[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Ammoniates of the Ammonium Halides[1]

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Pressure–composition isotherms at −35.5° for the binary systems NH_4X-NH_3, where X = F, Cl, Br and I, have been determined through the use of a quartz helix balance that is shown to be admirably suited to the study of binary systems involving one volatile component. Some ammoniates previously reported have been confirmed, others are reported for the first time, and these data are used to clarify certain conflicting evidence in the older literature.

Although evidence for the existence of stable 3-ammoniates of ammonium chloride, bromide and iodide appears to be entirely satisfactory, the literature relative to other ammoniates of these salts is both incomplete and contradictory. In the course of studies involving certain other series of ammoniates it therefore seemed worthwhile to establish the pressure–composition isotherms at −35.5° for these salts and for ammonium fluoride as well. These studies are described in the present communication.

Experimental

The apparatus employed in this investigation was an adaptation of the quartz helix sorption balance introduced by McBain and Bakr.[2] The recent improvements in design and construction of quartz helix balances described by Ernsberger and Drew[3] suggest the broad applicability of these techniques to problems that previously utilized equipment similar to that described by Howard, Friedrichs and Browne[4] for the study of binary systems having one volatile component.

In addition to a quartz helix balance suspended in a tube 30 mm. in diameter and 500 mm. in length, the apparatus consisted of a mercury manometer and a gas buret attached to an external system for the introduction or removal of gases. The tube containing the quartz helix was connected by ground glass joints to facilitate introduction and removal of samples. The temperature was controlled to within ±0.3° by means of a liquid ammonia bath stirred with dry air. The procedure for calibration of the quartz helix consisted of measuring elongation as a function of load at the desired temperature and under the load conditions of the particular experiment. A cathetometer reproducible to 0.1 mm. was used in all of these experiments.

Commercial anhydrous ammonia[5] was distilled into small tanks and dried over sodium amide. All ammonium halides used were reagent grade.

A typical experiment utilized 0.0994 g. of ammonium chloride in a 0.1293-g. Pyrex bucket. Under the load of 0.2287 g. at the temperature of this experiment, the increase in weight per unit length was 0.01834 g./cm. From the weight of the sample of ammonium chloride and the constant of the helix, the calculated elongation of the helix for an uptake of three moles of ammonia is 3 × (17.03 × 0.0994/53.50 × 0.01834) = 5.17 cm.; the observed elongation corresponding to the formation of the 3-ammoniate was 5.19 cm. or 3.01 moles NH_3/mole NH_4Cl (see Fig. 1).

After introduction of the sample and bucket into the tube, the system was alternately evacuated and filled with dry ammonia. Finally the system was evacuated, liquid ammonia was added to the cooling bath, and the initial equilibrium points were determined with the cathetometer. Ammonia gas was then introduced until its pressure was 570 mm. of mercury; this pressure was maintained approximately constant (by adjusting the level of the mercury in the gas buret mentioned above) until equilibrium between

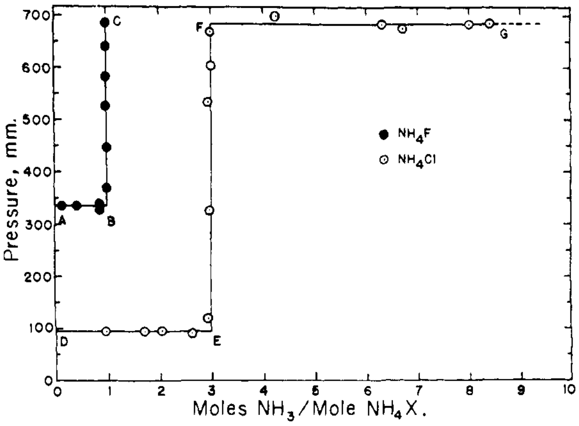

Fig. 1.—Pressure–composition isotherms for the systems NH_4F-NH_3 and NH_4Cl-NH_3 at −35.5°.

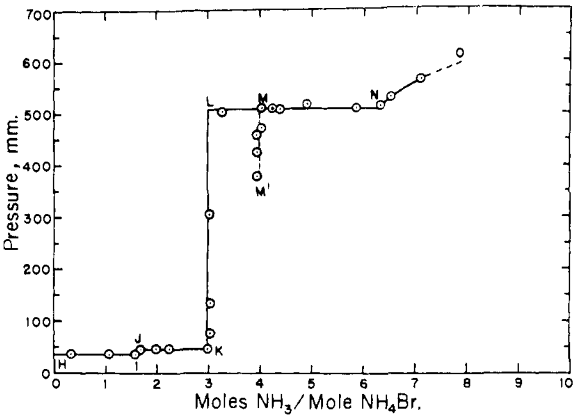

Fig. 2.—Pressure–composition isotherm for the system NH_4Br-NH_3 at −35.5°.

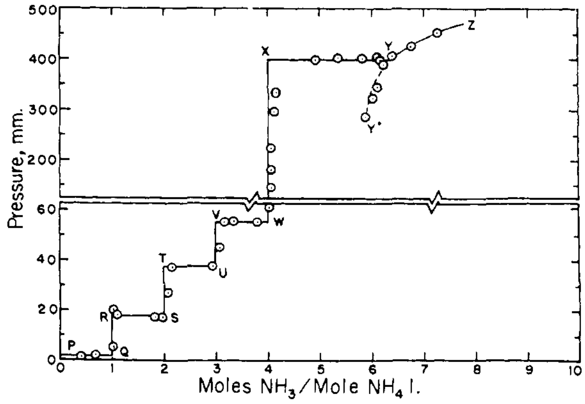

Fig. 3.—Pressure–composition isotherm for the system NH_4I-NH_3 at −35.5°.

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[1] This work was supported in part by the U. S. Navy Bureau of Ordnance, Contract N123s-67363, Task Order 2.

[2] J. W. McBain and A. M. Bakr, THIS JOURNAL, **48**, 690 (1926).

[3] F. M. Ernsberger and C. M. Drew, *Rev. Sci. Instruments*, **24**, 117 (1953); F. M. Ernsberger, *ibid.*, **24**, 998 (1953).

[4] D. H. Howard, F. Friedrichs and A. W. Browne, THIS JOURNAL, **56**, 2332 (1934).

[5] This material was generously supplied by the Polychemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

the 3-ammoniate and the vapor phase was established. The pressure was subsequently either reduced or increased by small increments and the resulting system again allowed to come to equilibrium. This procedure was repeated until the pressure–composition isotherms were determined; equilibrium positions were approached from both high and low pressures. The time necessary to achieve equilibrium conditions varied from 1 to 24 hr.

The pressure–composition isotherms at −35.5° are shown in Figs. 1, 2 and 3. In Fig. 4, the approximate rate of uptake of ammonia at constant pressure for several experiments is plotted as a function of time. The composition of the phases coexistent under the equilibrium conditions corresponding to the pressure-composition isotherms is listed in Table I.

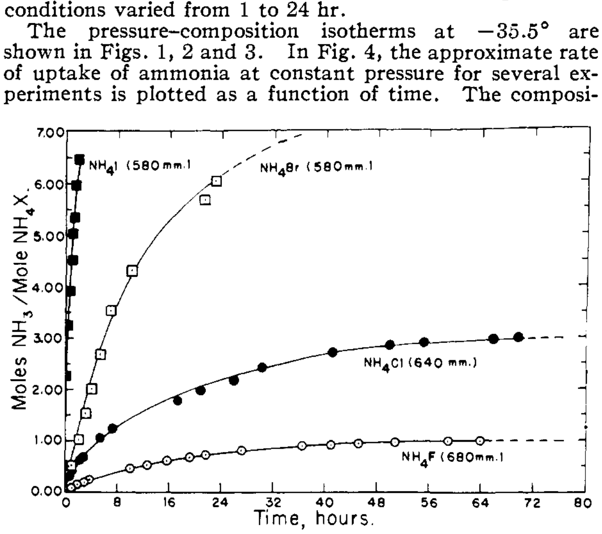

Fig. 4.—Rate of uptake of ammonia by the ammonium halides at constant temperature and pressure.

TABLE I

COMPOSITION OF PHASES AT EQUILIBRIUM

Fig. no.	Curve	Phases
1	AB	$NH_4F(s)$, $NH_4F{\cdot}NH_3(s)$, $NH_3(g)$
	BC	$NH_4F{\cdot}NH_3(s)$, $NH_3(g)$
	DE	$NH_4Cl(s)$, $NH_4Cl{\cdot}3NH_3(s)$, $NH_3(g)$
	EF	$NH_4Cl{\cdot}3NH_3(s)$, $NH_3(g)$
	FG	$NH_4Cl{\cdot}3NH_3(s)$, satd. soln., $NH_3(g)$
2	HI	$NH_4Br(s)$, $NH_4Br{\cdot}xNH_3(s)$, $NH_3(g)$
	IJ	$NH_4Br{\cdot}xNH_3(s)$, $NH_3(g)$
	JK	$NH_4Br{\cdot}xNH_3(s)$, $NH_4Br{\cdot}3NH_3(s)$, $NH_3(g)$
	KL	$NH_4Br{\cdot}3NH_3(s)$, $NH_3(g)$
	LM	$NH_4Br{\cdot}3NH_3(s)$, satd. soln., $NH_3(g)$
	MM′	$NH_4Br{\cdot}4NH_3(s)$, $NH_3(g)$, (metastable)
	MN	$NH_4Br{\cdot}4$ or $3NH_3(s)$, satd. soln., $NH_3(g)$
	NO	Dil. soln., $NH_3(g)$
3	PQ	$NH_4I(s)$, $NH_4I{\cdot}NH_3(s)$, $NH_3(g)$
	QR	$NH_4I{\cdot}NH_3(s)$, $NH_3(g)$
	RS	$NH_4I{\cdot}NH_3(s)$, $NH_4I{\cdot}2NH_3(s)$, $NH_3(g)$
	ST	$NH_4I{\cdot}2NH_3(s)$, $NH_3(g)$
	TU	$NH_4I{\cdot}2NH_3(s)$, $NH_4I{\cdot}3NH_3(s)$, $NH_3(g)$
	UV	$NH_4I{\cdot}3NH_3(s)$, $NH_3(g)$
	VW	$NH_4I{\cdot}3NH_3(s)$, $NH_4I{\cdot}4NH_3(s)$, $NH_3(g)$
	WX	$NH_4I{\cdot}4NH_3(s)$, $NH_3(g)$
	XY	$NH_4I{\cdot}4NH_3(s)$, satd. soln., $NH_3(g)$
	YY′	$NH_4I{\cdot}6NH_3$(?, solid present), $NH_3(g)$, (metastable)
	YZ	Dil. soln., $NH_3(g)$

Discussion

On the basis of freezing point curves for the binary systems NH_4X–NH_3, Kendall and Davidson[6] confirmed the 3-ammoniates where X = Cl, Br and I; reported the detection of $NH_4I{\cdot}4NH_3$; and concluded that NH_4F does not form ammoniates. They expressed doubt relative to the existence of the ammoniates $NH_4Cl{\cdot}6NH_3$ and $NH_4Br{\cdot}6$ and 1 NH_3 described by Troost[7,8] and by Roozeboom[9,10] and made no reference to the 1-, 3- and 6-ammoniates of NH_4I reported by these same workers. Since the methods as employed by Kendall and Davidson are clearly inapplicable to the detection of less stable ammoniates and since Troost gave no data relative to the composition of solid phases and a very inadequate account of his experimental procedures, the present work was done to provide a complete characterization of these systems in terms of pressure–composition diagrams. Results reported by earlier workers together with conclusions from the present studies are summarized in Table II.

TABLE II

AMMONIATES OF THE AMMONIUM HALIDES

Ammoniate	M.p., °C.	References
$NH_4I{\cdot}NH_3$	. . .[a]	8, 13, 16, 18
$2NH_3$	. . .[b]	16, 18
$3NH_3$	−8, −12	6, 8, 13, 16, 18
$4NH_3$	−5.1	6, 16, 18
$6NH_3$	−28	8, 13
$NH_4Br{\cdot}NH_3$	. . .[a]	8, 9, 10, 13
$3NH_3$	6[c]	6, 8, 9, 10, 13, 16, 18
$4NH_3$	. . .[b]	18
$6NH_3$	−20	8, 13
$NH_4Cl{\cdot}3NH_3$	7[d]	6, 7, 11–18
$6NH_3$	−18	7, 13
$NH_4F{\cdot}NH_3$	. . .[a]	18

[a] Does not exhibit a definite melting point. [b] Not reported. [c] 8.7 and 13.7 also reported. [d] 7.6, 9.8 and 10.7 also reported.

Although NH_4F is substantially insoluble in ammonia, it does form (only) a 1-ammoniate which has an approximate dissociation pressure of 335 mm. at −35.5° (Fig. 1). This solvate could not have been detected by the methods used by Kendall and Davidson[6] and involves a gas–solid reaction strictly analogous to the formation of the 3-ammoniate of $(NH_4)_2SO_4$ which was characterized by Drew, *et al.*,[19] by means of a pressure–composition isotherm at −32.5° and the temperature dependence of its dissociation pressure.

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(6) J. Kendall and J. G. Davidson, THIS JOURNAL, **42**, 1140 (1920).

(7) M. L. Troost, *Compt. rend.*, **88**, 578 (1879).

(8) M. L. Troost, *ibid.*, **92**, 715 (1881).

(9) H. W. B. Roozeboom, *Z. physik. Chem.*, **2**, 460 (1888).

(10) H. W. B. Roozeboom, *Rec. trav. chim.*, **4**, 361 (1885).

(11) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Third Edition, Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 571, 579, 580, 1091, 1092.

(12) G. Patscheke and C. Tanne, *Z. physik. Chem.*, **A174**, 135 (1935); W. C. Johnson and O. F. Krumboltz, *ibid.*, **A167**, 249 (1933); E. I. Akhumov and E. A. Eserova, *Zhur. Obshchei Khim.*, **6**, 1418 (1936).

(13) "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Vol. 7, McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 240, 241.

(14) S. Abe, K. Watanabe and R. Hara, *J. Soc. Chem. Ind., Japan, Suppl. Binding*, **38**, 642 (1935).

(15) S. Abe, K. Watanabe, S. Sigetomi and R. Hara, *ibid.*, **39**, 18 (1936).

(16) G. Spacu and P. Voichescu, *Z. anorg. allgem. Chem.*, **233**, 197 (1937).

(17) G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.*, 4938 (1952).

(18) This work.

(19) C. M. Drew, H. W. Kruse, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **71**, 1494 (1949).

The binary system NH_4Cl–NH_3 has been the subject of extensive investigations by Abe and co-workers[14,15] who have reported dissociation pressures for the 3-ammoniate for the temperature range −53 to 5°; the value of 95 mm. at −35.5° (Fig. 1) is in excellent agreement with their results. For the dissociation of $NH_4Cl{\cdot}3NH_3$, the pressure–temperature plot shown in Fig. 5 includes the original data of Troost as well as those from the present studies. The one point that lies considerably off the curve for the expected linear relationship (that for curve B for NH_4Cl in Fig. 5 and connected by a dashed line) is attributable to Troost's admitted difficulty in maintaining temperature constant in the low temperature range over long periods of time. Since this difficulty was not encountered in the present work, Troost's data were extrapolated to points found in the present studies at −35.5° ($1/T \times 10^3 = 4.21$).

More recently, Fowles and Pollard[17] have extended the investigation of the dissociation pressure of the 3-ammoniate to include the temperature range −23 to −63°; the work of Troost, Abe, *et al.*, and Spacu and Voichescu did not involve measurements below −53°. The careful work of Fowles and Pollard has shown that only the 3-ammoniate exists at −44 and −63° and that it is stable up to at least −23°. These results are in complete accord with Troost's work and are comparable to those given in Fig. 1. However, the procedures employed by these workers would verify the formation of a 6-ammoniate only if the saturated solution in equilibrium with it were stable with respect to the 3-ammoniate and its saturated solution. The pressure for this latter invariant system is reported by Abe, *et al.*

An interpolation of the data of Abe and co-workers for the vapor pressure of ammonia in equilibrium with a saturated solution of NH_4Cl and $NH_4Cl{\cdot}3NH_3(s)$ gives a value of 663 mm. at −35.5°, *i.e.*, only 20 mm. below the condensation pressure (683 mm.) of ammonia at this temperature. Thus it would be exceedingly difficult to determine the composition of the saturated solution by means of the pressure–composition isotherm at this temperature and equally difficult to detect the ammoniate $NH_4Cl{\cdot}6NH_3$. In addition, Patscheke and Tanne[12] have reported that the composition of the saturated solution in equilibrium with the 3-ammoniate is 1 mole NH_4Cl/28.2 moles NH_3 at −39.3°, 1/10.7 at −20.5°, 1/7.48 at −11.8°, and 1/4.58 at 0.9°. Thus, the work of Abe, *et al.*, on the vapor pressure of the invariant system at constant temperature may be correlated with the data of Patscheke and Tanne. If a 6-ammoniate exists at −35.5°, Troost's results suggest that its dissociation pressure would be about 600 mm. (see Fig. 5). Consequently, it would be implicit that the 6-ammoniate in equilibrium with its saturated solution would be either unstable or metastable at −35.5° because the dissociation pressure for the invariant system involving the dissociation of the 6-ammoniate is less than that for the invariant system consisting of the 3-ammoniate and its saturated solution. If Troost's value of −18° for the melting point of the 6-ammoniate is correct, this ammoniate should exhibit its maximum stability at a temperature just below its melting point. Accordingly, the accumulated evidence does not rule out the existence of $NH_4Cl{\cdot}6NH_3$ but does place a limit on the range of conditions under which it may exhibit stability.

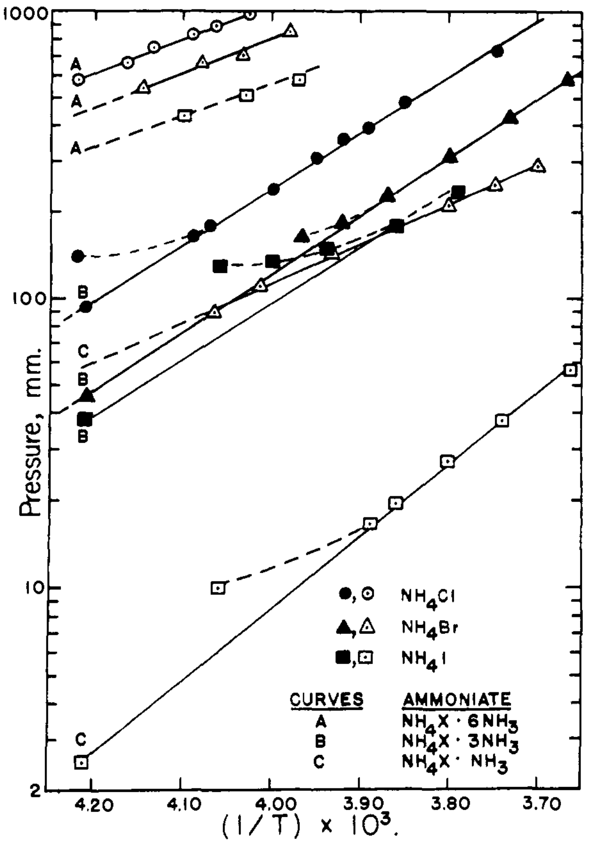

Fig. 5.—Ammonia pressures for invariant systems resulting from dissociation of ammoniates of the ammonium halides. (With the exception of the points corresponding to −35.5° ($1/T \times 10^3 = 4.21$), the data plotted are those of Troost[7,8] and Roozeboom[9,10].)

The pressure–composition isotherms for NH_4Br and NH_4I (Figs. 2 and 3) show that the composition of the saturated solution in equilibrium with the 4-ammoniates is 1 mole NH_4Br or NH_4I/6.30 moles NH_3. The phase, $NH_4Br{\cdot}xNH_3$, lends some support to the previously reported 1-ammoniate; the difference in vapor pressure of ammonia (Fig. 2, curves HI and JK) is significant and quite reproducible, but too small to justify attempts to determine the composition of the phase. One may either assume a 1-ammoniate and extrapolate Troost's data for $NH_4Br{\cdot}NH_3$ (Fig. 5, curve C) to the present data for $NH_4Br{\cdot}xNH_3$ (dissociation pressure of 37 mm. at −35.5°) or assume that the composition of the phase at the lower temperature is $NH_4Br{\cdot}1.5NH_3$ (Fig. 2). In the former case, a considerable number of points would fall far off the curve; in the latter case the 1-ammoniate would appear to be unstable relative to the 3-ammoniate at lower temperatures since the dissociation pressure for $NH_4Br{\cdot}NH_3$ would be greater than that of $NH_4Br{\cdot}3NH_3$ (46 mm. at −35.5°). The curve MM′ in Fig. 2 is indicative of a metastable 4-ammoniate obtained by the slow removal of ammonia from a dilute solution over a period of several days; this condition is strictly analogous to metastable systems described by Browne, *et al.*[4]

Figure 3 shows that the system NH_4I-NH_3 involves the 1-, 2-, 3- and 4-ammoniates; the dissociation pressures are 2.5, 18, 38 and 56 mm., respectively. Spacu and Voichescu[16] report dissociation pressures for the 2-, 3- and 4-ammoniates at −36° as 19, 37 and 49 mm., respectively. Curve YY′ is suggestive of the 6-ammoniate.[4,8] The data of Troost are correlated with these data in Fig. 5; the solid curves for the 3-ammoniates were drawn parallel because the heats of formation of these ammoniates would be expected to be of the same order of magnitude. Similarly, the curves for the 6-ammoniates were also drawn parallel.

Data relating to rates of uptake of ammonia at constant pressure are plotted in Fig. 4. Under the conditions of these experiments, NH_4Br and NH_4I are characterized by the rapid formation of a liquid layer and the establishment of a heterogeneous system for which one may obtain rate data that do no more than confirm the phase changes. On the other hand, NH_4F and NH_4Cl are ammoniated to $NH_4F \cdot NH_3$ and $NH_4Cl \cdot 3NH_3$ without the appearance of a liquid phase; thus these reactions should be expected to be pseudounimolecular. The plot (Fig. 6) of log concentration (% unreacted) *vs.* time in hours for NH_4F at 680 mm. and NH_4Cl at 570 mm.[20] leads to first-order rate constants of 0.0627 hr.$^{-1}$ for NH_4F and 0.0424 hr.$^{-1}$ for NH_4Cl. Although both of these salts undergo a four- to eightfold increase in volume upon ammoniation, the effect of particle size on the rate of ammoniation was not considered; the rate data obtained are based upon the ammoniation of halides not previously expanded by reaction with gaseous ammonia.

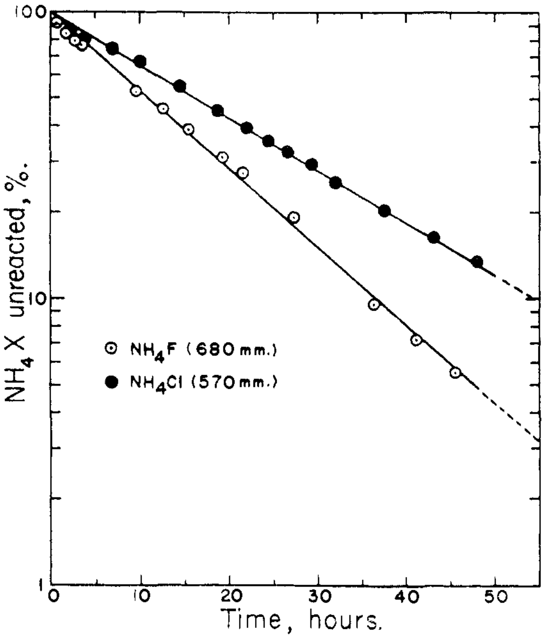

Fig. 6.—First-order rate plots for the ammoniation of ammonium fluoride and ammonium chloride.

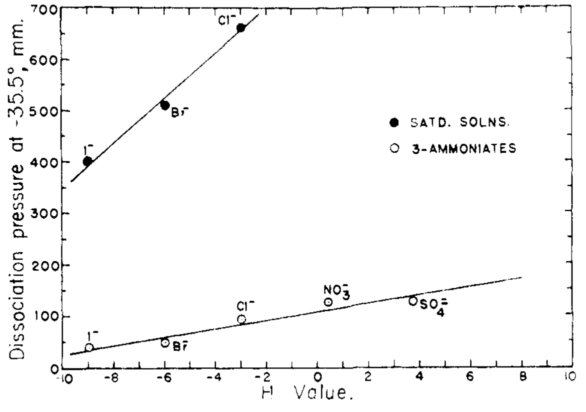

Fig. 7.— Correlation of dissociation pressures with a basicity scale.

In Fig. 7 a correlation of the dissociation pressures for two series of invariant systems is plotted as a function of the H value described by Edwards.[21] The H values used are estimates based upon the normal pK_a values for the conjugate acids in aqueous solution with the addition of a constant, thus $H = pK_a + 1.74$. The correlation is surprisingly good, and is much better than is obtained by comparison with either an electronegativity series or a nucleophilic scale.

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[20] The data for NH_4Cl are from a series different from that represented by Fig. 4.

[21] J. O. Edwards, This Journal, **76**, 1540 (1954).