

Still another variation of Equation 1 applied to two substances exerting the same pressure at different temperatures may be written without any assumptions beyond those of the thermodynamic Clapeyron equation itself:

$$\frac{dT/T}{dT'/T'} = \frac{d \log T}{d \log T'} = \frac{l' \Delta v}{l \Delta v'} \quad (18)$$

where Δv and $\Delta v'$ are the respective differences between specified volumes of vapor and liquid.

This gives an integral form (with respect to temperature):

$$\frac{l}{\Delta v} \log T = \frac{l'}{\Delta v'} \log T' + C \quad (19)$$

Specific volumes at different pressures are often readily available—for example, for both water and saturated steam. Specific gravities (or specific volumes) of solutions are also readily available. The specific volume of the vapor leaving the solution is the specific volume of steam saturated with respect to the solution but superheated with respect to water. The vapors are at the same pressure but have the same number of degrees superheat as the elevation of boiling point of the solution. Thus, for the important case of aqueous solutions, values of the latent heat may be exactly determined without assumptions. With these values of latent heat as a basis, the heats of dilution and enthalpies may also be obtained readily for any aqueous solutions, mixtures, or compounds on which is available a minor amount of vapor pressure data. The neglect of the value of the volumes of the condensed phases may be used with only minor loss of the exactness of Equation 19, since a quotient is changed only slightly by changing both the numerator and denominator by almost the same amount (which is in itself insignificant as noted above). Thus for values at the same pressures:

$$\log T = \frac{l'v}{lv'} \log T' + C \quad (20)$$

No elaboration or examples of the use of Equations 18, 19, or 20 will be given here; but their greater accuracy would balance their greater inconvenience in use in some cases.

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Literature Cited

- (1) Badger and Baker, *Trans. Am. Inst. Chem. Engrs.*, **13**, 151 (1920).
- (2) Baker and Pettibone, *IND. ENG. CHEM.*, **21**, 562 (1929).
- (3) Bertetti and McCabe, *Ibid.*, **28**, 248 (1936).
- (4) Blue and Giaque, *J. Am. Chem. Soc.*, **57**, 991 (1935).
- (5) *Ibid.*, **58**, 832 (1936).
- (6) Brown, *J. Franklin Inst.*, **219**, 405 (1935).
- (7) Calingaert and Davis, *IND. ENG. CHEM.*, **17**, 12-87 (1925).
- (8) Cox, *Ibid.*, **15**, 592 (1923).
- (9) Giaque and Powell, *J. Am. Chem. Soc.*, **61**, 1971 (1939).
- (10) Greenewalt, *IND. ENG. CHEM.*, **17**, 522 (1925).
- (11) Hirschler, *J. Am. Chem. Soc.*, **58**, 2472 (1936).
- (12) Hodgman, *Handbook of Chemistry and Physics*, 23rd ed., Cleveland, Chemical Rubber Publishing Co., 1939.
- (13) *International Critical Tables*, New York, McGraw-Hill Book Co., 1926-30.
- (14) Kemp and Egan, *J. Am. Chem. Soc.*, **60**, 1521 (1938).
- (15) Kemp and Giaque, *Ibid.*, **59**, 79 (1937).
- (16) Kiehl and Wallace, *Ibid.*, **49**, 381 (1927).
- (17) Landolt and Börnstein, *Physikalisch-Chemische Tabellen*, 5th ed., Berlin, Julius Springer, 1931.
- (18) *Ibid.*, Vol. II, Part 2, p. 1289.
- (19) *Ibid.*, Vol. II, Part 2, p. 1559.
- (20) Lange, *Handbook of Chemistry*, 3rd ed., Sandusky, Ohio, Handbook Publishers, 1939.
- (21) Livingston and Heisig, *J. Am. Chem. Soc.*, **52**, 2409 (1930).
- (22) MacDougal, *Ibid.*, **58**, 2585 (1936).
- (23) Monrad, *IND. ENG. CHEM.*, **21**, 139 (1929).
- (24) Monrad and Badger, *Ibid.*, **21**, 40 (1929).
- (25) Olsen, *Chemical Annual*, New York, D. Van Nostrand Co., 1934.
- (26) Othmer, *IND. ENG. CHEM.*, **20**, 743 (1928).
- (27) Overstreet and Giaque, *J. Am. Chem. Soc.*, **59**, 254 (1937).
- (28) Partington and Winterton, *J. Chem. Soc.*, **1930**, 635.
- (29) Perry, *Chemical Engineers' Handbook*, New York, McGraw-Hill Book Co., 1934.
- (30) *Ibid.*, p. 346.
- (31) Perry and Smith, *IND. ENG. CHEM.*, **25**, 195 (1933).
- (32) Powell and Giaque, *J. Am. Chem. Soc.*, **61**, 2366 (1939).
- (33) Roehl, *IND. ENG. CHEM.*, **30**, 1320 (1938).
- (34) Roehl, *J. Am. Chem. Soc.*, **58**, 1291 (1936).
- (35) Taylor and Taylor, *IND. ENG. CHEM.*, **27**, 673 (1935).
- (36) Wright, *J. Phys. Chem.*, **36**, 2793 (1932).

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Preparation of Anhydrous Aluminum Bromide

PAUL K. WINTER AND PAUL L. CRAMER

General Motors Corporation, Detroit, Mich.

AMONG the advantages possessed by aluminum bromide over aluminum chloride as a catalyst in certain organic reactions are its greater solubility in hydrocarbons, resulting in a homogeneous reaction mass, and its higher catalytic activity. In addition, the bromide may be readily purified by simple distillation whereas the chloride sublimes.

The increasing use of anhydrous aluminum bromide has created a need for a simple and convenient method of preparing it. Various procedures have been reported in the past (1, 2, 4, 7, 8, 9, 12, 13), each with its own meritorious features and often for a special purpose. The use of diluent

gases or liquid solvents as a means of controlling the reaction temperature results in a reduced rate of production and complicates the problem of purification. The object of the present proposed method is to provide a reasonably pure product in any desired quantity, in one operation, with a relatively high rate of production, and with a minimum of operating difficulties.

The apparatus is shown in the diagram. The bromine is introduced near the bottom of the reaction flask where it comes into contact with the aluminum chips or pellets. The flask may be warmed gently at first to start the reaction, but

in a short time the reaction supplies enough heat to vaporize the incoming bromine and to distill the aluminum bromide out through the side arm on the neck of the flask, where it condenses and flows into the auxiliary purifier. The molten aluminum bromide refluxes down through the mass of aluminum chips in the flask, and serves to prevent local overheating and consequent fusion of the metal. The bottom of the flask is protected against occasional molten globules of aluminum by a layer of glass wool. The bromine tube must not be joined to the flask by a permanent glass seal, because it must be removed and cleaned occasionally when the lower end becomes clogged with solid impurities coming from the technical grades of bromine and aluminum. A ground-glass joint will serve nicely but is not necessary; the loose joint shown in the diagram may be sealed satisfactorily by an easily broken cement of pumice, water glass, and water. The level of this joint should be above that of the exit tube to avoid having the aluminum bromide reflux over it. The mouth of the flask is closed by a loosely fitting glass stopper.

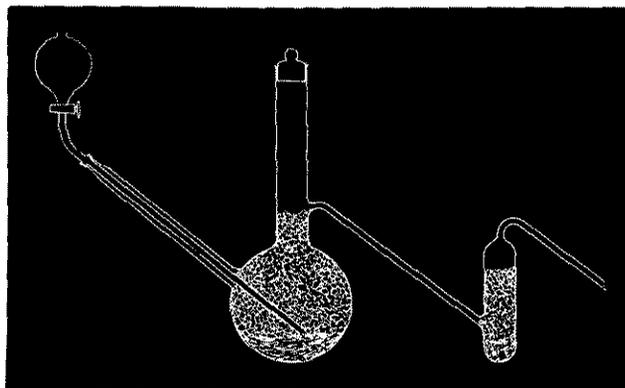
As the reaction proceeds, aluminum is consumed largely from the center of the flask, and the bromine finally begins to channel up through and be carried over with the aluminum bromide. When this occurs, the supply of bromine is shut off, the stopper in the neck of the flask is removed, a hole is punched through to the interior of the mass of aluminum chips by means of a heavy glass rod, and the flask is refilled with aluminum chips.

A simple and convenient method for preparing anhydrous aluminum bromide is reported. The important features of this method are: the introduction of the bromine near the bottom of the reaction vessel (through a tube which is not vertical, since a wide channel is quickly eaten out adjacent to a vertical tube) so that it may be distilled upward through the mass of aluminum and react in the vapor phase; the control of the temperature within the flask by the refluxing of the molten aluminum bromide over the metal; and the purification of the product as fast as it is formed.

The initial product as it distills from the reaction flask is usually nearly water-white, and may be collected at that point in a reaction vessel for immediate use or in a flask for storage. Sometimes, however, it is contaminated by a little free bromine and by impurities carried over mechanically. For this reason it is best to run it directly from the reaction flask to the bottom of a small distilling vessel filled with aluminum chips. Auxiliary heating is required to distill the aluminum bromide out of the purifier. A clean water-white product is thus obtained in a continuous process. For convenience in storing and subsequent use, the best receiving vessel is a distillation flask, whose neck and side arm are constricted for convenience in sealing the flask after it is filled. Before the reaction is started, the whole system should be flushed out with a dry gas (air or nitrogen) in order to avoid hydrolysis of the aluminum bromide. The side arm of the receiver should be provided with a guard tube to prevent the entrance of moisture. When the flask is about three fourths full, the reaction is stopped, and both the neck and the side

arm are sealed. The aluminum bromide thus collected can be stored indefinitely without deterioration, and smaller quantities can be withdrawn by cutting off the tip of the side arm and distilling the desired amount into the dry reaction vessel; then the side arm may be sealed again.

The size of the apparatus is governed by the production rate desired. A one-liter reaction flask can easily produce a kilogram or more of aluminum bromide per hour. The rate of production is controlled by the flow of bromine, and is limited by the condensing capacity of the receiver and by the maximum safe temperature within the reaction flask, which is just under the melting point of the aluminum. The apparatus described has ample capacity to supply aluminum bromide for laboratory uses, and there is no apparent reason why the principles involved might not be employed on a much larger scale, should the occasion arise.



This apparatus has been used with bromine of National Formulary V specifications, and with aluminum purchased from the Aluminum Company of America, and described by them as 99 + per cent ingots. Without further purification, the aluminum bromide thus produced melted at 97.2° and boiled at 254° C. (760 mm. pressure). There is some discrepancy in the values of these physical constants reported in the literature. For example, the melting point and boiling point are given by Fischer and Rahlfs (5) as 97° and 255° C., by Mallet (11) as 93° and 263.3° C. (747 mm.), by Weber (14) as 90° and 265–270° C., by International Critical Tables (6) and a handbook of chemistry (10) as 97.5° and 268° C. Kendall, Crittenden, and Miller (9) give the melting point as 97.1° C., Fischer (4) as 97.5°, and Biltz and Voigt (3) as 97°. The relatively high melting point and low boiling point in the present instance indicate a reasonably pure product.

Literature Cited

- (1) Barre, *Bull. soc. chim.*, **11**, 433 (1912).
- (2) Bell, R. P., *J. Chem. Soc.*, **134**, 338 (1932).
- (3) Biltz, W., and Voigt, W., *Z. anorg. allgem. Chem.*, **126**, 39 (1923).
- (4) Fischer, W., *Ibid.*, **200**, 332 (1931).
- (5) Fischer, W., and Rahlfs, O., *Ibid.*, **205**, 37 (1932).
- (6) International Critical Tables, Vol. I, pp. 136, 164, New York, McGraw-Hill Book Company, 1926.
- (7) Kablukov, Iv., *J. Russ. Phys. Chem. Soc.*, **40**, 485 (1908).
- (8) Kaveler, H. H., and Monroe, C. J., *J. Am. Chem. Soc.*, **50**, 2421 (1928).
- (9) Kendall, J., Crittenden, E. D., and Miller, H. K., *Ibid.*, **45**, 963 (1923).
- (10) Lange, N. A., *Handbook of Chemistry*, 1st ed., p. 111, Sandusky, Ohio, Handbook Publishers, 1934.
- (11) Mallet, J. W., *Trans. Roy. Soc. (London)*, **171**, 1003 (1880); *Chem. News*, **41**, 212 (1880).
- (12) Richards, T. W., and Krepelka, H., *J. Am. Chem. Soc.*, **42**, 2221 (1920).
- (13) Treadwell, W. D., and Stern, H., *Helv. Chim. Acta*, **7**, 627 (1924).
- (14) Weber, R., *Pogg. Ann.*, **101**, 469 (1857); **103**, 264 (1857).