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RECEIVED for review February 26, 1969. Accepted June 13, 1969. Work conducted under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, Project **9713**, Program Element **681308**, and the Bureau of Mines, U.S. Department of the Interior. Contribution No. **164** from the thermodynamics laboratory of the Bartlesville Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla. 74003

Enthalpies of Formation of Ethylenediamine, 1,2,-Propanediamine, 1,2,-Butanediamine, 2-Methyl-1,2-propanediamine, and Isobutylamine

C—N and N—F Thermochemical Bond Energies

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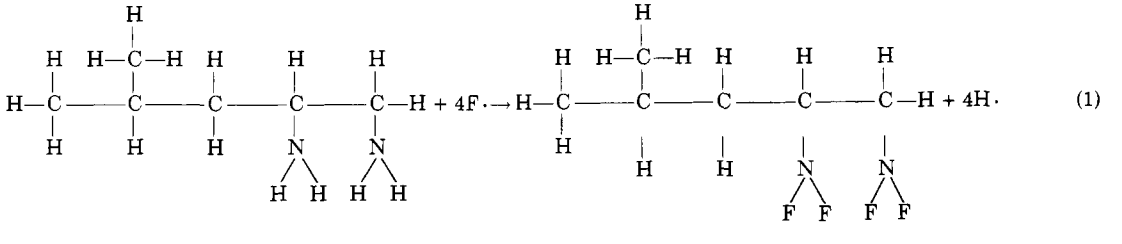
The enthalpies of combustion of ethylenediamine, 1,2-propanediamine, 1,2-butanediamine, 2-methyl-1,2-propanediamine, and isobutylamine, as determined by oxygen-bomb combustion calorimetry, were used to derive the following values, in kcal. per mole, for the enthalpies of formation of the liquid, $\Delta Hf^{\circ}_{298.15}$, from graphite and gaseous hydrogen and nitrogen: ethylenediamine, −15.06 ± 0.13; 1,2-propanediamine, −23.38 ± 0.10; 1,2-butanediamine, −28.74 ± 0.19; 2-methyl-1,2-propanediamine, −32.00 ± 0.16; and isobutylamine, −31.68 ± 0.12. These values were combined with enthalpies of vaporization derived from vapor pressure measurements to obtain values of the enthalpies of formation in the gaseous state. For these molecules, the C—N thermochemical bond energy was derived and compared to that in the simple alkyl amines. The N—H thermochemical bond energy in a 1,2-diamine was compared to the N—F thermochemical bond energy in a 1,2-bis(difluoroamino)alkane.

IN 1962 the difluoroamino compound, 1,2-bis(difluoroamino)-4-methylpentane, was studied in this laboratory (7), and a value of the N—F thermochemical bond energy was derived. This derivation required selections of values of C—H, N—H, and C—N thermochemical bond energies from other molecules. Pure samples of 1,2-diamines were not available then, but if thermochemical studies could have been made on such compounds, then obviously the N—F thermochemical bond energy in a 1,2-bis(difluoroamino)alkane could have been compared directly to the N—H thermochemical bond energy in a 1,2-diamine by consideration of reactions such as Reaction 1.

It is assumed that all bond energies other than N—H and N—F are fixed during the reaction. However, this assumption is not entirely valid, because bond energies in complex molecules are rather labile. This treatment and its comparison to earlier bond energy calculations (7) are instructive, nevertheless.

In this laboratory and others, enthalpies of formation of most of the alkyl amines having four or less carbon atoms in the molecule have been measured. The present study adds values of the enthalpy of formation of isobutylamine and the 1,2-diamines with four or less carbon atoms. The carbon-nitrogen bond energies in the alkyl amines were compared to those in the 1,2-diamines.



(1)

Table I. Carbon Dioxide Recovery

Compound	% Recovery	Number of Experiments
Ethylenediamine	$100.01_1 \pm 0.01_1$	7
1,2-Propanediamine	$100.00_8 \pm 0.00_6$	7
1,2-Butanediamine	$99.97_5 \pm 0.01_4$	6
2-Methyl-1,2-propanediamine	$100.01_2 \pm 0.01_4$	7
Isobutylamine	$100.01_2 \pm 0.01_0$	8

EXPERIMENTAL

Apparatus and Procedures. The rotating-bomb calorimeter BMR-2 and platinum-lined bomb Pt-3b, internal volume 0.349_4 liter, have been described (*8, 9*). Rotation of the bomb was not necessary for the present experiments. Calorimetric procedures were the same as those reported previously from this laboratory (*10, 11, 17*). The liquids were confined in borosilicate glass ampoules. One milliliter of water was added to the bomb, and the bomb was flushed and charged to 30 atm. with pure oxygen. Each experiment was initiated at 23° C., and because of the masses of combustibles chosen, the final temperatures were very nearly 25° C.

Three series of combustion experiments were done. 1,2-Propanediamine and 2-methyl-1,2-propanediamine were studied in the first series of experiments, ethylenediamine and 1,2-butanediamine in the second, and isobutylamine in the third.

The calorimeter was calibrated by combustion of benzoic acid, NBS Sample 39I, which evolves 26.434 ± 0.003 absolute kilojoules per gram under certificate conditions. Conversion to standard conditions (*12*) gives −6313.02 ± 0.72 cal. per gram for the energy, $\Delta Ec^\circ/M$, of the idealized combustion reaction. Eight benzoic acid combustion experiments during the first series of experiments gave ε(calor.) = 4005.07 ± 0.15 cal. per deg. (mean and standard deviation), and nine benzoic acid combustion experiments during the second series gave ε(calor.) = 4004.91 ± 0.32 cal. per deg. A slight modification of the calorimeter was necessary between the second and third series. Eight benzoic acid combustion experiments during the third series gave ε(calor.) = 4004.54 ± 0.11 cal. per deg.

The samples of auxiliary oil, empirical formula $CH_{1.894}$, and cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, used to initiate the combustion reactions have been described (*8, 9*). The value of $\Delta Ec^\circ/M$ for the oil was $-10984.3_0 + 0.1_5$ cal. per gram (mean and standard deviation).

Amine Samples. Three of the diamines, ethylenediamine, 1,2-propanediamine, and 2-methyl-1,2-propanediamine, were obtained commercially. The sample of 1,2-butanediamine was obtained through the courtesy of Ralph Roberts of the Office of Naval Research and Kurt Baum of the Aerojet-General Corporation. All four materials were purified by means of preparative-scale gas-liquid chromatography. Study of the melting point as a function of the fraction melted showed the purities of ethylenediamine, 1,2-propanediamine, and 2-methyl-1,2-propanediamine to be 99.9, 99.7, and 99.4 mole %, respectively. Analytical gas-liquid chromatography showed no impurities in the 1,2-butanediamine sample.

The sample of isobutylamine was obtained commercially. Analytical gas-liquid chromatography showed two trace isomeric impurities, 0.004% *sec*-butylamine and 0.05% *n*-butylamine, that would have little effect on the enthalpy of combustion. All compounds were dried by vapor passing over freshly activated molecular sieve.

Carbon Dioxide Recovery. Carbon dioxide was recovered from some of the combustion experiments as another indication of sample purity. Anhydrous lithium hydroxide was used as the absorbent (*10*). Recoveries of carbon dioxide, based on masses of combustibles and the stoichiometry of the combustion reaction, are summarized in Table I. Experiments were rejected if soot was found in the bomb. After the carbon dioxide was absorbed from the combustion products, the gas was passed through a furnace in the analytical train which would oxidize carbon monoxide or other combustibles. No evidence for such materials was found. The quantitative carbon dioxide recoveries gave good evidence that the materials were pure, but the presence of isomeric impurity was left undetected.

Table II. Physical Properties at 298.15° K.

	ρ, Grams/Ml.	c_p, Cal./Deg./Gram	$(\partial E/\partial P)_T$, Cal./Atm./Gram
Ethylenediamine	0.891	0.70	−0.01
1,2-Propanediamine	0.864	0.69	−0.01
1,2-Butanediamine	0.861	0.68	−0.01
2-Methyl-1,2-propanediamine	0.847	0.67	−0.01
Isobutylamine	0.724	0.63	−0.01

RESULTS

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*3*) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and the thermochemical calorie (*4*). The laboratory standards of mass and resistance had been calibrated at the National Bureau of Standards. For reducing weights in air to weights in vacuo, correcting to standard states, and correcting the energy of the actual bomb process to that of the isothermal process, the values of Table II were used for density, ρ, specific heat, c_p, and $(\partial E/\partial P)_T$ of the amines. The density values were measurements made in this laboratory. The values of c_p and $(\partial E/\partial P)_T$ were estimates.

Calorimetric Results. Detailed results of typical calorimetric experiments are given in Table III. Computation of results followed the form given in reference (*12*). Results of all experiments are summarized in Table IV. The values of $\Delta E_c^\circ/M$ are based upon sample mass and refer to the reactions as follows:

Ethylenediamine

$$C_2H_8N_2(liq) + 4\ O_2(g) = 2\ CO_2(g) + N_2(g) + 4\ H_2O(liq) \quad (2)$$

1,2-Propanediamine

$$C_3H_{10}N_2(liq) + 1\tfrac{1}{2}\ O_2(g) = 3\ CO_2(g) + N_2(g) + 5\ H_2O(liq) \quad (3)$$

1,2-Butanediamine and 2-Methyl-1,2-propanediamine

$$C_4H_{12}N_2(liq) + 7\ O_2(g) = 4\ CO_2(g) + N_2(g) + 6\ H_2O(liq) \quad (4)$$

Isobutylamine

$$C_4H_{11}N(liq) + 2\tfrac{7}{4}\ O_2(g) = 4\ CO_2(g) + 1\tfrac{1}{2}\ H_2O(liq) + \tfrac{1}{2}\ N_2(g) \quad (5)$$

Derived Results. Table V lists the derived results. Uncertainties given are the "uncertainty interval" (*16*). No allowance was made for uncertainty caused by isomeric impurity. In the least pure compound, 2-methyl-1,2-propanediamine, isomeric impurity could increase the uncertainty interval by as much as 0.02 to 0.03 kcal. mole^{-1}. To calculate values of the enthalpies of formation, the following values were used for the standard enthalpies of formation of gaseous carbon dioxide and liquid water, respectively; −94.051 and −68.315 kcal. per mole (*18*). Uncertainties attached to the enthalpies of formation of gaseous carbon dioxide and liquid water were 0.011 (*15*) and 0.010 (*14*) kcal. per mole, respectively.

Table III. Summary of Typical Calorimetric Experiments[a]

	Ethylenediamine	1,2-Propanediamine	1,2-Butanediamine	2-Methyl-1,2-propanediamine	Isobutylamine
m'(compound), g.	0.998490	0.903137	0.841806	0.888427	0.748068
m''(oil), g.	0.051315	0.062271	0.073691	0.033132	0.060538
m'''(fuse), g.	0.001212	0.001059	0.001218	0.001014	0.001228
Δt_c, deg.	1.99610	1.99992	2.00975	1.99009	2.00532
$n'(H_2O)$, mole .05535 0.05535	0.05535	0.05535			
ε(calor.)$(-\Delta t_c)$, cal.	−7994.21	−8009.81	−8048.87	−7970.43	−8030.40
ε(cont.)$(-\Delta t_c)$, cal.[b]	−10.96	−10.85	−10.82	−10.71	−10.71
$\Delta E_{ign.}$, cal.	0.78	0.77	0.51	0.47	0.59
$\Delta E^{cor.\ to\ std.\ states}$, cal.	1.35	1.61	1.76	1.71	1.17
$\Delta E^{dec.}(HNO_3)$, cal.	29.19	26.32	22.49	23.59	16.31
$-m''\Delta Ec^\circ/M$(oil), cal.	563.66	684.00	809.45	363.93	664.97
$-m'''\Delta Ec^\circ/M$(fuse), cal.	4.91	4.29	4.93	4.11	4.97
$m'\Delta Ec^\circ/M$(compound), cal.	−7405.28	−7303.67	−7220.55	−7587.33	−7353.10
$\Delta Ec^\circ/M$(compound), cal./gram	−7416.48	−8087.00	−8577.43	−8540.19	−9829.43

[a] Reaction temperature is 298.15° K. Symbols and terminology, except as noted, are those of reference (*12*). [b] ε'(cont.)$(t' - 25°) + \varepsilon'$(cont.)$(25° - t_f + \Delta t_{cor.})$.

Table IV. Summary of Combustion Experiments
$\Delta Ec^\circ/M$(compound), cal./gram

Ethylenediamine	1,2-Propanediamine	1,2-Butanediamine	2-Methyl-1,2-propanediamine	Isobutylamine
−7416.48	−8086.04	−8577.43	−8540.19	−9828.98
−7415.49	−8087.64	−8579.76	−8541.35	−9830.35
−7414.25	−8086.63	−8579.22	−8539.28	−9829.21
−7421.90	−8086.38	−8576.28	−8543.73	−9828.76
−7412.72	−8087.00	−8574.27	−8539.57	−9829.23
−7416.54	−8087.40	−8578.27	−8541.36	−9830.19
−7415.99	−8087.29	−8578.03	−8541.47	−9828.94
−7416.70	−8087.77	−8578.48	−8538.83	−9829.43
−7416.65		−8578.38		
−7415.35				
		Mean		
−7416.21	−8087.02	−8577.79	−8540.72	−9829.50
		Std. Dev.		
±0.75	±0.22	±0.55	±0.56	±0.21

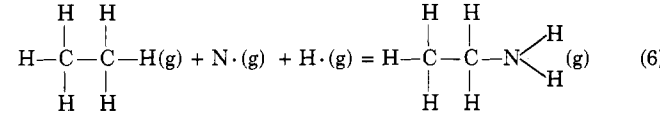
Values of the enthalpy of vaporization were derived by means of the Clapeyron equation from inclined-piston vapor pressure measurements (*5*). The enthalpies of formation are for the real gas state and may differ by several hundredths of a kcal. per mole from the standard enthalpy of formation.

DISCUSSION

Comparison with Previous Work. National Bureau of Standards Technical Note **270-3** (*18*) gives −5.82 kcal. per mole as the enthalpy of formation of liquid ethylenediamine, a value evidently derived from the pioneering work of Berthelot (*2*). No literature values for the other compounds are available.

C—N Thermochemical Bond Energy. The enthalpies of formation of the gaseous 1,2-diamines can be used with enthalpy-of-formation data itemized in Table VI to calculate and compare the C—N thermochemical bond energies in the amines and diamines. The carbon-hydrogen thermochemical bond energy, E(C—H), was taken to be 99.39 kcal. from methane. The nitrogen-hydrogen thermochemical bond energy, E(N—H), was taken to be 93.43 kcal. from ammonia.

Consider the following typical hypothetical reaction at 298.15° K.



(6)

Ethylamine was used as an example. For this reaction,

$$\Delta H = \Delta Hf[C_2H_7N(g)] - \Delta Hf[C_2H_6(g)] - \Delta Hf[N\cdot(g)] - \Delta Hf[H\cdot(g)] = E(C—H) - E(C—N) - 2E(N—H)$$

If enthalpies of formation and E(C—H) and E(N—H) are substituted in this equation, the carbon-nitrogen thermochemical bond energy, E(C—N), is 68.6 kcal. This calculation was made for all the amines in Table VI and for the diamines from this research. Values of E(C—N) are tabulated in Table VII alongside the carbon-nitrogen skeletons of the molecules. If the values of E(C—N) in Table VII are compared horizontally, the sum of the two C—N bond energies is approximately the same, whether both bonds appear in the diamine or appear separately in the simple amines.

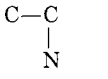
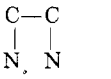
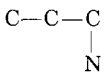
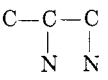
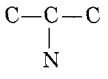
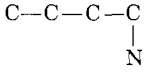
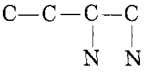
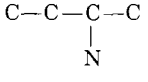
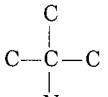
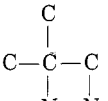
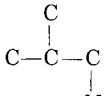
Table V. Derived Results at 298.15° K., Kcal./Mole

	Ethylenediamine	1,2-Propanediamine	1,2-Butanediamine	2-Methyl-1,2-propanediamine	Isobutylamine
ΔEc°	−445.71 ± 0.12	−599.46 ± 0.08	−756.16 ± 0.18	−752.90 ± 0.14	−718.92 ± 0.10
ΔHc°	−446.30 ± 0.12	−600.35 ± 0.08	−757.35 ± 0.18	−754.09 ± 0.14	−720.25 ± 0.10
ΔHf°(liq)	−15.06 ± 0.13	−23.38 ± 0.10	−28.74 ± 0.19	−32.00 ± 0.16	−31.68 ± 0.12
ΔHv	10.99 ± 0.05	10.57 ± 0.05	11.06 ± 0.05	10.43 ± 0.05	8.11 ± 0.05
ΔHf(g)	−4.07 ± 0.14	−12.81 ± 0.11	−17.68 ± 0.20	−21.57 ± 0.17	−23.57 ± 0.13

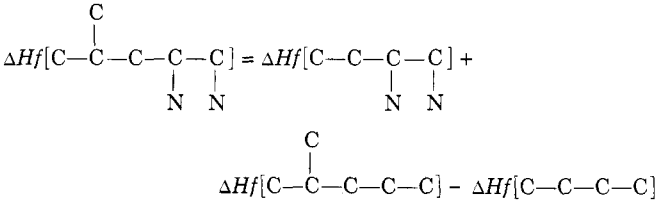
Table VI. Standard Gaseous Enthalpies of Formation at 298.15° K. Used in Bond Energy Calculations, Kcal./Mole

Hydrocarbons			Amines			Miscellaneous		
CH_4	(18)	−17.88	C_2H_7N	(13)	−11.27	NH_3	(18)	−11.02
C_2H_6	(18)	−20.24	n-C_3H_9N	(17)	−16.77	N·	(18)	112.979
C_3H_8	(1)	−24.82	iso-C_3H_9N	(17)	−20.02	C·	(18)	171.291
C_4H_{10}	(1)	−30.15	n-$C_4H_{11}N$	(6)	−22.5	H·	(18)	52.095
iso-C_4H_{10}	(1)	−32.15	sec-$C_4H_{11}N$	(6)	−25.2	F·	(18)	18.88
2-Methylpentane	(1)	−41.66	$tert$-$C_4H_{11}N$	(17)	−28.90			
			iso-$C_4H_{11}N$		−23.57			

Table VII. The C—N Thermochemical Bond Energy, Kcal./Bond at 298.15° K.

	68.6		69.5
	69.6		71.6
	72.8		
	70.0		71.4
	72.7		
	74.4		72.3
	69.0		

N—F Thermochemical Bond Energy. The values of the $-CH_2-$ increment to the enthalpies of formation of ethylenediamine, 1,2-propanediamine, and 1,2-butanediamine indicate that the increment beyond C_4 probably will be the normal incremental value from the alkanes. The enthalpy of formation of gaseous 4-methyl-1,2-pentanediamine at 298.15° K. can be estimated as follows.



The enthalpy of formation of 4-methyl-1,2-pentanediamine, $\Delta Hf^{\circ}_{298.15}$, is -29.1_9 kcal. per mole. This compound now can be compared to 1,2-bis(difluoroamino)-4-methylpentane (Reaction 1). E(N—F) is 65.3 kcal. This is essentially the same value that would have been found for E(N—F) in reference (7) if the C—N thermochemical bond energy from the diamines had been used rather than the C—N thermochemical bond energy from dimethylamine.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of the following employees of the Bureau of Mines, Bartlesville (Okla.) Petroleum Research Center: H. L. Finke and J. F. Messerly, who contributed values of purity from their low-temperature calorimetric studies, and Ann Osborn, who contributed enthalpies of vaporization derived from vapor pressure measurements.

NOMENCLATURE

∂	=	differential operator
T	=	temperature, ° K.
m	=	mass, grams
n	=	number of moles
P	=	pressure, atm.
ε(calor.)	=	energy equivalent of calorimeter, cal. per deg.
ε(cont.)	=	energy equivalent of contents, cal. per deg.
$\Delta E_{dec.}$	=	energy of decomposition, cal.
$\Delta E_{ign.}$	=	electrical iginition energy, cal.
$\Delta E_{cor.\ to\ std.\ states}$	=	energy for reduction to standard states, cal.
$\Delta Ec^{\circ}/M$	=	standard energy of idealized combustion reaction, cal. per gram
ΔEc°	=	standard energy of idealized combustion reaction, kcal. per mole
ΔHc°	=	standard enthalpy of combustion, kcal. per mole
ΔHv	=	enthalpy of vaporization to real gas
ΔHf°(l)	=	standard enthalpy of formation of liquid, kcal. per mole
ΔHf°(g)	=	standard enthalpy of formation of gas, kcal. per mole
E	=	thermochemical bond energy, kcal.
i	=	superscript indicating initial state
f	=	superscript indicating final state

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RECEIVED for review February 26, 1969. Accepted June 13, 1969. Work conducted under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, Project **9713**, Program Element **681308**, and the Bureau of Mines, U. S. Department of the Interior. Contribution No. **165** from the thermodynamics laboratory of the Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla. 74003.

Melting Points of Ethane and Three of Its Deuterated Modifications

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A pulsed nuclear magnetic resonance method has been used to determine both the apparent melting point and the impurity correction for samples of ethane and three of its deuterated modifications. The true melting points were found to be: CH_3CH_3 89.82° K., CH_3CD_3 89.13° K., CHD_2CHD_2 89.89° K., and CHD_2CD_3 89.82° K.

IN THE PAST, considerable confusion has surrounded an accurate determination of the melting point of ethane. As late as 1960, the Handbook of Chemistry and Physics (*6*) quoted a value of 101.2° K., measured at the turn of the century (*7*). Results obtained later, notably 89.47° (*11*), 89.89° (*12*), and 90.35° K. (*3*), have slowly been incorporated into reference books during the last ten years. As late as 1949, Gutowsky *et al.* (*5*) quoted the melting point of ethane as 101.0° K., while reporting the observation of a narrow liquid-like nuclear magnetic resonance line at about 91° K.

In the course of attempts to understand spin-lattice relaxation in liquid and solid ethane (*4, 8*), the authors learned of this uncertainty in the ethane melting point and were unable to find any melting point measurements for the deuterated modifications of ethane. To measure these melting points, a nuclear magnetic resonance (NMR) technique (*1*) was developed which appears to give both the melting points of the samples and the true melting points as reliably as the conventional heat capacity method (*12*). By the true melting point of a substance, the authors mean the melting temperature of a sample of that substance whose impurity content is small enough or innocuous enough to have no measurable effect on the experimental determination of this temperature.

EXPERIMENTAL

The melting points and their impurity corrections were determined using this pulsed NMR method. According to the Raoult theory of impurity premelting (*10*), the fraction of the sample which is liquid, $A(T)$, at any temperature T below the apparent melting point, $(T_m)_A$, follows the equation

$$A(T) = \left[1 + \frac{(T_m)_A - T}{\Delta}\right]^{-1} \quad (1)$$

where Δ is equal to the difference between T_m, the true melting point, and $(T_m)_A$. Δ is also proportional to the fraction of impurity molecules which depress the melting point—that is, of a type soluble in the melt but not appreciably soluble in the crystals—and the proportionality constant is the (mole fraction) freezing point depression constant. $A(T)$ is measured directly by observing the amplitude of the spin echo of pulsed NMR. The two parameters, $(T_m)_A$ and Δ, are adjusted for a best fit to the experimental points and then added to provide the true melting point. For samples of ethane of reasonable purity, C.P. grade, neither the validity of the method nor the true melting points obtained depend upon the sample purity (*1*).

The CH_3CH_3 sample was prepared from Phillips Petroleum Co. research grade ethane. As with all the samples, it was exposed to a Misch metal getter in order to remove paramagnetic oxygen (*9*) and then sealed in a glass sample tube of 3.5-mm. i.d. and approximately 80-mm. length. Thus, all our measurements were taken along the vaporization curve. The melting range for this sample (Figure 1) was about 0.1° K., and its impurity correction was 0.007° K. Consequently, this sample is considerably purer than that of Witt and Kemp (*12*), and of comparable purity to that of Clusius and Weigand (*3*). The CH_3CD_3, CHD_2CHD_2, and CHD_2CD_3 samples were obtained from Merck, Sharp, and Dohme of Canada, Ltd. The overriding impurities in these samples were reported by the manufacturer to be other deuterated modifications of ethane. Analysis by the National Bureau of Standards of the lots from which our samples came indicated that each contained 93 to 95%