aldehydes, Sauter[13] attacks the existence of "inner" reflections (lower orders of the (001) plane) observed by Ott. In consideration of the results obtained in this thesis, there appears to be every reason to anticipate results such as obtained by Ott on polymer formaldehydes, since the spacings observed lie in a range suitable for observation.

Summary

1. A large number of two-component mixtures of the normal fatty acids C_{10} to C_{18} have been studied. The chain length difference of the two components varied from one to eight carbon atoms. The mixtures with difference in chain length up to three carbon atoms were studied for various concentrations. In all cases mixed crystal formation was established.
2. Very complex mixtures of fatty acids (containing as many as nine components) were also measured and the existence of solid solution demonstrated.
3. These results are discussed in connection with their chemical significance.

[13] E. Sauter, *Z. physik. Chem.*, **B18**, 417 (1932).

BALTIMORE, MARYLAND

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Heat Capacities of Gaseous Mono- and Dimethylamine[1]

BY W. A. FELSING AND F. W. JESSEN

Object of the Investigation.—The purpose of this investigation was the experimental determination of the heat capacities of mono- and dimethylamine in the gaseous state. This study is a continuation of a series by Felsing and co-workers[2] dealing with the thermodynamic constants of monomethylamine with a view to the possible use of this substance as the refrigerating fluid in the absorption type of refrigerating units. The inclusion of dimethylamine in this study serves to present, also for the first time, heat capacity data for this substance, which itself presents possibilities as a refrigerating fluid. A study of the thermal decomposition of the methylamines yields data at elevated temperatures leading to the evaluation of their free energies of formation from the elements. Such experiments, to be reported in a later paper, have been made; to evaluate the free energy content at 25°, however, requires a knowledge of the heat capacities of these gaseous amines. These data, hence, form the objectives of this investigation.

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[1] From a portion of a thesis submitted by F. W. Jessen in partial fulfilment of the requirements for the Ph.D. degree.

[2] Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929); Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); C. T. Ashby, M. A. Thesis, University of Texas, 1931.

Previous Investigations.—The literature records no data for the heat capacities of the methylamines as gases. Planck and Vahl[3] cite a single value for the heat capacity of *liquid* monomethylamine at 20° and Vahl[4] cites one at 15°.

The Method of this Investigation.—The method best suited for an accurate determination of the heat capacities of substances such as the amines seemed to be the closed system continuous flow method of Scheel and Heuse.[5] This method was adopted, accordingly, utilizing such modifications as suggested by Thayer and Stegman and by Haas and Stegman.[6] Some minor modifications were made during this investigation. Special attention was paid to the very exact temperature control of the thermostat in which the calorimeter was immersed (*i. e.*, ±0.005°).

The Calorimeter.—The calorimeter in design followed that of Scheel and Heuse in general and was constructed of Pyrex glass. The heating unit was made of 300 cm. of double silk-covered manganin wire wound on a small glass tube, shellacked to ensure complete insulation. The brass tube T (see figure) was machined to fit the glass tube F of the calorimeter, inside of which it was placed and to which it was attached by means of de Khotinsky cement. The copper tube E was closed at its lower end by means of a fine copper gauze, soldered on. The space between the inner walls of this tube and the heater coil was packed with finely shredded copper, B, to ensure adequate thermal contact of the gas with the heater unit. The resistance of the heater unit was found to be 109.30 ohms, determined potentiometrically against a 10-ohm standard resistance calibrated by the U. S. Bureau of Standards.

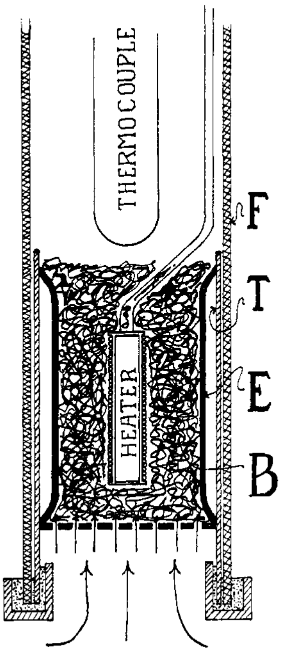

Fig. 1.—Details of calorimeter unit.

The Thermoelements.—All temperature measurements were made with a 15-junction copper–nickel thermoelement constructed according to the recommendations of La Mer and Robertson.[7] Although Tsutui[8] questions the dependability of the copper–nickel junction, it was found in this investigation that the calibration at different times gave identical results. A 10-junction copper–constantan element was constructed to check against the copper–nickel element. The thermoelements were 86 cm. long; the ends were staggered to avoid undue bulking. Both the cold and hot junctions were encased in a very thin-walled (0.15 mm. thickness) seamless silver tube, closed at one end and having a total length of 15 cm. Naphthalene was used to ensure good thermal contact of the junctions with the silver sheath. The calibrated thermoelements were used differentially to measure the temperature differences of the gas before entering and after leaving the heating unit.

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(3) Planck and Vahl, *Fortschr. Geb. Ingenierw.*, [A] **2**, 11 (1931).

(4) Vahl, *Z. Ges. Kälte-Ind.*, **38**, 177 (1931); **39**, 7 (1932).

(5) Scheel and Heuse, (a) *Ann. Physik*, **37**, 79 (1912); (b) **40**, 473 (1913).

(6) (a) Thayer and Stegman, *J. Phys. Chem.*, **35**, 1505 (1931); (b) Haas and Stegman, *ibid.*, **36**, 2127 (1932).

(7) La Mer and Robertson, *ibid.*, **35**, 1953 (1931).

(8) Tsutui, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **11**, 93 (1929).

Calibration of the Apparatus.—The apparatus was highly evacuated for six to eight hours before filling with pure air (moisture and carbon dioxide free). The specific heat of the gas was calculated by the relation, also used by Thayer and Stegman

$$\tilde{C}_p \text{ (watt-sec./g.)} = (E/M\Delta T)\ [1 - K/M^2]$$

where E is the energy input in watts, M is the mass of gas passing through the heater unit per second, ΔT is the temperature rise, and K is the heat loss constant of the calorimeter. The value of K was determined in the usual way by varying the rate of flow of the gas and the heat input to maintain a constant temperature rise. The value of K for this apparatus for air was found to be 4.92×10^{-5}. The molal heat capacity of air at 25° was found in this investigation to be 6.960 cal./mole, which value is in excellent agreement with recent determinations of Scheel and Heuse,[5b] of Grüneisen and Merkel,[9] of Hebb,[10] of Shields[11] and of Thayer and Stegman.[6b]

The Heat Capacities of Mono- and Dimethylamine Gases.—Monomethylamine and dimethylamine gases were generated by the action of 40% potassium hydroxide on their highly purified hydrochlorides. The gases were dried by passage through long tubes filled with potassium hydroxide pellets and they were condensed in a reservoir surrounded by a mush of carbon dioxide and ether. After evacuation they were distilled from the reservoir, now surrounded by an ice–salt mixture, into another reservoir surrounded by the carbon dioxide–ether mush. Only about two-thirds of the liquid in each case was thus distilled into the new reservoir. This procedure was repeated several times to ensure a pure, dry product. The final product was then passed as a gas into the closed heat capacity system.

The heat capacities were determined at temperatures ranging from 0 to 50°. Table I presents the data obtained for both mono- and dimethylamine. These heat capacity data were plotted to large scale and the values of C_p determined as functions of the temperature. The following relations were obtained, which may be expected to determine the molal heat capacities even to temperatures considerably higher than the experimental limit of 50°.

$$\tilde{C}_p\ CH_3NH_2 \text{ (g.) (cal./mole)} = 9.530 + 0.1108T - 1.212 \times 10^{-4}T^2$$

and

$$\tilde{C}_p\ (CH_3)_2NH \text{ (g.) (cal./mole)} = 5.595 - 0.1148T + 2.750 \times 10^{-4}T^2$$

The Heat Capacity Ratios.—It seemed desirable to determine also the heat capacity ratios for these amines, specially since no such data for them are recorded in the literature. The method adopted was that of Kundt,[12] as modified by Saha.[13] Some modifications in connection with the production of sound were also introduced. At one end of the gas tube a telephone receiver connected to a variable high frequency vacuum tube oscillator, as described by Oldfather,[14] served as the source of sound. The receiver was placed inside a machined brass fitting, a special graphitic packing being employed to secure a gas-tight joint between the glass tube and the coupling enclosing the telephone receiver. The remainder of the

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(9) Grüneisen and Merkel, *Ann. Physik.*, [4] **72**, 193 (1923).

(10) Hebb, *Trans. Roy. Soc. Canada*, [3] **13**, 101 (1919).

(11) Shields, *Phys. Rev.*, **10**, 525 (1917).

(12) Kundt, *Pogg. Ann.*, **127**, 497 (1866); **135**, 337, 527 (1868).

(13) Saha, *Indian J. Phys.*, **6**, 445 (1931).

(14) Grace Oldfather, M. A. Thesis, University of Texas, 1929.

TABLE I

THE HEAT CAPACITIES OF MONO- AND DIMETHYLAMINE GASES

T, °C.	ΔT, °C.	M (g. gas/sec.)	E (watts) (RI^2)	K ($\times 10^4$)	C_p watt-sec./g.	C_p cal./mole
			I. Monomethylamine			
0	5.3550	0.01280	0.15780	0.492	1.6110	11.97
	5.4862	.01249	.15780	.492	1.5770	11.72
	5.5788	.01271	.15780	.492	1.5462	11.48
					Average	11.72
25	5.4876	.01232	.17500	.492	1.7485	12.98
	5.3255	.01093	.17500	.492	1.7700	13.14
	5.6402	.01248	.17500	.492	1.6992	12.62
					Average	12.91
50	5.4720	.01049	.19264	.492	1.8528	13.76
	5.8815	.00936	.19264	.492	1.8450	13.69
	5.3785	.01248	.19264	.492	1.8760	13.92
					Average	13.79
			II. Dimethylamine			
10	4.3430	0.01440	0.11920	0.471	1.4685	15.802
12	4.3350	.01413	.11920	.471	1.4850	15.975
25	4.5620	.01634	.14175	.471	1.5670	16.870
	4.5784	.01705	.14175	.471	1.5225	16.380
					Average	16.575
40	4.8355	.01241	.14175	.471	1.6750	18.030
50	4.9986	.01324	.15780	.471	1.7450	18.770
	4.9942	.01378	.15780	.471	1.7230	18.550

apparatus and its operation involved no new features. All determinations were carried out at 25° in a specially constructed thermostat.

The procedure of a determination involved the evacuation of the apparatus to pressures less than 0.001 mm., filling with pure, dry air, setting the oscillator at a definite constant frequency, and determining the nodal distances. After evacuating as before, pure, dry amine was admitted and, with the identical oscillator frequency, the nodal distances were again determined. The values for the ratio, γ, were calculated by the usual relation $\gamma = 1.403(M/29.0)(l_2^2/l_1^2)$, where 1.403 is the value of γ for air; 29.0 is the molal weight of air; M is the molecular weight of the amine; and l_1 and l_2 are the experimentally determined nodal distances for air and the amine, respectively.

TABLE II

THE HEAT CAPACITY RATIOS OF SEVERAL AMINES AT 25°

Substance	CH_3NH_2[15]	$(CH_3)_2NH$	$(CH_3)_3N$	$C_2H_5NH_2$[15]
$\gamma = C_p/C_v$	1.202	1.149	1.184	1.135

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[15] Since this paper was submitted for publication, Mehl [*Beihefte Z. ges. Kälte-Ind.*, Reihe 1, Heft 3 (1933)] published a value for $\gamma = 1.18 \pm 0.01$ for CH_3NH_2 (p. 27) and $\gamma = 1.13 \pm 0.01$ for $C_2H_5NH_2$ (p. 20).

The calculated values are listed in Table II; values for trimethylamine and monoethylamine are also included.

Summary

1. The need for heat capacity data for the amines and the absence of such data in the literature are pointed out.

2. Experimental values for heat capacities are presented tabularly and the heat capacity–temperature relations for the mono- and dimethylamines are presented for a temperature range from 0 to 50°. The accuracy of the measurements is given.

3. Experimental values for the heat capacity ratio, γ, are presented for the methylamines and for monoethylamine.

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The Conductance of Bases in Liquid Ammonia

BY WILLIAM W. HAWES[1]

I. Introduction

It is well known that a molecular species which consists principally of an element of the second period differs markedly in its physical and chemical properties generally when compared with its analogs of the succeeding periods. That the same trend would be shown if the species under consideration were ionic seems likely and we would expect the electrolytic conductance of solutions of a compound of this type to show an abrupt change from the behavior of the commoner types of electrolytic solutions. The evidence in support of this hypothesis is meager but examination of the available data does show discontinuities that are probably characteristic of the second period elements. However, the specific effect is usually involved and is, therefore, difficult of generalization.

Perhaps the approach to the problem most likely of success is a comparative study of dissociation of electrolytes consisting of the simplest ions of second period elements. This would necessarily have to be carried out in a solvent of dielectric constant sufficiently low that its solutions of ordinary electrolytes would be measurably undissociated. Unfortunately, this field of investigation is very restricted because such compounds are ordinarily insoluble in suitable media. The only systems that are readily available are the alkali metal amides in solution in liquid ammonia. Ammonia is well suited to this purpose since no electrolyte as far as is known at present is completely dissociated in this solvent and also, the conductance values of a large variety of electrolytes are available for comparison.

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(1) National Research Fellow in Chemistry.