Research Project 44,[16] Table IV lists the calculated values of the heat capacity, heat content function, free energy function and entropy in the ideal gas state from 298.16 to 1500° K. Internal consistency of the functions occasionally demands more significant figures in these tabulated values than are justified by the accuracy of the original data.

TABLE IV

THE VALUES OF THE HEAT CAPACITY, HEAT CONTENT FUNCTION, FREE ENERGY FUNCTION AND ENTROPY OF NAPHTHALENE IN THE IDEAL GAS STATE

T, °K.	C^{p}_0, cal./deg. mole	$(H^0 - H^0_0)$, kcal./mole	$-(F^0 - H^0_0)/T$, cal./deg. mole	S^0, cal./deg. mole
298.16	31.03	4.910	63.83	80.30
300	31.25	4.968	63.93	80.49
400	42.81	8.683	69.39	91.10
500	52.46	13.46	74.80	101.73
600	60.16	19.11	80.15	112.00
700	66.31	25.44	85.40	121.75
800	71.32	32.33	90.53	130.94
900	75.43	39.68	95.49	139.57
1000	78.87	47.40	100.32	147.72
1100	81.76	55.43	104.98	155.38
1200	84.22	63.73	109.46	162.58
1300	86.31	72.26	113.84	169.42
1400	88.10	80.99	118.04	175.89
1500	89.62	89.88	122.10	182.02

Table V shows a comparison of the calculated and experimental values of the heat capacity and entropy. Agreement is within experimental error. For this comparison the accuracy of the data does not warrant consideration of anharmonicity in the statistical calculations.

TABLE V

COMPARISON OF THE EXPERIMENTAL AND CALCULATED VALUES OF THE HEAT CAPACITY AND ENTROPY

T, °K.	C^0_{p}, cal./deg. mole Expt.	Calcd.	S^0, cal./deg. mole Expt.	Calcd.
451.0	48.18 ± 0.48	47.99	96.85 ± 0.44	96.54
522.7	54.17 ± .54	54.31	104.41 ± .44	104.04

Acknowledgment.—We wish to express our appreciation to the American Petroleum Institute, Research Project 44, for financial support of this investigation.

BERKELEY, CALIF. RECEIVED AUGUST 2, 1950

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[16] Selected Values of Properties of Hydrocarbons, Circular of the National Bureau of Standards, C461, U. S. Government Printing Office, Washington, D. C., 1947.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Aluminum Bromide Monoetherate on Addition of Various Bases at 25°[1]

BY ROSS E. VAN DYKE AND THOMAS S. HARRISON[2]

Pyridine and benzonitrile react with aluminum bromide monoetherate $AlBr_3 \cdot (CH_3)_2O$ with evolution of ether. Pyridine quantitatively evolves ether forming the complex $C_5H_5N{:}AlBr_3$ with subsequent formation of higher complexes. The reaction with benzonitrile involves two competitive reactions with completeness of ether evolution remaining uncertain. Acetone, on the other hand, does not replace ether but rather coördinates with the monoetherate. Conductometric studies of these reactions present a comparison of the strengths of the various complexes as electrolytes. Conductance data for the addition of pyridine to nitrobenzene solutions of aluminum bromide are presented.

I. Introduction

The preceding paper[3] presents results to show that the stability of various aluminum bromide addition compounds with nitrogen and oxygen bases in solution depends upon the extent of interaction of the salt with the solvent molecule. In this connection it should be of considerable interest to further evaluate the relative stability of various addition compounds in the same solvent. Aluminum bromide forms a very stable monoetherate with dimethyl ether. This compound is quite stable in nitrobenzene and is a much weaker electrolyte in this solvent than is aluminum bromide. Thus, the monoetherate was chosen for this series of investigations.

The conductance of aluminum bromide monoetherate $AlBr_3 \cdot (CH_3)_2O$ in nitrobenzene has been studied on addition of pyridine, benzonitrile and acetone at 25°. These data are compared with results obtained when these bases are added to solutions of aluminum bromide itself in this solvent. Included in this paper are the results obtained on addition of pyridine to solutions of aluminum bromide.

II. Experimental

(1) **Materials.**—Nitrobenzene[4] was washed successively with hydrochloric acid, alkali, pretreated with aluminum chloride and again washed with alkali and water. After preliminary drying with calcium chloride, the product was distilled several times under reduced pressure at 30° and then subjected to fractional crystallization as described in an earlier paper.[5] The product had a specific conductance of 1–2 × 10^{-10} mho. Benzonitrile was purified according to the procedure described in the preceding paper.[3] Anhydrous aluminum bromide was prepared, purified and collected in bulblets of various sizes according to procedures described previously.[5] Dimethyl ether was a Matheson product which was carefully dried over activated aluminum oxide in a stainless steel cylinder. The gas was further dried over barium oxide on withdrawal. Acetone and pyridine were purified as described in the preceding paper.[3]

(2) **Apparatus and Procedure.**—Resistance measurements were made with a Leeds and Northrup bridge of the Jones type with conductance cells thermostated in oil at 25 ±

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[1] This paper is based on a portion of a thesis presented by Thomas S. Harrison in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University.

[2] Grasselli Division, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

[3] Van Dyke and Harrison, THIS JOURNAL, 73, 402 (1951).

[4] Kindly donated by Calco Chemicals Division, American Cyanamid Company.

[5] Van Dyke and Kraus, THIS JOURNAL, 71, 2694 (1949).

0.01°. Conductance cells of the erlenmeyer type with varying constants were handled according to previously described procedures[6] with due precautions as to atmospheric moisture contamination. Introduction of liquid and gaseous complexing agents was accomplished by techniques described in the preceding paper.[3] Solutions of aluminum bromide monoetherate were prepared from solutions of aluminum bromide to which an equimolar quantity of dimethyl ether was added.

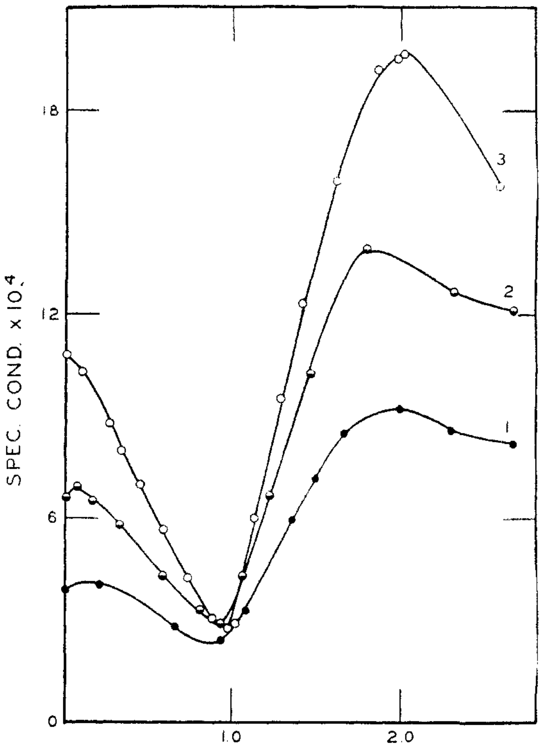

Fig. 1.—The conductance of aluminum bromide in nitrobenzene on addition of pyridine at 25°: (1) 0.0893 molal, (2) 0.1528 molal, (3) 0.2593 molal.

Table I

The Conductance of Aluminum Bromide and Aluminum Monoetherate in Nitrobenzene on Addition of Pyridine at 25°

A. Aluminum bromide		B. Aluminum bromide monoetherate	
Mmoles $AlBr_3$, 10.034; molality, 0.2593		Mmoles $AlBr_3.(CH_3)_2O$, 16.220; molality, 0.2556	
$\kappa \times 10^4$	Molar ratio $C_5H_5N/AlBr_3$	$\kappa \times 10^4$	Molar ratio $C_5H_5N/AlBr_3 \cdot (CH_3)_2O$
10.78	0.000	1.479	0.000
10.31	.0968	2.150	.1879
8.808	.2574	2.412	.3986
8.032	.3320	2.620	.5655
6.952	.4460	2.798	.7443
5.666	.5832	2.992	.9180
4.248	.7320	3.595	.9950
3.064	.8744	6.815	1.141
2.769	.9637	10.42	1.312
2.904	1.004	14.22	1.522
4.285	1.055	17.29	1.723
6.016	1.123	19.20	1.899
9.533	1.279	19.28	1.935
12.29	1.407	19.23	1.988
15.90	1.608	18.67	2.090
19.20	1.858	17.88	2.243
19.49	1.983	16.81	2.493
17.64	2.148	16.05	2.753
15.75	2.591		

III. Results

(1) **Pyridine.**—The conductance of aluminum bromide in nitrobenzene on addition of pyridine has been determined for three concentrations of salt *m* = 0.2593, 0.1528, 0.0893. These data are presented graphically in Fig. 1; one series of numerical data are presented in Table I, A.

The conductance of aluminum bromide monoetherate in nitrobenzene on addition of pyridine has been determined for three different solutions of concentration *m* = 0.5175, 0.2556, 0.1484. These data are shown graphically in Fig. 2. Numerical values are given for only one solution in Table I, B.

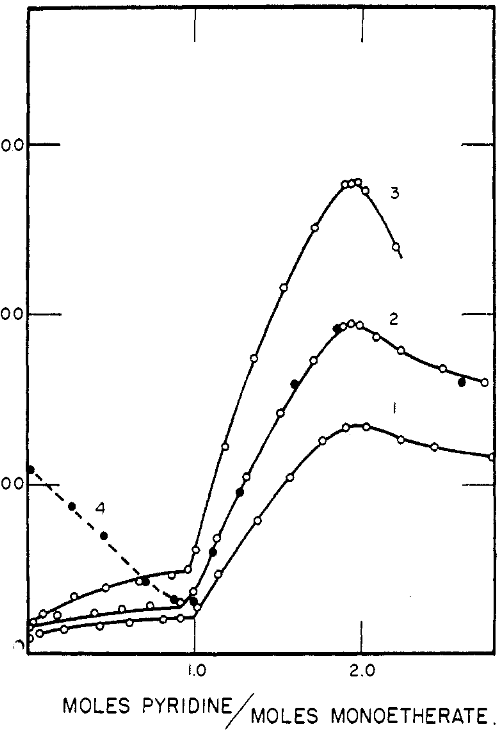

Fig. 2.—Conductance of aluminum bromide monoetherate on addition of pyridine at 25°: (1) 0.1484 molal, (2) 0.2556 molal, (3) 0.5175 molal, (4) 0.2593 molal solution of $AlBr_3$ on addition of pyridine.

Table II

The Conductance of Aluminum Bromide Monoetherate in Nitrobenzene on Addition of Benzonitrile at 25°

Mmoles $AlBr_3 \cdot (CH_3)_2O$, 11.326;	molality, 0.2010
$\kappa \times 10^4$	Molar ratio $C_6H_5CN/AlBr_3 \cdot (CH_3)_2O$
1.442	0.000
7.135	.2735
11.82	.6415
14.77	1.033
15.59	1.195
16.73	1.517
17.49	1.847
17.92	2.158
18.25	2.500
18.31	2.853
18.33	3.266

(2) **Benzonitrile.**—The conductance of aluminum bromide monoetherate in nitrobenzene on

addition of benzonitrile was studied at three concentrations of salt m = 0.5545, 0.2010, 0.1025. These results are shown graphically in Fig. 3; data for one of these solutions is presented in Table II.

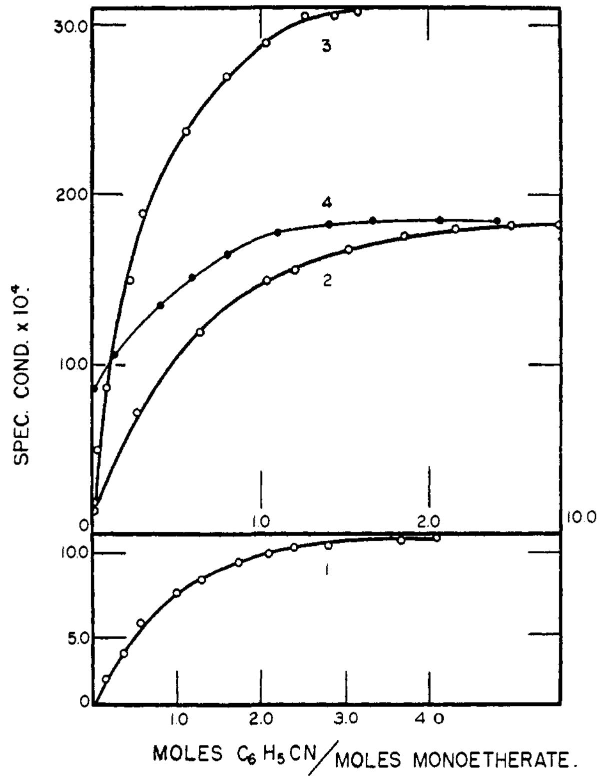

Fig. 3.—Conductance of aluminum bromide monoetherate on addition of benzonitrile at 25°: (1) 0.1025 molal, (2) 0.2010 molal, (3) 0.5545 molal, (4) 0.2115 molal solution of $AlBr_3$ on addition of benzonitrile.

(3) **Acetone.**—The conductance of aluminum bromide monoetherate in nitrobenzene on addition of acetone has been determined for three different solutions of concentration m = 0.3600, 0.1846, 0.0893. These data are presented graphically in Fig. 4 along with numerical values for one solution in Table III.

TABLE III

THE CONDUCTANCE OF ALUMINUM BROMIDE MONOETHERATE IN NITROBENZENE ON ADDITION OF ACETONE AT 25°

Mmoles $AlBr_3\cdot(CH_3)_2O$, 10.044; molality, 0.1846

$\kappa \times 10^4$	Molar ratio $(CH_3)_2CO/AlBr_3\cdot(CH_3)_2O$
0.851	0.000
2.405	.0955
5.812	.2720
8.555	.4265
12.68	.6970
15.36	.9060
16.28	.9980
17.15	1.083
19.13	1.326
20.71	1.637
21.41	2.016
21.83	2.543
22.22	3.307

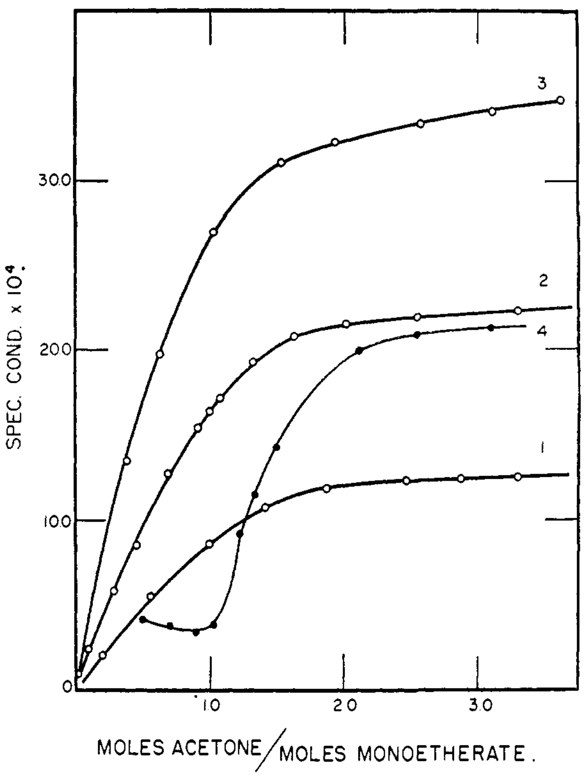

Fig. 4.—Conductance of aluminum bromide monoetherate on addition of acetone at 25°: (1) 0.0893 molal, (2) 0.1846 molal, (3) 0.3600 molal, (4) solution of equimolar quantities of $AlBr_3$ and $AlBr_3\cdot(CH_3)_2O$ on addition of acetone (total $AlBr_3$ content 0.1832 molal).

IV. Discussion

(1) **Pyridine.**—As shown in Fig. 1, the results for addition of pyridine to nitrobenzene solutions of aluminum bromide are more readily interpreted than those obtained with benzonitrile as solvent. In the more dilute solutions the conductance increases, passes through a maximum at a molar ratio of approximately 0.10 followed by a nearly linear decrease to a ratio value of 1.0. In the more concentrated solution (curve 3) the conductance decreases on first addition of pyridine with no evidence of a maximum appearing. The curves pass through a minimum at a molar ratio close to unity, followed by rapid linear increases in conductance with further addition of pyridine. As the ratio value approaches 2.0, the conductance levels off and finally decreases with precipitation of a pyridine complex. Analysis of the solid complex corresponded to the compound $AlBr_3\cdot 3C_5H_5N$ as might be expected. The maxima in dilute solutions are probably due to formation of two species of complex (*e. g.*, $C_5H_5N:AlBr_3$ and $AlBr_3\cdot 2C_5H_5N$) with the formation of the addition compound $C_5H_5N:AlBr_3$ as the predominant reaction.

(2) **Addition of Pyridine to $(CH_3)_2O\cdot AlBr_3$.**—The addition of pyridine to nitrobenzene solutions of aluminum bromide monoetherate causes a vigorous evolution of ether. As shown in Fig. 2 this reaction is responsible for the nearly linear increase in conductance as the molar ratio of added pyridine to monoetherate increases to a

value of 1.0. For molar ratios beyond 1.0, the conductance curve is almost identical with that obtained upon addition of pyridine to the aluminum bromide solution. The agreement of the data shown in curves 2 and 4 (Fig. 2) for almost equal concentrations appears remarkably close. It is clear that the initial reaction is one of quantitative replacement of the ether by pyridine to form the complex $C_5H_5N:AlBr_3$. The completeness of this reaction is remarkable in view of the fact that addition of trimethylamine to nitrobenzene solutions of the monoetherate does not evolve ether. However, a quantitative study of this system appears impossible because the amine complexed monoetherate appears to be involved in a slow decomposition reaction with the solvent nitrobenzene.

(3) **Benzonitrile.**—On addition of benzonitrile to solutions of the monoetherate (Fig. 3), the conductance increases rapidly along a smooth curve approaching a limiting value at a molar ratio in excess of 2.0. The curves show no evidence of a break or marked change in slope in the region of unit molar ratio as was observed on pyridine additions. However, dimethyl ether was evolved on addition of nitrile, the reaction being less vigorous than that in the case of pyridine addition. Comparing curves 2 and 4 of Fig. 3 it is seen that the maximum values of conductance are nearly equal for these solutions of almost equal aluminum bromide concentration. This indicates that the solutions probably contain the same molecular species at this point. These facts suggest that two reactions occur simultaneously rather than consecutively in which one reaction is completed before the second begins as was the case with pyridine addition to the monoetherate. The displacement of ether by benzonitrile forming the complex $C_6H_5CN:AlBr_3$ is probably competing with a reaction involving addition of nitrile to the monoetherate to form the complex $(CH_3)_2O:AlBr_3 \cdot C_6H_5CN$. These complexes then further react with benzonitrile to form the complex $AlBr_3 \cdot 2C_6H_5CN$.

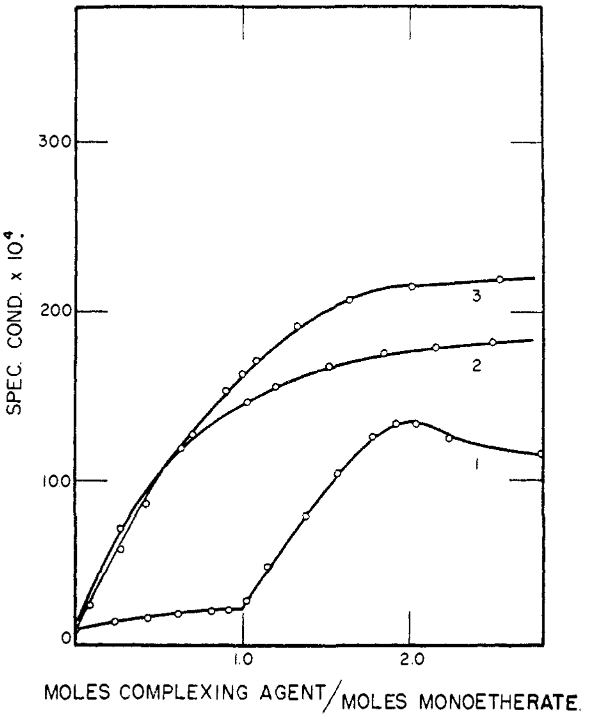

Fig. 5.—Comparison plot for various complexing agents at 25°: (1), 0.1484 molal solution + pyridine; (2), 0.2010 molal solution + benzonitrile; (3), 0.1846 molal solution + acetone.

(4) **Acetone.**—When acetone is added to a monoetherate solution, the conductance increases rapidly along a smooth curve for molar ratios as great as 1.5. Beyond this region the conductance begins to level off and approaches a nearly constant maximum value. No evidence of ether evolution was observed. In view of this fact, acetone was added to a solution containing equimolar quantities of aluminum bromide and aluminum bromide monoetherate. The results of this experiment are shown in curve 4, Fig. 4. On first additions of acetone to this solution the conductance curve closely approximates that obtained when acetone was added to aluminum bromide solutions.[6] At the minimum in the conductance curve, the solution presumably contains equimolar quantities of monoetherate and monoacetonate. Upon further addition of acetone the curve is much the same as the other curves of Fig. 4. It seems clear from this experiment that acetone does not displace dimethyl ether, but rather complexes with the monoetherate. While the concentrations of aluminum bromide in solutions represented by curves 2 and 4 are nearly equal, the maximum conductance in curve 4 is somewhat below that of curve 2. This appears reasonable in view of the fact that the monoetherate is a much weaker electrolyte than the monoacetonate for these concentrations.

In Fig. 5 a comparison plot is shown for solutions of approximately equal monoetherate concentration on addition of pyridine, benzonitrile and acetone. Of particular interest is the comparison of curves 2 and 3 for benzonitrile and acetone. For molar ratios up to approximately 0.8 the two curves are nearly colinear. Beyond this point the curve for acetone addition continues with nearly the same slope, whereas curve 2 begins to level off much more rapidly. The difference here appears to be due to the fact that the acetone always complexes to form a stronger electrolyte, while some of the benzonitrile is utilized in ether displacement.

BALTIMORE, MARYLAND RECEIVED AUGUST 24, 1950

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[6] Van Dyke, THIS JOURNAL, **73**, 398 (1951).