Agreement with values obtained by a gravimetric method by Sarver and Brinton[15] can be seen to be only fair. The estimated specific conductances have also been compared with the values of Rimback and Schubert[16] and those of Sarver and Brinton.

Standard free energy changes for the reactions of interest have been given in Table VII for the three elements. Structures of rare-earth oxalates have not been determined; however, it has been reported that both lanthanum and cerium form a 9-hydrate whereas the heavier rare earths precipitate as a 10-hydrate. The decrease in hydration of cerium and lanthanum may be the result of a higher coördination of oxalates about these ions. The absence of evidence of trivalent oxalate complex in the case of the heavier neodymium and ytterbium ions with smaller ionic radii may well be caused by steric factors.

TABLE VII

STANDARD FREE ENERGY CHANGES OF THE REACTION INVOLVING CERIUM, NEODYMIUM AND YTTERBIUM AT 25°

	Ce, kcal.	Nd, kcal.	Yb, kcal.
$\Delta F°_{\mathrm{I}}$	$+1.12$	<-2.67	<-2.67
$\Delta F°_{\mathrm{II}}$	$+4.40$	$+5.87$	$+6.26$
$\Delta F°_{\mathrm{III}}$	$+8.90$	$+9.83$	$+9.96$
$\Delta F°_{\mathrm{sp_1}}$	$+39.87$	$+42.43$	$+39.35$
$\Delta F°_{\mathrm{sp_2}}$	$+16.67$	$+16.91$	$+13.26$

The stability of the monoxalate and dioxalate complexes seemed surprisingly independent of ionic radius as indicated by the similarity in values of $\Delta F°_{\mathrm{II}}$ and $\Delta F°_{\mathrm{III}}$. This was particularly apparent with the pair, neodymium and ytterbium. Although $\Delta F°_{\mathrm{II}}$ and $\Delta F°_{\mathrm{III}}$ were slightly larger for neodymium than for ytterbium as had been expected, the difference must be considered negligible in view of the fairly large difference of ionic radius which must be nearly 0.2 Å. It may be noted that if the two elements have nearly equal values for K_{II} and for K_{III}, the solubility curves differ only by a vertical displacement. This feature of the neodymium–ytterbium systems is apparent in Fig. 2. The fairly large difference in the solubilities of the oxalates of these two elements must then have resulted largely from differences in the crystal energies.

Another feature of these systems was the stability of the dioxalate complexes relative to the monoxalate. Thus the values of $\Delta F°_{\mathrm{II}}$ seemed particularly large when compared with the corresponding values of $\Delta F°_{\mathrm{III}}$ which would contain contributions from the separation of a greater charge and the low entropy of a trivalent RE ion. It would appear therefore that the presence of one oxalate expedites the addition of a second ion.

AMES, IOWA RECEIVED JULY 31, 1950

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[15] L. A. Sarver and H. M. P. Brinton, THIS JOURNAL, **49**, 943 (1927).

[16] E. Rimback and A. Schubert, *Z. physik. Chem.*, **67**, 198 (1909).

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

The Thermodynamic Properties of Naphthalene

BY GORDON M. BARROW[1] AND A. L. McCLELLAN[2]

The heat of vaporization of naphthalene has been measured and found to be 11,086 ± 30 cal./mole at 209 mm. pressure and 440.9°K. From vapor heat capacity determinations at 451.0 and 522.7°K. the heat capacity in the ideal gas state at these temperatures has been obtained. Values of the entropy and heat capacity of solid and liquid naphthalene were taken from the literature and used with the heat of vaporization determined here to calculate 95.9 ± 0.4 cal./deg. mole for the entropy of naphthalene in the ideal gas state at 440.9°K. Thermodynamic functions have been calculated from spectroscopic data for the range 298.16 to 1500°K. Comparison shows agreement between calculated and experimentally determined properties.

Naphthalene, one of the simplest polycyclic compounds, is the logical starting point for an extension of the calculated thermodynamic properties of hydrocarbons as compiled by the American Petroleum Institute, Research Project 44. A reliable vibrational assignment obtained in this Laboratory provides a basis for the necessary statistical calculations, and experimental vapor heat capacity and entropy determinations verify the calculated values.

Experimental

Materials and Apparatus.—The material used in the heat of vaporization and heat capacity determinations was Baker and Adamson resublimed naphthalene, repeatedly crystallized from ether and suction dried. The measurements were made in a flow calorimeter similar in design to those described by Pitzer[3] and by Waddington, Todd and Huffman.[4] A more complete description of this apparatus will be given in a later paper. Although the calorimeter was primarily intended for determining the vapor heat capacities and heats of vaporization of compounds liquid at room temperature and boiling below 180°, only slight modifications were necessary for the measurements on naphthalene.

A suitable boiling point of naphthalene, was obtained by controlling the pressure of the system at 209 mm. during all the measurements. At this pressure the boiling point was 167.7°. Solidification of the naphthalene was prevented by passing steam through the reflux condenser and enclosing the exposed tubing in hot air jackets.

With these additions the heat capacities and heats of vaporization were determined in the usual way as discussed, for example, by Pitzer.[3]

Heat of Vaporization.—Four separate determinations of the heat of vaporization at 209 mm. and 440.9°K. were made at various flow rates. The results, after the usual corrections[2] for heat lost in the vaporizer heater leads and the change in liquid volume, are

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[1] Physical Chemistry Laboratory, Oxford, England.

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[3] K. S. Pitzer, THIS JOURNAL, **63**, 2413 (1941); K. S. Pitzer and W. D. Gwinn, *ibid.*, **63**, 3313 (1941); R. Spitzer and K. S. Pitzer, *ibid.*, **68**, 2537 (1946).

[4] G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947).

11,092
11,057
11,100
11,097
Average 11,086 ± 30 cal./mole

Previous estimates in the literature[5,6] based on vapor pressure data and the Clausius–Clapeyron equation give a value of 11,280 cal./mole for the heat of vaporization. This value, when corrected for the gas imperfection, as determined by the Berthelot equation, and the liquid volume, gives the result 11,110 cal./mole in satisfactory agreement with that obtained here. The critical data, $T_c = 480°$ and $P_c = 41$ atm., used in the Berthelot equation were taken from the work of Schroer.[7]

Vapor Heat Capacities.—The vapor heat capacities at 209 mm. were measured at two temperatures. Heat capacities in the ideal gas state were obtained by the addition of gas imperfection corrections, determined from the Berthelot equation of state, to the measured values. These data are shown in Table I.

TABLE I

EXPERIMENTAL VAPOR HEAT CAPACITIES AT 209 MM., GAS IMPERFECTION CORRECTIONS AND HEAT CAPACITY IN THE IDEAL GAS STATE (CAL./DEG. MOLE)

T, °K.	C_p(209 mm.)	C_p (209 mm.) − C_p^0	C_p^0
451.0	48.34	0.16	48.18
522.7	54.27	.10	54.17

At atmospheric pressure gas imperfection corrections calculated from the Berthelot equation of state are inaccurate.[8] However, little error can be introduced here because of the reduced pressure at which the heat capacities were measured.

Entropy.—The entropy of solid naphthalene at 298.16°K. has been determined by Huffman, Parks and Daniels[9] from heat capacity measurements down to 90°K. and by Southard and Brickwedde[10] from measurements down to 15°K. The results are in good agreement, the latter authors giving the value 39.89 cal./deg. mole for the entropy of solid naphthalene at 298.16°K.

The entropy between 298.16 and 440.9°K., the temperature at which the heat of vaporization was determined, was obtained from the graphical integration of the heat capacity measurements of Spaght, Thomas and Parks[11] together with the entropy of fusion, 12.92 cal./deg. mole. The value taken for the heat of fusion was 4560 cal./mole[12] at the melting point, 79.9°.

Again using the gas imperfection correction computed from the Berthelot equation, we obtain the entropy of naphthalene in the ideal gas state. This calculation is summarized in Table II.

TABLE II

CONTRIBUTIONS TO THE ENTROPY (IN CAL./DEG. MOLE) OF NAPHTHALENE IN THE IDEAL GAS STATE AT 440.9°K.

S solid at 298.16°K.		39.89 ± 0.12
ΔS solid at 298.16°K. − solid at 353.1°K.	7.65	
ΔS solid at 353.1°K. − liquid at 353.1°K.	12.92	
ΔS liquid at 353.1°K. − liquid at 440.9°K.	12.75	
ΔS liquid at 440.9°K. − vapor at 440.9°K., 209 mm.	25.15	
S vapor at 440.9°K. and 209 mm. pressure		98.4
ΔS real gas − perfect gas 440.9°K., 209 mm.	0.06	
ΔS perfect gas, 209 mm. − 760 mm.	−2.57	
S^0 P = 1 atm., T = 440.9°K.		95.9 ± 0.4

Calculated Thermodynamic Functions

The infrared[13] and Raman spectra[14] of naphthalene have been studied by several investigators. The only complete vibrational assignment is that of Pimental and McClellan which is shown in Table III.

TABLE III

VIBRATIONAL ASSIGNMENT OF NAPHTHALENE

Infrared		Raman	
Class	Frequency, cm.⁻¹	Class	Frequency, cm.⁻¹
A_u	581	A_g	512
	726		764
	841		778
	1146		946
			1025
B_{1u}	80		1380
	747		1460
	821		3001
	949		3058
B_{2u}	478	B_{1g}	390
	787		726
	1129		1144
	1269		1240
	1390		1440
	1590		1575
	2942		2980
	3034		3025
B_{3u}	620	B_{2g}	191
	779		1168
	975		1254
	1012		
	1214	B_{3g}	406
	1508		742
	2984		972
	3070		1624

The moments of inertia were calculated using the skeletal structure reported by Abrahams, Robertson and White[15] together with the value 1.09 Å. for the C–H bond length. All angles were assumed to be 120°. The computed moments of inertia are: 2.67×10^{-38}, 6.67×10^{-38}, and 9.35×10^{-38} g. cm.^{2}.

The translational, rotational, and vibrational contributions to the thermodynamic functions were calculated from this vibrational assignment and these moments of inertia using the formulas and physical constants published by the A.P.I.

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(5) O. A. Nelson and C. E. Senseman, *Ind. Eng. Chem.*, **14**, 58 (1922); **15**, 621 (1923).

(6) J. S. N. Cramer, *Rec. trav. chim.*, **62**, 606 (1943).

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(10) J. C. Southard and F. G. Brickwedde, *ibid.*, **55**, 4378 (1933).

(11) M. E. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

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(13) F. K. Bell, THIS JOURNAL, **47**, 2811 (1925); P. Lambert and J. Lecomte, *Compt. rend.*, **194**, 960 (1932); G. C. Pimentel and A. McClellan, in the process of publication.

(14) R. Norris, *Proc. Indian Acad. Sci.*, **16A**, 250 (1942); T. M. K. Nedungadi, *ibid.*, **15A**, 376 (1942); H. Luther, *Z. Elektrochem.*, **52**, 210 (1948).

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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_p^0, 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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[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 $1\text{–}2 \times 10^{-10}$ 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).