of benzene was found to be 3×10^{-9} mho. Hydrogen bromide at 402 mm. pressure was introduced into the system in 50-c.c. portions. After one such addition a trace of lower phase separated; the specific conductivity of the upper phase was $1·9 \times 10^{-5}$ mho. With successive introductions the volume of the lower phase increased at the expense of the upper, the total volume remaining constant. Over the whole range the specific conductivity of the upper phase was constant at $1·9 \times 10^{-5}$ mho, and that of the lower phase constant at $1·0 \times 10^{-2}$ mho.

After five such additions of hydrogen bromide, the total pressure in the system was 121 mm., and the reaction vessel was immersed in an oil-bath and slowly heated. As the temperature rose, so also did the equilibrium pressure, and the volume of the *upper* phase increased at the expense of the *lower,* until at 60° the lower phase had largely disappeared. At this point the upper phase had a pronounced reddish tinge, and a specific conductivity of $0·9 \times 10^{-4}$ mho. On slow cooling of the system, the changes were all reversed. The lower phase increased at the expense of the upper until at 15° it reached its original volume. The conductivities of the upper and the lower phase recovered their original values, and the pressure finally reached 127 mm. The only change was that the lower phase was slightly darker.

In a separate experiment pure benzene was found to have an apparent specific conductivity of 2×10^{-9} mho, and the value was not changed on dissolution of hydrogen bromide in it until the partial pressure of the latter was 106 mm. The true value for the specific conductivity of benzene is certainly much less than this, and probably less than the value of 1×10^{-13} reported by Wohl and Wertyporoch (*loc. cit.*). The value given here is to be regarded as the limiting value of our measuring apparatus, rather than that due to impurities in the benzene. The benzene used showed no colour on being sealed with pure aluminium bromide for several months, which is a very sensitive test for impurity, especially moisture. Our conductivity value for aluminium bromide must be regarded as only very approximate since it is so near the limiting value for the apparatus, so that its agreement with the figure of 3×10^{-9} reported by Wohl and Wertyporoch (*loc. cit.*) is probably fortuitous. Wohl and Wertyporoch report a value of 10^{-2} for the red oil, which agrees with ours.

A single experiment was made with a solution of 3·2 g. of aluminium bromide in about 3·0 g. of *n*-hexane (from B.D.H.), not specially purified. The conductivity of *ca.* 10^{-9} mho was unchanged on addition of hydrogen bromide, and there was no separation into two phases, as is to be expected from the work of Fontana and Herold (*J. Amer. Chem. Soc.*, 1948, **70**, 2883).

Stability of the lower phase. If some of the lower red phase is sealed in an ampoule *in vacuo* it becomes black during a few days. Irreversible changes obviously take place, independently of the presence of any impurity. In the absence of hydrogen bromide, we have found it possible to keep aluminium bromide–benzene mixtures indefinitely in sealed ampoules without coloration (Eley and King, *Trans. Faraday Soc.*, 1951, **47**, 1287).

DISCUSSION

We conclude from the foregoing results that, while in the system C_6H_6–HBr–Al_2Br_6 the interaction of any two components separately is of a mild physical nature, *i.e.*, involves only van der Waals and polarisation forces, in the ternary system a much more profound interaction occurs, involving the ionisation of covalent bonds. This may be classed as chemical in nature, and nothing similar is noted if benzene be replaced by a saturated hydrocarbon such as *n*-hexane (Fontana and Herold, *loc. cit.*). As is well known, two liquid phases are formed, and we have shown that the red oil, or lower red phase, is in thermodynamic equilibrium with all the other phases present, *i.e.*, upper liquid phase, gas, and excess of solid (if any). This follows from the possibility of reversing the process of formation by lowering the partial pressure of hydrogen bromide, or by raising the temperature. That the presence of hydrogen bromide is essential for formation of the red oil is in agreement with the results of Norris and his co-workers (*J. Amer. Chem. Soc.*, 1939, **61**, 1167; 1940, **62**, 1298, 1428). The position is complicated by the tendency for the red oil to become black, obviously owing to side-reactions, when kept even in sealed tubes. It has not been found possible to isolate a crystalline complex from the red oil, which has a composition varying somewhat with conditions, around $Al_2Br_6,HBr,6C_6H_6$; an oil of this composition was reported by Norris and Ingraham (*loc. cit.*) and Korshak, Lebedev, and Fedoseev (*loc. cit.*). It is noteworthy that there is no analytical evidence for the presence of $HAlBr_4$ in this lower red phase, or for that matter in the upper phase where the amount of hydrogen bromide dissolved by a solution of aluminium bromide in benzene is almost the same as that dissolved by pure benzene.

The thermodynamic reversibility of the system is also evident in that it obeys the phase rule. Thus, reference to Fig. 2 shows a portion of the graph where the pressure is constant, independently of the amount of hydrogen bromide added. Over this region four phases are present (solid aluminium bromide, two liquid phases, and vapour) and for a three-component system at constant temperature we should expect zero variance under these conditions. Where only three phases are present (no excess of solid) the pressure increases with the amount of hydrogen bromide added.

Dilke, Eley, and Perry (*Research*, 1949, **2**, 538) observed the slow formation of a red complex oil between aluminium chloride and xylene in the absence of added hydrogen chloride. This may have been due in part to the formation of hydrogen chloride *in situ*, since the system was not anhydrous in the sense used here. Probably also some of the irreversible side reaction noted above occurred. Aluminium chloride we now know to be rather unsuitable for work of this kind, since its high lattice energy and related low solubility in aromatic hydrocarbons serve to make any reaction of this kind very slow, even if hydrogen halide be present. Further, the aluminium chloride was commercial material purified by only two sublimations, and we have subsequently found (Eley and Watts, *J.*, 1952, 1914) that at least eight sublimations are necessary for complete purification of this product.

If the red oil is a definite compound, then experiment shows that its melting point must be lower than that of benzene.

The highly conducting nature of solutions of this type was established by Wohl and Wertyporoch (*Ber.*, 1931, **64**, 1357). The conductivity data show that both aluminium bromide and hydrogen bromide in benzene are non-ionised. On addition of hydrogen bromide to aluminium bromide in benzene a weakly ionised system of $\kappa = 1{\cdot}9 \times 10^{-5}$ mho eventually results. At this concentration of ions the system becomes unstable and splits into a weakly ionised upper phase having $\kappa = 1{\cdot}9 \times 10^{-5}$, and the lower "red oil" phase, which is strongly ionised, having $\kappa = 1{\cdot}0 \times 10^{-2}$. Subsequent addition of hydrogen bromide causes little change in the composition of either phase, but merely causes the growth of the lower at the expense of the upper phase. This view accords with both analytical and conductivity data.

The system shows some analogies to the phenol–water system, which also gives two liquid phases, but there are important differences. Increase of temperature with the phenol–water system causes the two phases to become more alike, with little change in relative volume, until at the critical solution temperature the two phases become identical.

In the case of aluminium bromide increase in temperature merely causes the upper phase to grow in volume at the expense of the lower, *i.e.*, reverses the effect of increase in pressure. This may be due mainly to removal of hydrogen bromide from solution, its solubility in benzene decreasing with increase in temperature.

The nature of the ions present in the lower phase requires further investigation, since the analytical data, suggesting a system of composition 1 Al_2Br_6 : 1 HBr, tend to rule out $HAlBr_4$ and therefore H^+ and $AlBr_4^-$.

The actual lower phase itself is reminiscent of a coacervate, the liquid phase which separates from the interaction of oppositely charged, highly solvated colloids. It may be similar in nature, a highly concentrated system of positive and negative ions which " imbibes " a more or less definite quantity of solvate benzene. If so, it might properly be called a " molecular coacervate," so as to imply that the ions are of molecular rather than colloidal dimensions. We hope to subject the matter to further examination—*X*-ray diffraction experiments may perhaps assist at this point. The importance of the " red oil " lies in the probability that it forms the main sphere of reaction in many kinds of Friedel–Crafts catalysis.

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