given. Plastics containing up to 40% hydrocarbon by weight are covered.

2. The mean moment per (CH₂CHCl) group is shown to approach 1.73 D with increasing dilution, which is the theoretical limit for a linear polar polymer of alternating structure, assuming free rotation. Positive deviations at high concentrations of polymer or low temperatures are explained qualitatively as an increase of average moment due to configurations in which the chain molecules are not in their most probable state.

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The Heat Capacity of Gaseous Paraffin Hydrocarbons, Including Experimental Values for n-Pentane and 2,2-Dimethylbutane

BY KENNETH S. PITZER

Although several accurate experimental entropies are now available for the paraffin series, the gaseous heat capacity data are sparse and mostly of doubtful accuracy. Several years ago the writer started work on gaseous specific heat measurements by the flow method, which seemed the most direct among those capable of giving reasonable accuracy and which has given some of the best results in the past. It was decided at the beginning that the calorimeter was to be designed for substances boiling above room temperature, and that the results must be absolute and not merely relative to some one compound. Some preliminary results already have been published,[1] and the work presented below tends to confirm their correctness.

The general method used by Bennewitz and Rossner[2] was adopted but with complete change of detailed design. As is shown in Fig. 1, this general method consists of establishing the flow of vapor by electrical evaporation of the liquid at a constant rate. In our final apparatus a continuous cycle is employed, the condensed vapor being returned to the vaporizer chamber as liquid at the boiling point. Suffice it to say here that the accuracy of the resulting heat capacities appears to range from about 0.3% near room temperature to about 1% at 200°C. Heats of vaporization reliable to about 0.3% are also obtained.

In the discussion of the results in terms of statistical calculations, it is shown that the barriers to internal rotation in n-butane and pentane are probably about 3600 cal. per mole instead of the 30,000 and 16,000 cal. values which also have been proposed.

(1) K. S. Pitzer, THIS JOURNAL, **62**, 1224 (1940).

(2) K. Bennewitz and W. Rossner, Z. physik. Chem., **B39**, 126 (1938).

Design and Operation of Apparatus

The essentials of a good flow calorimeter include (1) a constant, accurately measured rate of flow, (2) a heater to introduce an accurately measured amount of heat into the gas, (3) thermometers that measure the temperature of the gas itself, and (4) a design which prevents excessive heat loss between heater and thermometer and which permits accurate correction for the loss occurring.
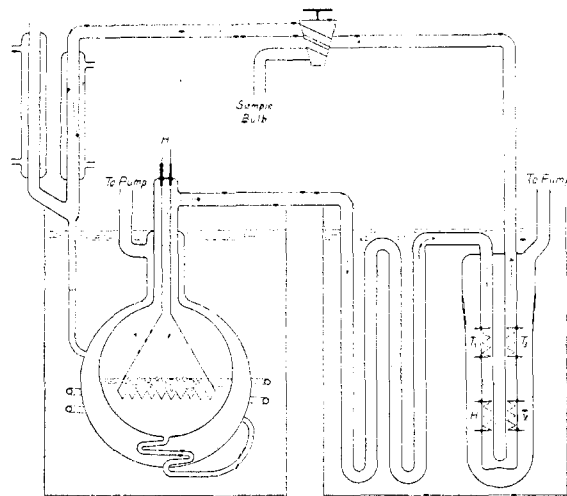

Fig. 1.—Diagram of the apparatus. Certain parts are omitted for simplicity.

A diagram of the calorimeter is shown in Fig. 1. The gas flow was produced by electrically evaporating the liquid at a constant, accurately measured rate. A spherical, double-walled glass vessel was constructed from 1- and 2-liter flasks, which had a long straight double-walled neck at the top. At the bottom a small tube spirals from the inner container to the outside. The heater is a large double spiral of no. 22 chromel wire (11 ohms) mounted somewhat below the center of the inner vessel. Preliminary experiments showed that at least 300 watts could be introduced with this heater into typical organic liquids without excessive wire temperatures. In operation the liquid level is 1 to 2 cm. above the heater wire. The liquid boils smoothly around the heater, the flow being satisfactorily

constant without any ballasting devices. The rate of flow is measured by condensing and collecting timed samples in a removable sample bulb fitted with stopcocks and a ground-glass joint. Once the heat of vaporization has been established definitely, rates of flow are determined from the electrical measurements of the heating energy alone.

The space between the silvered walls in the vaporizing vessel is continuously evacuated to less than 10^{-5} mm. pressure. The entire vessel is immersed in a thermostat regulated to within $0.1°$ of the boiling point. Closer regulation could be attained but is not needed. Except when a sample is being collected, the vapor enters permanent condensers and the resulting liquid enters the vaporizing vessel through the small tube at the bottom. The liquid passes through about 1.5 meters of 4 mm. i. d. tubing in the thermostat before entering the vessel.

All tubing carrying vapor outside of the thermostats is surrounded by electrically heated jackets. As shown in Fig. 1 two condensers are used, one on a side-arm. At the higher rates of flow approximate liquid–vapor equilibrium is attained below both condensers, leaving the liquid very near its boiling point.

The heat capacity unit consists, as is shown in Fig. 1, of a U-tube, about 8 mm. i. d. with, in order, one platinum resistance thermometer, a platinum wire heater, and two more platinum resistance thermometers. All of this is in an outer bulb which is continuously evacuated by the same pumping system as the vaporizer unit. A second thermostat contains the heat capacity unit and more than one meter of tubing through which the gas passes before entering the measuring unit. The tubing within the evacuated bulb is wrapped with aluminum foil to reduce heat exchange by radiation. This bulb is in two parts joined with a ground glass joint. The joint is sealed with a continuous ring of finely drawn solder wire which makes a tight joint but may be melted out when desired.
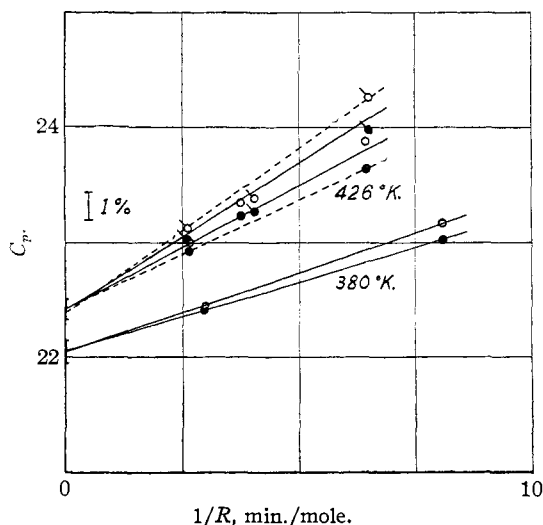

24

$\int 1\%$

C_p

426 °K.

380 °K.

22

0   1/R, min./mole.   10

Fig. 2.—The apparent heat capacity of carbon tetrachloride at various rates of flow. Solid circles are based on data from T_2 (see Fig. 1) and open circles, from T_3. Two different series are indicated at 426°K.

The heater consists of spirals of about 0.2-mm. platinum wire. Two 40-ohm sections are operated in parallel. Resistance measurements during operation as a heater show that the wire temperature exceeds that of the gas by only a few degrees. The leads are tungsten wires sealed through the glass, from which potential and current leads are taken.

The resistance thermometers consist of spirals of 0.1-mm. c. p. platinum wire wound on mica crosses. Each has about 20 ohms resistance at the ice-point. The leads are similar to the heater. Preliminary measurements, with thermocouples soldered to tungsten wires in turn sealed into the glass walls, showed that the walls approach the gas temperature within a few tenths of a degree. The resistance thermometer frame touches the glass only at a few points, and but two long fine wires connect to the tungsten seals (3 cm. from mica frame to tungsten). Thus it is apparent that the effective temperature of the platinum must be very close to that of the gas.

The thermometers were calibrated at the ice, steam, and sulfur points according to the international temperature scale. All three thermometers came from the same spool of wire and showed the same behavior within close limits. The equation obtained was

$$R/R_0 = 1 + 0.003973t - 5.85 \times 10^{-7}t^2$$

This one equation was used for all three thermometers, but in a manner carefully avoiding the exaggeration of the slight differences between them.

A constricted section in the tubing immediately after the heater assured turbulent mixing even at the lowest rates of flow employed.

All electrical measurements were made on a White potentiometer. Heater potentials were measured through a volt box while currents were measured by the potential drops across 0.01-ohm standard resistances. A single measuring current passes through all three thermometers in series and through a 25-ohm constant resistance, potential readings being taken across each. The absolute accuracy of the potential measurements is to about 0.02%; however, relative readings are considerably more accurate. Thus temperature differences leading to resistance changes of about 8% can be read with an error of less than 0.1%.

The principal reason for having two thermometers after the heater was to obtain a measure of the heat loss as the gas flows along the tube. In practice measurements are made at different rates of flow and the apparent heat capacities plotted against the reciprocal of the rate. Extrapolation to zero (i. e., infinite rate) should give the true heat capacity if the only correction is this heat loss. Since apparent heat capacities can be calculated with either thermometer, the two sets of results should extrapolate to the same limit, and thus offer a check on each other. Figure 2 shows the data for carbon tetrachloride at two temperatures. At a given temperature the points showing the greater slope are, of course, from the thermometer farther along the tube.

The two sets of measurements at 380°K. were made first. After one series of measurements at 426°K. it was apparent that it would not be safe, in general, to depend on results for only two rates of flow. All results on other substances are based on measurements using at least three different rates of flow. Although the data at 426°K. show considerable fluctuation, the extrapolation to zero heat loss

(1/R) is quite definite when one considers the two different series of measurements.

Experimental Measurements

As stated above, measurements were made on carbon tetrachloride in addition to n-pentane and 2,2-dimethylbutane. The former served as a check since its heat capacity is known reasonably well from spectroscopic data. The 2,2-dimethylbutane also had been measured in the preliminary apparatus and therefore served as a check between the two.

Purification of Materials.—The carbon tetrachloride and n-pentane came from commercial sources. After drying, the former appeared very pure on fractionation in a column of about 20-plate efficiency, and the middle cut was used. The n-pentane was first purified by crystallizing fractionally onto a copper coil through which liquid or cold gaseous air was passed. About 40% of the starting material was crystallized in all. This good fraction was then washed with concentrated sulfuric acid until no further reaction was apparent and then fractionally distilled. Over 90% distilled within 0.1°, the middle 60% being taken for the experiments.

The 2,2-dimethylbutane was a combination of two samples: one received from the Standard Oil Company of California, the other from Dr. F. D. Rossini of the National Bureau of Standards. Freezing point measurements indicated a purity of about 99%. Since the boiling point is very constant it seems that the impurity must be extremely similar. Very probably its effect on the heat capacity is less than the calorimetric error.

Heat Capacity Measurements.—Table I contains the results of these heat capacity measurements, together with one value for 2,2-dimethylbutane obtained with the older calorimeter. The gas imperfection corrections were calculated on the assumption of Berthelot's equation of state $(C_p - C_p^0 = 81RPT_c^3/32P_cT^3)$. No values of the critical temperature and pressure for 2,2-dimethylbutane were found in the literature, the values 490°K. and 30 atm. being assumed. Since the corrections are quite small these estimates can-

TABLE I

EXPERIMENTAL HEAT CAPACITIES OF GASEOUS CARBON TETRACHLORIDE, n-PENTANE, AND 2,2-DIMETHYLBUTANE

Units are cal. per degree per mole.

Substance	T, °K.	C_p (1 atm.)	$(C_p - C_p^0)$	C
CCl$_4$	380	22.05 ± 0.1	0.38	21.67
CCl$_4$	426	22.42 ± .1	.25	22.17
n-C$_5$H$_{12}$	331	31.71 ± .1	.45	31.26
n-C$_5$H$_{12}$	373	34.7 ± .2	.3	34.4
n-C$_5$H$_{12}$	427	38.2 ± .2	.2	38.0
(CH$_3$)$_3$C-C$_2$H$_5$	361	40.8 ± .2	.4	40.4
(CH$_3$)$_3$C-C$_2$H$_5$	391	42.9 ± .2	.3	42.6
(CH$_3$)$_3$C-C$_2$H$_5$	448	48.0 ± .4	.2	47.8
(with old calorimeter)				
(CH$_3$)$_3$C-C$_2$H$_5$	417	44.7 ± .5	0.2	44.5

not lead to serious error. Figure 3 shows these results, together with the curve for carbon tetrachloride from the statistical calculations of Vold.[3] The agreement on carbon tetrachloride is evidently perfect. One must consider that Vold used frequencies determined in the liquid, and the approximate rigid rotator–harmonic oscillator formulas. The errors from these two sources should be in opposite directions with a net effect not larger than 1%.
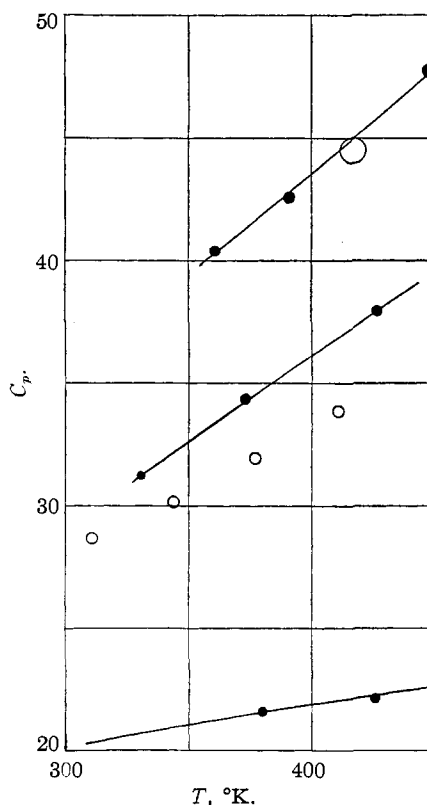

Fig. 3.—Experimental heat capacities of gaseous 2,2-dimethylbutane, n-pentane, and carbon tetrachloride, respectively, from top to bottom. The curve for carbon tetrachloride is one calculated from spectroscopic data. The open circles for n-pentane are from Sage, Webster and Lacey. All other points are from this research.

Also shown in Fig. 3 are the data of Sage, Webster and Lacey[4] on pentane at various temperatures. Bennewitz and Rossner[2] have given the value 34.2 cal. per deg. for pentane at 410°K. The agreement of these data with our results is not good. It is believed that results of this research are much more reliable since this calorimeter is known to give correct, absolute results

(3) R. D. Vold, This JOURNAL, **57**, 1192 (1935).
(4) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 1309 (1937).

for carbon tetrachloride. Both of the other groups of experimenters presented data as merely relative to other substances. It is possible that the errors in their work varied from one substance to another.

Kistiakowsky and Rice,[5] by an independent method, obtained results for propane differing somewhat from Sage, Webster and Lacey's. The writer previously found the heat capacity of n-heptane to differ from Bennewitz and Rossner's value.

Heat of Vaporization Measurements.—Values were also obtained for the heats of vaporization which are listed in Table II. No trend with rate of flow was observed. The only corrections applied were for the buoyancy and air content of the sample bulb. The agreement with the results of others is excellent, except for the value of Bennewitz and Rossner[2] on n-pentane. These authors also give the peculiar boiling point 31.4° for this substance. The heat of vaporization value given for Messerly and Kennedy[6] was obtained from
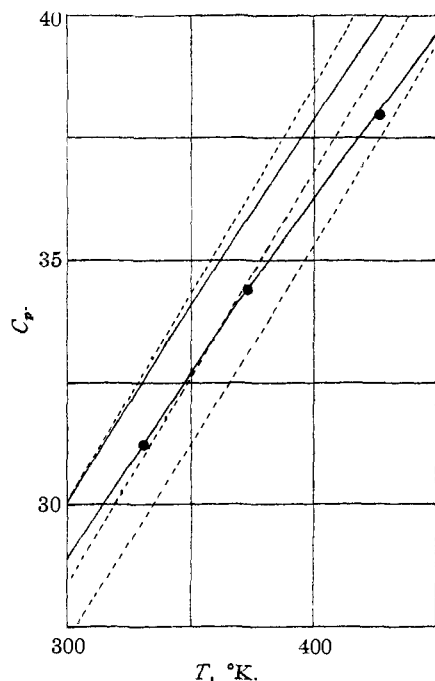

Fig. 4.—A comparison of calculated and experimental heat capacities for gaseous n-pentane. Points are experimental; dotted curves calculated by Messerly and Kennedy using, from the top, respectively, 950, 1050 and 1150 cm.$^{-1}$ for the lower hydrogen bending frequencies; solid curves calculated by the writer with similar variation of hydrogen bending frequencies.

their average calorimetric heat of vaporization at 293.5°K. by the use of the value -11.2 cal. per deg. for $(C_{p(\text{gas})} - C_{p(\text{liq.})})$. This last value is obtained from their liquid heat capacities and our values for the gas.

TABLE II

THE HEATS OF VAPORIZATION OF CARBON TETRACHLORIDE, n-PENTANE, AND 2,2-DIMETHYLBUTANE

Substance	T, °K.	Rate, moles/min.	ΔH^0, cal./mole
CCl₄	349.8	0.3414	7180
		.2471	7160
		.1549	7168
	This research, selected value		7170 ± 20
	Mathews[7]		7161
n-C₅H₁₂	309.1	0.1385	6160 ± 20
		(2 measurements)	
	Messerly and Kennedy[6]		6148
	(corr. see text)		
	Sage, Evans, and Lacey[8]		6161
	Bennewitz and Rossner[2]		6060
(CH₃)₃C–C₂H₅	422.8	.1022	6357
		.1881	6357
	(from old calorimeter)		6350 ± 30
	Selected value, this research		6355 ± 20

The results from the old calorimeter on both the heat capacity and heat of vaporization of 2,2-dimethylbutane are in good agreement with the new values. This, of course, lends support to the other results from the old apparatus on n-heptane and 2,2,4- and 2,3,4-trimethylpentanes.

Discussion

n-**Pentane.**—Two statistical calculations have been made for n-pentane, one by Messerly and Kennedy[6] and one by the writer.[9] Both give the correct entropy for n-pentane at 298°K. Figure 4 shows the curves calculated by the two methods. Messerly and Kennedy's curves were obtained for a range of values for the lower group of hydrogen bending frequencies and 1455 cm.$^{-1}$ for the higher group. Although the experimental points are never very far from their curve with 1050 cm.$^{-1}$ for this lower group of frequencies, nevertheless the measured points cross this curve so definitely that one cannot consider the agreement completely satisfactory. The writer,[9] in his statistical calculations, used 1000 and 1400 cm.$^{-1}$ for these groups of frequencies. The curve obtained is definitely too high. However, if we change the lower group

(5) G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940).

(6) G. H. Messerly and R. M. Kennedy, THIS JOURNAL, **62**, 2988 (1940).

(7) J. H. Mathews *ibid.*, **48**, 562 (1926).

(8) B. H. Sage, H. D. Evans, and W. N. Lacey, *Ind. Eng. Chem.*, **31**, 763 (1939).

(9) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); see also K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

arbitrarily to 1090 cm.$^{-1}$ and the upper group to Messerly and Kennedy's value of 1455 cm.$^{-1}$, we obtain a curve which passes almost exactly through the measured points.

With one of the statistical treatments showing such superiority, it becomes a matter of interest to find the essential difference in terms of the molecular structures assumed. Although there are many minor differences, the critical point is dependence of potential energy on skeletal internal rotation, *i. e.*, rotation about the two central bonds. Here Messerly and Kennedy assume, following earlier work on n-butane,[10,11] that all potential minima are of the same depth. They then determine the torsional frequencies, and thereby the potential barriers, by making the calculated entropy agree with the experimental value.

However, the writer classified these potential minima as of different depths, but in terms of a single parameter. This parameter, a, was defined as the difference in energy between the potential minima in n-butane. Here the "straight," or planar, *trans* form is presumably of lowest energy. The optically isomeric forms obtained by 120° rotation in either direction are then assigned an energy a cal./mole higher because of repulsion of the methyl groups. This treatment was applied not only to butane and pentane but to all n-paraffins through octane, classifying all positions in terms of this one parameter. Then, a and the potential barrier height, V_0, were evaluated from the entropies of n-butane and n-heptane, obtaining 800 and 3600 cal. per mole, respectively. At that time the entropy of n-pentane was known only very approximately. The calculated value at 298.1°K., 83.27 cal. per degree, agrees very well with the new experimental value of Messerly and Kennedy, 83.13 ± 0.2.

One may regard the distribution of molecules among these various potential minima of different depths, as leading to a heat capacity term. This term is, of course, zero in the Messerly and Kennedy calculations, but is 0.65 cal. per degree at 298°K. in the writer's treatment and decreases with rising temperature. Also, the heat capacity of internal rotation for a 3600 cal. per mole barrier is highest at about 350°K., while for the 16,000 cal. per mole barrier used by Messerly and Kennedy it is rising slowly but steadily through

(10) J. G. Aston and G. H. Messerly, THIS JOURNAL, **62**, 1917 (1940).

(11) K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

the entire range of interest. Both of these effects serve to decrease the slope of the writer's curve as compared to Messerly's.

In addition to fitting the gas heat capacity better, the molecular structure assumed by the writer seems more plausible than a 30,000 cal. per mole barrier in butane and 16,000 cal. per mole barrier in pentane.

2,2-Dimethylbutane.—The only statistical calculations for this substance are the relatively crude ones made by the writer[9] for all the simpler branched chain paraffins. These results deviate from the experimental values by a moderate amount, just as for n-pentane. Probably they could be brought into agreement by similar changes in vibration frequencies.

Measurements are now in progress in this Laboratory which will lead to an accurate entropy of 2,2-dimethylbutane. It seems best to postpone any revisions of the statistical calculations for this substance until the entropy value is available.

General Equations for the Paraffins.—The modifications in the hydrogen bending frequencies, suggested above, are reasonably satisfactory in view of spectroscopic data. Furthermore, their contribution to entropies at room temperature is small, so that only slight modifications are needed there. Nevertheless, it seems best to postpone a general revision of the thermodynamic functions for even the normal paraffins until an essentially final set of values can be given. For the calculation of equilibria, the old values are still quite satisfactory since the effect of these changes is very small. For calculations using the heat capacity directly, the following empirical equation has been derived which should serve reasonably well.

$$C_p^0 = 5.65n - 0.62 + t(0.0111n + 0.0158) \quad (1)$$

where n is the number of carbon atoms and t is in degrees centigrade. This equation appears to apply to any paraffin hydrocarbon above ethane, whether branched or not, and even fits the ethane data fairly well. The accuracy can be judged best from Fig. 5. Above 450°K. the errors may increase to several per cent. As nearly as one can judge at present from the statistical data, the equation is not grossly in error even at 1000°K.

The data shown in Fig. 5 for ethane and propane are from the work of Kistiakowsky and Rice.[5,12] All other data are from this research

(12) G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **7**, 281 (1939).

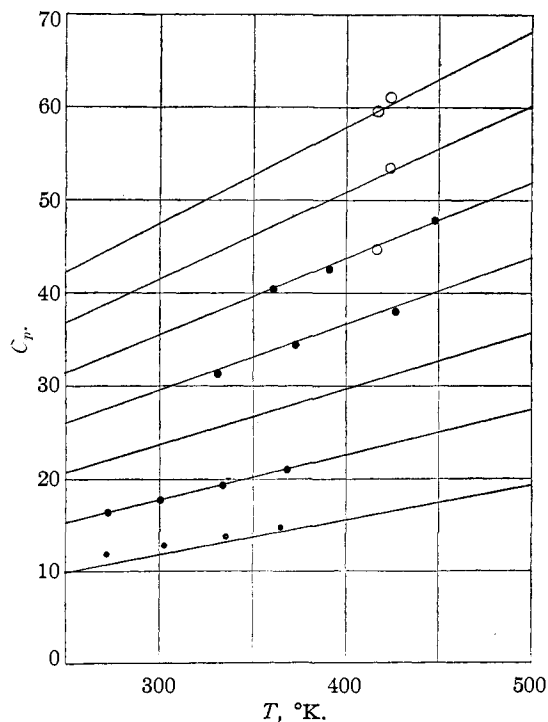or from the preliminary values already published by the writer.

Fig. 5.—A comparison of equation 1 with the experimental values for various paraffins. The curves and points are for octanes, heptanes, - - - - -, and ethane from top to bottom.

The writer acknowledges the assistance of Mr. William D. Gwinn in the construction of the calorimeter. It is also a pleasure to thank Dr. F. D. Rossini of the National Bureau of Standards, and Dr. William Claussen of the Standard Oil Co. of California, for arranging loans of samples of 2,2-dimethylbutane.

Summary

A description is given of a calorimeter of the flow type which measures both the heat capacity of the gas and the heat of vaporization. In this calorimeter the liquid is continuously vaporized electrically and, after passing the heat capacity unit, is condensed, brought to the boiling point, and returned to the vaporizing unit. The rate of flow, and thereby the heat of vaporization, is measured by diverting the gas flow into a separate condenser and sample bulb for an accurately timed interval. The heat capacity unit consists of a thermally insulated tube containing in order, one platinum resistance thermometer, an electrical heater, and two more platinum resistance thermometers. Corrections for heat loss along the tube can then be made either on the basis of the difference between the last two thermometers, or on the variation of apparent heat capacity with rate of flow. Results are obtained which agree with the statistically calculated heat capacity of carbon tetrachloride vapor. Measurements are reported for the heat of vaporization of n-pentane and 2,2-dimethylbutane, and for the heat capacities of these vapors from their boiling points to about 450°K. Literature values for n-pentane agree with these results for the heat of vaporization, but not for the vapor heat capacities.

The two statistical calculations previously published for n-pentane are compared with these heat capacity data. This shows that the 3600 cal. per mole potential barrier to internal rotation proposed by the writer is much more nearly correct than the 16,000 cal. value proposed by Messerly and Kennedy. Similarly, for n-butane, the true barrier is probably much nearer 3600 than the 30,000 value proposed by Aston and Messerly.

It is found that the equation $C_p = 5.65n - 0.62 + t(0.0111n + 0.0158)$ fits the available data for all gaseous paraffins above ethane, both normal and branched. This equation should be useful for many practical calculations.