

within $\pm 0.3\%$, and to make measurements in which accidental errors are reduced to values within this limit of precision. However, the elimination of constant errors from design and the construction of flow calorimeters which will give accurate measurements of specific heat to better than a few per cent. is much more difficult. Also these results would suggest that some of the high degree of accuracy which has been claimed for published data on heat capacity might be actually a high degree of precision.

Some essentials of a properly designed flow calorimeter include: (a) a minimum rate of heat loss, obtained by reducing the radiating surface to a minimum, by evacuating the jacket space around the calorimeter, and by using properly spaced radiation shields to prevent radiated heat from being used twice; (b) a proper arrangement of the vapor heater and thermometers to eliminate constant errors due to the effect of direct radiation and conduction

from the heater; and (c) a construction which uses a minimum volume of material of low heat capacity to reduce the time-lag to temperature changes.

One of the authors (J. B. M.) is grateful to E. I. du Pont de Nemours and Co., Inc., for a fellowship which made this work possible.

Summary

A study was made of flow calorimeters for the determination of the heat capacity of organic vapors. The simpler calorimeter, following the design of Callendar, was preferred.

A recycling vaporizer for producing a constant rate of vapor flow was designed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Heat Capacity of Organic Vapors. IV. Benzene, Fluorobenzene, Toluene, Cyclohexane, Methylcyclohexane and Cyclohexene

By JAMES B. MONTGOMERY¹ AND THOMAS DE VRIES

This paper is a continuation of a program for measuring the heat capacity of organic vapors. The heat capacities of benzene, fluorobenzene, toluene, cyclohexane, methylcyclohexane and cyclohexene vapors have been measured at atmospheric pressure at temperatures from their boiling points to 410°K. With the exception of benzene, little information is available on the heat capacity of these compounds. There are no published data for fluorobenzene and cyclohexene.

Experimental

The heat capacity of the vapor was determined by a flow-calorimeter method, using the modified Callendar direct-flow calorimeter described in the preceding paper of this series.² To correct for heat losses in the calorimeter, the observed heat capacities were plotted against the reciprocal of the rate of flow and extrapolated to infinite rate of flow. At each temperature approximately ten determinations were made at different rates of flow. The method of least squares was used to make the extrapolations. The precision of the results is within $\pm 0.3\%$.

Purification of Chemicals.—The observed boiling points and refractive indexes of the compounds are compared with reported values in Table I. The compounds were rectified in a twelve plate column, and only the middle fractions with boiling point ranges within 0.1° were used. Several compounds were distilled from a flask before rectification in a column.

(1) This paper is an abstract from the thesis submitted by J. B. Montgomery in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Montgomery and De Vries, *THIS JOURNAL*, **64**, 2372 (1942).

TABLE I
PHYSICAL CONSTANTS OF COMPOUNDS

Compound	Boiling point, °C.		Refractive index, n_D^{20}	
	Obs.	Lit.	Obs.	Lit.
Benzene	80.0	80.09 ^a	1.5004	1.5017 ^b
Fluorobenzene	84.6	84.85 ^c	1.4657	1.4677 ^b
Toluene	110.8	110.70 ^d	1.4962	1.49675 ^d
Cyclohexane	80.6	80.80 ^e	1.4262	1.4262 ^f
Methyl- cyclohexane	100.7	100.8 ^g	1.4224	1.4230 ^f
Cyclohexene	82.8	83.25 ^h	1.4465	1.44646 ⁱ

^a Smith and Matheson, *Bur. Stand. J. Research*, **20**, 641 (1938). ^b Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1939, pp. 794, 781.

^c Timmermans and Hennaut-Roland, *J. chim. phys.*, **32**, 501, 589 (1935). ^d Mathews, see ref. 4. ^e Timmermans and Martin, *J. chim. phys.*, **23**, 733 (1926). ^f Wibaut and Langedijk, *Rec. trav. chim.*, **59**, 1220 (1940). ^g Hicks-Bruun and Bruun, *Bur. Stand. J. Research*, **8**, 525 (1932). ^h Timmermans, *Bull. soc. chim. Belg.*, **30**, 62 (1921). ⁱ Vogel, *J. Chem. Soc.*, 1323 (1938).

Benzene.—Thiophene-free benzene from the Barrett Company was dried over phosphorus pentoxide, rectified and stored over sodium.

Fluorobenzene.—The fluorobenzene was prepared by the method of Flood.³ It was dried over calcium chloride, distilled through a Glinsky type column and rectified.

Toluene.—A Merck and Company purified grade of toluene was treated successively with concentrated sulfuric acid, 5% sodium hydroxide solution and water. It was dried with calcium chloride, allowed to stand over mercury

(3) Flood, "Org. Syntheses," **13**, 46 (1933).

for ten days, dried over phosphorus pentoxide, rectified and stored over sodium.⁴

Cyclohexane.—An Eastman Kodak Co. practical grade of cyclohexane was treated with nitrating acid to remove benzene, washed, dried over calcium chloride, distilled, rectified and stored over sodium.

Methylcyclohexane.—The methylcyclohexane, obtained from the Paragon Testing Laboratories, was treated with nitrating acid, distilled, dried over sodium, rectified and stored over sodium.

Cyclohexene.—The cyclohexene was prepared by the method of Coleman and Johnstone,⁵ dried over calcium chloride and rectified.

Results.—The results are summarized in Table II and in Fig. 1. Data from this investigation are indicated by open circles which are connected by lines to facilitate comparison. All data are reported in terms of the defined calorie equal to 4.1833 Int. joules. The experimental results were corrected for gas imperfections by means of the Berthelot equation. The critical point data for benzene, fluorobenzene, toluene and methylcyclohexane were taken from the literature.⁶ The critical temperature for cyclohexene was estimated to be 534°K. The critical

pressures of methylcyclohexane and cyclohexene were estimated to be 34.6 and 31.6 atmospheres, respectively. The uncertainty involved in these estimations and calculations is negligible, since the gas imperfection correction is of the order of one per cent.

TABLE II
EXPERIMENTAL HEAT CAPACITIES
(Units are cal. per mole per degree C.)

T, °K.	C_p (1 atm.)	C_p	C_p (calcd.)	% Diff.
Benzene				
370	25.43	25.1	24.6	-2.0
390	26.81	26.5	25.9	-2.3
410	27.81	27.6	27.1	-1.8
Fluorobenzene				
370	28.98	28.6	26.8	-6.3
390	30.24	29.9	28.1	-6.0
410	31.45	31.2	29.4	-5.8
Toluene				
390	33.93	33.5	31.6	-5.7
410	35.35	35.0	33.2	-5.1
Cyclohexane				
370	33.41	33.0	34.8	+5.5
390	35.38	35.0	36.5	+4.6
410	37.13	36.8	38.4	+4.4
Methylcyclohexane				
390	43.69	43.2	42.4	-1.9
410	45.63	45.2	44.5	-1.5
Cyclohexene				
370	32.08	31.9	30.5	-4.4
390	33.91	33.8	32.1	-5.0
410	35.62	35.5	33.7	-5.1

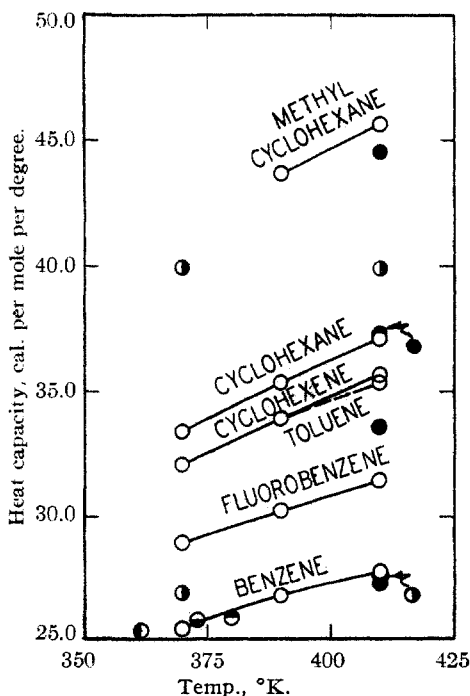


Fig. 1.—Experimental heat capacities: ●, Bennewitz and Rossner (benzene, toluene, cyclohexane, methylcyclohexane); ○, Jatkar (benzene, cyclohexane); ○, Dixon and Greenwood; ○, Déjardin; ○, Wiedemann.

(4) Mathews, *This Journal*, **48**, 562 (1926).

(5) Coleman and Johnstone, "Org. Syntheses," **5**, 33 (1925).

(6) "International Critical Tables," Vol. III, p. 248; Nogornov and Rotinyantz, *Ann. inst. anal. phys. chim.*, **3**, 162 (1926).

The results for benzene agree reasonably well with previous work. The result taken from Dixon and Greenwood's⁷ measurement of C_p/C_v at 363°K. by a velocity of sound method was 2.5% above the extrapolated curve. Déjardin's result⁸ from C_p/C_v at 373°K. was 0.8% above the curve. Wiedemann's⁹ average value of 25.9 cal. per mole degree over the temperature range from 308 to 453°K. was 0.6% below the curve. Regnault's¹⁰ average value of 29.3 for the temperature range from 389 to 491°K. falls on a straight-line extrapolation of the experimental curve. Bennewitz and Rossner's¹¹ value at 410°K., obtained with a flow calorimeter, was 1.6% lower than the measurement in this investigation.

Bennewitz and Rossner also reported the follow-

(7) Dixon and Greenwood, *Proc. Roy. Soc. (London)*, **105A**, 199 (1924).

(8) Déjardin, *Ann. phys.*, (9) **11**, 253 (1919).

(9) Wiedemann, *Wied. Ann.*, **2**, 195 (1877).

(10) Regnault, *Mem. de l'Acad.*, **26**, 1 (1862).

(11) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

ing values at 410°: toluene, 33.6 cal. per mole degree; cyclohexane, 37.3; and methylcyclohexane, 44.5. With the exception of cyclohexane, these values are lower than the results found in this investigation. Other investigators have obtained higher results than Bennewitz and Rossner for acetone,¹² heptane and pentane.¹³

Discussion

For the more complex organic molecules, which have not yet yielded to the methods of calculating heat capacity from spectroscopic data, semi-empirical equations for the calculation of heat capacity have great practical importance. An excellent general equation is the one which was proposed by Bennewitz and Rossner¹¹ and modified by Fugassi and Rudy¹⁴ and by Dobratz.¹⁵ In this equation, the vibrational contribution to heat capacity is calculated by means of the Einstein functions, using valence-bonding frequencies evaluated from Raman spectra and deformation frequencies empirically calculated from experimental data.

(12) De Vries and Collins, unpublished data.

(13) Pitzer, *THIS JOURNAL*, **62**, 1224 (1940); *ibid.*, **63**, 2413 (1941).

(14) Fugassi and Rudy, *Ind. Eng. Chem.*, **30**, 1029 (1938).

(15) Dobratz, *ibid.*, **33**, 759 (1941).

Heat capacities calculated with the modified equation of Dobratz are represented in Table II. The agreement with toluene, fluorobenzene, cyclohexane and cyclohexene is not very satisfactory. In both the aromatic and alicyclic series the calculated results are relatively lower for the compounds in which the ring symmetry has been destroyed by substituted groups. The discrepancy between the experimental and calculated results suggests that the empirically assigned deformation frequencies should be corrected to bring the calculated values into closer agreement with recent experimental data. Further work is in progress on this problem.

One of the authors (J. B. M.) is grateful to E. I. du Pont de Nemours and Co., Inc., for a fellowship which made this work possible.

Summary

Measurements have been reported for the heat capacities of benzene, fluorobenzene, toluene, cyclohexane, methylcyclohexane and cyclohexene vapors at atmospheric pressure from their boiling points to 410°K.

The experimental results have been compared with semi-empirically calculated heat capacities.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation and Physical Properties of Trimeric Phosphonitrilic Chloride

BY R. STEINMAN, F. B. SCHIRMER, JR., AND L. F. AUDRIETH

The phosphonitrilic chlorides, which may be represented by the empirical formula PNCl_2 , may be looked upon as the ammono analogs of phosphoryl chloride. Like their aquo analog they are capable of undergoing a wide variety of solvolytic reactions. However, they differ from phosphoryl chloride in their ability to undergo polymerization with formation of compounds of high molecular weight, some of which resemble rubber in appearance and properties. In addition to these highly polymerized forms a series of stable polyhomologs is known ranging from $(\text{PNCl}_2)_3$ to $(\text{PNCl}_2)_7$.

The preparation of the phosphonitrilic chlorides involves the partial ammonolysis of phosphorus pentachloride. Ammonia,¹ ammonium chloride and ammonobasic mercuric chloride² have

been employed as ammonolytic agents. However, only ammonium chloride has been used successfully, first by Stokes,³ who heated mixtures of the reactants in closed tubes under pressure, and later by Schenck and Römer,⁴ who employed *s*-tetrachloroethane as a medium for the reaction. Mixtures of the various polyhomologs are always obtained.

It has also been reported by Besson and Rosset⁵ that phosphonitrilic chlorides may be obtained by heating together equimolecular quantities of phosphorus pentachloride and ammonium chloride; in other words, neither solvent nor reaction under pressure are necessary. Unfortunately, neither yields nor conditions are specified by

(1) Liebig and Wöhler, *Ann.*, **11**, 139 (1834).

(2) Gladstone and Holmes, *J. Chem. Soc.*, **17**, 226 (1864).

(3) Stokes, *THIS JOURNAL*, **17**, 275 (1895); **19**, 782 (1897).

(4) Schenck and Römer, *Ber.*, **57B**, 1343 (1924).

(5) Besson and Rosset, *Compt. rend.*, **143**, 37 (1906).