concentration of 1:6, and thereafter a slight decrease. Similar behavior has been observed in solutions of zinc chloride[2b] and hydrogen chloride.[13]

If the relative intensity of the two components of the band can be taken as a measure of the extent of inter-molecular association in water, then water in a 3.7 M solution of potassium thiocyanate at 25° has a structural temperature around 60°, and in a 9.3 M solution over 100°. This striking effect of potassium ion and thiocyanate ion on the structure of water is in conformity with the low hydration of both ions and the resulting far extending ion-fields, as discussed by Ulich.[14]

Acknowledgment.—The author wishes to express his thanks to the China Institute in America, New York, for a scholarship covering the period during which the work here reported was carried out.

Summary

The Raman spectra of aqueous solutions of potassium thiocyanate and of pure water at various concentrations and temperatures have been described. The results show a great increase in the structural temperature of water in potassium thiocyanate solutions caused by the perturbing ionic field created by the solute.

MADISON, WISCONSIN RECEIVED JUNE 29, 1946

[13] L. Ochs, J. Guéron and M. Magat, *J. phys. radium*, (8) **1**, 85 (1940).

[14] H. Ulich, *Angew. Chem.*, **49**, 279 (1936).

[CONTRIBUTION FROM BUREAU OF MINES, PETROLEUM EXPERIMENT STATION]

An Improved Flow Calorimeter. Experimental Vapor Heat Capacities and Heats of Vaporization of *n*-Heptane and 2,2,3-Trimethylbutane[1]

BY GUY WADDINGTON,[2] SAMUEL S. TODD[3] AND HUGH M. HUFFMAN[4]

Introduction

The dearth of reliable heat capacity values for vapors has been emphasized in recent years by the increasing need of the petroleum and allied industries for such information. Theoretical and quasi-theoretical calculations of heat capacities and other thermodynamic quantities from spectral data, by the methods of statistical mechanics, have done much to supplement and to extend existing experimental data. However, as the accuracy and self-consistency of thermodynamic values ultimately rest upon the quality of the available experimental evidence, it is evident that additional accurate measurements are desirable.

To fill this need, the Petroleum and Natural Gas Division of the Bureau of Mines, U.S. Department of the Interior, has instituted, as part of its thermodynamic research program, a project for the development and application of accurate methods for determining heat capacities of hydrocarbon vapors and their derivatives. This paper describes the apparatus and experimental procedure now in use and also presents molal heat capacities and heats of vaporization for *n*-heptane and 2,2,3-trimethylbutane.

Modified versions of Swann's[5] continuous flow method have given good results in the hands of careful experimenters. Of the early work, that of Scheel and Heuse[6] and of Osborne,[7] *et al.*, may be mentioned, while recent contributors in this field include De Vries,[8] Felsing,[9] Pitzer[10] and Scott[11] and their co-workers.

The method used by Osborne[7] and by Scott[11] reduced losses to a minimum by creating nearly adiabatic conditions in the calorimeter, while the others involved heat-loss corrections obtained from measurements at several flow rates. In this Laboratory the design due to Pitzer[10] was used as a starting point for the following reasons: (1) the heat losses may be made small and can be corrected for by a linear relationship if all important variables are taken into account; (2) it is well-adapted to the study of compounds the boiling points of which are above room temperature; (3) it permits the incorporation of changes of design and operating procedure, which may lead to improvements in precision.

Very briefly, the method consists of passing a measured constant flow of vapor, generated by electrical evaporation in a cycling vaporizer, through a calorimeter in which the vapor is heated electrically by a measured and constant power input. The apparent heat capacity $C_{p\text{obs.}}$ is given by $E/F\ \Delta T$, where ΔT is the temperature increase produced when E units of energy per unit of time are imparted to a vapor flowing at a rate of F moles per unit of time. The experi-

---

[1] Published by permission of the Director of the Bureau of Mines, U. S. Dept. of the Interior. Not copyrighted.

[2] Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[3] Associate Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[4] Principal Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[5] Swann, *Proc. Roy. Soc.* (London), **82A**, 147 (1909).

[6] K. Scheel and W. Heuse, *Ann. Physik*, [4] **37**, 79 (1912).

[7] N. S. Osborne, H. F. Stimson and T. S. Sligh, *Natl. Bur. Standards Sci. Technol. Papers*, **20**, 119 (1925).

[8] James B. Montgomery and Thomas De Vries, THIS JOURNAL, **64**, 2372 (1942).

[9] Benjamin P. Dailey with W. A. Felsing, *ibid.*, **65**, 42 (1943).

[10] Kenneth S. Pitzer, *ibid.*, **63**, 2413 (1941).

[11] Russell B. Scott and Jane W. Mellors, *J. Research Natl. Bur. Standards*, **34**, 243 (1945).

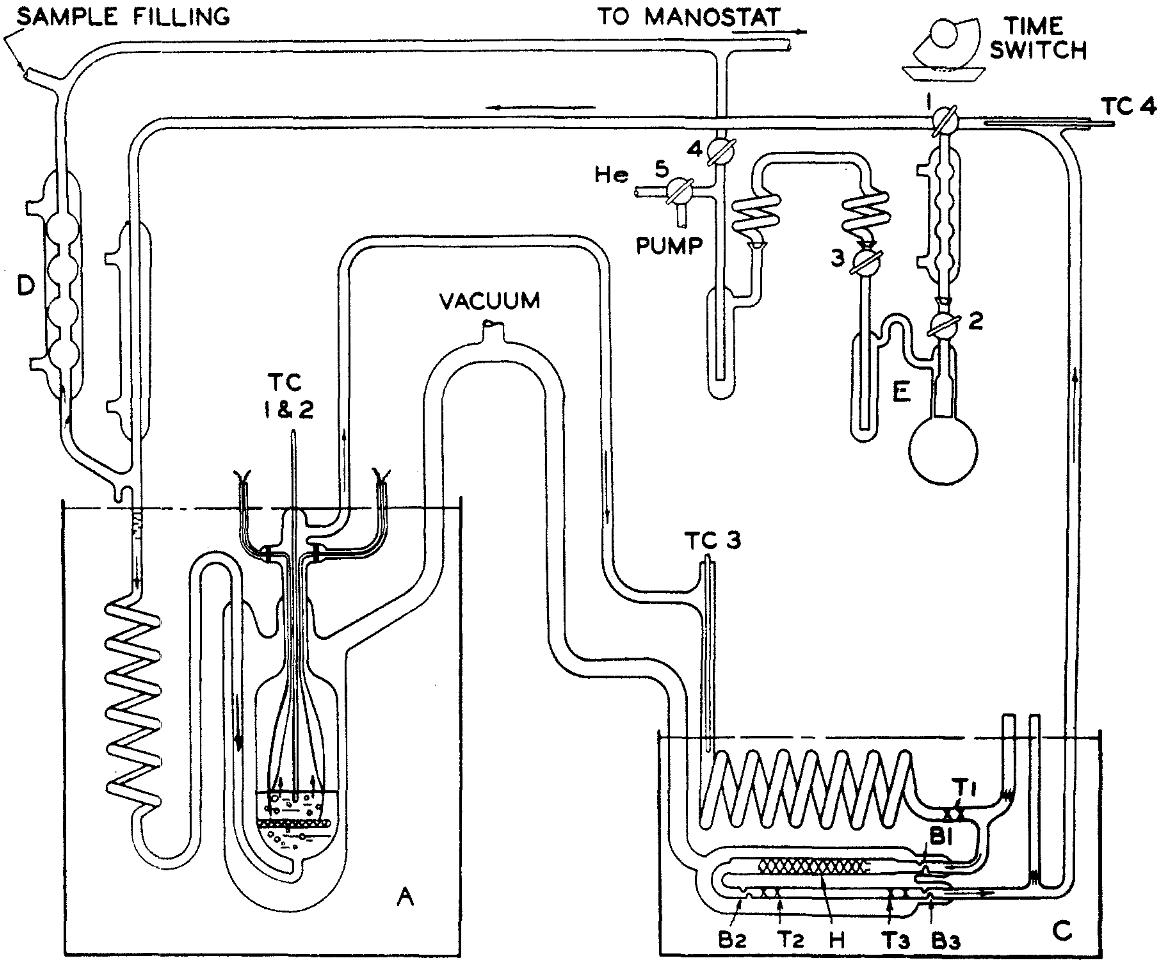

Fig. 1.—Essential features of the apparatus for measuring heats of vaporization and the heat capacities of vapors.

mental data are precisely represented by the relationship $C_{p_{\text{obs.}}} = C_p + k/F$ where C_p is the true heat capacity. Hence a plot of $C_{p_{\text{obs.}}}$ *vs.* $1/F$ extrapolated to zero value of $1/F$ gives the correct value of C_p. The fact that the experimental points of the present work deviate on the average from a straight line by less than ± 0.05% is convincing evidence for the validity of the correction for heat losses. The design of the apparatus used in the present work is such that the precision of the measured heat capacities is within ± 0.1%.

Experimental

Apparatus.—The construction and operation of the calorimetric system may be followed by reference to Fig. 1. For simplicity certain parts are omitted. The main features are: (1) the cycling vaporizer A, contained in a constant-temperature bath; (2) the calorimeter C situated in a second thermostated bath; (3) the flow-calibration system E.

Hydrocarbon vapors are produced at a steady rate by boiling 150 to 250 ml. of the liquid hydrocarbon in the vacuum-jacketed vaporizer A with electrical energy from storage batteries. The heater is an 11-ohm helix of no. 24 AWG manganin wire with double glass-fiber insulation. The wire is close-wound on a glass spiral made from 4-mm. Pyrex rod fused to the wall of the boiling vessel, which is cylindrical and has a length of 20 cm. and a diameter of 6 cm. Current and potential leads of no. 20 and no. 24 AWG silver wire, respectively, are taken from the heater at points below the surface of the liquid hydrocarbon and leave the vaporizer at the top, through tungsten seals, under the surface of the bath liquid from which they are isolated by small glass tubing. The hydrocarbon vapor, prevented from condensing by electrically heated flow lines, after flowing through the calorimeter C, is condensed, brought up to the bath temperature by flowing through a long helix and returned to the vaporizer. Heat exchange between the vaporizer and its environment is negligible when the bath, which is controlled to better than ± 0.003°, is maintained at a temperature about 0.2° higher than the temperature of the boiling hydrocarbon and when a pressure of less than 10^{-5} mm. is maintained in the silvered jacket space. The temperature difference between the bath and the boiling liquid or vapor is measured by the copper–constantan difference couple, TC_1, which can be placed at any depth in the deep thermocouple-well shown. Another copper–constantan couple, TC_2, indicates the boiling temperature of the liquid, and a platinum resistance thermometer is used to measure the bath temperature.

Adjusting the relative flow of water in the two condensers, so that a small fraction of the total condensation occurs in condenser D, returns the liquid to the vaporizer system at near the boiling temperature. Helium is maintained in the rest of the system. Pressure is controlled to better than ± 0.1 mm. (as observed on a mercury manometer and also estimated from small boiling-temperature variations) by having a slow stream of helium continuously entering the system and escaping through a small capillary tube, alternately opened and closed by a soft rubber seat on he movable arm of a relay, actuated by a sulfuric acid manostat[12] mounted in an ice-bath, thus minimizing pressure drifts due to temperature effects. For operation below atmospheric pressure the relay is in a continuously pumped vacuum desiccator.

The flow calorimeter is situated in a second thermostated bath, which is controlled to ± 0.002° at low temperatures and ± 0.005° at high temperatures. The flowing vapor is brought to within ± 2.0° (indicated on copper–constantan difference couple, TC_3) of the bath temperature before it enters the bath, by controlling the heat input to the flow line. It then passes through a helix made from 2 m. of 8-mm. i.d. glass tubing and past the platinum resistance thermometer T_1, which, by comparison with another platinum resistance thermometer (not shown) in the bath itself, gives necessary knowledge of the temperature equilibrium between the rapidly flowing vapor and the bath.

The thin-walled Pyrex U-tube, silvered on the outside, containing the calorimeter heater H and two platinum resistance thermometers T_2 and T_3, is surrounded by a silvered jacket connected to the high-vacuum system. The heater consists of 4 m. of no. 30 AWG Nichrome wire wound in three concentric helices spaced from one another by small glass rods. The two inner helices, in series with one another, are in parallel with the outermost helix giving an effective resistance of about 24 ohms. The unit is spaced from the glass tube, which is 10 mm. i.d. at this point, by a snugly fitting, steep-pitched helix of glass insulated no. 20 AWG copper wire, which also serves as an electrical lead. Bringing the current and potential leads out of the calorimeter *against* the entering vapor stream tends to eliminate conduction losses along the leads. The potential and current leads leave the glass flow line outside of the calorimeter proper through tungsten seals and are isolated from the bath liquid by glass tubing. Electrical energy is supplied to the heater by storage batteries. Baffles B_1 and B_3 minimize radiation losses along the length of the tube, while B_2 helps to mix the gas after heating. Thermometers T_2 and T_3 are isolated from radiation from the heater by being in a separate arm of the U. The current and potential leads from T_2 (in series with T_3), insulated by thin glass tubes, pass lengthwise through the mica cross of T_3 and then, with the potential leads from T_3, are threaded through small holes in mica strips which carry them out of the calorimeter, in the direction of the flowing gas, to hard-soldered connections with tungsten wires sealed through the glass walls.

The temperature of the exit lines is adjusted so that the vapor passes through three-way stopcock 1 at 20° above the boiling temperature of the compound. This stopcock can direct the vapor to the flow calibration system or to the vaporizer. It is specially ground and is lubricated with a thin film of lithium stearate grease,[13] which retains its consistency to at least 100°. The flow calibration unit consists of a condenser, a detachable double trap E for collecting samples for timed intervals, a protective trap and stopcocks 4 and 5. The lubricant used on the ground-glass joint above stopcock 2 is insoluble in hydrocarbons.[14] The stem of stopcock 1 has attached to it a stainless steel sector which dips into a pool of mercury when the stopcock is turned, thus completing the circuit to an electric timer. The time interval, usually five or six minutes, is measured with an estimated accuracy of ± 0.05 sec.

The platinum resistance thermometers are of the coiled-filament strain-free type[15] and have ice-point resistances of about 24 ohms. The five thermometers were compared, at the ice point and at other temperatures covering the range of the experiments, with a platinum resistance thermometer calibrated and certified by the National Bureau of Standards. During calibration the assembled calorimeter was mounted in the thermostated bath and a slow stream of helium was passed over thermometers T_1, T_2 and T_3 to promote thermal homogeneity. From the calibration experiments constants of the Callendar equation were derived for each thermometer. A 1-ma. measuring current is used for the five resistance thermometers connected in series. The power inputs to the vaporizer and calorimeter are determined by measuring the currents through the heaters and the potentials across them. A White double potentiometer, in conjunction with suitable calibrated resistors, standard cell and high-sensitivity galvanometer, is used for all electrical measurements.

---

(12) E. B. Hirshberg and E. H. Huntress, *Ind. Eng. Chem., Anal. Ed.*, **5**, 344 (1933).

(13) I. E. Puddington, THIS JOURNAL, **65**, 990 (1943).

(14) T. P. Sager, *Ind. Eng. Chem., Anal. Ed.*, **4**, 388 (1932).

(15) C. H. Meyers, *Bureau Standards J. Research*, **9**, 807 (1932).

Method of Measurement: (a) Rate of Flow and Heat of Vaporization.—The detachable double trap E, previously evacuated and weighed, is placed in position. Air is pumped from the connecting tubes and helium admitted to the collecting system at a pressure equal to that in the other parts of the apparatus. Then, with the vapor smoothly cycling, stopcocks 2, 3 and 4 open, and suitable cooling agents on all traps, stopcock 1 is turned, starting the electric timer and diverting the hydrocarbon into the receiver for the desired interval. The vaporizer heater potentials and currents are recorded at regular intervals, and the temperature of the issuing vapor is measured on thermocouple TC_2 at the beginning and end of the run. On completion of the collection, the hydrocarbon is frozen with liquid nitrogen and the helium pumped off. The receiver is detached and weighed, using a glass tare of equal volume and calibrated weights. No buoyancy corrections are necessary. The mass collected varied from 25 to 90 g.

The total electrical energy delivered to the vaporizer during the collection period is obtained from the measured time interval and from interpolated mean values of the potential and current. The drift in the power input, from the storage batteries, is always very uniform and during a ten minute period is usually 0.01 to 0.05%. The uncertainty in interpolation is probably less than the absolute accuracy of the energy measurement, which is about 0.02%. Three corrections must be applied to obtain the total energy involved during the vaporization of the collected sample. (1) The boiling temperature, as measured on TC_2, may increase or decrease by as much as 0.05° between the beginning and end of the collection period. The change in the heat of vaporization with temperature may be neglected; but because of the large masses involved, the change in temperature of the liquid and of the glass vessel causes the transfer of significant quantities of heat which can be calculated from the observed change in temperature, the known specific heats, the mass of glass and the average mass of liquid. Since the temperature change is small the expression (heat capacity glass + heat capacity liquid) ΔT gives a sufficiently accurate estimate of the energy to be subtracted from the measured energy. The total correction ranges from 0 to 20 calories per mole. (2) When the hydrocarbon is boiling, a temperature gradient exists between the surface of the liquid and the level of the heater. This gradient depends on the increase of pressure with depth and its value may be calculated from the density of the liquid and vapor pressure data or it may be measured by observations of temperature with TC_2 at different depths in the liquid. When m_1 grams of hydrocarbon are vaporized, the change of state involved is the conversion of m_1 grams of liquid, at the mean temperature of the heater level, into m_1 grams of vapor at the temperature of the surface. This means that the heat of vaporization, as determined at the temperature of the surface, must have a correction applied for the transfer of m_1 grams of liquid from the heater level temperature to the surface temperature. In addition all parts of the wall of the containing vessel decrease in temperature by a uniform amount ΔT_2 determined by the *change* in depth of the liquid above the heater. The form of the correction necessitated by these two depth factors is $m_1C_{p_1}\Delta T_1 + m_2C_{p_2}\Delta T_2$ where m_1, C_{p_1}, m_2 and C_{p_2} refer to the mass and heat capacity of the hydrocarbon and glass involved, respectively, ΔT_1 is the difference between the mean heater-level temperature and the surface temperature and ΔT_2 is the change in wall temperature caused by the change in depth. The first term is the more important. The correction varies from 10 to 35 cal. per mole, depending on the fullness of the vaporizer, the amount removed and the pressure at which the experiment is performed. (3) The current leads inside the vaporizer are insulated with loosely woven fiberglass sleeves which, due to capillarity, are wet by the hydrocarbon. The correction for unmeasured energy in the leads must therefore include both the immersed part and the wet portion of the leads above the surface. The sum of these two parts is constant at a given temperature. The correction is about 25 cal. per mole.

Having applied the three corrections described, the heat of vaporization is calculated from the relationship $\Delta H_v = Q(1 - v/V),/M$ where Q is the corrected energy delivered to the vaporizer while M moles are being collected and the factor $(1-(v/V))$ makes allowance for the fact that the space vacated by the evaporating liquid becomes filled with vapor which is not condensed and weighed. The molal volume of the vapor V may be obtained with sufficient accuracy from the Berthelot equation and v, the molal volume of the liquid, is derivable from density data.

To illustrate the combined effect of the corrections applied the data given for *n*-heptane at 58.06° (see Table I) would have a precision of ± 30 cal. per mole with no corrections applied instead of the ± 2 cal. per mole reported. The precision indicated is a measure of the extreme range of the measured values. The apparent heat capacities determined during flow-calibration experiments check to within 0.05% of those determined under normal conditions when the hydrocarbon cycles and the liquid level in the vaporizer remain constant. This is good evidence for the validity of special corrections made during the flow measurement. Once proportionality between power input and mass rate of flow has been established for a given boiling temperature, a determination of power input provides a measure of flow rate. Experiments show this direct proportionality to be independent of flow rate and of the duration of the flow measurement if the boiling temperature is kept the same at the different rates of flow.

(b) Heat Capacity Measurements.—Apparent heat capacities are determined at four or more flow rates from observations of the temperature increase produced by a measured power input to the calorimeter heater. Resistance thermometers T_2 and T_3 give independent values of the apparent heat capacity at each flow rate. A plot of these values against the reciprocal of the flow rate is linear, the mean deviation from linearity in this work being about ± 0.05% (see Fig. 2). Extrapolation to zero value of the reciprocal corrects for the heat losses which even at the highest temperature and lowest flow rate are less than 2%.

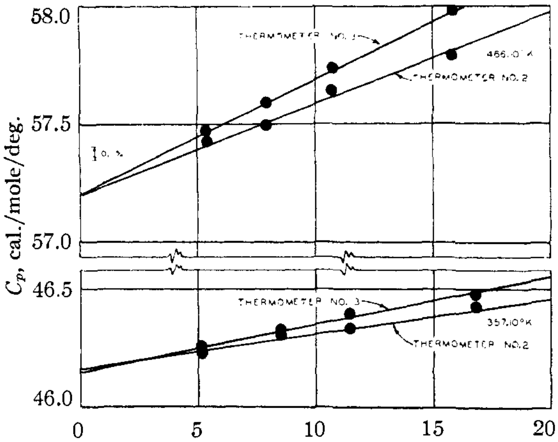

Fig. 2.—The apparent heat capacity of *n*-heptane as a function of flow rate.

Actual measurements are made by observing temperatures on resistance thermometers T_1, T_2 and T_3 with vapor flowing but *before* heating the vapor and then repeating all observations *after* the measured power input to the calorimeter has had enough time to bring the entire calorimeter to a steady state. The time required to attain a steady state is 3 to 15 minutes, depending on the flow rates, which range from 0.05 to 0.25 mole per minute. The temperature of the bath is measured with a resistance thermometer at the beginning and end of the experiment. The reading of each thermometer is recorded at regular intervals during the experimental period. Thermometer readings on T_2 and T_3 are made at fifteen-second intervals over a four-minute period and the results averaged. The range of the readings caused by slight irregularities in flow rate, is ±0.003 to ±0.008 deg. Small thermal effects in the thermometer circuit, caused by thermal gradients in the heated vapor after it leaves the calorimeter, are measured with no current flowing through the thermometers and appropriate corrections are applied to the observed temperatures. The actual temperature increments produced by the measured power input are then obtained from the final and initial temperatures observed on thermometers T_2 and T_3 (*i.e.*, T_2 final–T_2 initial). A small correction is applied if the mean bath temperature drifts during the measurements. Only *one* thermometer enters significantly into the determination of an individual ΔT value, thus tending to eliminate errors due to differences in thermometer calibrations and to Joule–Thompson cooling caused by the pressure drop through the calorimeter. Under conditions of low temperature, low pressure and high flow rate, the latter effect would cause significant errors. Over the 8° temperature rise used in practice, the temperature coefficient of the Joule–Thompson cooling is such as to introduce an effect of measurable magnitude under some conditions but an adequate correction is applied. Experiments have shown that the apparent heat capacities are independent of the magnitude of the ΔT used, provided the *mean* temperature of a series of measurements is the same.

From the previously determined relationship between power input to the vaporizer and mass of vapor flowing the flow rate is determined by a measurement of power supplied to the vaporizer. Small corrections are applied for the energy generated in the immersed portion of the current leads and for the fact that the liquid returned to the vaporizer carries some heat with it due to its being superheated by approximately 0.2°.

The calorimeter power input is corrected for the unmeasured energy generated in the leads at the entrance to the calorimeter. Experiments have shown this effect to be about 0.03% of the total.

During a given series of experiments the temperature and hence the pressure in the vaporizer are brought to a chosen value by adjusting the controlled helium pressure at each flow rate. Over the range of flow rates and pressures studied, the pressure drop between the vaporizer and the condensers varied from 1 to 35 mm., being at a maximum for the highest flow rate and lowest operating pressure. From the geometry of the system and a knowledge of the total pressure drop the actual pressure in the calorimeter can be closely estimated. When this pressure differs significantly from the pressure in the vaporizer, a correction is applied to the measured heat capacity to make its value correspond to the vaporizer pressure. This correction involves a measured value of $(\Delta C_p/\Delta p)_T$ and the pressure drop between the vaporizer and the calorimeter. Its maximum value is 0.1%.

Heat capacity values calculated from data obtained with thermometers T_2 and T_3 agree on the average to within 0.05% when operating conditions are closely controlled.

Materials.—The *n*-heptane, obtained from a commercial source, was distilled in a 77-plate column at about 3 cc. per hour at a reflux ratio of about 400:1. From its melting point curve the sample was found to have a purity of 99.97 mole per cent., assuming the impurity to be liquid-soluble, solid-insoluble; it had the constants d^{20}_4 0.6837; n^{20}D 1.3877.

The 2,2,3-trimethylbutane, obtained from General Motors Corp., was distilled similarly to the n-heptane. A melting-point analysis by the National Bureau of Standards showed its purity to be 99.69 mole per cent. Its density and refractive index were: d^{20}_4 0.6900, n^{20}D 1.3894. The most probable impurity, 2,4-dimethylpentane, since it is isomeric with triptane, would have a negligible effect on the measured heat capacities.

Heats of Vaporization.—If corrections are made for all energy exchanges, flow calibration experiments will yield accurate values of heats of vaporization, provided the boiling gives an essentially dry vapor. The absence of spray was suggested by the fact that the heat of vaporization was not affected by change of flow rate or by the presence or absence of a glass-wool spray trap.

Pitzer,[10] using the same method on other compounds, obtained reasonable agreement with literature values of heats of vaporization. The precision of the present work is higher than that reported by Pitzer, but literature values suitable for checking accuracy are not available at any of the temperatures studied. Table I gives the results of six separate measurements of the rate of flow and the corresponding heats of vaporization for 2,2,3-trimethylbutane at 80.80°. The other heats of vaporization given in the table are the average values of 3 to 6 determinations. The corrections outlined earlier in this paper were applied systematically. The *precision* is approximately ± 0.1%. However, pending further studies, the *accuracy* is tentatively estimated as ± 0.3%.[15a]

TABLE I

THE HEATS OF VAPORIZATION OF 2,2,3-TRIMETHYLBUTANE AND n-HEPTANE

1 cal. = 4.1833 int. joules; at. wt. carbon = 12.01; at. wt. hydrogen = 1.008.

p, mm.	T, °C.	Flow moles/min.	ΔH_v cal./mole	ΔH_v Clapeyron
		2,2,3-Trimethylbutane		
758.4	80.80	0.056	6912	
		.068	6921	
		.069	6914	
		.103	6918	
		.226	6918	
		.228	6924	
		Mean	6918 ± 6	
195.7	40.68	6 expts.	7461 ± 4	
		n-Heptane		
597.7	90.48	3 expts.	7715 ± 2	7734
391.2	77.33	3 expts.	7938 ± 5	7945
195.2	58.06	4 expts.	8244 ± 2	8245

The Clausius–Clapeyron equation $\Delta H_v = T\Delta V\ (\mathrm{d}p/\mathrm{d}t)$ may be used to calculate heats of vaporization if accurate values of vapor pressures and molal volumes of vapor and liquid are available. Experimental evidence obtained in heat capacity measurements at different pressures indicates that the gas imperfection predicted by the Berthelot equation is too small for the compounds studied in the temperature range of interest, hence it has not been used here to obtain the molal volume of the vapor. In the case of n-heptane parameters[16] of the Kellogg equation[17] were available and have been used to calculate molal volumes of the vapor which when combined with molal volumes of the liquid and $\mathrm{d}p/\mathrm{d}t$ derived from vapor pressure data[18] yield the heats of vaporization given in the last column of Table I which agree with experiment to better than 0.3%. The same method of calculation applied to propane, n-butane and n-pentane gives similar agreement with literature values of the heats of vaporization. If systematic errors in the heats of vaporization should be present, these may have no effect on the accuracy of the heat capacities since it is only necessary to establish a *proportionality* between mass of vapor passing through the calorimeter per unit of time and electrical power supplied to the vaporizer.

Experimental Heat Capacities.—Table II gives values of the heat capacities of n-heptane and 2,2,3-trimethylbutane at the temperatures and pressures studied. In obtaining $(\Delta C_p/\Delta p)_T$ values from determinations at one temperature and two or more pressures constant absolute errors in C_p will cancel. For this reason results are reported to the nearest 0.005 cal./deg./mole since the precision of the results suggests that

TABLE II

EXPERIMENTAL HEAT CAPACITIES, CAL./DEG./MOLE

1 cal. = 4.1833 int. joules; at. wt. carbon = 12.01; at. wt. hydrogen = 1.008.

			n-Heptane			
T°, K.→	357.10	373.15	400.40	434.35	466.10	
P, mm.						
195.5	46.140	47.805	50.555	53.965	57.075	
391.2	46.515	48.095				
597.7		48.410	50.930	54.200	57.215	
			2,2,3-Trimethylbutane			
T°, K.→	328.80	348.85	369.20	400.40	434.30	461.80
P, mm.						
195.7	43.085	45.345	47.585	51.020	54.615	
758.4			48.130	51.315	54.815	57.515

[15a] Since the writing of this paper a measurement of the heat of vaporization of benzene has been made at 80.10°. The mean of three experiments is 7,348 ± 2 cal./mole which is within 0.07% of the reliable value 7,353 cal./mole derived from the work of Fiock, Ginnings and Holton, *J. Research Natl. Bureau of Standards*, **6**, 881 (1931). This result suggests that the accuracy of the heats of vaporization reported for n-heptane and 2,2,3-trimethylbutane may be in the neighborhood of ±0.1%.

[16] Unpublished values derived from the experimental work of Smith, Beattie and Kay (see ref. 22) were courteously supplied by the M. W. Kellogg Co.

[17] M. Benedict, G. B. Webb and L. C. Rubin, *J. Chem. Phys.*, **8**, 334 (1940).

[18] A. P. I. Research Project at the National Bureau of Standards. "Selected Values of Properties of Hydrocarbons," Table 2k (Part 2), paraffins C_7, dated May 31, 1944.

differences between measured heat capacities may possess higher accuracy than the quantities from which they are derived.

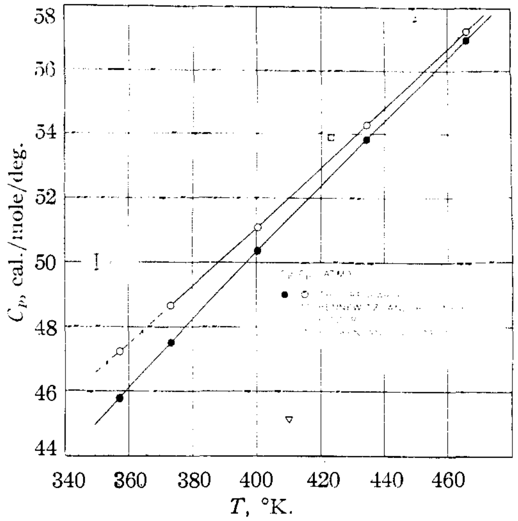

Fig. 3.—The heat capacity of *n*-heptane. The lower curve is for the ideal gas state and the upper curve for 1 atm. pressure. The dashed portion is not experimentally realizable.

The upper curve of Fig. 3 shows values for *n*-heptane of C_p^1, the heat capacity of the vapor at 1 atmosphere pressure, as a function of temperature. Comparison with the work of others shows Pitzer's[19] one experimental point at 423°K. to be about 1% higher while Eucken and Sarstedt[20] using a quite different variation of the flow method report a value at 450°K. more than 3% higher than the results reported here. Bennewitz and Rossner's[21] value at 410°K. is about 10% lower than that found in the present work.

Correction for Gas Imperfection.—C_p^0, the heat capacity of the vapor in the ideal state, is usually obtained from the experimental data by application of the relationship $C_p - C_p^0 = -T\int_0^p (\partial^2 v/\partial T^2)_p \, dp$ or other equivalent thermodynamic equations. Frequently the second derivative has been evaluated from the Berthelot equation of state. This procedure may be adequate for simple molecules, since for them the correction is small, but in the present work with C_7 molecules it became evident that either an accurate equation of state would be necessary for each compound studied or that another method of making the correction should be used if the C_p^0 values were to retain the accuracy of the experimental data. By experimentally determining the heat capacities at two or more pressures at the same temperature, and plotting C_p *vs.* p, a linear extrapolation to zero pressure may be made, thus giving C_p^0 and $(\Delta C_p/\Delta p)_T$ without recourse to any equation of state. This was done at all temperatures for *n*-heptane and at three temperatures for 2,2,3-trimethylbutane. The linearity of the three *n*-heptane points at 373.15°K. is considerably better than the precision of the heat capacity measurements (±0.1%) from which it is inferred that the use of only two pressures at the other temperatures will not lead to serious error.

TABLE III

HEAT CAPACITIES IN THE IDEAL GAS STATE

CAL./DEG./MOLE

1 cal. = 4.1833 int. joules; at. wt. carbon = 12.01; at. wt. hydrogen = 1.008

			$C_p^1 - C_p^0$ cal./deg./mole/atm.			
T, ° K.	C_p^1	C_p^0	Expt.	Berthelot	Beattie–Bridgman	Kellogg
			n-Heptane			
357.10	47.22	45.77	1.45	0.65	0.32	1.28
373.15	48.66	47.51	1.15	.57	.29	1.06
400.40	51.08	50.37	.71	.46	.25	.79
434.35	54.30	53.85	.45	.36	.20	.57
466.10	57.27	57.00	.27	.29	.17	.42
			2,2,3-Trimethylbutane			
328.80	44.08	42.74	(1.34)	0.71		
348.85	46.07	45.09	(.98)	.60		
369.20	48.13	47.39	.74	.50		
400.40	51.32	50.92	.40	.40		
434.30	54.82	54.54	.28	.31		
461.80	57.52	57.36	(.16)	.26		

Table III gives values of C_p^1, C_p^0 and C_p^1 and $C_p^1 - C_p^0$ for *n*-heptane and 2,2,3-trimethylbutane. C_p^0 and C_p^1 were obtained by use of the experimental values of $(\Delta C_p/\Delta p)_T$. Since the values of $C_p^1 - C_p^0$ obtained experimentally are considerably larger than those predicted by the Berthelot equation of state, it becomes of interest to examine results obtained from equations of state based on experimental data. This is possible for *n*-heptane since parameters of the Beattie–Bridgman[22] and Kellogg[16] equations have been evaluated for this compound. The Berthelot equation results were obtained from the relationship $C_p^1 - C_p^0 = 81RT_c^3P/32P_cT^3$ using 540.17°K. and 27.00 atm. for the critical temperature and pressure of *n*-heptane[23] while for 2,2,3-trimethylbutane 531.5°K. and 29.75 atm.[24] were used.

The Beattie–Bridgman correction utilized the approximate relationship[25]

$$C_p^1 - C_p^0 = \frac{2A_0}{RT^2} + \frac{12c}{T^4}$$

The Kellogg[16,17] equation was used in the suffi-

---

(19) Kenneth S. Pitzer, THIS JOURNAL, **62**, 1224 (1940).

(20) A. Eucken and B. Sarstedt, *Z. physik. Chem.*, **B50**, 143 (1941).

(21) K. Bennewitz and W. Rossner, *ibid.*, **B39**, 126 (1938).

(22) L. B. Smith, J. A. Beattie and W. C. Kay, THIS JOURNAL, **59**, 1587 (1937).

(23) J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1936).

(24) Graham Edgar and George Calingaert, *ibid.*, **51**, 1540 (1929).

(25) J. A. Beattie, *Phys. Rev.*, **34**, 1615 (1927).

ciently exact form $P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a + c/T^2)\ d^3$. From this equation $C_p^1 - C_p^0$ is readily obtained by use of the thermodynamic relationships

$$C_p - C_v^1 = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p$$

$$C_v^1 - C_v^0 = T\int_{\infty}^{v'}\left(\frac{\partial^2 p}{\partial T^2}\right)_v \mathrm{d}V, \text{ and}$$

$$C_p^0 - C_v^0 = R$$

This procedure avoids the cumbersome second derivative of volume with respect to temperature at constant pressure.

The differences between the results from the three equations suggest that caution should be used in obtaining C_p^0 from experimental data by the use of equations of state, particularly at low temperatures. For n-heptane at 373.15° the error in C_p^0 when the Berthelot equation is used is about 1.3%. The increase of $C_p^1 - C_p^0$ with decrease in temperature is predicted reasonably well by the Kellogg equation but the agreement is not perfect.

Accurate experimental values of $(\Delta C_p/\Delta p)_T$ provide a useful check on the assignment of parameter values in the construction of empirical equations of state. This is particularly true in the low-temperature, low-pressure region where PVT data are not ordinarily available. In addition a knowledge of $(\Delta C_p/\Delta p)_T$ as a function of temperature gives information concerning the temperature dependence of the second virial coefficient since $(\Delta C_p/\Delta p)_T = -T(\partial^2 B/\partial T^2)_P$ where B is defined by $pV = RT + Bp$.

For 2,2,3-trimethylbutane heat capacities were measured at one pressure only at 357.10, 373.15 and 466.10°K. The $C_p^1 - C_p^0$ values (in parentheses in Table III) at these points were obtained by an extrapolation method from the equation $(\Delta C_p/\Delta p)_T = -T(\partial^2 B/\partial T^2)_P$ with B being of the form $B_0 - (A/T) - (C/T^3)$. This type of equation fits the data from both compounds and gives a linear plot of $T^2\ (\Delta C_p/\Delta p)_T$ *vs.* $1/T^2$.

The extrapolated values of $C_p^1 - C_p^0$ obtained from this plot at the temperatures mentioned appear to be only slightly less reliable than measured values at other temperatures.

Discussion

The emphasis in this investigation has been on accuracy. An analysis of the many known variables entering into the measurements indicates that the precision of the results should be in the neighborhood of ±0.1% and this is checked not only by the reproducibility of a given point but by internal consistency of a high order. For example the heat capacities of n-heptane at 373.15°K. and pressures of 195.5, 391.2 and 597.7 mm., when plotted against pressure, deviate from the linearity expected for a low pressure vapor by less than 0.05% even though the measurements involved the determination of three heats of vaporization ranging from 7,715 to 8,244 cal./mole. This precision has been confirmed by other work now in progress. C_p^0 for the two compounds studied may be represented by the empirical equations

n-heptane: $C_p^0 = -0.2365 + 0.14864T - 0.00005583T^2$
2,2,3-trimethyl-
butane: $C_p^0 = 1.800 + 0.153201T - 0.000053907T^2$

All experimentally derived points are fitted by these two curves to ±0.05%. The triptane point at 461.80°K. obtained by the extrapolation method previously described deviates from the equation by 0.16%. The precision of the measurements is such that a clear-cut distinction is made between the heat capacities of the two isomeric compounds.

While the precision of the measurements is satisfactory the question of accuracy must be approached with caution. In the dynamic system employed, it is difficult to be sure that proper corrections have been applied for all variables which influence the final values. In principle the accuracy of the calorimetric measurements can be checked by comparison with statistically calculated values. However, the increasing uncertainties and incompleteness of spectral analysis and the greater gas imperfections as molecular complexity increases make accuracy a matter to be resolved through the accumulation of data, by varying experimental methods in different laboratories, which will possess internal consistency and be consistent with other related thermodynamic quantities which have been determined independently.

Acknowledgment.—We thank Richard M. Gooding of this Laboratory for the distillation and measurement of the physical constants of the two compounds as well as for the estimate of impurity in the n-heptane by the melting point method. We are grateful to F. D. Rossini of the National Bureau of Standards for determining the purity of the 2,2,3-trimethylbutane and to General Motors Corp., which supplied the sample of this compound.

Summary

An improved constant-flow calorimeter for vapors is described. Details involved in the experimental procedure and in the treatment of the data are outlined. Results obtained have a precision of ±0.1%.

The heat capacities of n-heptane and 2,2,3-trimethylbutane have been measured at several pressures over the temperature range 330 to 465°K. From measured values at two or more pressures at the same temperature the heat capacity of the vapor in the ideal state is obtained by linear extrapolation to zero pressure. It is believed that this method of making the correc-

tion for gas imperfection is more accurate than the use of available equations of state.

C_p^0 for the two compounds studied may be represented by the following empirical equations with a mean deviation of less than 0.1%

n-Heptane $C_p^0 = -0.236 + 0.14864T - 0.000055583T^2$

2,2,3-Trimethylbutane: $C_p^0 = 1.800 + 0.15320T - 0.000053907T^2$

The method of measurement also yields precise heats of vaporization. For n-heptane the heats of vaporization reported at 90.48, 77.33 and 58.00° are 7,715, 7,938 and 8,244 cal./mole respectively while for 2,2,3-trimethylbutane the values at 80.80 and 40.68° are 6,918 and 7,461 cal./mole.

BARTLESVILLE, OKLAHOMA RECEIVED AUGUST 8, 1946

[CONTRIBUTION NO. 134 FROM THE GOODYEAR RESEARCH LABORATORY]

Molecular Size Distribution in Three Dimensional Polymers. V. Post-gelation Relationships

BY PAUL J. FLORY

In previous papers[1-4] of this series statistical methods were applied to the structural interpretation of three dimensional polymers, *i.e.*, polymers some of the structural units of which are polyfunctional in the sense that they connect with more than two other neighboring units of the polymer. Critical conditions for the occurrence of gelation were explored, and methods were set forth for computing the extent of reaction at the gel points in condensation processes involving polyfunctional units[1] or in addition polymerizations accompanied (or followed) by cross-linking reactions.[3,4] The theory of gelation resulting from cross-linking was extended by Stockmayer[5] and by Walling.[6]

Gelation occurs in three dimensional condensation polymerizations at somewhat higher extents of reaction than predicted by theory owing to intramolecular condensations[1,7] which are not taken into account by the theory.[8] The discrepancy generally is small, and the essential correctness of the statistical theory is adequately confirmed by the correlation between observed and calculated gel points.

The writer applied the statistically derived molecular size distribution relationships beyond the gel point as well as to polymers which had not been carried to gelation. By appropriately summing over the distribution functions for all *finite* species, it was possible to derive the weight fraction of sol, average molecular weights of the sol, and the concentration of cross linkages in the sol; gel properties were obtained by difference. Stockmayer[9] generalized and extended the size distribution relationships, but was hesitant to apply them beyond the gel point. His criticisms of the writer's efforts in this direction centered upon the approximation[2,3] according to which intramolecular ("cyclic") connections in finite (sol) molecules are neglected while acknowledging that they must be present in the infinite network (gel) structures. On the other hand, the derivation of the size distribution equations applies equally to the sol existing beyond the gel point, or to the polymer preceding gelation.[10] The distribution equations are oblivious of the gel (except by omission), hence the frequent occurrence of intramolecular connections in the gel does not constitute a violation of the basic approximation.

While the logic of this procedure appears to be satisfactory, it must be admitted that derivation of gel properties by difference is not as straightforward as might be desired. In this paper polymers *randomly* cross-linked to the extent that they contain a gel fraction will be treated by a more general procedure applicable to *any* distribution of chain lengths. The method here employed is independent of size of complexity distribution equations (except in calculating weight average molecular weight); it is more direct and simpler than the procedures previously applied to the problem of post-gelation constitution. The results obtained confirm and extend previous conclusions.

Theoretical Treatment

Molecular size distribution functions[2,3,9] for three dimensional polymers may show a single maximum at relatively low molecular weight, but beyond this maximum they decrease monotonically toward zero. This is true after as well as before gelation. It is evident, therefore that an intermediate fraction between finite sol molecules

---

(1) P. J. Flory, THIS JOURNAL, **63**, 3083 (1941).

(2) P. J. Flory, *ibid.*, **63**, 3091 (1941).

(3) P. J. Flory, *ibid.*, **63**, 3096 (1941).

(4) P. J. Flory, *J. Phys. Chem.*, **46**, 132 (1942).

(5) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(6) C. Walling, THIS JOURNAL, **67**, 441 (1945).

(7) W. H. Stockmayer and L. L. Weil, unpublished. See "Advancing Fronts in Chemistry," Reinhold Publishing Corp., New York, N. Y., Chapter 6 by W. H. Stockmayer.

(8) A theory which will take into account intramolecular connections obviously is needed but, as Stockmayer has pointed out (paper given before the Division of High Polymer Physics of the American Physical Society, January, 1946), the mathematical difficulties appear to be insuperable.

(9) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).

(10) P. J. Flory, *Chem. Rev.*, **39**, 137 (1946).