(33%) polyvinylpyridine; it was essentially a copolymer of vinylpyridine and N-methyl-4-vinylpyridinium bromide. As seen in Fig. 3, the conductance was much higher even than that of the plasticized picrate. Sample 8 was 88% quaternized; as expected from the higher electrolyte content, the conductance is still higher. Finally, on plasticizing (No. 13), the conductance rose nearly two decades more. These plastic electrolytes have very large positive temperature coefficients of conductance; for No. 13, κ_0 approximately trebles for each 10° rise in temperature. We thus have at our disposal a system of electrolytes whose conductance is of the order of ordinary electrolytic solutions, with the significant difference that they are plastic solids rather than liquids. Further work is in progress.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Heats of Vaporization and Vapor Heat Capacities of Some Dimethylcyclohexanes[1]

BY J. P. MCCULLOUGH,[2] W. B. PERSON AND RALPH SPITZER

The vapor heat capacities and heats of vaporization of cyclohexane and four isomeric dimethylcyclohexanes have been measured in a flow calorimeter system. The vapor heat capacity results, in cal. deg.$^{-1}$ mole^{-1}, may be represented in the range of experimental measurements (approximately 400–500°K.) by the empirical equations

cis-1,2-Dimethylcyclohexane: $C_p = -51.34 + 0.34991T - 2.4515 \times 10^{-4}\,T^2$
trans-1,2-Dimethylcyclohexane: $C_p^0 = -50.96 + 0.35146T - 2.427 \times 10^{-4}\,T^2$
cis-1,3-Dimethylcyclohexane: $C_p^0 = -57.92 + 0.38060T - 2.764 \times 10^{-4}\,T^2$
trans-1,4-Dimethylcyclohexane: $C_p^0 = -19.76 + 0.21844T - 1.057 \times 10^{-4}\,T^2$

A comparison of the experimental heat capacity data with values calculated by the method of methyl increments shows the latter to be significantly high, but the structural concepts involved in the semi-theoretical computation are given further verification by the internally consistent results for the dimethylcyclohexanes.

In view of the continuing need for accurate thermodynamic data a flow calorimeter similar to that used by Waddington, Todd and Huffman[3] has been constructed. Their design is well adapted for measuring the vapor heat capacities and heats of vaporization of substances boiling above room temperature.

An important application of thermal data has been in the elucidation of the structures of complex molecules. Beckett, Pitzer and Spitzer[4] have used the information gained in their study of cyclohexane and methylcyclohexane to compute the heat capacities of the dimethylcyclohexanes. The vapor heat capacities of several dimethylcyclohexanes have been measured in order to determine the reliability of such approximate methods of calculation.

Experimental

Apparatus and Procedure.—Since the flow calorimeter built for this investigation is similar in construction and operation to that described by Waddington, *et al.*,[3] only a brief account of the method will be given here.

The vapor heat capacity of a substance is determined by observing its temperature rise when it is passed over an electrical heater at a constant, known rate of flow. The heater and two platinum resistance thermometers are enclosed in a vacuum-jacketed, silvered calorimeter designed to minimize both heat losses and indirect heating effects on the thermometers.[3] A thermostated bath surrounds the calorimeter and brings the vapor entering it to a constant temperature. Under these conditions the vapor heat capacity is defined by

$$C_p = W/F\Delta T - h/F\Delta T = C_{p(\text{app.})} - h/F\Delta T$$

where W is the power input of the calorimeter heater, F is the rate of flow of vapor and h is the heat loss from the calorimeter to its surroundings. Independent values of the temperature rise, ΔT, are obtained from observations with the two thermometers. For a particular mean vapor temperature and a constant ΔT, the heat loss, which is primarily due to radiation, is essentially constant regardless of flow rate. Hence, C_p may be evaluated by measuring $C_{p(\text{app.})}$ ($= W/F\ \Delta T$) at several rates of flow, plotting $C_{p(\text{app.})}$ *vs.* $1/F$ and extrapolating the resulting straight line to $1/F = 0$.

The steady flow of vapor required for heat capacity measurements is maintained by boiling the liquid in a vacuum-jacketed, silvered vaporizer located in a second thermostated bath. The vapor is passed through the calorimeter, condensed and returned to the boiler. A relationship between the power input of the electrical boiler heater and the vapor flow rate is determined in separate experiments in which the cycling vapor is diverted to a collection system where it is condensed and trapped in a weighed, detachable receiver. The weight of material produced by a measured quantity of energy during a measured interval of time provides the necessary flow calibration data. By applying suitable corrections to the proportionality thus obtained the heat of vaporization may be computed.[3]

Waddington and co-workers[5] have shown that the use of empirical equations of state to calculate $(\partial C_p/\partial P)_T$ is not reliable. They demonstrate that the heat capacity of a hydrocarbon vapor is a linear function of pressure up to one atmosphere and that measurements of C_p at two or more pressures suffice to determine both the heat capacity in the ideal gas state, C_p^0, and the quantity $(\partial C_p/\partial P)_T$.

Materials.—The dimethylcyclohexanes used in this work were made available by the American Petroleum Institute Research Project 45 at the Ohio State University and the Esso Laboratories of Standard Oil Development Company. The sources and purities of the various samples were

cis-1,2-Dimethylcyclohexane, 99.95 mole % ± 0.02%	(API RP 45)
trans-1,2-Dimethylcyclohexane, 99.82 mole % ± 0.08%	(API RP 45)
cis-1,3-Dimethylcyclohexane, 99.85 mole % ± 0.05%	(API RP 45)
trans-1,4-Dimethylcyclohexane, 99.83 mole %	(Esso Laboratories)

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[3] G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947).

[4] C. W. Beckett, K. S. Pitzer and Ralph Spitzer, *ibid.*, **69**, 2488 (1947).

[5] G. Waddington, J. C. Smith, D. W. Scott and H. M. Huffman, *ibid.*, **71**, 3902 (1949). See also earlier references cited there.

The purity of the thiophene-free benzene was estimated to be 99.5 mole % by determination of its freezing point. The cyclohexane was Lilly's spectrographic grade and was further purified by fractionation in an efficient column. Its purity was estimated to be 99.9 mole % ± 0.1% by time-temperature freezing point determinations. These purity measurements were made using an apparatus and method similar to that described by Glasgow, *et al.*[6]

Results

Heats of Vaporization.—Measurements of the heat of vaporization of benzene were made for comparison with the results of other investigators. The value obtained at 60.5° from 9 determinations with flow rates from 0.044 to 0.234 mole min.$^{-1}$ was 7610 ± 24 cal. mole^{-1}. Scott, *et al.*,[7] report a value of 7606 cal. mole^{-1} at 60.9° (corresponding to 7611 cal. mole^{-1} at 60.5°).

Higher precision was obtained in subsequent measurements, but comparison of the heats of vaporization of the dimethylcyclohexanes with the accurate 25° values of Osborne and Ginnings[8] showed abnormal deviation from linearity in plots of $\Delta H_{\text{vap.}}$ *vs.* T. For this reason the accuracy of the data of Table I is estimated to be about ±0.3%, although the values for *cis*-1,3-dimethylcyclohexane may be less reliable.

Table I

Heats of Vaporization

1 cal. = 4.1833 int. joules

Compound	Temp., °C.	$\Delta H_{\text{vap.}}$, cal. mole^{-1}
Cyclohexane	54.1	7500 ± 6[b] (3 detn.)
	73.3	7260 ± 3 (3 detn.)
cis-1,2-dmch[a]	96.7	8480 ± 4 (3 detn.)
	113.7	8250 ± 10 (2 detn.)
trans-1,2-dmch[a]	100.1	8210 ± 5 (3 detn.)
	114.1	8000 ± 6 (3 detn.)
cis-1,3-dmch[a]	88.0	8350 ± 10 (3 detn.)
	111.8	7960 ± 19 (3 detn)
trans-1,4-dmch[a]	67.5	8520 ± 10 (4 detn.)
	84.0	8270 ± 10 (2 detn.)
	103.3	8010 ± 10 (3 detn.)

[a] Dimethylcyclohexane. [b] Deviations given represent maximum spread of experimental results.

Vapor Heat Capacities.—Results obtained from measurements of the vapor heat capacities of benzene and cyclohexane are recorded in Table II along with data from other investigations. It may be seen that the differences between the present values and those reported in the literature do not exceed the uncertainties assigned to the latter, *i.e.*, ±0.2% for benzene[7] and ±1% for cyclohexane.[9]

Table II

Vapor Heat Capacity in Cal. Deg.$^{-1}$ Mole^{-1} of Benzene and Cyclohexane

1 cal. = 4.1833 int. joules; 0°C. = 273.16°K.

Compound	Temp., °K.	P, mm.	C_p	$C_p^1 - C_p^0$	C_p^0 (obsd.)	C_p^0 (lit.)
Benzene	370.2	398	25.17	0.57[a]	24.87	24.93[a]
Cyclohexane	370.9	605	33.19			
		455	33.02			
		315	32.84	0.90	32.48	32.60[b]
	468.5	310	42.78		42.69 (est.)	42.60[b]

[a] Estimated from data of reference 7. [b] Estimated from data of reference 9.

Experimental vapor heat capacity data for four dimethylcyclohexanes are summarized in Table III. Each value of C_p was determined by measuring $C_{p(\text{app.})}$ with two independent resistance thermometers at four rates of flow.[3] In general the deviation of points from linearity in plots of $C_{p(\text{app.})}$ *vs.* $1/F$ did not exceed ±0.1% of C_p except at the higher temperatures where the spread of points was as much as ±0.2%. Data were obtained at three pressures for cyclohexane at 370.9°K. and for *trans*-1,2-dimethylcyclohexane at 407.2°K. In both instances the deviations from linearity in plots of C_p *vs.* P were less than ±0.1%. In spite of this relatively good precision the experimental values of $C_p^1 - C_p^0$ are probably not more accurate than ±0.5% of C_p^0 since the high boiling points of the compounds investigated made it difficult to operate over as wide a range of pressure as is necessary for accurate extrapolation to zero pressure. For this reason the values of C_p^0 in Table III are assigned an uncertainty of ±0.5%. Again, the results for *cis*-1,3-dimethylcyclohexane may be less accurate.

Table III

Vapor Heat Capacity in Cal. Deg.$^{-1}$ Mole^{-1} of Four Dimethylcyclohexanes

1 cal. = 4.1833 int. joules; 0°C. = 273.16°K.

Compound	Temp., °K.	P, mm.	C_p	$C_p - C_p^0$	C_p^0 (obsd.)	C_p^0 (calcd.)[c]
cis-1,2-dmch[a]	407.0	485	51.04			
		285	50.80	0.91	50.46	52.0
	437.0	485	54.90			
		285	54.84	0.23	54.75	55.9
	501.7	285	62.55		62.5[b]	63.7
trans-1,2-dmch[a]	407.2	582	52.73			
		390	52.52			
		260	52.22	1.11	51.91	52.8
	437.3	582	56.47			
		390	56.42	0.20	56.32	56.8
	501.9	390	64.30		64.3[b]	64.5
cis-1,3-dmch[a]	407.1	599	52.37			
		289	51.78	1.45	51.23	52.1
	436.9	599	55.95		55.6[b]	56.0
	501.2	605	63.42		63.4[b]	63.8
trans-1,4-dmch[a]	370.1	260	47.12		46.6[b]	
	406.1	480	52.14			
		260	51.85	1.00	51.51	52.4
	467.9	480	59.50			
		260	59.41	0.31	59.30	60.2

[a] Dimethylcyclohexane. [b] Estimated. [c] Interpolated from Table X, reference 4.

In those cases where measurements were made at only one pressure, $C_p^1 - C_p^0$ and C_p^0 were estimated from data at other temperatures. The estimate was based upon a correlation of $C_p^1 - C_p^0$ with the second virial coefficient, B, of the equation of state, $PV = RT + BP$, and introduces appreciable error at the lower temperatures only.[7]

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(6) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

(7) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(8) N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

(9) Ralph Spitzer and K. S. Pitzer, This Journal, **68**, 2537 (1946).

Discussion.—Values of C_p computed by Beckett, Pitzer and Spitzer[4] are included in Table III for comparison with experimental data. Briefly, their method of calculation consists of determining the heat capacity increment due to a substituent methyl group from data for cyclohexane and methylcyclohexane. The methyl increment is assumed to be the difference between the vapor heat capacities of the two compounds when the individual contributions of chair–boat and polar–equatorial tautomerism have been subtracted from each.[4]

The figures calculated by the methyl increment method are from 2 to 3% greater than the observed values at the lower temperatures and from 0.5 to 1.5% at the higher. Using the same procedure to compute the vapor heat capacities of the mesitylenes from data for benzene and toluene,[10] the deviations from experimental results are within the 1% accuracy of the latter. The measurements on cyclohexane reported here were made in an effort to determine if the experimental data of Spitzer and Pitzer[9] were the cause of the large discrepancies found for the dimethylcyclohexanes. It is unlikely that deviations greater than 1% can be ascribed to this source.

Experimental methyl increments are presented in Table IV along with some details of the calculation. Parameters for evaluation of the tautomeric contributions were taken from the paper of Beckett, Pitzer and Spitzer.[4] A value of 0.97 kcal. mole^{-1} was used for the *n*-butane-like strain energy, *a*, as suggested there. This figure is in best agreement with available heat of isomerization data,[11] and reasonable changes in it do not appreciably improve the calculated results. In Table IV the *base* heat capacity is found by subtracting the tautomeric contributions from C_p^0; ΔM is the methyl increment, the difference between the *base* figure for an alkycyclohexane and that for cyclohexane. It was assumed in computing the heat capacities in the last column of Table III that the methyl increment for dimethylcyclohexane is twice that for methylcyclohexane,[4] but this is only approximately true. Nevertheless, with the exception of the more highly strained *cis*-1,2-dimethylcyclohexane the increments for the dimethyl compounds are constant within experimental limits of error, thus providing further verification of the types of tautomerism postulated by Beckett, Pitzer and Spitzer.[4]

The agreement between the calculated and experimental results shown in Table III is probably as good as can be expected considering both the degree of interference of the methyl groups with the ring structure and the reliability of the experimental data used in the calculation.

TABLE IV

EXPERIMENTAL METHYL INCREMENTS IN CAL. DEG.$^{-1}$ MOLE^{-1}

Compound	Temp., °K.	Tantomeric contribution		C_p^0	C_p (base)	ΔM
		Chair–boat	Equa.–polar			
Cyclohexane	400	0.27		35.82[b]	35.55	
Methylcyclohexane	400	.09	0.87	44.35[b]	43.39	7.84
cis-1,2-dmch[a]	400	.09		49.40	49.31	13.76
trans-1,2-dmch[a]	400	.18	.66	50.79	49.95	14.40
cis-1,3-dmch[a]	400	.09	.07	50.10	49.94	14.39
trans-1,4-dmch[a]	400	.18	.36	50.71	50.17	14.62
Cyclohexane	500	.69		45.47[b]	44.78	
Methylcyclohexane	500	.23	.83	55.21[b]	54.15	9.37
cis-1,2-dmch[a]	500	.23		62.33	62.10	17.32
trans-1,2-dmch[a]	500	.46	.83	64.10	62.81	18.03
cis-1,3-dmch[a]	500	.23	.20	63.28	62.85	18.07

[a] Dimethylcyclohexane. [b] Ref. 4.

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[10] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

[11] R. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 173 (1947).