vidual electrodes were rejected where it deviated from the average by more than about 0.1 mv. The agreement among the silver–silver chloride electrodes was better, in general, than that for the hydrogen electrodes and narrower limits were used for the former than for the latter.

An attempt to make a run with m_1, m_2 and m_3 approximately 0.005 resulted in potentials that drifted badly and these results were discarded entirely.

The measured values of the potential differences in absolute volts were divided by the factor 1.000330 to convert them into international volts.[16] This was done so that the E^0 values of Harned and Ehlers[9] and the constants of Manov, Bates, Hamer and Acree[17] could be used in the calculations.

The data were treated as indicated in the introduction and representative extrapolations at three temperatures are shown in Fig. 1.

The results showing K at the various temperatures are shown in Table II. The experimental values of $-\log K$ were fitted by the method of least squares by the empirical equation $-\log K = (A/T) + CT - D$, yielding the values 1143.71, 1.2979 and 0.0023142 for A, D and C, respectively. The calculated values of $-\log K$ using these constants are shown in Table II. The standard deviation of the calculated values from the experimental ones is 0.00063 in $-\log K$.

Standard thermodynamic quantities for the ionization reaction may be calculated from the above constants by well-known relations.[18] It is worthy of note that $\Delta C_p^0 = -2(2.3026)CRT$ yields -6.3 cal. mole^{-1} deg.$^{-1}$ at 25° which appears to be the smallest value for this quantity to appear in the literature for this type of reaction although it barely fits the range predicted on empirical grounds by Harned and Owen[19] for the standard heat capacity change for the ionization of a zwitterion.

TABLE II

THE IONIZATION CONSTANT OF SULFANILIC ACID IN WATER FROM 0 TO 50°

T, °C.	$K \times 10^4$	$-\log K$ obsd.	$-\log K$ calcd.	$\Delta \times 10^4$
0	3.01_6	3.520_6	3.5213	+ 7
5	3.48_8	3.457_4	3.4576	+ 2
10	4.00_3	3.397_6	3.3965	−11
15	4.58_8	3.338_4	3.3380	− 4
20	5.21_8	3.282_5	2.2819	− 6
25	5.92_5	3.227_3	3.2280	+ 7
30	6.66_8	3.176_0	3.1764	+ 4
35	7.48_2	3.126_0	3.1267	+ 7
40	8.34_1	3.078_8	3.0790	+ 2
45	9.24_9	3.033_9	3.0332	− 7
50	10.25_2	2.989_2	2.9892	± 0

Standard deviation = 0.0063

Acknowledgment.—The authors are grateful to the Research Corporation for a grant in support of this investigation.

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[16] National Bureau of Standards, Circular 475, 1949.

[17] G. G. Manov, R. B. Bates, W. J. Hamer and S. F. Acree, THIS JOURNAL, **65**, 1765 (1943).

[18] Ref. 8, p. 583.

[19] Ref. 8, p. 533.

EUGENE, ORE. RECEIVED SEPTEMBER 18, 1950

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

Experimental Vapor Heat Capacities and Heats of Vaporization of Seven Octanes

BY GORDON M. BARROW[1]

The vapor heat capacities at about 130, 190 and 250° and the heats of vaporization have been measured for *n*-octane, 3-ethylhexane, 2,3-dimethylhexane, 3,4-dimethylhexane, 2-methyl-3-ethylpentane, 3-methyl-3-ethylpentane and 2,3,4-trimethylpentane. The heat capacities of *n*-octane and 2,3,4-trimethylpentane have also been measured at a reduced pressure to obtain gas imperfection data. From average values of the gas imperfection corrections of these two compounds the heat capacities of all seven octanes in the ideal gas state have been obtained. A comparison of the results for *n*-octane with those of *n*-hexane and *n*-heptane and also with the statistically calculated values has been given. From this it appears that, while the calculated values are essentially reliable, they tend to be about 1% high for the *n*-paraffins.

The available thermodynamic properties of many of the paraffin hydrocarbons are the result of a necessarily approximate statistical calculation. It is desirable, therefore, to have experimentally determined values as checks on these calculations. Furthermore, the extension of this method of calculation to the branched compounds is sufficiently difficult that detailed statistical calculations do not appear to be feasible. Vapor heat capacity data for these compounds would then provide the basis for the empirical determination of otherwise undetermined factors.

The results presented here on the vapor heat capacities of seven of the paraffin octanes are part of the program in connection with the American Petroleum Institute Research Project 44 to provide the experimental results necessary to confirm and extend the tabulated thermodynamic properties of the paraffin hydrocarbons.

Apparatus and Material.—The vapor heat capacities and the heats of vaporization were measured in a new flow calorimeter. The calorimeter unit is similar to that recently described by Waddington, Todd and Huffman,[2] and will be described further elsewhere.

The vaporizer unit is essentially the same as that previously described by Pitzer.[3] The vaporizer heater consists of a 25 ohm coil of No. 30 chromel resistance wire supported on a light glass frame and suspended from a small glass float. With this arrangement the depth to which the heater was submerged remained constant. Two short sections of glass tubing attached to the float rode on the vertical tungsten leads and kept the float centered in the vaporizer.

The octanes used were already of high purity when re-

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[1] Physical Chemistry Laboratory, Oxford, England.

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

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

ceived and no further purification was necessary. The *n*-octane sample was obtained from Dr. F. D. Rossini through the A. P. I. Research Project 6. The remaining six octanes were provided by Dr. K. W. Greenlee through the A. P. I. Research Project 45, Cecil E. Boord Director, at The Ohio State University.

The purities of these compounds, in mole per cent., obtained from freezing or melting point data where possible or otherwise estimated, are as follows: *n*-octane, 99.65; 3-ethylhexane, 99$^+$; 2,3-dimethylhexane, 99$^+$; 3,4-dimethylhexane, 98$^+$; 2-methyl-3-ethylpentane 99.0; 3-methyl-3-ethylpentane, 99.7; 2,3,4-trimethylpentane, 99.5.

Procedure.—The heats of vaporization and the heat capacities were determined in the usual way. The procedure has been described fully by both Pitzer[3] and Waddington, Todd and Huffman.[2]

In the extrapolations of the measured apparent heat capacities to infinite flow rate the plots of apparent heat capacity *versus* the reciprocal of the flow rate gave, for both therometers after the heater, good linear relations. Furthermore, the intersection of the two curves through the apparent heat capacities with the zero value of the reciprocal of the flow rate always gave values of the true heat capacity differing by less than 0.1%.

Results

The measured heats of vaporization are presented in Table I.

TABLE I

THE HEATS OF VAPORIZATION OF SEVEN PARAFFIN OCTANES

	1 atmos.		361 mm.	
	T, °C.	ΔH_v, cal./mole	T, °C.	ΔH_v, cal./mole
n-Octane	125.3	8263	100.5	8691
	125.0	8296[a]		
3-Ethylhexane	118.2	8032		
2,3-Dimethylhexane	115.2	7935		
3,4-Dimethylhexane	117.3	7952		
2-Methyl-3-ethylpentane	115.2	7878		
3-Methyl-3-ethylpentane	118.0	7837		
2,3,4-Trimethylpentane	113.1	7822	88.3	8244
	113.1	7829[a]		
	113.1	7810[b]		

[a] R. F. Leinger, Ph.D. Thesis, University of California, 1945. [b] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **63**, 2419 (1941).

These results are the averages of four determinations. The average deviations from these values were about 10 cal./mole. No dependence of the heat of vaporization on the flow rate was observed. Corrections have been made for the heat lost in the leads to the vaporization heater and for the additional vapor required to fill the volume of the liquid removed during a determination of the heat of vaporization.

The experimental heat capacities at atmospheric pressure are presented in Table II. Values for the heat capacity at 361 mm. for the highest boiling (*n*-octane) and the lowest boiling (2,3,4-trimethylpentane) of the seven octanes studied here are given in Table III. These results are believed to be reliable to at least 1%.

TABLE II

EXPERIMENTAL VAPOR HEAT CAPACITIES AT 1 ATMOSPHERE PRESSURE AND THE HEAT CAPACITIES IN THE IDEAL GAS STATE FOR SEVEN PARAFFIN OCTANES

	T, °K.	C_p, cal./deg. mole	C_p^0, cal./deg. mole
n-Octane	405.7	59.02	58.0
	462.5	65.25	64.7
	522.7	70.68	70.6
3-Ethylhexane	397.1	58.71	57.7
	462.7	65.07	64.5
	522.7	71.47	71.4
2,3-Dimethylhexane	397.4	58.56	57.5
	463.7	65.90	65.3
	522.2	71.76	71.7
3,4-Dimethylhexane	406.7	59.59	58.6
	462.3	65.65	65.1
	522.6	71.86	71.8
2-Methyl-3-ethylpentane	399.7	59.09	58.1
	461.9	65.81	65.2
	522.2	71.71	71.6
3-Methyl-3-ethylpentane	403.3	60.19	59.1
	462.6	66.50	65.9
	521.7	72.71	72.6
2,3,4-Trimethylpentane	402.8	60.33	59.3
	463.6	66.76	66.2
	521.6	72.57	72.5

TABLE III

EXPERIMENTAL VAPOR HEAT CAPACITIES AT 361 MM. PRESSURE FOR *n*-OCTANE AND 2,3,4-TRIMETHYLPENTANE

	T, °K.	C_p, cal./deg. mole
n-Octane	408.1	58.86
	461.4	64.86
	521.3	70.61
2,3,4-Trimethylpentane	403.0	59.74
	460.8	66.13
	521.0	72.45

Gas Imperfection and Heat Capacity in the Ideal Gas State.—The inadequacy of the Berthelot equation for calculation of the gas imperfection corrections has recently been shown for the hexanes[4] and a similar situation would certainly be expected for the octanes. Furthermore, the results for the hexanes indicate that the gas imperfection corrections for all the isomers are not very different and that the use of an average gas imperfection correction should not introduce an error of more than 0.1 or 0.2 cal./deg. mole, and this only at the lowest temperature.

From the measured heat capacities at the two pressures, the gas imperfection corrections of Table IV for *n*-octane and 2,3,4-trimethylpentane have been obtained by assuming a linear relation of heat capacity with pressure. The validity of this relation has been confirmed for similar compounds by Waddington, Smith, Scott and Huffman.[4] The corrections calculated for the Berthelot equation are also included in Table IV.

To obtain the results at the temperatures listed, smooth curves were drawn through the three experimental points in each case. The listed temperatures of Table IV are sufficiently close to these points so that the error introduced by these approximate curves is not appreciable.

Any error in the experimental values is considerably exaggerated by the extrapolation to zero pressure. The agreement of the gas imperfection corrections for the two compounds is considerably better than might be expected from the claimed accuracy of the experimental results.

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(4) G. Waddington, J. C. Smith, D. W. Scott and H. M. Huffman, THIS JOURNAL, **71**, 3902 (1949); G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

TABLE IV

GAS IMPERFECTION CORRECTIONS TO THE VAPOR HEAT CAPACITIES OF n-OCTANE AND 2,3,4-TRIMETHYLPENTANE

		C_p, cal./deg. mole		$C_p^1 - C_p^0$, cal./deg. mole	
		760 mm.	361 mm.	Obsd.	Berthelot
130°	n-Octane	58.53	58.06	0.89	0.57
	2,3,4-Trimethylpentane	60.19	59.58	1.16	.51
			Av.	1.0	
190°	n-Octane	65.15	64.86	0.55	.38
	2,3,4-Trimethylpentane	66.52	66.20	0.61	.34
			Av.	0.6	
250°	n-Octane	70.55	70.57	−0.04	.26
	2,3,4-Trimethylpentane	72.50	72.41	0.17	.23
			Av.	0.1	

From the average gas imperfection corrections, the heat capacities in the ideal gas state are calculated from the experimental values and are given together with the experimental values in Table II.

The heat capacities of all the branched chain compounds studied here are higher than those of the normal compound. The differences between the heat capacity of the branched isomers and that of the normal compound are seen to be less than 3%.

TABLE V

COMPARISON OF THE CALCULATED AND OBSERVED IDEAL GAS STATE HEAT CAPACITIES IN CAL./DEG. MOLE OF n-HEXANE, n-HEPTANE AND n-OCTANE

		Calcd.	Obsd.	Difference	Increment Calcd.	Increment Obsd.
403.2°K.	n-Hexane	44.30	43.67	0.63		
	n-Heptane	51.50	50.66	.84	7.20	6.99
	n-Octane	58.7	58.1	.6	7.20	7.4
473.2°K.	n-Hexane	50.25	49.84	.40		
	n-Heptane	58.38	57.65	.73	8.13	7.81
	n-Octane	66.51	66.0	.5	8.13	8.3

Comparison with Other Data.—The vapor heat capacities of n-hexane[5] and n-heptane[6] have recently been accurately measured and a comparison of these values with the values for n-octane obtained here is of interest. As a basis for the comparison, the heat capacities calculated by Pitzer[7] and published by the A. P. I. Research Project 44[8] are also included in Table V.

The calculation of the thermodynamic functions requires, essentially, the assumption that the functions for a given n-paraffin can be obtained from those of the n-paraffin of one less carbon atom by the addition of an appropriate, and calculable, increment. Furthermore, it is required that this increment be independent of chain length for n-paraffins of more than four carbon atoms.

Although the observed heat capacities of Table V are not known to sufficient accuracy to test the constancy of the CH_2 heat capacity increment, they do confirm the general correctness of the calculated value of this quantity. The calculated heat capacities, however, are all of the order of 1% higher than the experimental values.

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(5) G. Waddington and D. R. Douslin, THIS JOURNAL, **69**, 2275 (1947).

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

(7) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); *Ind. Eng. Chem.*, **36**, 829 (1944).

(8) Selected Values of Properties of Hydrocarbons, Circular of the National Bureau of Standards C 461, U. S. Government Printing Office, Washington, D. C., 1947.

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[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Photochemistry of Proteins. XII. A Contribution to the Photochemistry of Amino Acids[1]

BY INES MANDL AND A. D. MCLAREN[2]

In the course of study of the comparative rates of inactivation of enzymes and viruses under oxygen and nitrogen it seemed worthwhile to observe the behavior of related substances under similar conditions. More ammonia is liberated from acidic DL-alanine solutions under oxygen than under nitrogen by radiation from an Hanovia quartz mercury vapor lamp. Under nitrogen, the products ammonia, lactic acid and pyruvic acid were formed but no acetaldehyde was found. The product L-lactic acid was obtained from L-alanine in 0.10 N hydrochloric acid. After irradiation of L-aspartic acid, L-malic acid was found. The production of optically active hydroxy acids from optically active amino acids is a new observation and requires a new scheme for the photolysis of amino acids.

Introduction

The photochemistry of amino acids has been recently reviewed.[3] As far back as 1908 photolysis to ammonia, carbon dioxide and aldehydes in the presence of air was investigated by Neuberg.[4] Henri, Weizmann and Hirshberg[5] and Weizmann, Bergmann and Hirshberg[6,7] have found ammonia, carbon monoxide and hydroxy acids among the photolysis products of alanine and aspartic acid irradiated under nitrogen. Their quantum yield data have been recalculated.[3] In view of the im-

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(1) From the Ph.D. Thesis of Ines Mandl, Polytechnic Institute of Brooklyn, April, 1949.

(2) For previous papers see A. D. McLaren and P. Finkelstein, THIS JOURNAL, **72**, 5423 (1950), and G. Oster and A. D. McLaren, *J. Gen. Physiol.*, **33**, 215 (1950), Paper XI.

(3) A. D. McLaren, "Advances in Enzymology," **9**, 75 (1949).

(4) C. Neuberg, *Biochem. Z.*, **13**, 305 (1908); **29**, 279 (1910).

(5) V. Henri, C. Weizmann and Y. Hirshberg, *Compt. rend.*, **198**, 168 (1934); **199**, 1205 (1935).

(6) C. Weizmann, E. Bergmann and Y. Hirshberg, THIS JOURNAL, **58**, 1675 (1936).

(7) C. Weizmann, Y. Hirshberg and E. Bergmann, *ibid.*, **60**, 1799 (1938).