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VAPOR PRESSURES AND SATURATED LIQUID AND VAPOR DENSITIES OF ISOMERIC HEPTANES AND OCTANES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
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By

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Approved by

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INTRODUCTION

In the separation of useful products from crude petroleum by distillation, basic data on the vapor pressure and densities of the liquid and vapor phases of pure hydrocarbons are of great technical importance. Crude oil is composed of literally thousands of compounds of which the paraffin hydrocarbons are the most abundant. The majority of these are isomers, compounds of the same molecular weight but with different molecular structure and physical properties. To determine the vapor pressure and densities up to the critical point of all of the isomers would be a herculean task. Since the difference in properties of the isomers is due solely to differences in molecular structure, it seems plausible that values of these properties for any isomer might be estimated from a correlation with the molecular structure. Data for such a correlation are available only for the paraffin hydrocarbons containing six or fewer carbon atoms. These are quite inadequate to establish empirical relations. To provide additional data for this purpose, the vapor pressures and densities of the 9 isomeric heptanes and 17 of the 18 isomeric octanes were determined up to their critical points. This report gives a summary of the experimental data and the development of the methods of correlation.

DESCRIPTION OF MATERIALS

The isomeric heptanes and octanes used for this work were made available by the American Petroleum Institute through the API Research Project 44 at the Carnegie Institute of Technology. The samples were purified by the API Research Project 6 from material supplied from the following laboratories: Ethyl Corporation, Detroit, Michigan; API Research Project 45 at the Ohio State University; Socony-Vacuum Laboratories, Paulsboro, N.J.; General Motors Corporation, Detroit, Michigan; Penn State Hydrocarbon Laboratory, Pennsylvania State College, State College, Pennsylvania. Table 1 lists the compounds, their purity and the source of the starting material.

The methods employed in the purification include the following: regular distillation, azeotropic distillation, adsorption, crystallization and formation of molecular or clathrate compounds. Purity of the compound was determined by freezing point determination. The apparatus and procedures have been described in detail elsewhere (18). The samples were received in glass ampoules and were used without further purification. The standard boiling point, liquid density at 20° and 25°C. and the vapor pressure-temperature relation up to 1500 mm Hg. have been determined by Rossini and coworkers (19).

TABLE 1

SAMPLE PURITY

Parenthesized values of purity indicate an estimated value.

Name of Compound#	Purity Mole Percent	Source of Starting Material
n-Heptane*	99.92	Phillips Lot No. 643
2-Methylhexane (B)	99.91 ± 0.07	Ethyl
3-Methylhexane (A)	(99.80 ± 0.15)	Ethyl
3-Ethylpentane	99.94 ± 0.03	APIRP 45
2,2-Dimethylpentane	99.81 ± 0.06	Socony Mobil
2,3-Dimethylpentane	(99.85 ± 0.10)	General Motors
2,4-Dimethylpentane	99.88 ± 0.05	APIRP 6
3,3-Dimethylpentane (B)	99.96 ± 0.04	APIRP 45
2,2,3-Trimethylbutane (B)	99.991 ± 0.008	General Motors
n-Octane	99.95 ± 0.04	APIRP 6
2-Methylheptane	99.66 ± 0.18	APIRP 45
3-Methylheptane (A)	99.62 ± 0.23	APIRP 45
4-Methylheptane	99.89 ± 0.07	APIRP 45
3-Ethylhexane	(99.75 ± 0.20)	APIRP 45
2,2-Dimethylhexane (B)	99.89 ± 0.11	APIRP 45
2,3-Dimethylhexane (B)	(99.85 ± 0.10)	APIRP 45
2,4-Dimethylhexane	(99.75 ± 0.20)	Penn State
2,5-Dimethylhexane (B)	(99.97 ± 0.005)	Penn State
3,3-Dimethylhexane (A)	99.75 ± 0.20	APIRP 45
3,4-Dimethylhexane	(99.75 ± 0.20)	APIRP 45
2-Methyl-3-ethylpentane	99.78 ± 0.11	APIRP 45
3-Methyl-3-ethylpentane	99.93 ± 0.04	APIRP 45
2,2,3-Trimethylpentane	99.68 ± 0.20	General Motors
2,2,4-Trimethylpentane (B)	99.95 ± 0.04	APIRP 6
2,3,3-Trimethylpentane (A)	99.79 ± 0.05	Penn State
2,3,4-Trimethylpentane	99.83 ± 0.06	APIRP 45

The designations, such as (A) and (B), mean there are different batches of the sample.

* The n-Heptane sample was obtained commercially from the Phillips Petroleum Corportion and was not an API sample.

EXPERIMENTAL METHOD AND APPARATUS

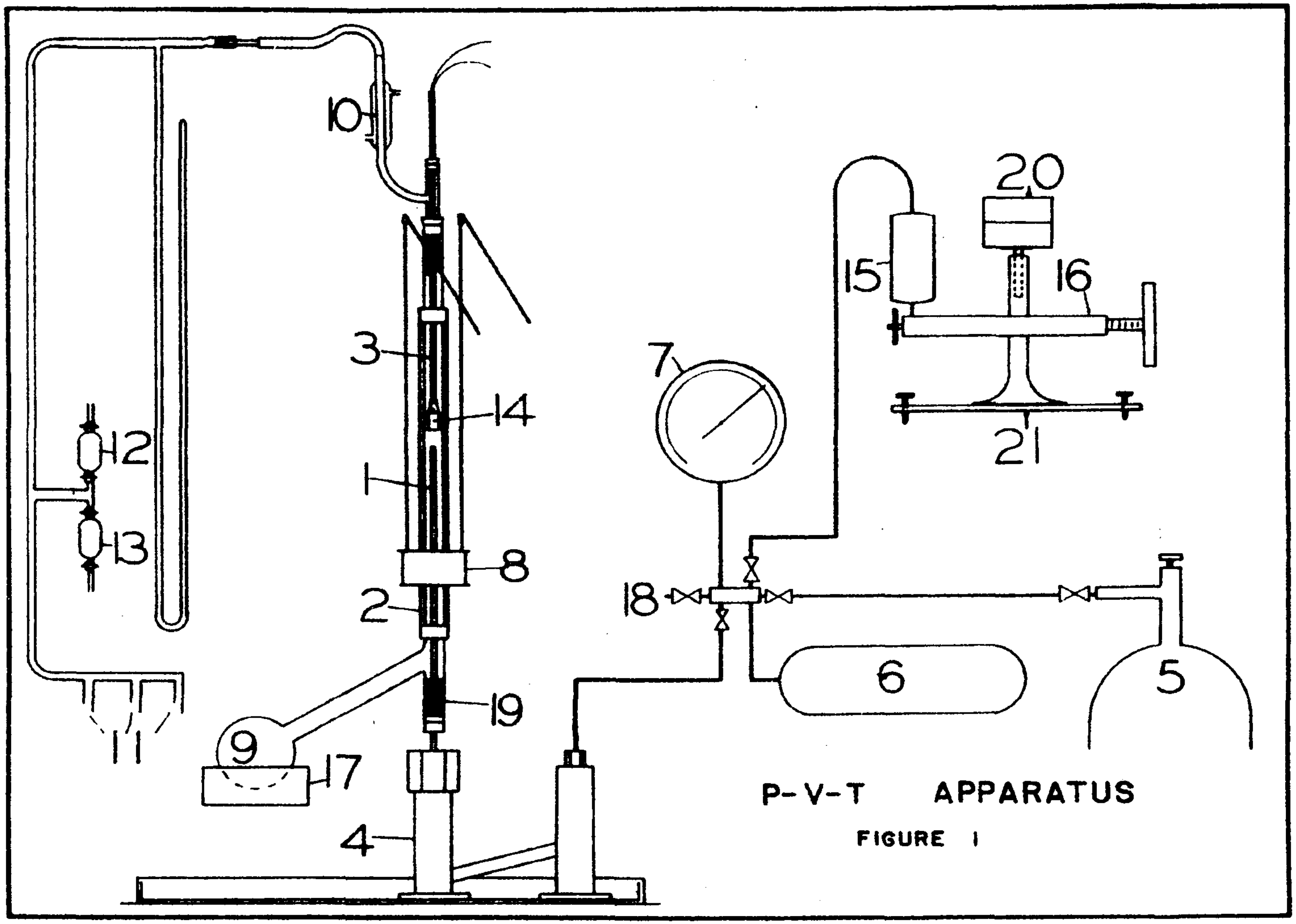
OUTLINE OF METHOD

The static method of determination of vapor pressure was employed. Figure 1 shows a sketch of the apparatus. A small air-free sample of the liquid hydrocarbon was confined over mercury in a thick-walled capillary tube, 1, hereafter called the experimental tube, which was heated to a constant temperature by the vapors of a series of pure organic compounds in the jacket, 2. The temperature was measured by the platinum resistance thermometer, 3. The capillary was held in one leg of a mercury-in-steel U-tube, 4, the other leg of which was connected by copper tubing to a high pressure gas cylinder, 5, and surge tank, 6, for regulating and controlling the pressure on the sample and to a pressure gage, 7, and dead weight gage, 16, for measuring the pressure. The volume of sample was determined by measuring the length of the capillary occupied by the sample; this length was related to the volume by a prior calibration of the tube. Equilibrium between the liquid and vapor phases was quickly reached by moving a small steel ball up and down through the sample by means of a magnet around the outside of the tube.

APPARATUS

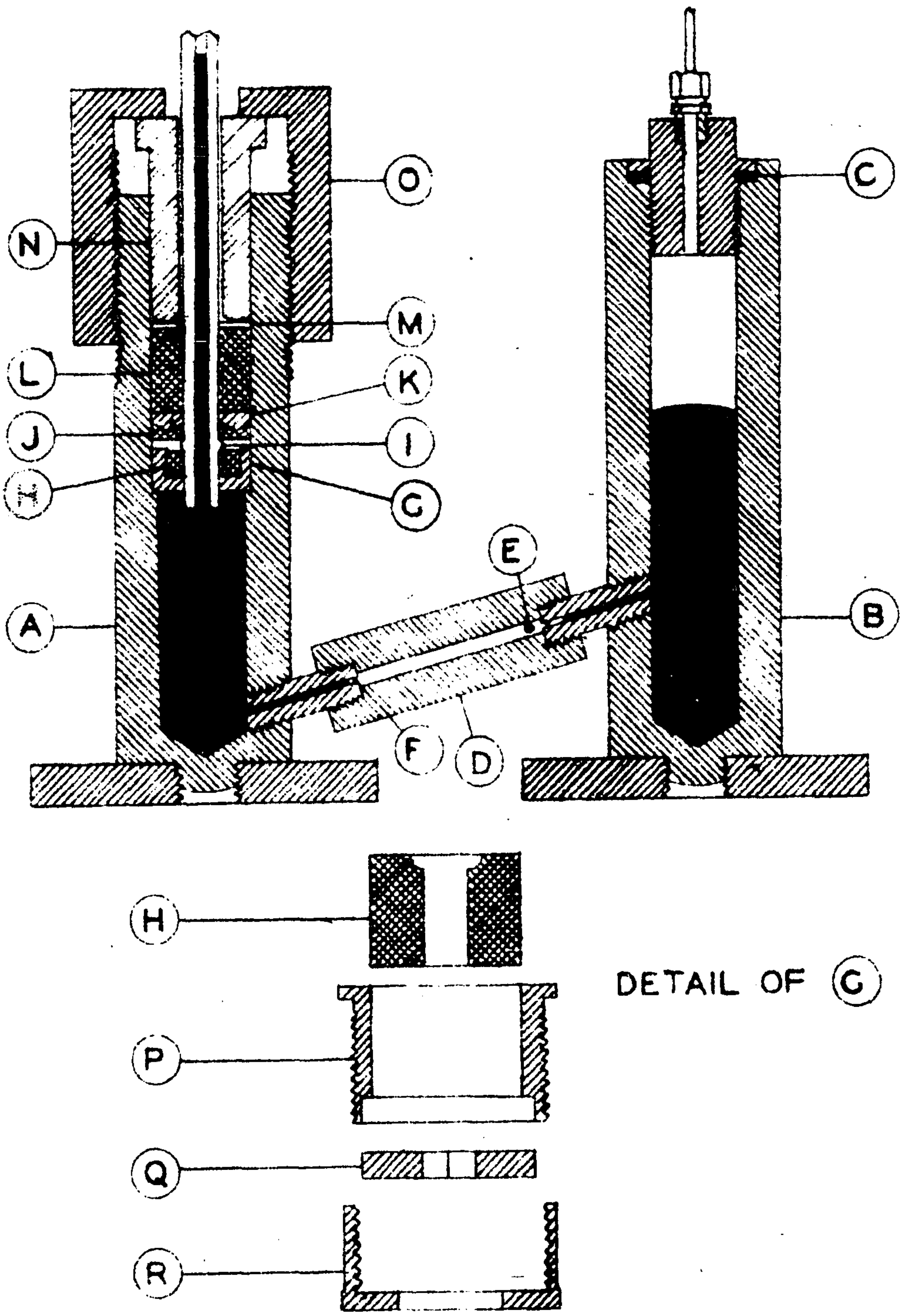
Compressor Block

A cross-sectional view of the compressor block is shown in Figure 2. The block was a mercury-in-steel U-tube. Leg A was fitted with a stuffing box for holding the experimental tube while



P-V-T APPARATUS

FIGURE 1



COMPRESSOR BLOCK

FIGURE 2

leg B was closed by a plug and connected to a tank of compressed gas. The pressure of the gas acting on the mercury surface in B was transmitted through the mercury to the sample in tube. The check valve D contained a steel ball, E, which in the event of the bursting of the tube, was driven into the seat F and thus prevented the escape of the mercury.

The method of holding the experimental tube was as follows: Near the open end of the tube an expanded section, l, was made which rested against a small rubber cylinder, H, in the loose-fitting cylindrical steel cup, G. Surrounding the tube above the expanded section was first a rubber washer, J, then a loose-fitting steel thrust ring K, machined so as to form a bearing seat for the upper part of I and finally a close-fitting cylindrical rubber stopper L. The tube thus prepared fitted into A, the cap G, resting against the shoulder therein. The gland N, was then slipped over the tube and drawn, not too tightly against the rubber cylinder by the cap O.

The Experimental Tube

A sketch of the experimental tube is shown in Figure 3. The working section of the tube was constructed of precision bore pyrex glass. Its volume in terms of the distance from the outside tip of the tube, was determined. The tube was cleaned, dried and the empty tube was weighed. The tube was partially filled with pure mercury and mounted in a vertical position. By means of a cathetometer reading to 0.05 mm., the distance from the mercury meniscus to

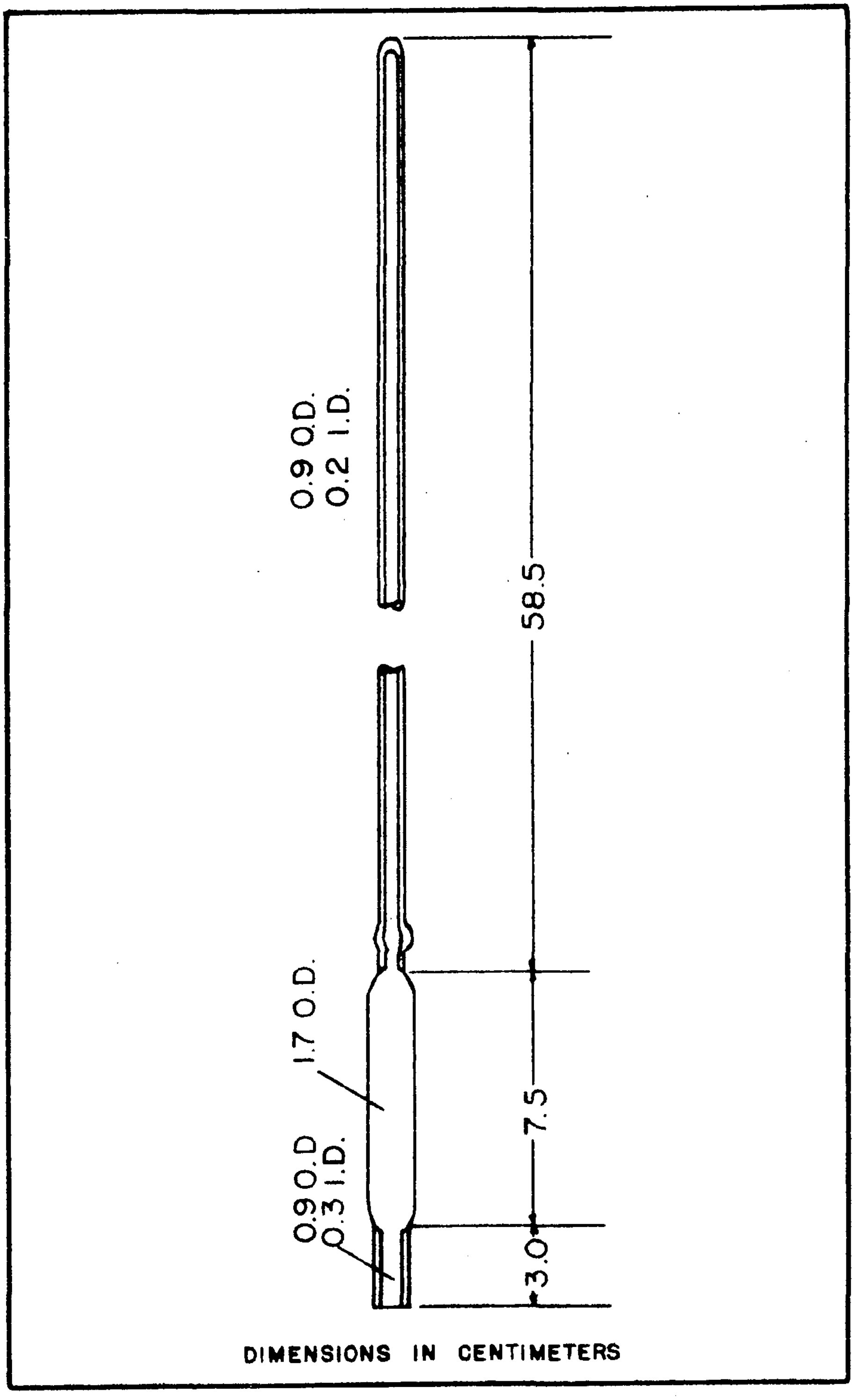


FIGURE 3, EXPERIMENTAL TUBE -2MM. BORE

the tube tip and the height of the mercury meniscus were measured. The tube containing the mercury was weighed and then the tube was remounted and more mercury was added; the distance and weight were redetermined. This procedure was repeated for several different volumes. From a knowledge of the weight, the specific volume and the temperature of the mercury, the volume of mercury was calculated for each determination. By taking the change of volume from one determination to the next, the change in volume per unit length was calculated. From the change in volume per unit length the average tube diameter was calculated. The average tube diameter and the height of the meniscus were used to calculate the complimentary volume of the mercury meniscus. The value of the compliment of the meniscus was calculated for each volume determination and added to the volume occupied by the mercury. A volume equation was then derived giving the volume as a function of length, by the method of least mean squares. (See Appendix II for calibration and equation details.)

The Temperature Bath

The experimental tube was surrounded by the jacket, 2, (Figure 1) and heated to a constant temperature by the vapors of a series of pure organic liquids whose boiling points lay within the temperature range desired. The liquid was heated in a side arm boiler, 9, the vapors rising through the side tube and around the experimental tube, were condensed in condenser, 10, at the top of the jacket, and liquid returned to the boiler. To prevent excessive heat loss the jacket was constructed with a double wall with the inner walls silvered and the inner space evacuated. Two narrow, unsilvered strips diametrically opposite each other were left to serve as a window for observing the experimental tube. The jacket rested on a tight fitting rubber stopper which was covered with mercury to prevent contamination of the boiling liquid by the rubber stopper, 19.

By reducing the pressure on the boiling liquid the temperature of the boiling point was lowered and any temperature, within a 30°C. range, constant to within 0.01°C. or better was obtained with a single liquid.

For the sake of control, the pressure in the boiler was indicated on a closed end manometer, and three five-gallon bottles were connected to the line at 11, to absorb small pressure fluctuations. These were insulated to eliminate pressure changes due to changes in the temperature of the gas in the bottles. Minute changes in pressure on the boiling fluid were made by means of small bulbs 12 and 13, one of which was open to the atmosphere and the other was connected to a vacuum pump. Carborundum crystals or clean glazed porcelain plate chips were added to the liquid to reduce bumping and produce even boiling.

The following compounds were used for the temperature bath; Carbon tetrachloride, 55°-75°C.; chlorobenzene, 75°-131°C.; bromobenzene, 131°-155°C.; aniline 155°-183°C.; naphthalene, 183° - 218°C.; diphenyl ether 218° - 255°C.; alpha-bromonaphthalene, 256° - 280°C.; benzophenone, 280° - 305°C.

Temperature Measuring Equipment

The temperature to which the experimental tube was heated was measured by means of a platinum resistance thermometer with a sensitive bridge for measuring the resistance of the coil. The resistance thermometer previously had been calibrated at the Bureau of Standards and was capable of measuring temperature to 0.001°C.

Apparatus for Stirring the Sample

In order to bring about equilibrium quickly between the liquid and vapor of the sample and mercury vapor in the narrow bore experimental tube, and to initiate vaporization when the pressure on the sample was reduced to the vapor pressure, a 1/16 inch diameter steel ball bearing was moved through the sample by means of a strong permanent magnet 8 around the outside of the jacket.

Pressure Measuring Equipment

Pressures up to about 45 pounds per square inch were measured with an open end mercury column and higher pressures by means of a pressure balance, 16. In the use of the pressure balance the approach to equilibrium between the pressure exerted on the piston by the weights on the pan and the line pressure, was indicated by a slow change in the position of the pan. This was detected quickly by an arrangement whereby the slightest downward movement of the pan made an electrical circuit which caused an electromic relay to turn.

on a signal light. With this arrangement it was possible to detect changes in pressure as small as 0.02 pounds per square inch. the effective diameter of the piston was determined by calibration against the vapor pressure of pure carbon dioxide (13). (See Appendix II for calibration details.)

EXPERIMENTAL PROCEDURES

Preparation of the Sample

The pure hydrocarbon sample was degassed by subjecting the sample repeatedly to the following cycle of operations: freezing the sample, pumping off the residual non-condensed gas over the solid, melting and distilling the sample at low pressure and freezing the condensate.

Loading the Experimental Tube

The apparatus for deaerating the sample and for transferring the degassed sample to the experimental tube is shown in figure 4. The apparatus was constructed of pyrex glass. In order to avoid the possibility of contaminating the hydrocarbon sample with stop cock lubricant, mercury sealed plug valves were used.

Referring to Figure 4, the pure liquid was contained in a glass break-off tube A which was sealed to the manifold of a high vacuum line. A mercury diffusion pump, backed by a mechanical oil pump, was used to produce a vacuum with a residual non-condensible gas pressure of less than 1×10^{-5} mm of mercury, as measured by

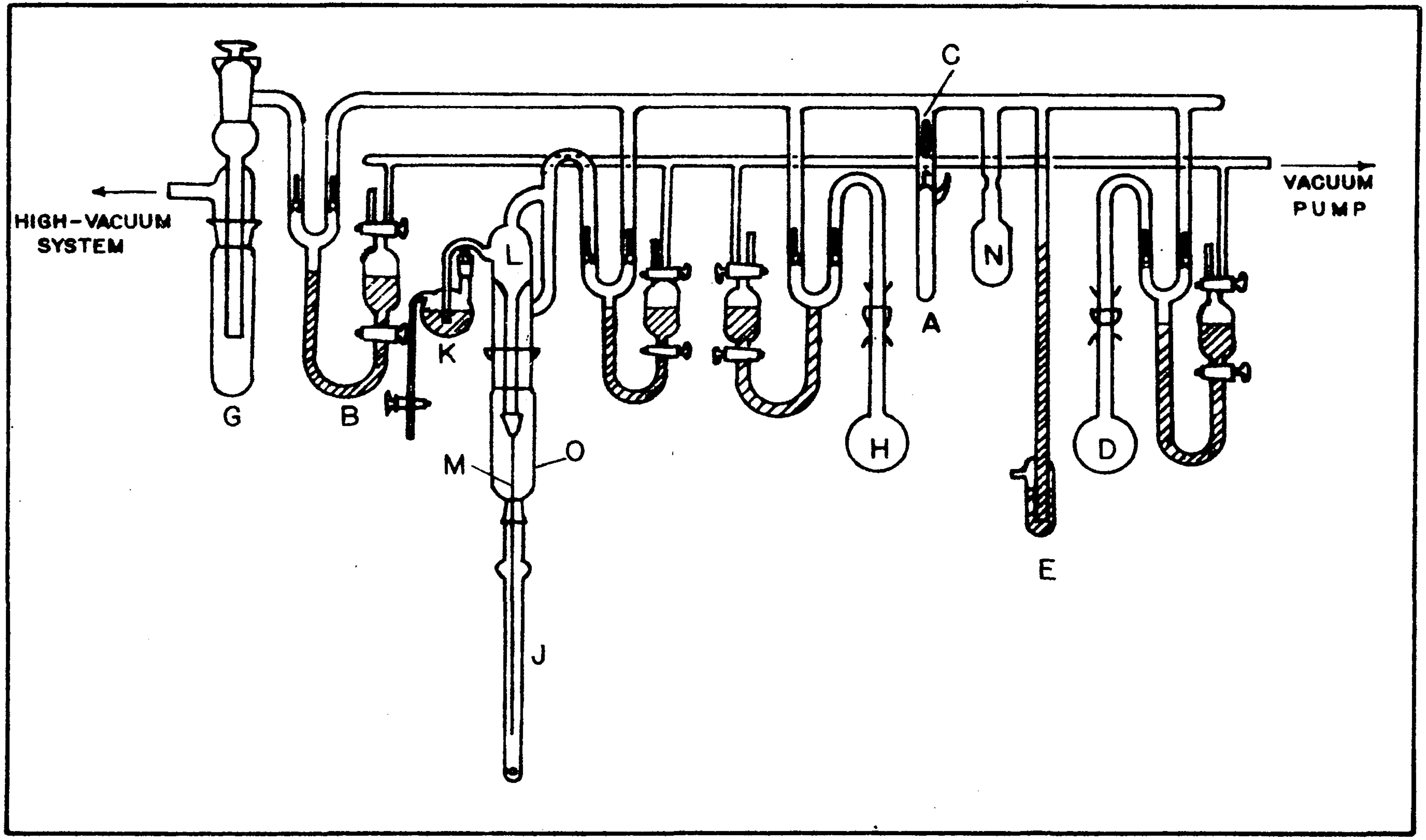


FIGURE 4, LOADING AND DEGASSING APPARATUS a McLeod gage. When such a pressure was attained in the system, valve B was closed, the break-off tip was broken by dropping the glass-covered iron rod C and the sample transferred to bulb D by cooling the bulb with a dry ice-acetone mixture. Valve B was then opened, and the system evacuated for 20 minutes, or until the pressure was less than could be read on the gage. Valve B was closed, the cold trap around bulb D removed, and the sample allowed to melt and warm up until a vapor pressure of about 10 mm was indicated on the barometric manometer D. The valve to D was then closed, and the tip of the experimental tube cooled, thereby condensing the vapor in the tip of the tube. Valve B was then opened, and the liquid in the experimental tube pumped into trap G and valve B closed again. Valve D was then opened, the cold bath placed around bulb H, and the sample transferred to H. Next, valve B was opened, and the residual gas over the solid in bulb H pumped off. The cycle was then repeated with the sample transferred back to bulb D. This purging of the apparatus with the vapors of the degassed sample was repeated six times which was considered sufficient to remove all traces of non-condensible gas.

Upon the completion of the degassing operation, a small sample of the degassed liquid was transferred by distillation to the experimental tube J, and was frozen in the tip with a dry ice-acetone mixture. By admitting air to flask K, mercury spilled into L and entered the experimental tube through the hair-size glass capillary M which extended into the tube to a point about 3 cms. above the surface of the frozen hydrocarbon sample. This method of introducing the mercury made it possible to displace most of the vapor from the experimental tube, thereby eliminating traces of air that might still be present in the vapor. The degassed hydrocarbon remaining in the flask D was transferred to the ampoule N which was then sealed off from the line.

Next, air was admitted to the system until atmospheric pressure was attained. Part O was lowered until capillary M could be detached from L at the ground joint and removed from the tube. During this latter operation, the open end of the experimental tube was completely covered with mercury. The packing assembly for holding the tube in the compressor block was put into place. Finally, with the end of the tube closed firmly with a finger, the tube was turned up into the mercury filled compressor block and fastened into place.

The 1/16 inch diameter steel ball which was used for stirring the sample during the vapor pressure determination was put into the tube at the time the apparatus was assembled.

Determination of the Amount of Sample

Before measuring the liquid volume of the sample, the heating jacket was put in place (figure 1) and the tube heated to about 200°C. The pressure was first adjusted so that the mercury level in the tube was lowered in order to release any liquid occluded between the glass wall and the mercury. Once this was done, the pressure was raised in order to bring all of the sample into the top of the tube. The jacket was then removed, and the tube allowed to cool, after which it was surrounded by a jacket filled with water at room temperature. Measurements of the distance between the top of the tube and the top of the mercury meniscus as well as the height of the mercury meniscus and the temperature of the water were made using a cathetometer reading to 0.05 mm. From a knowledge of the density of the liquid and the volume of the sample the weight of the sample was calculated. (See Appendix II for sample calculation of volume of sample.)

OPERATION OF THE APPARATUS

Referring to Figure 1 the pressure release valve 18 and the valve to the pressure balance were closed and the valve to the compressor block was opened. The valve to the compressed gas tank was then opened cautiously and the pressure, allowed to increase to a value that was certain to be higher than the vapor pressure to be measured. The electric heater, 17, was turned on and the experimental tube and constant temperature jacket brought up to temperature by the vapors from the boiling liquid in 9. The pressure on the boiling liquid was adjusted to give the temperature desired and the current to the heater set so that the position of the line of condensation of the vapor was steady at the top of the double wall section of the jacket. The pressure on the sample was then reduced slowly by cracking valve 18 while the sample was stirred until vaporization occurred and the mercury meniscus had fallen to a point in the tube slightly above the level of the mercury 19. valve 18 was then closed and the pressure balance cut in by opening the valve to it. The sample was stirred intermittently for about 20 minutes in order that equilibrium was established between the mercury vapor and the sample. The pressure was then raised by small increments, with intermittent stirring, until condensation of the vapor started. The beginning of condensation was detected by noting the effect of a very small change of pressure on the position of the mercury meniscus; a minute increase of pressure above the condensation pressure produces a relatively large decrease in the volume occupied by the sample, whereas a reduction of pressure produces relatively no change. Readings of the temperature, pressure and distance of the mercury meniscus from the tip of the tube were recorded for this point. The pressure was then reduced and the observations repeated. This was done until 2 consecutive sets of readings agreed to within the experimental error. The pressure was again increased and the sample stirred until only a small bubble of vapor remained in the tip of the tube when readings of the pressure, temperature and position of the mercury meniscus were again noted. Finally, the pressure was increased by an extremely small amount causing the bubble to disappear and a final reading of the position of the mercury meniscus only was noted.

CORRECTION AND CALCULATION OF THE DATA

The pressure as determined by the dead weight gage was corrected for (1) the difference in levels of the mercury (corrected to standard temperature) in the experimental tube and compressor block, (2) for the vapor pressure of mercury, (3) barometric pressure.

In calculating the volume of the sample, account was taken of the following factors: (1) the volume of the mercury meniscus, (2) the thermal expansion of the tube, (3) the volume of the steel ball stirrer. The volume of the mercury meniscus was calculated from the height assuming the meniscus to be a segment of a sphere with the base of the segment equal to the diameter of the tube. A value of 24×10^{-7} for the volumetric coefficient of expansion of pyrex glass was used for calculating the correction for thermal expansion of the tube. The diameter of the steel ball was measured and the volume calculated using the formula for a sphere.

The apparatus and experimental procedures described have been used in the study of pure substances and binary systems of which a few are (3),(4),(5),(6),(7),(8), and (9).

RESULTS

PRESENTATION OF SMOOTHED DATA

The volumes of the saturated liquid and the saturated vapor and their related pressures were measured at temperatures from 210°C. for heptanes and 240°C. for octanes, up to the critical temperatures. Below these temperature ranges, down to the standard boiling point temperature, measurements were made only on the liquid phase, the volume of the saturated vapor phase being larger than the volume of the useable portion of the experimental tube.

Measurements were made at temperature intervals ranging from about 10 degrees near the standard boiling point to about 5 degrees near the critical point.

One pressure-volume isotherm was determined for each of the compounds studied; for the heptanes, the temperature was 210°C. and for the octanes, it was 240°C. From these isotherms, the pressure change between the bubble and dew point could be determined, which served as an over-all indication of the purity of the experimental sample. It was found exceedingly difficult to reduce this difference to less than 0.2 to 0.3 of a pound per square inch. It is believed that this difference is due principally to residual non-condensible gas. Figure 5 shows the isotherm for n-heptane which is, in general, representative of the isotherms of the other compounds and indicates that the pressure at large values of the V/L ratio (volume of vapor

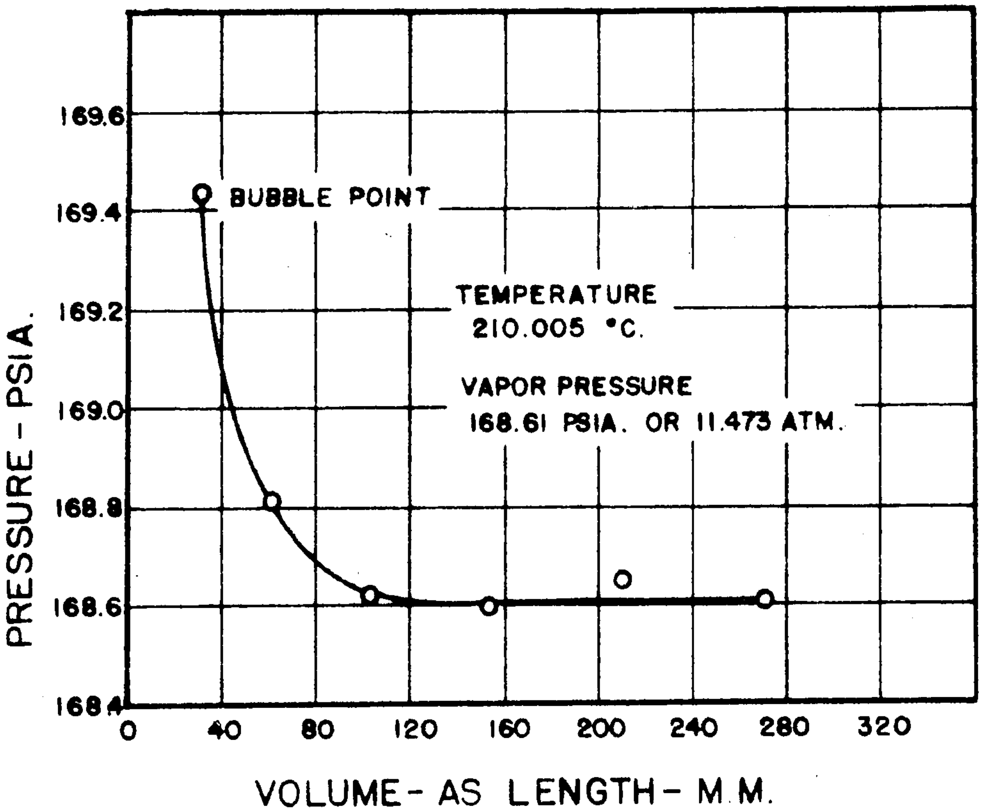


FIGURE 5 , PRESSURE-VOLUME ISOTHERM
FOR N-HEPTANE

to the volume of liquid) more nearly represents the true vapor pressure.

The experimental data for all samples that were studied are given in Appendix I. The pressures listed as "observed pressures" are the dew point and bubble point pressures. The column listed as "pressure deviation" refers to the difference between the pressure calculated from the equation:

$$\log P_{calc}\ (\text{atm.}) = A + B/T(^{\circ}K)$$

and the observed pressure at the experimental temperature. The value of the constants A and B in the equation were evaluated using the critical point and the standard boiling point of the compound. They are listed in Table 28 for each of the compounds studied. The pressure deviation were plotted against the temperature and a smooth curve drawn between the dew points and bubble points to correspond with the constant pressure section of the isotherm (see Figure 5). In general, the curve was plotted for values at large V/L ratios. These curves are shown in Figures 6 through 31. With the aid of the equations and the deviation curves the vapor pressure was calculated at 10 degree C. intervals from the standard boiling point to the critical point and are listed in Tables 2 through 27.

The experimentally measured volumes of the saturated liquid and vapor were expressed as densities in grams per cubic centimeter. Large scale plots of density versus temperature were constructed from which values of the densities of the liquid and vapor were read.

These values are listed in Tables 2 through 27. By plotting the arithmetical average of the densities of the liquid and vapor against the temperature and extrapolating the curve to the critical temperature, values of the critical density were obtained. These values are listed in Table 29 together with the critical temperature and pressure for all compounds studied.

ACCURACY OF THE DATA

As has been stated, temperatures could be read to within 0.001°C with the platinum resistance thermometer. The thermometer was confined within the vapor jacket (see page 11) and was well shielded from outside radiation. Fluctuations in the pressure over the boiling liquid sometimes amounted to temperature changes in the bath of the order of 0.02°C. over periods of 10 to 20 minutes. However, the thermometer responded rapidly to temperature changes so that it is believed that the temperature readings are accurate to within 0.02°C.

To get a value of the overall accuracy of the pressure measurements, the vapor pressure of water was determined at three temperatures covering the range in temperature encountered in the hydrocarbon measurements. The data were then compared with the vapor pressure data of Osborne and Meyers (14). The results are shown on the following page.

Test of Accuracy of Temperature and Pressure Measurements

Vapor Pressure of Water

Temp. °C.	Pressure Expt. Atm.	Pressure Literature Atm.	Deviation Atm.
157.39	5.708	5.705	0.003
216.775	21.519	21.519	0.000
240.332	33.261	33.235	0.026

Since the same apparatus and experimental procedures were used, it is believed that the accuracy of the data obtained for the hydrocarbons is about the same for the water.

An additional check on the precision of the measurements was made by a comparison of the vapor pressure and density data on, 2,2,4-trimethylpentane (iso-octane) with that of Kay and Warzel (11). This is shown in Table 30. The vapor pressures at temperatures below 210°C. are approximately 0.03 atmospheres higher than those reported by Kay and Warzel, whereas, above 210°C. up to the critical point, the agreement is within 0.01 atmosphere which is within the experimental accuracy of the measurement.

The precision of the measurements of the density is of the order of 0.0015 g/cc for the liquid and 0.002 g/cc for the vapor at near room temperature. As the temperature increases the precision increases for the liquid and stays the same for the vapor, becoming the same as the critical temperature is approached. In the critical region, the deviations become large and difficult to estimate. However, critical densities estimated by the law of rectilinear diameters are believed to be accurate to within 0.001 gm/cc.

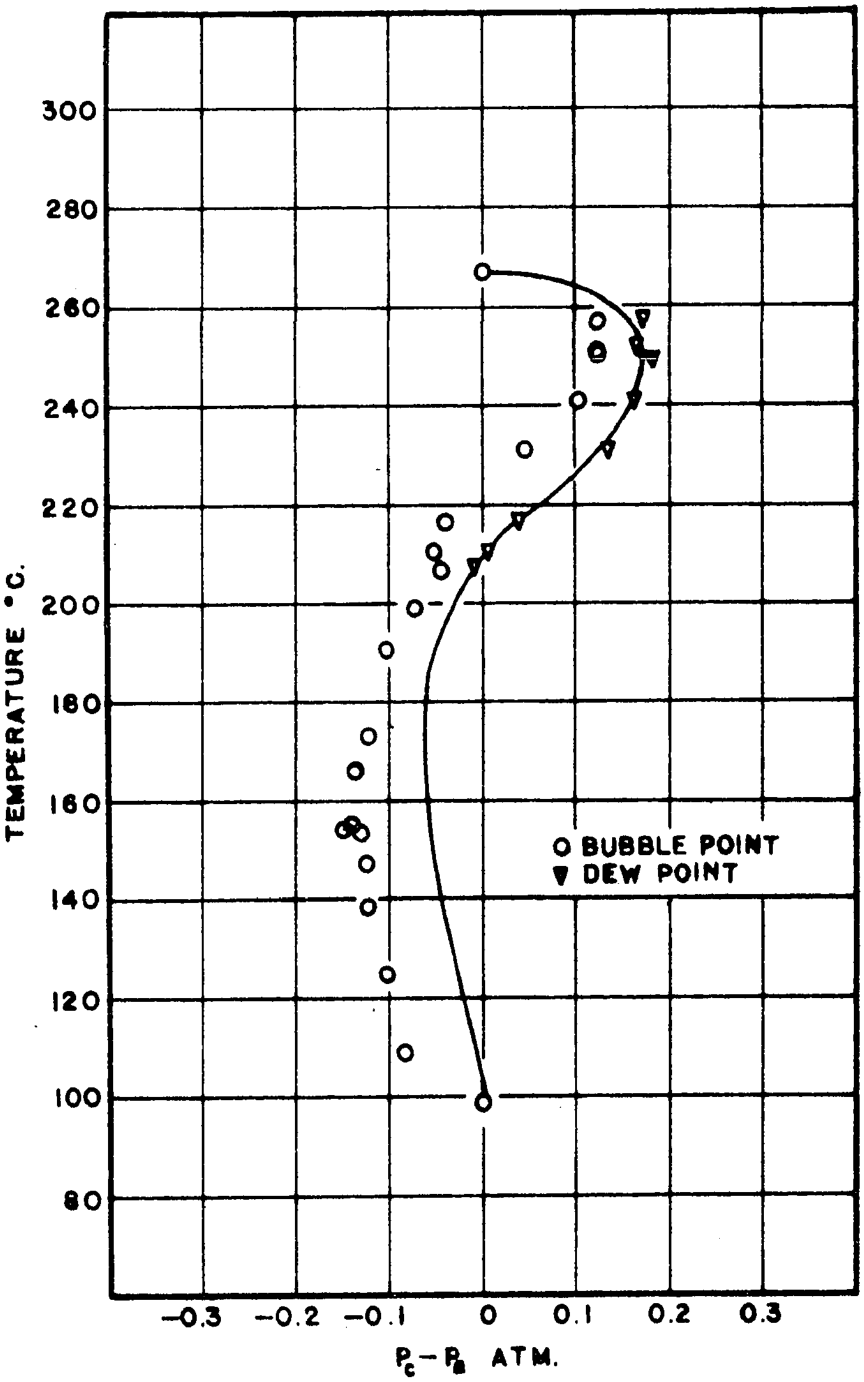


FIGURE 6, VAPOR PRESSURE DEVIATION CURVE FOR N-HEPTANE

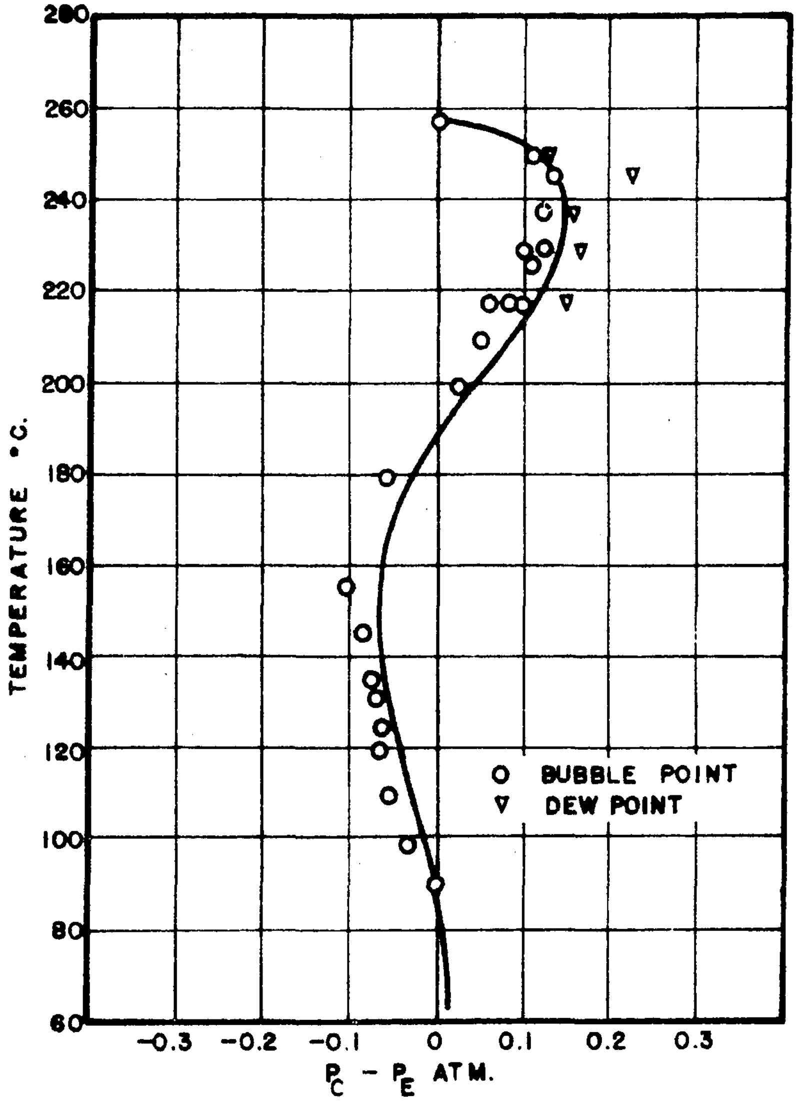


FIGURE 7, VAPOR PRESSURE DEVIATION CURVE
FOR 2-METHYLHEXANE

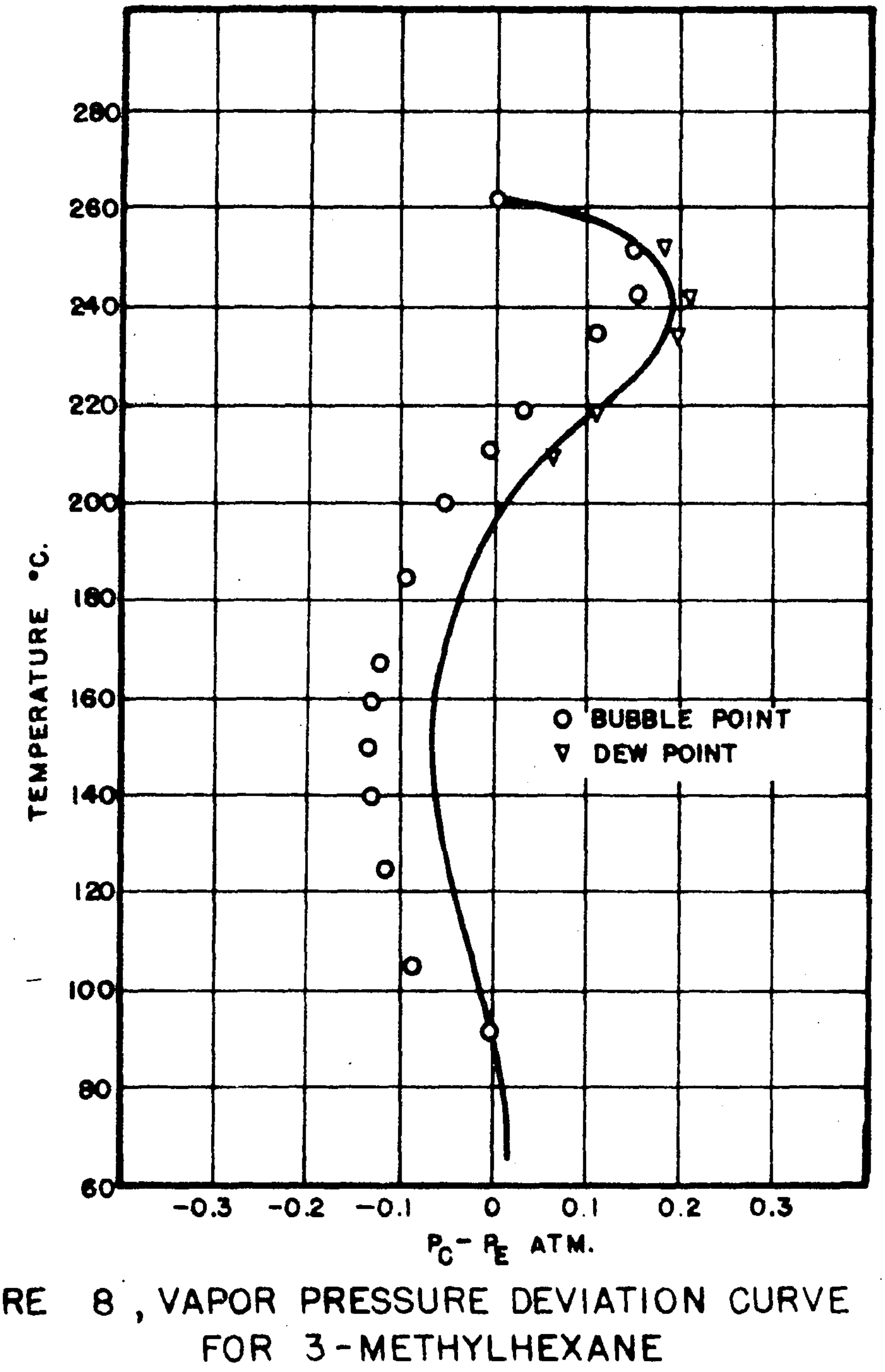


FIGURE 8 , VAPOR PRESSURE DEVIATION CURVE FOR 3-METHYLHEXANE

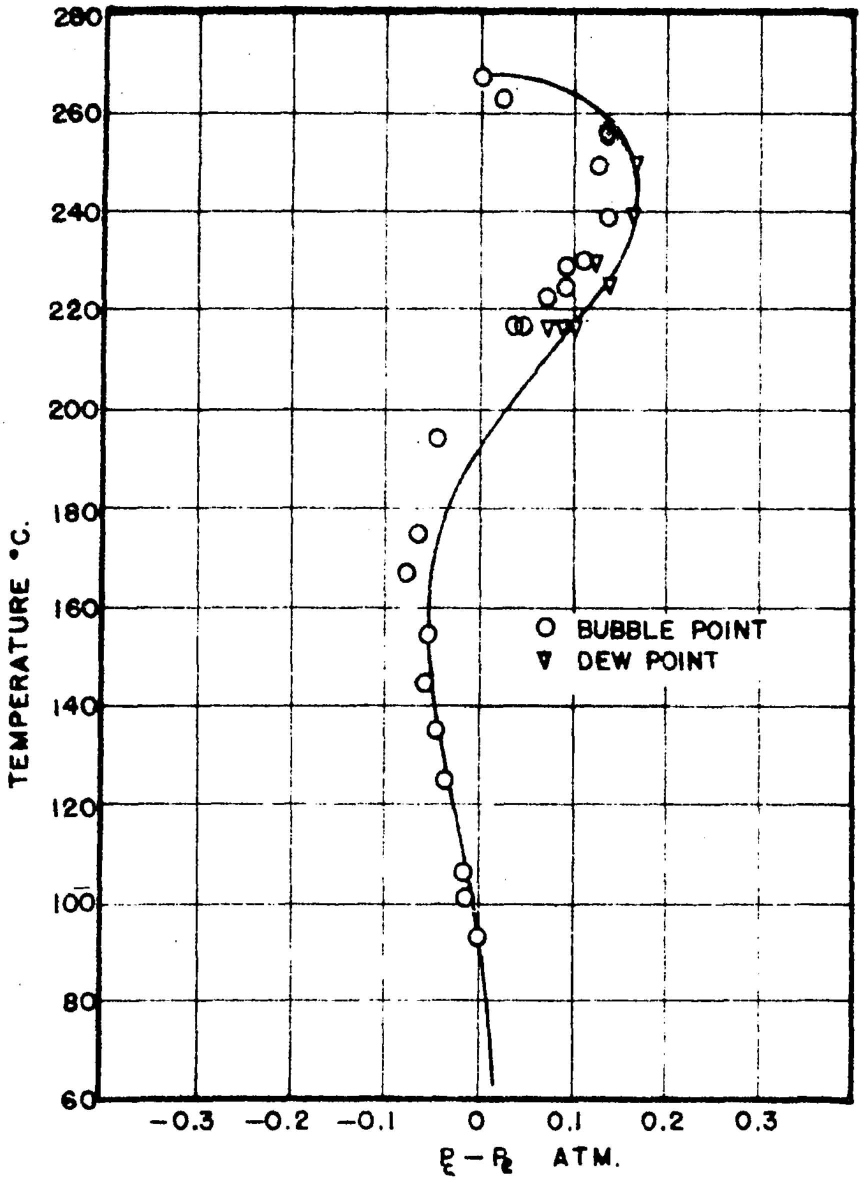


FIGURE 9 ,VAPOR PRESSURE DEVIATION CURVE FOR 3-ETHYLPENTANE

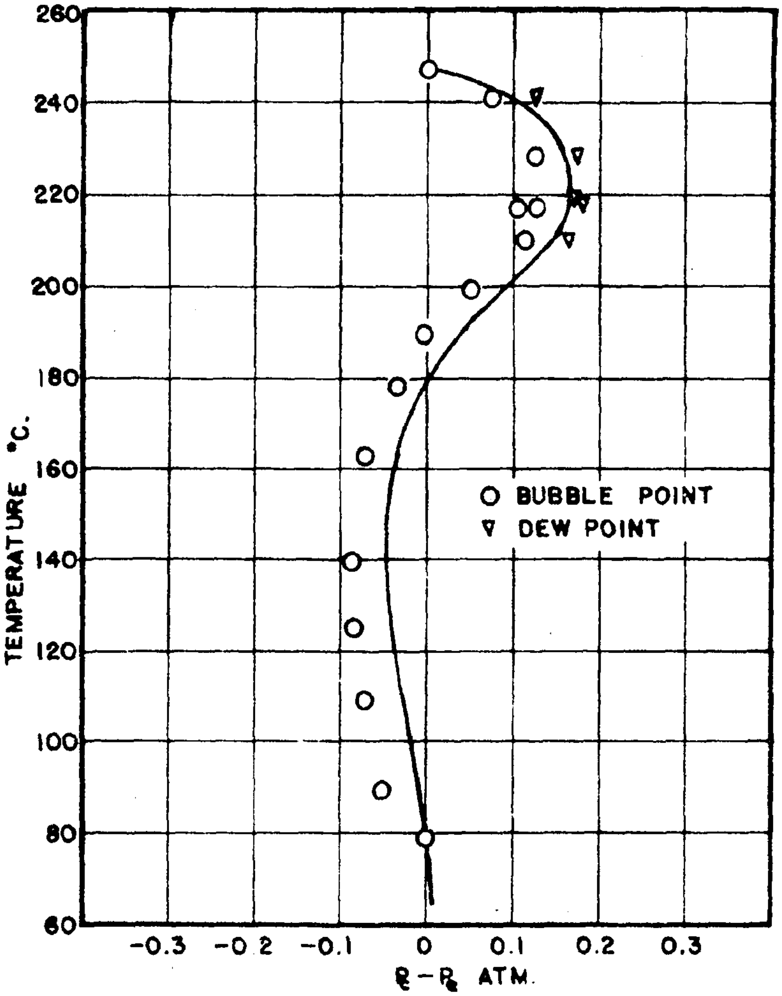


FIGURE 10, VAPOR PRESSURE DEVIATION CURVE FOR 2,2-DIMETHYLPENTANE

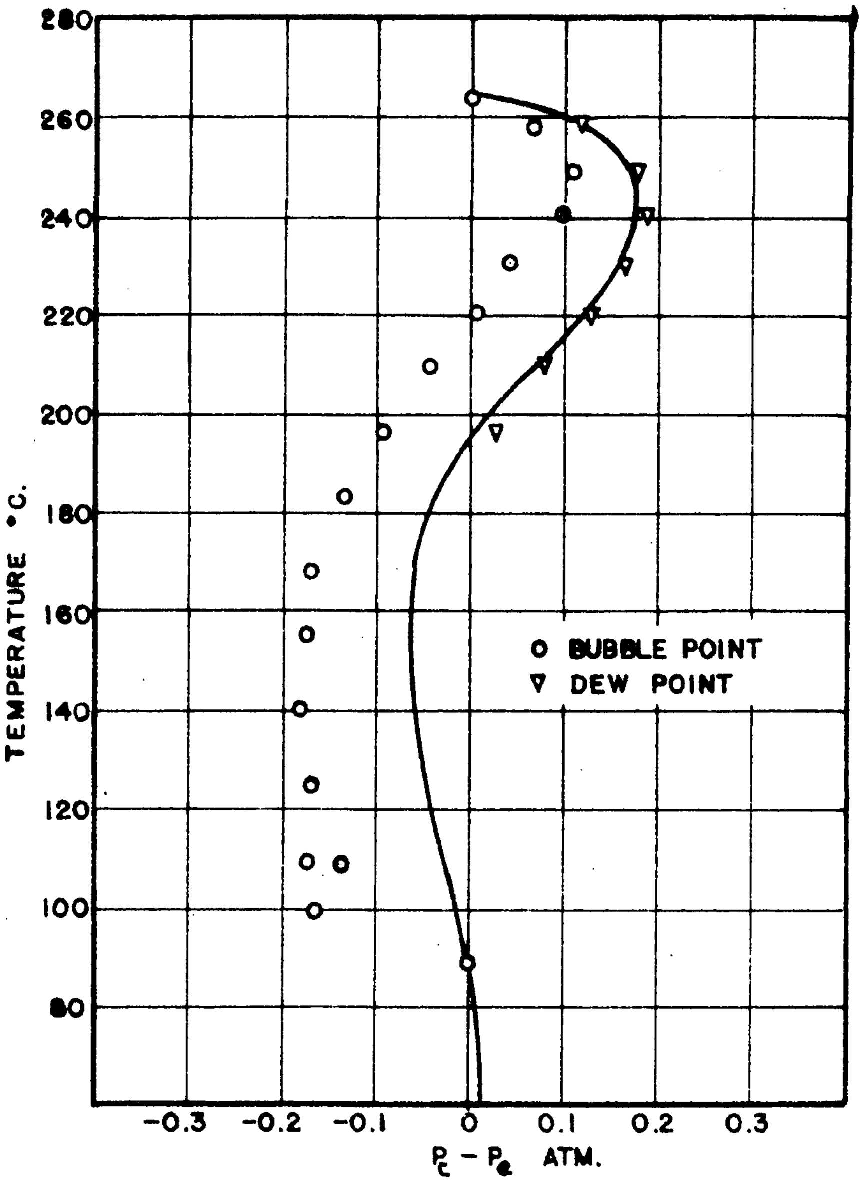


FIGURE 11, VAPOR PRESSURE DEVIATION CURVE FOR 2,3-DIMETHYLPENTANE

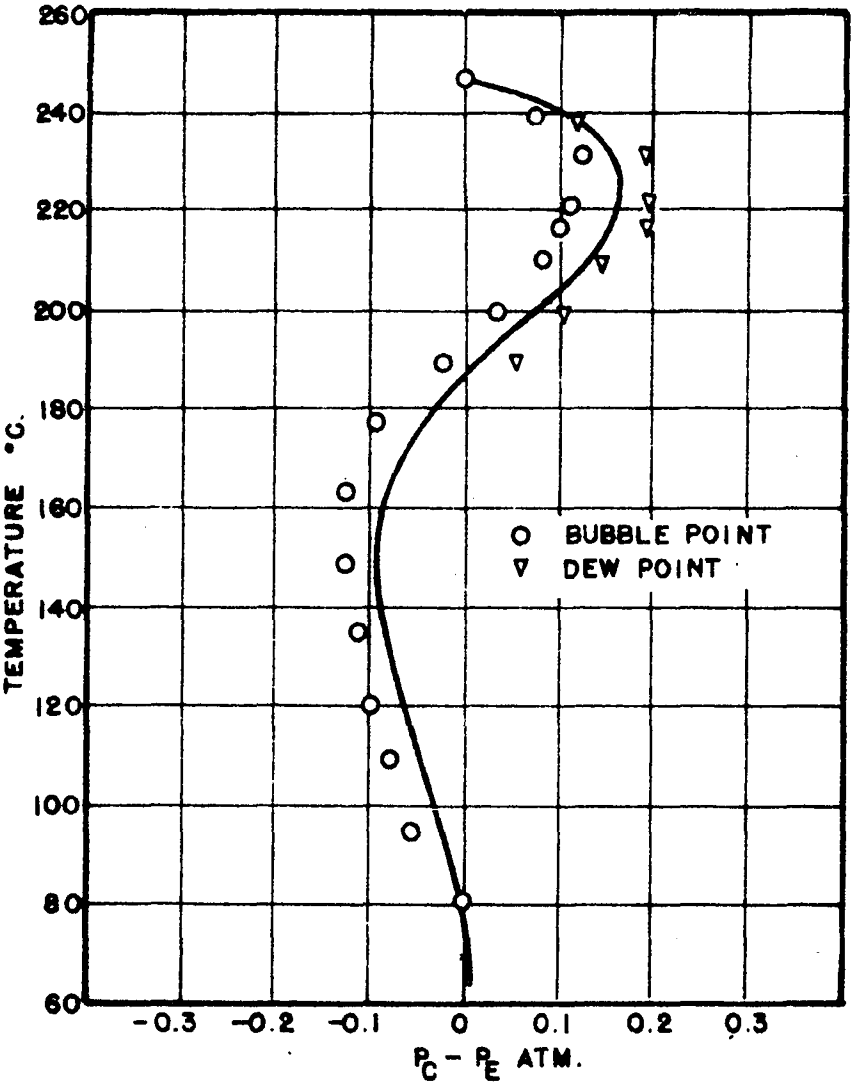


FIGURE 12, VAPOR PRESSURE DEVIATION CURVE FOR 2,4-DIMETHYLPENTANE

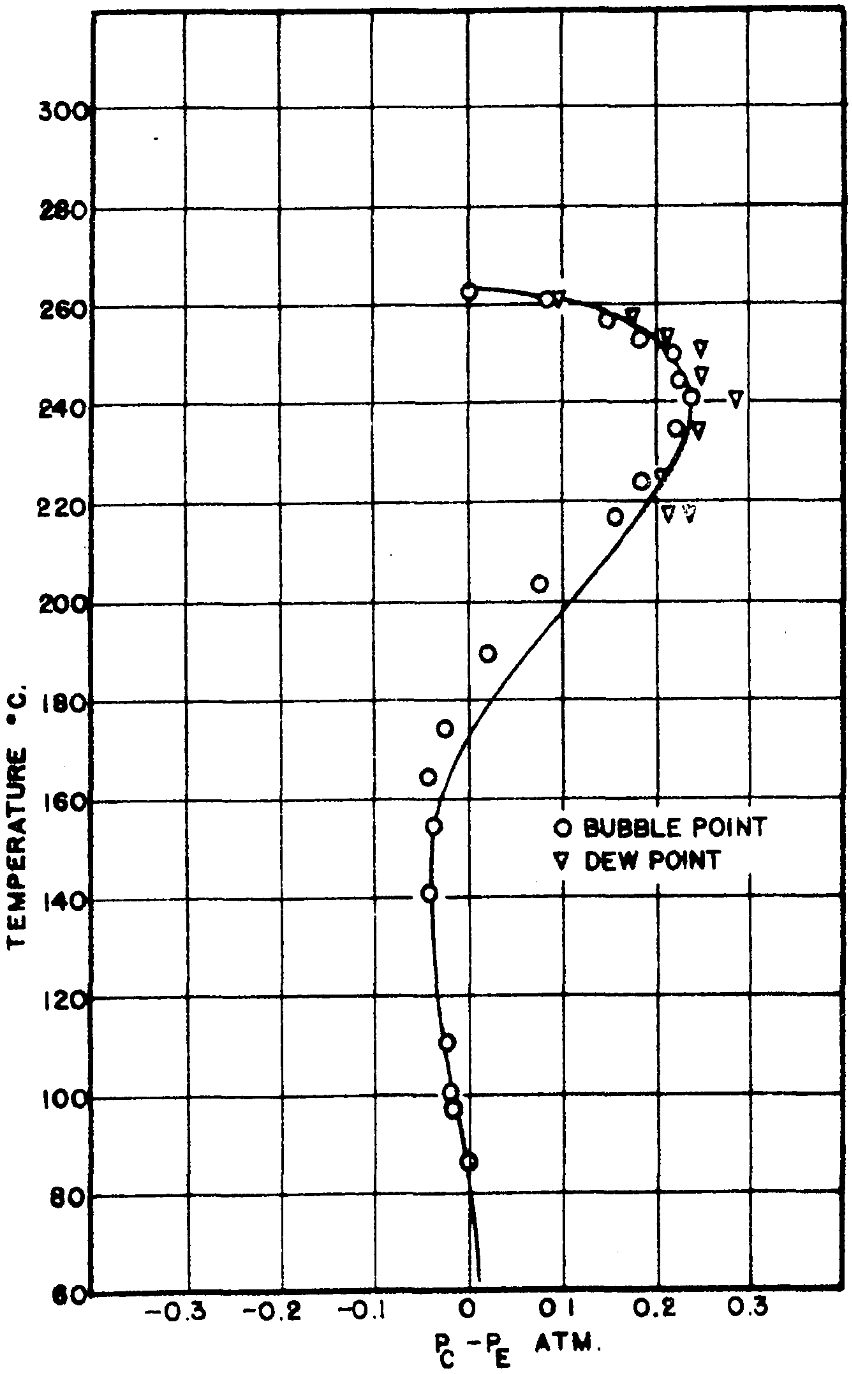


FIGURE 13, VAPOR PRESSURE DEVIATION CURVE FOR 3,3-DIMETHYLPENTANE

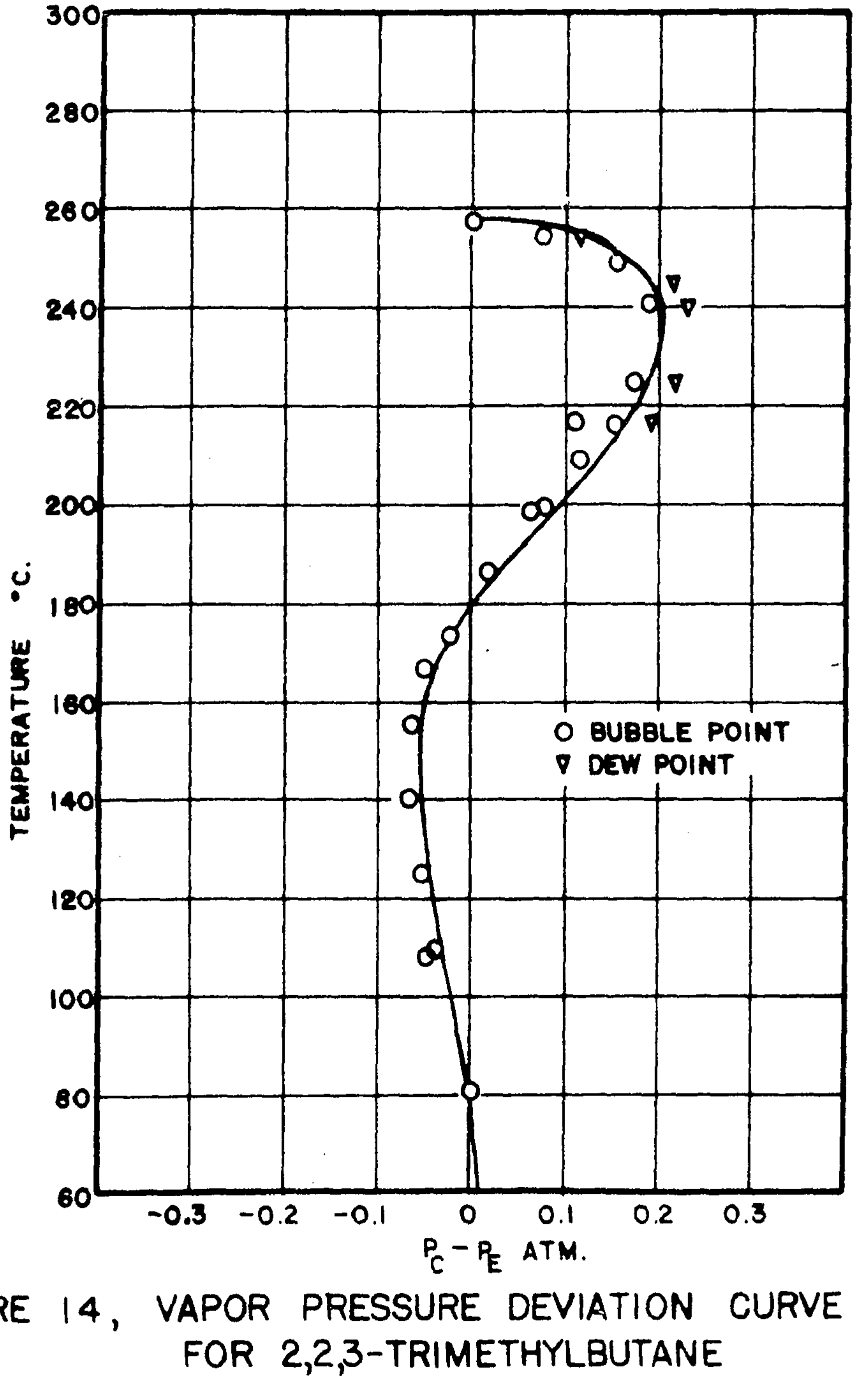


FIGURE 14, VAPOR PRESSURE DEVIATION CURVE FOR 2,2,3-TRIMETHYLBUTANE

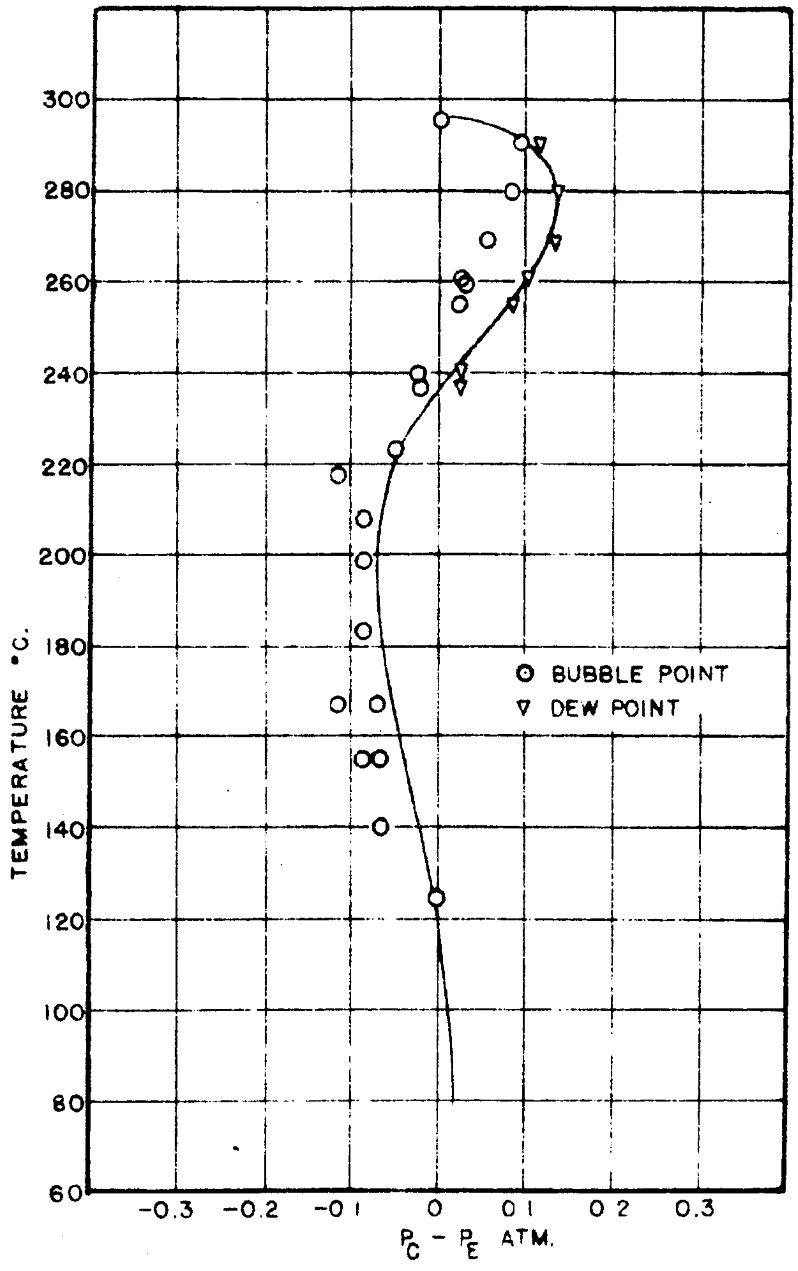


FIGURE 15, VAPOR PRESSURE DEVIATION CURVE FOR N-OCTANE

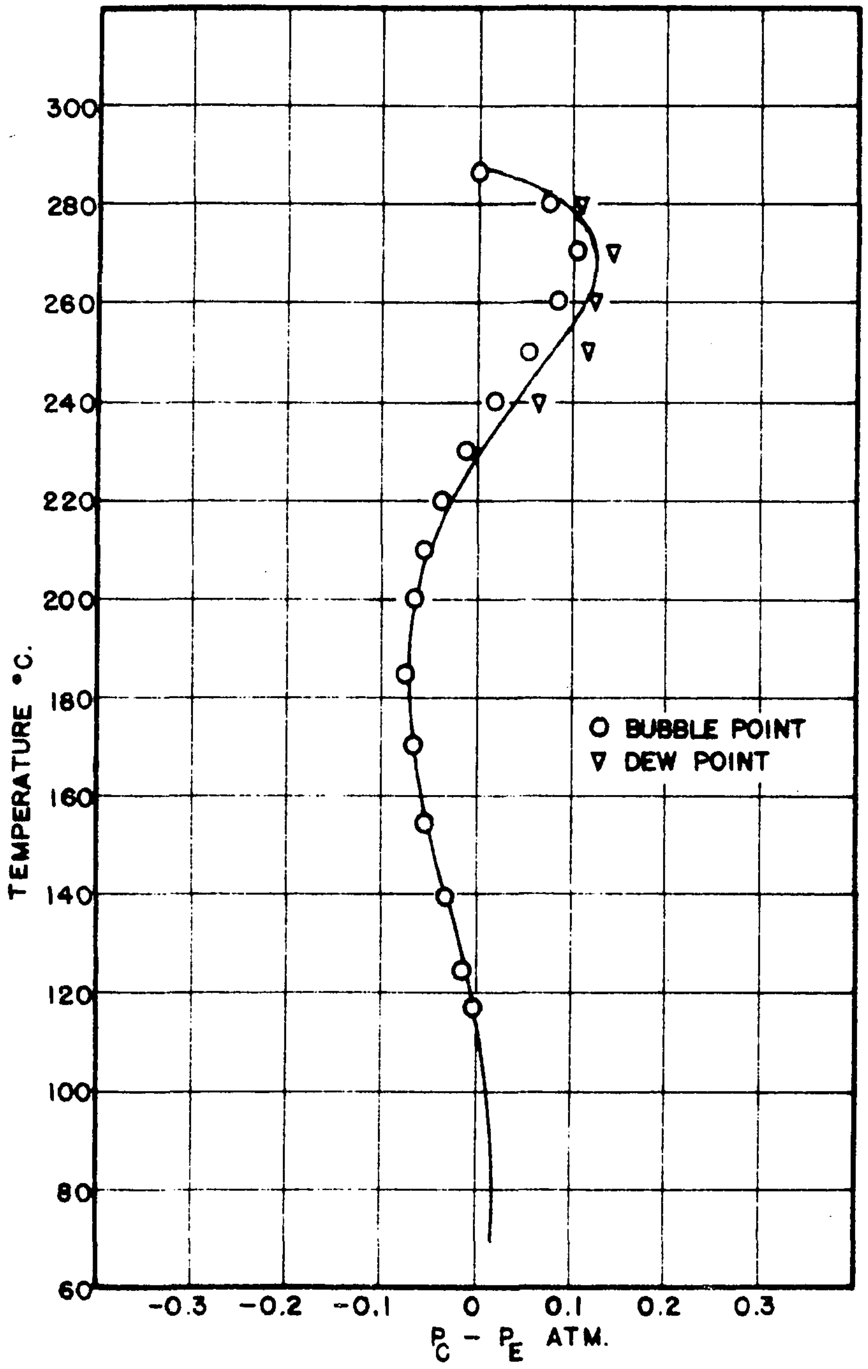


FIGURE 16, VAPOR PRESSURE DEVIATION CURVE FOR 2-METHYLHEPTANE

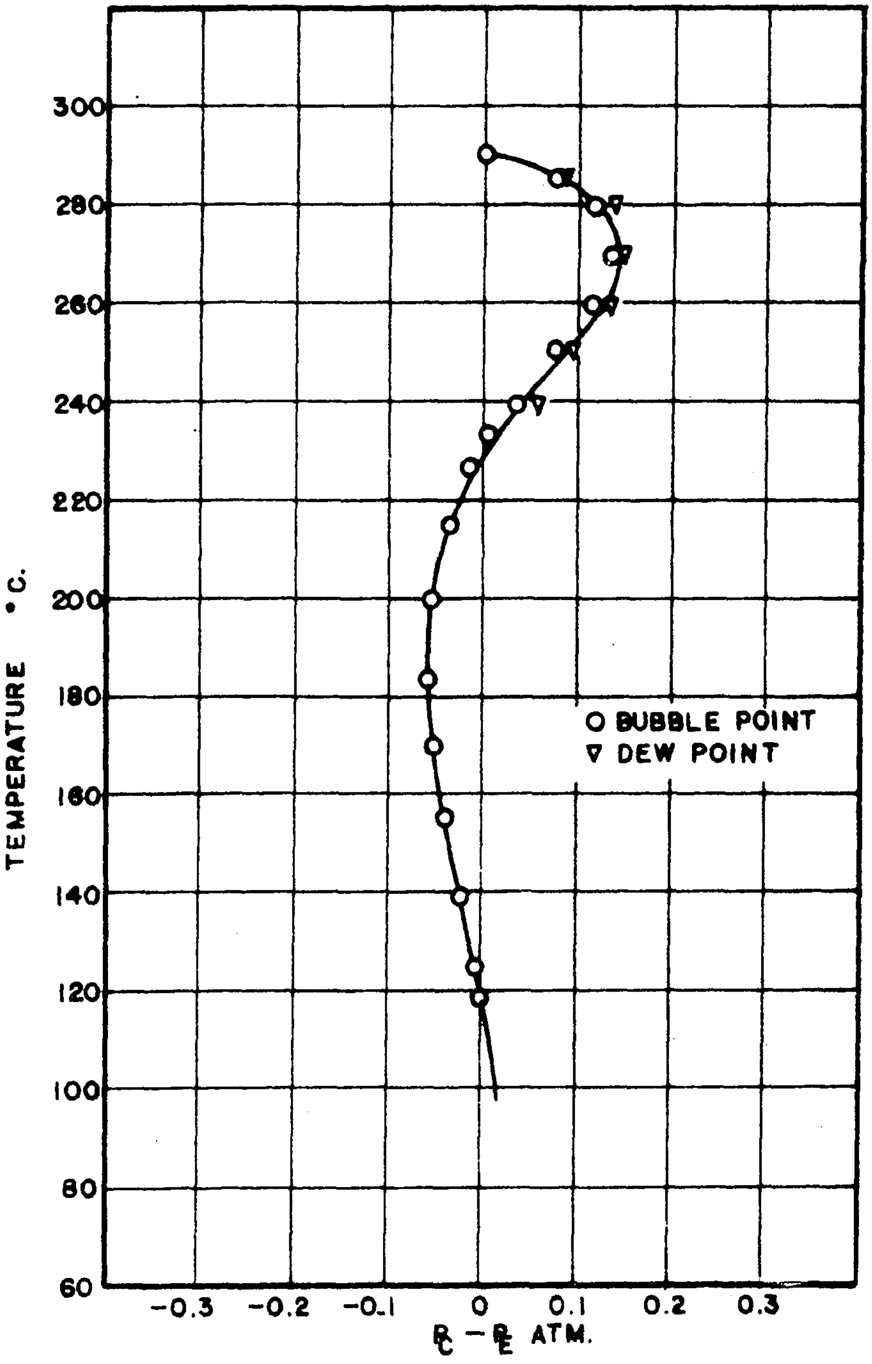


FIGURE 17, VAPOR PRESSURE DEVIATION CURVE FOR 3-METHYLHEPTANE

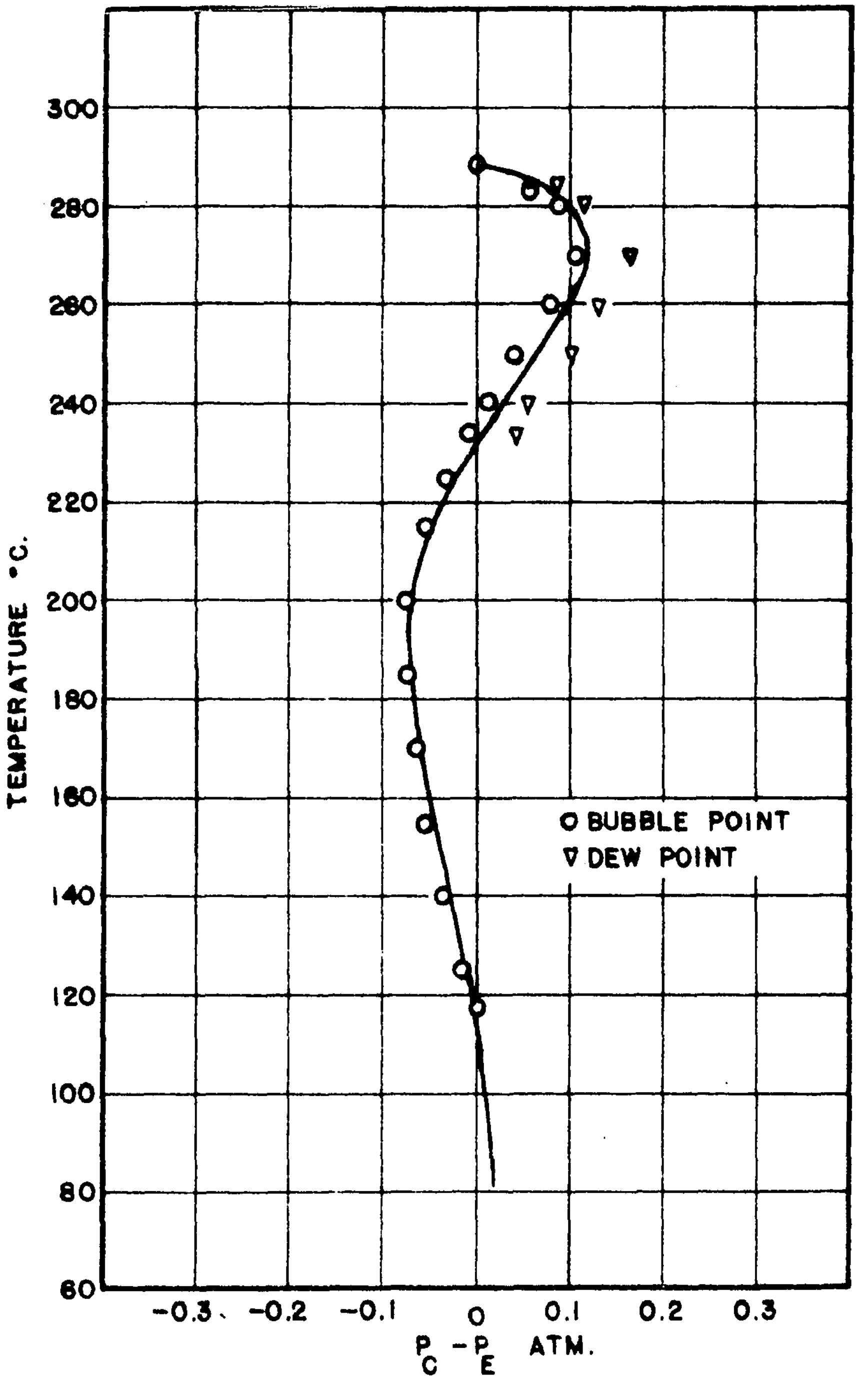


FIGURE 18, VAPOR PRESSURE DEVIATION CURVE
FOR 4-METHYLHEPTANE

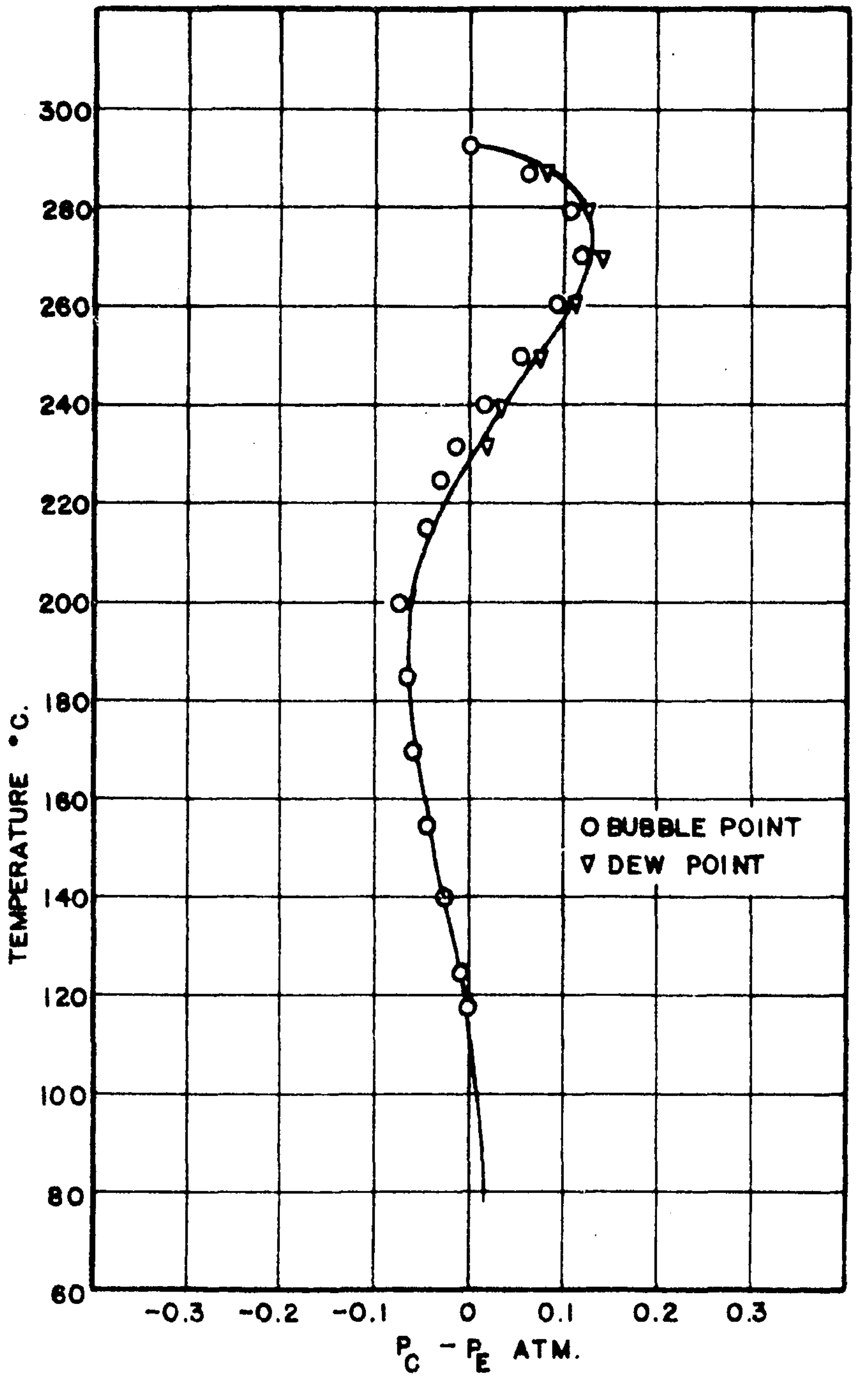


FIGURE 19, VAPOR PRESSURE DEVIATION CURVE FOR 3-ETHYLHEXANE

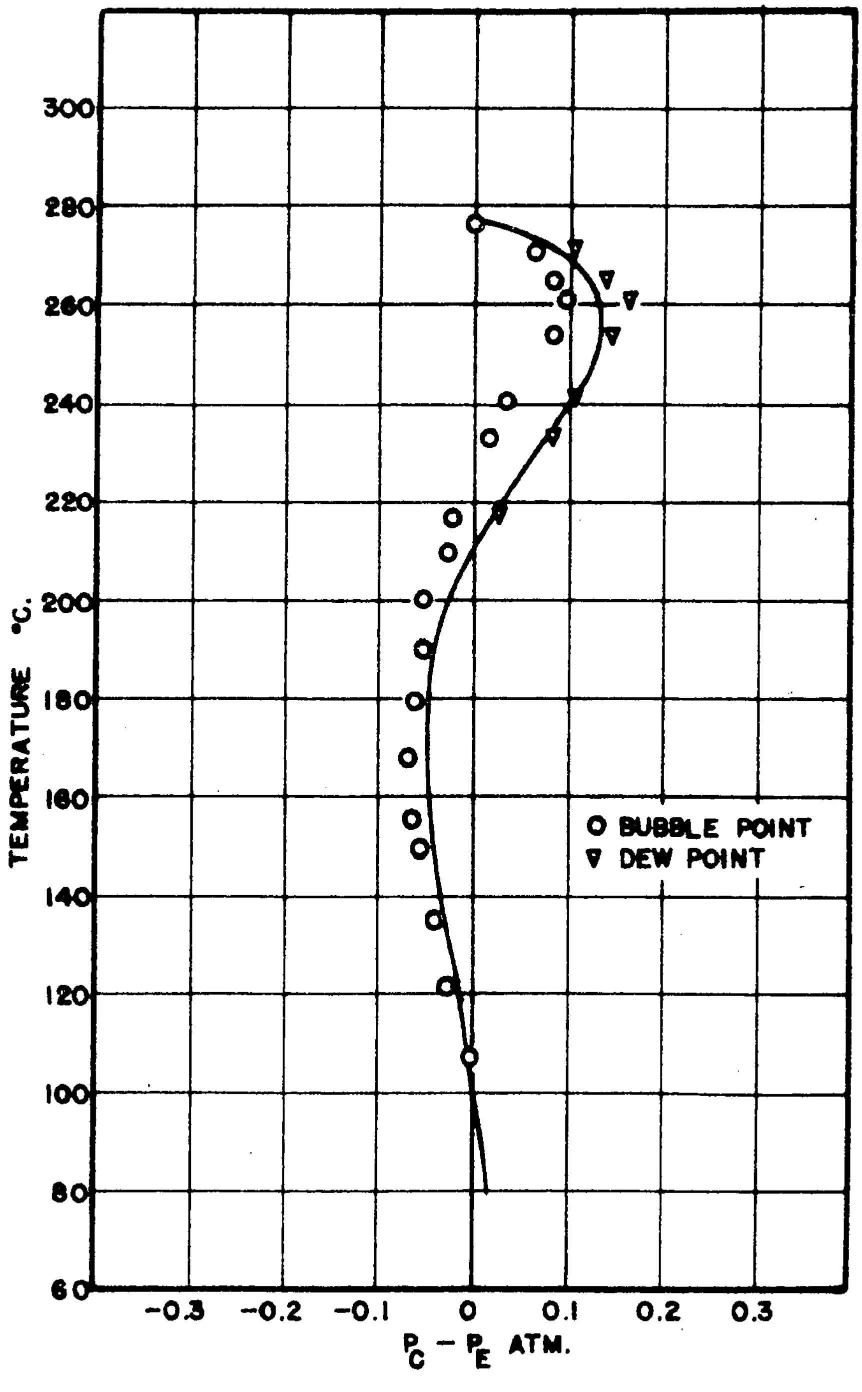


FIGURE 20, VAPOR PRESSURE DEVIATION CURVE FOR 2,2-DIMETHYLHEXANE

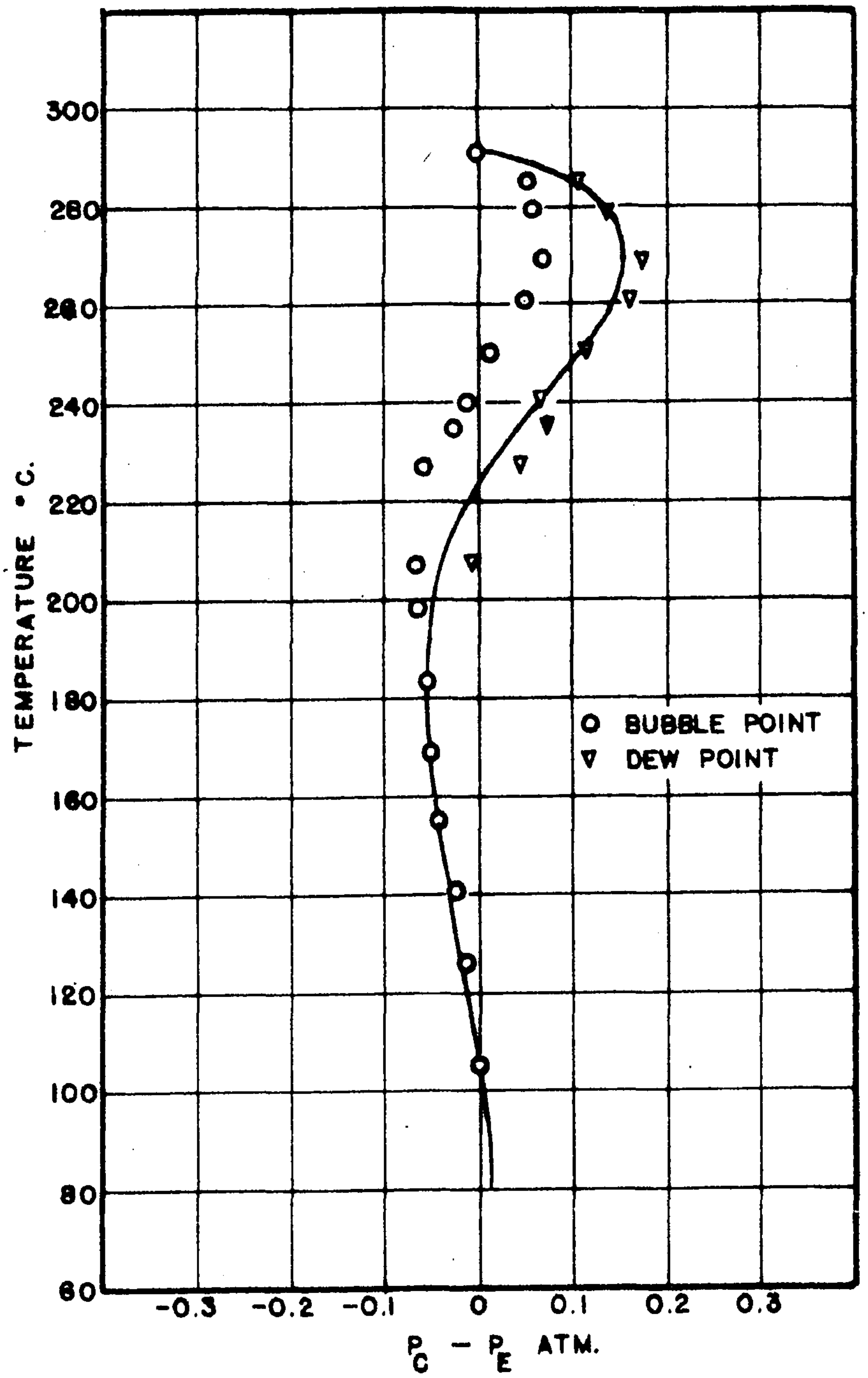


FIGURE 21, VAPOR PRESSURE DEVIATION CURVE
FOR 2,3-DIMETHYLHEXANE

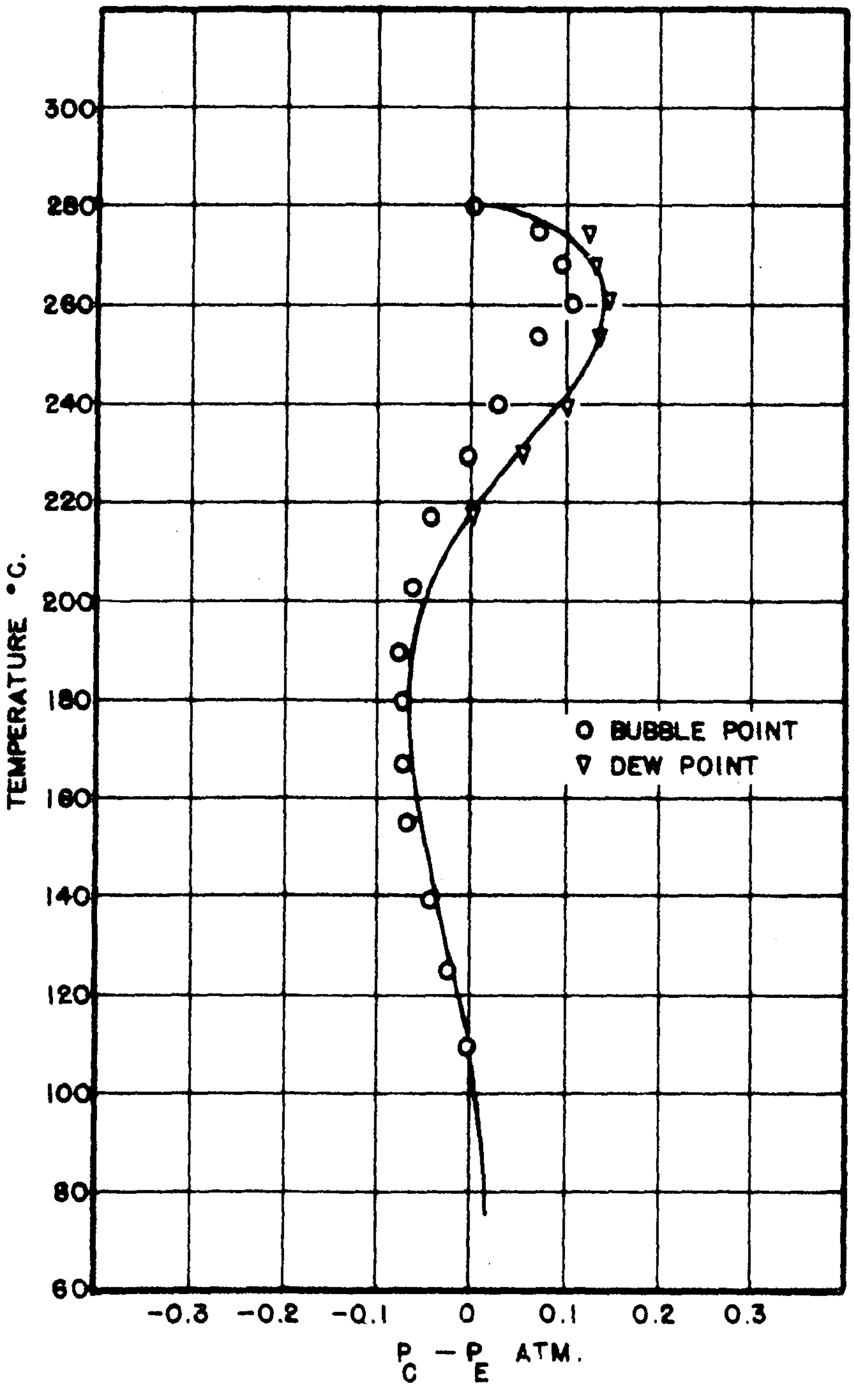


FIGURE 22, VAPOR PRESSURE DEVIATION CURVE FOR 2,4-DIMETHYLHEXANE

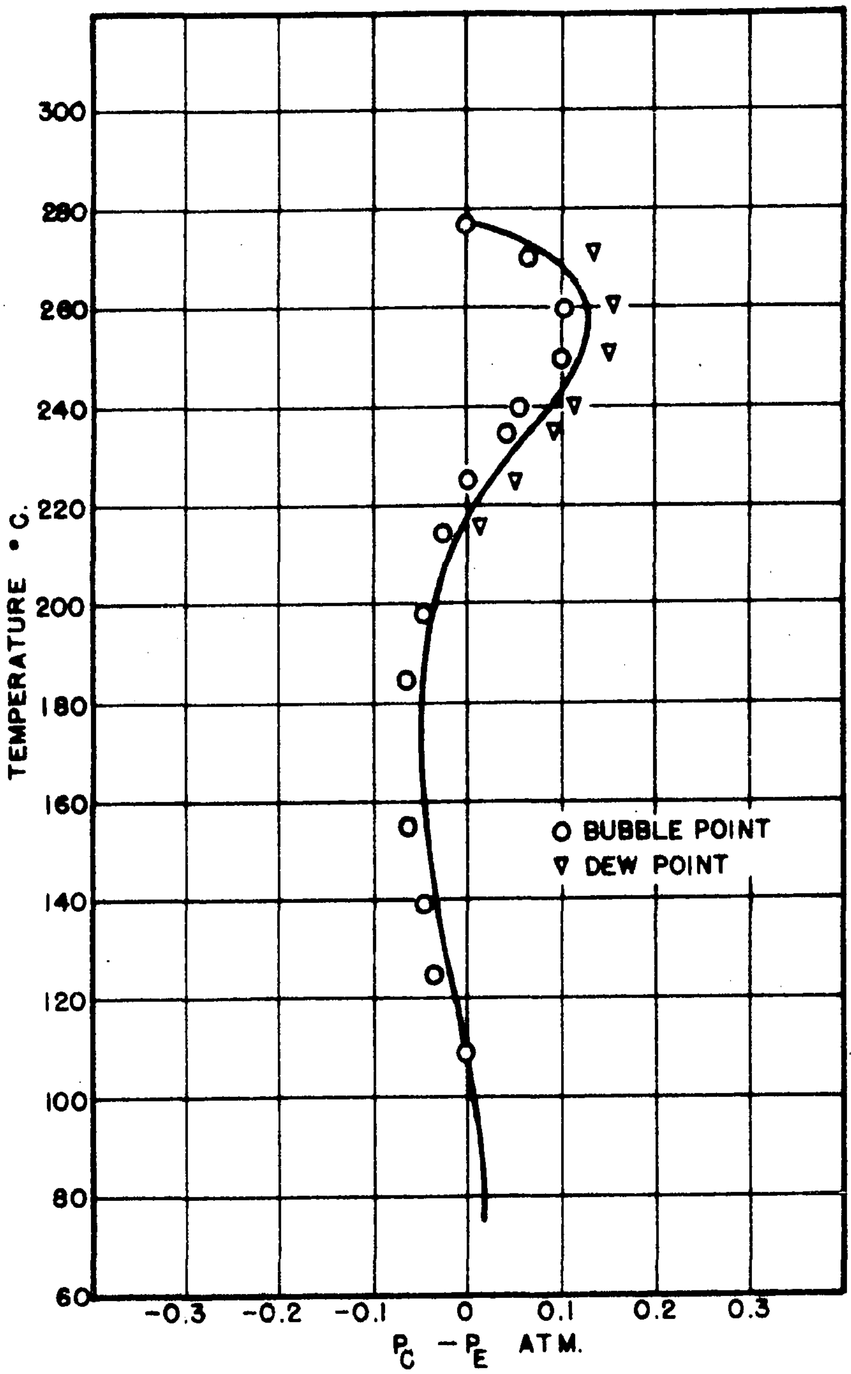


FIGURE 23, VAPOR PRESSURE DEVIATION CURVE FOR 2,5-DIMETHYLHEXANE

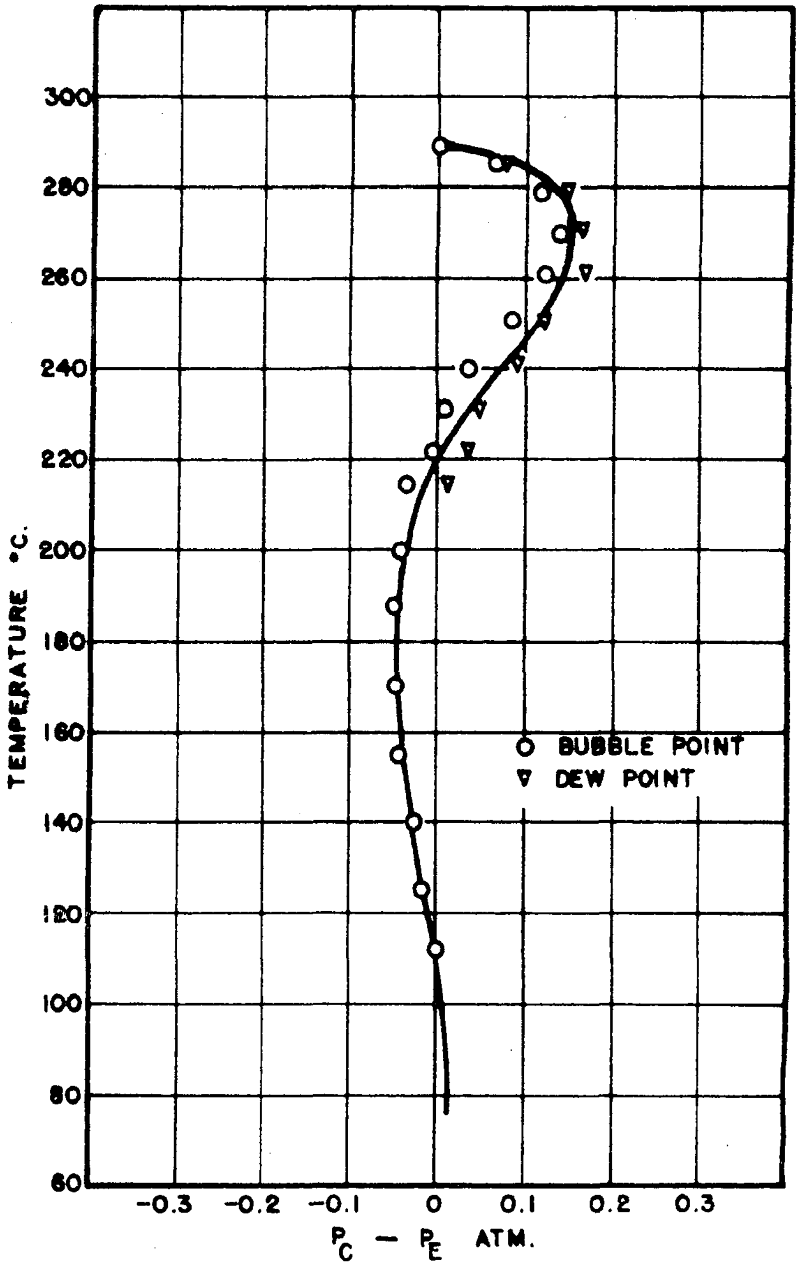


FIGURE 24, VAPOR PRESSURE DEVIATION CURVE FOR 3,3-DIMETHYLHEXANE

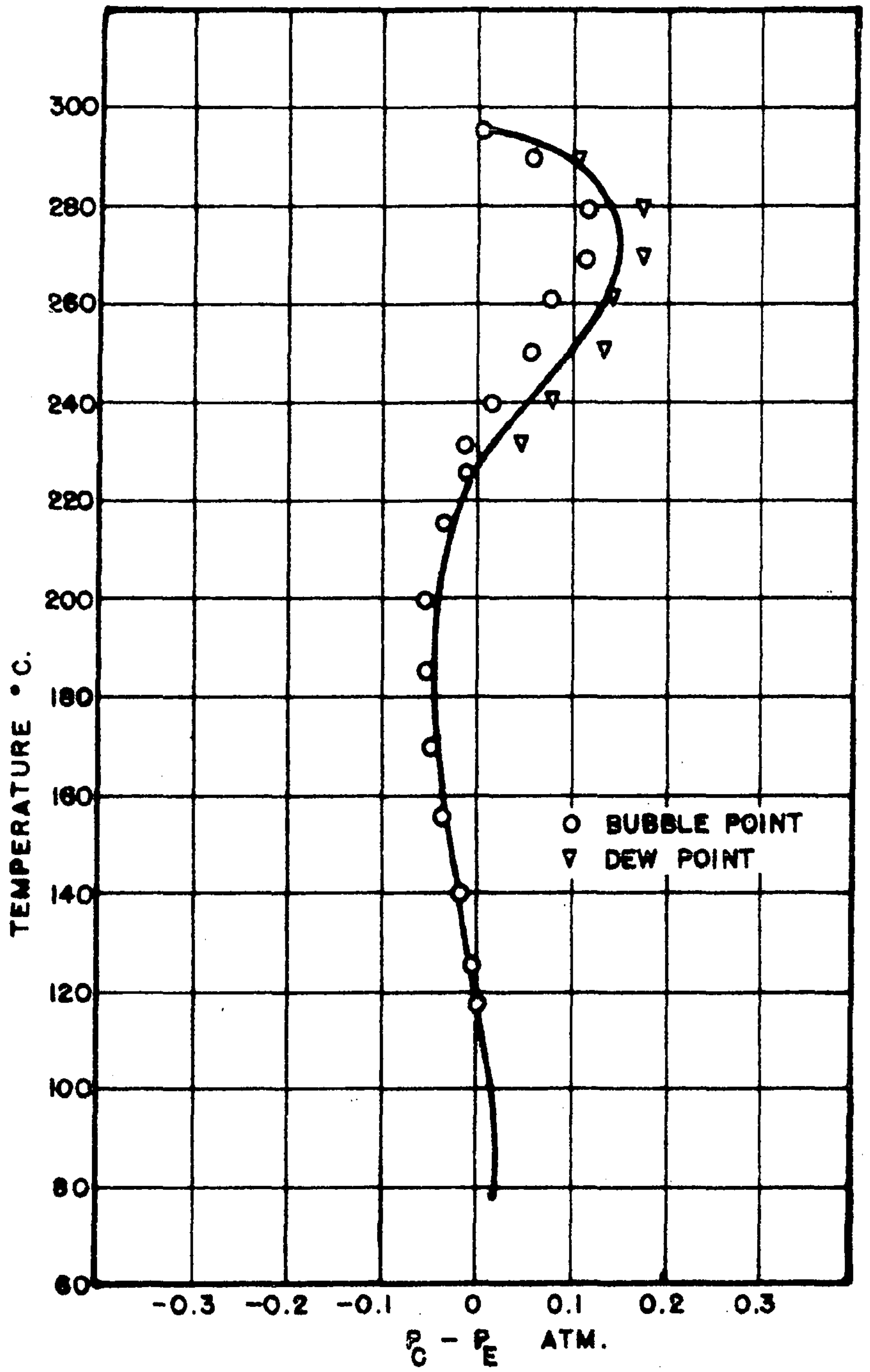


FIGURE 25, VAPOR PRESSURE DEVIATION CURVE FOR 3,4-DIMETHYLHEXANE

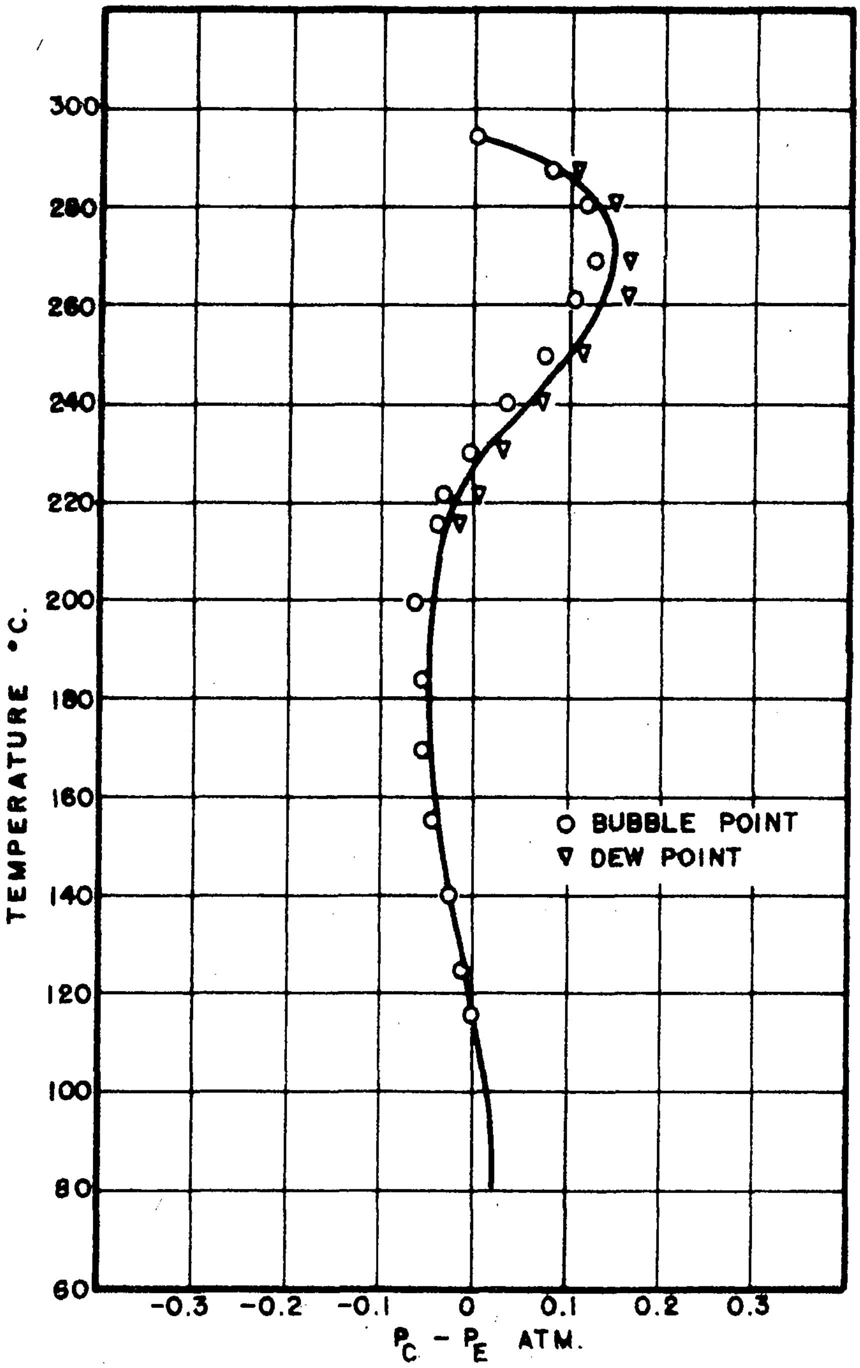


FIGURE 26, VAPOR PRESSURE DEVIATION CURVE FOR 2-METHYL-3-ETHYLPENTANE

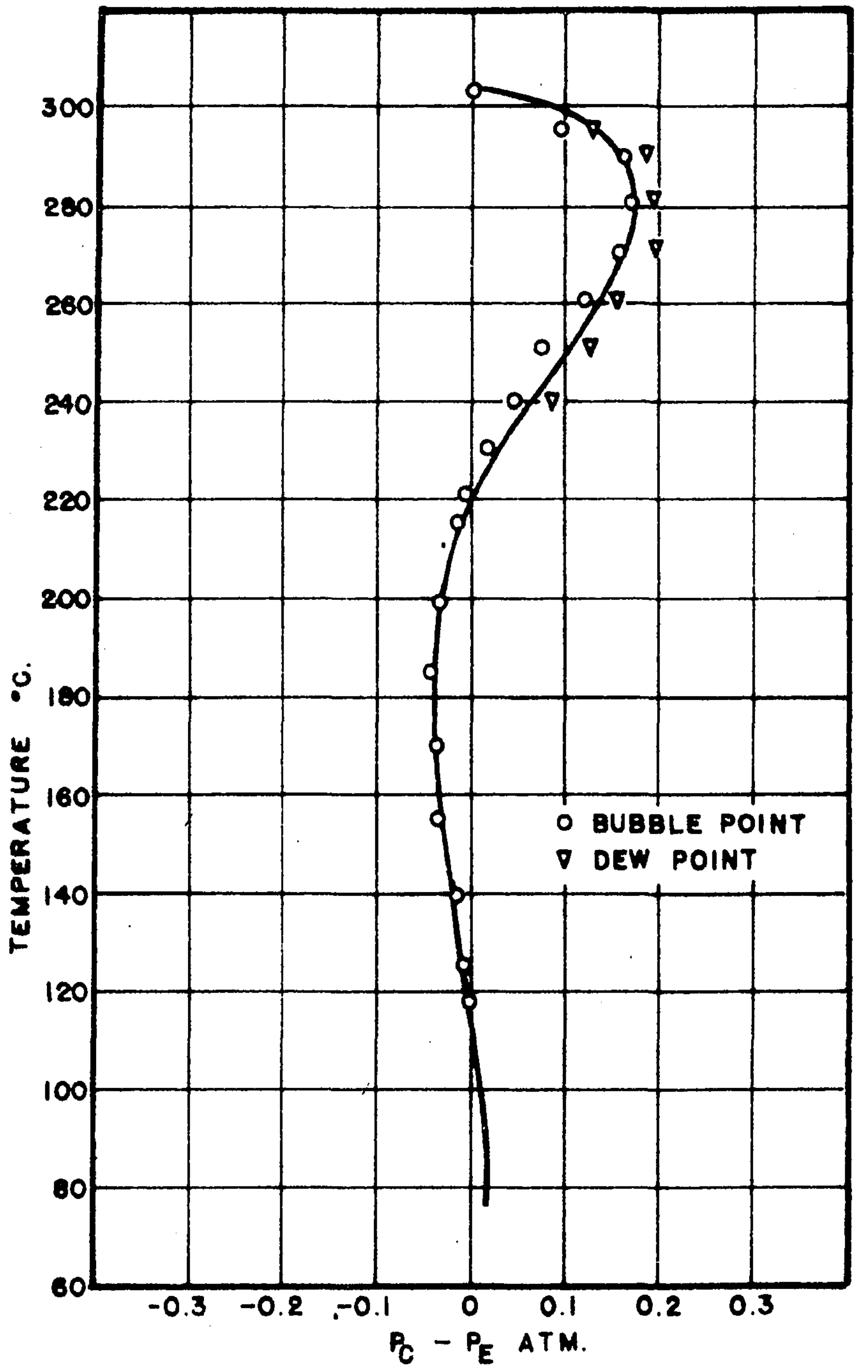


FIGURE 27, VAPOR PRESSURE DEVIATION CURVE FOR 3-METHYL-3-ETHYLPENTANE

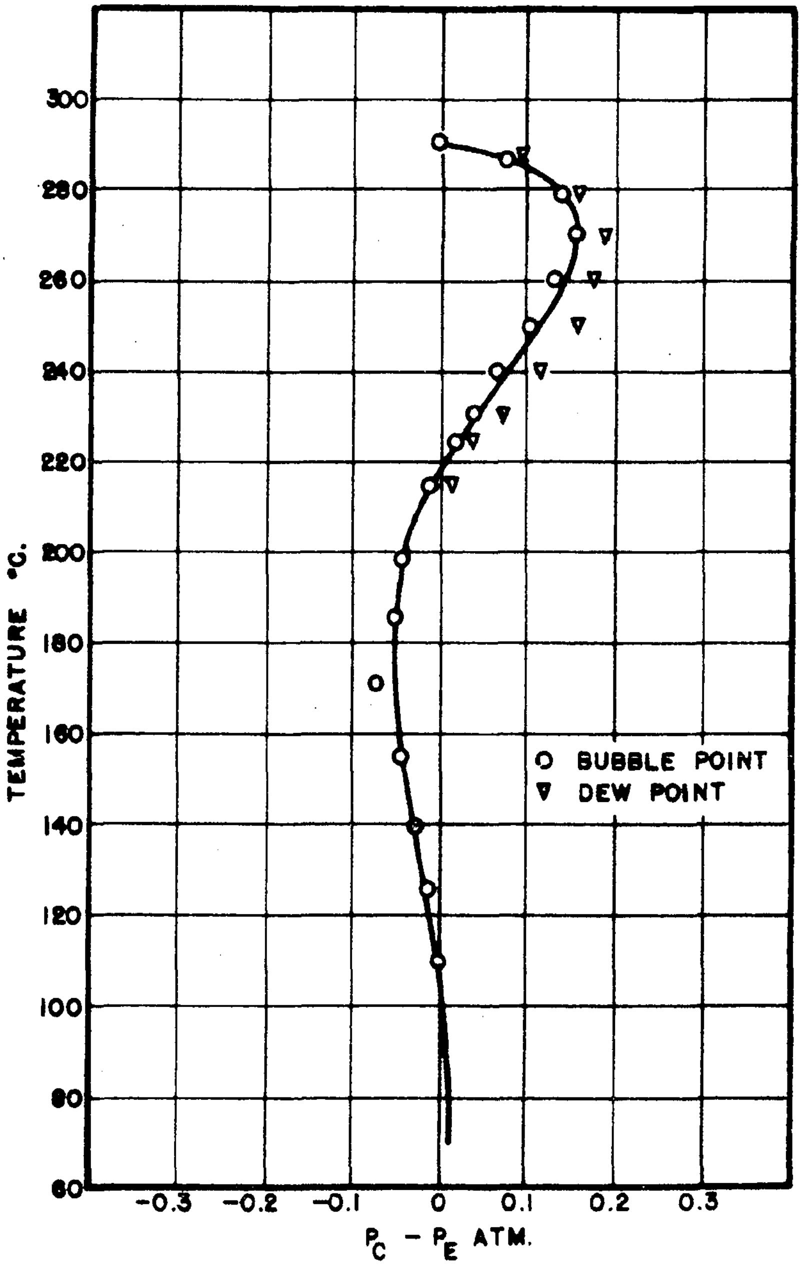


FIGURE 28, VAPOR PRESSURE DEVIATION CURVE FOR 2,2,3-TRIMETHYLPENTANE

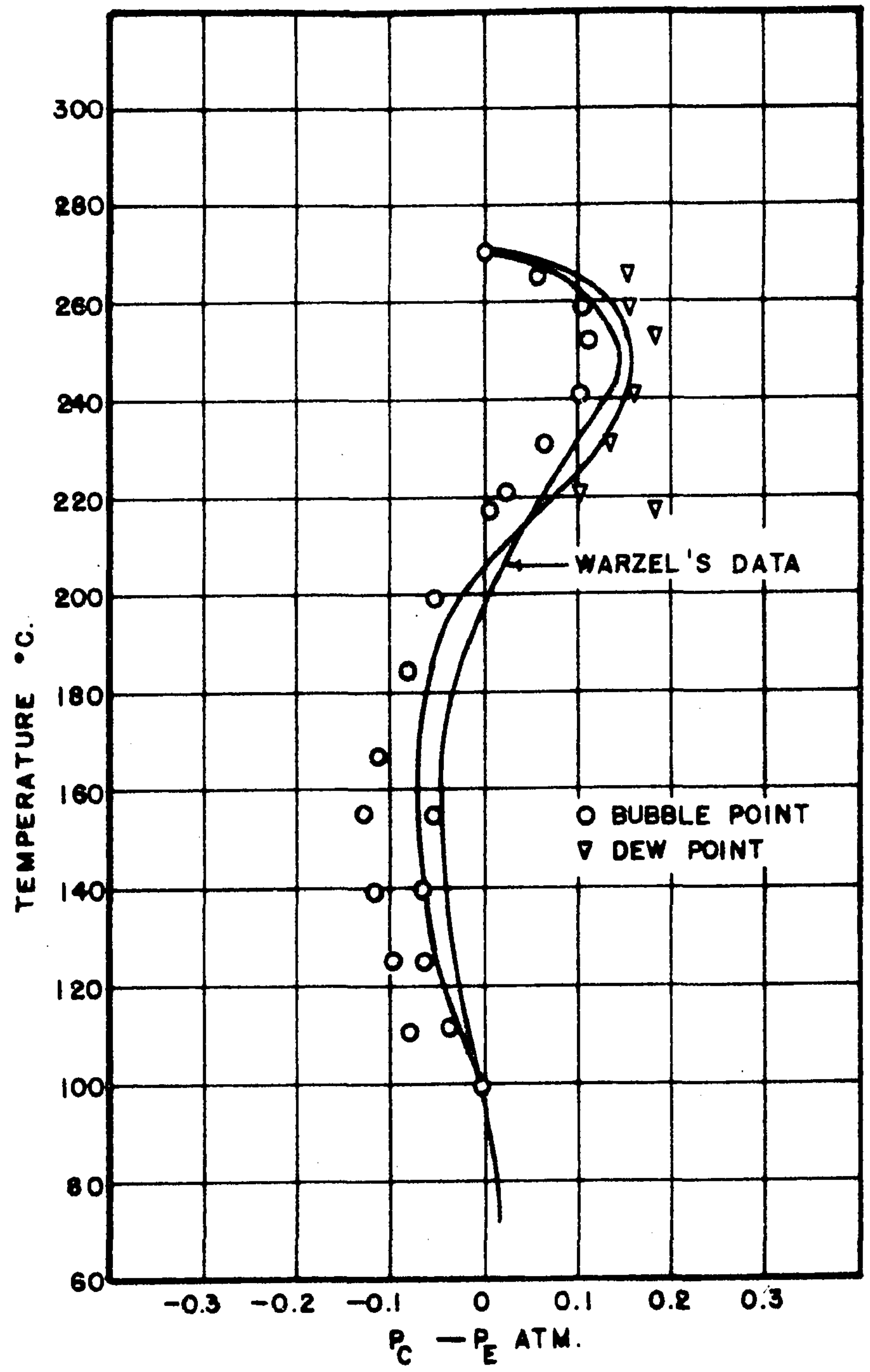


FIGURE 29, VAPOR PRESSURE DEVIATION CURVE FOR 2,2,4-TRIMETHYLPENTANE

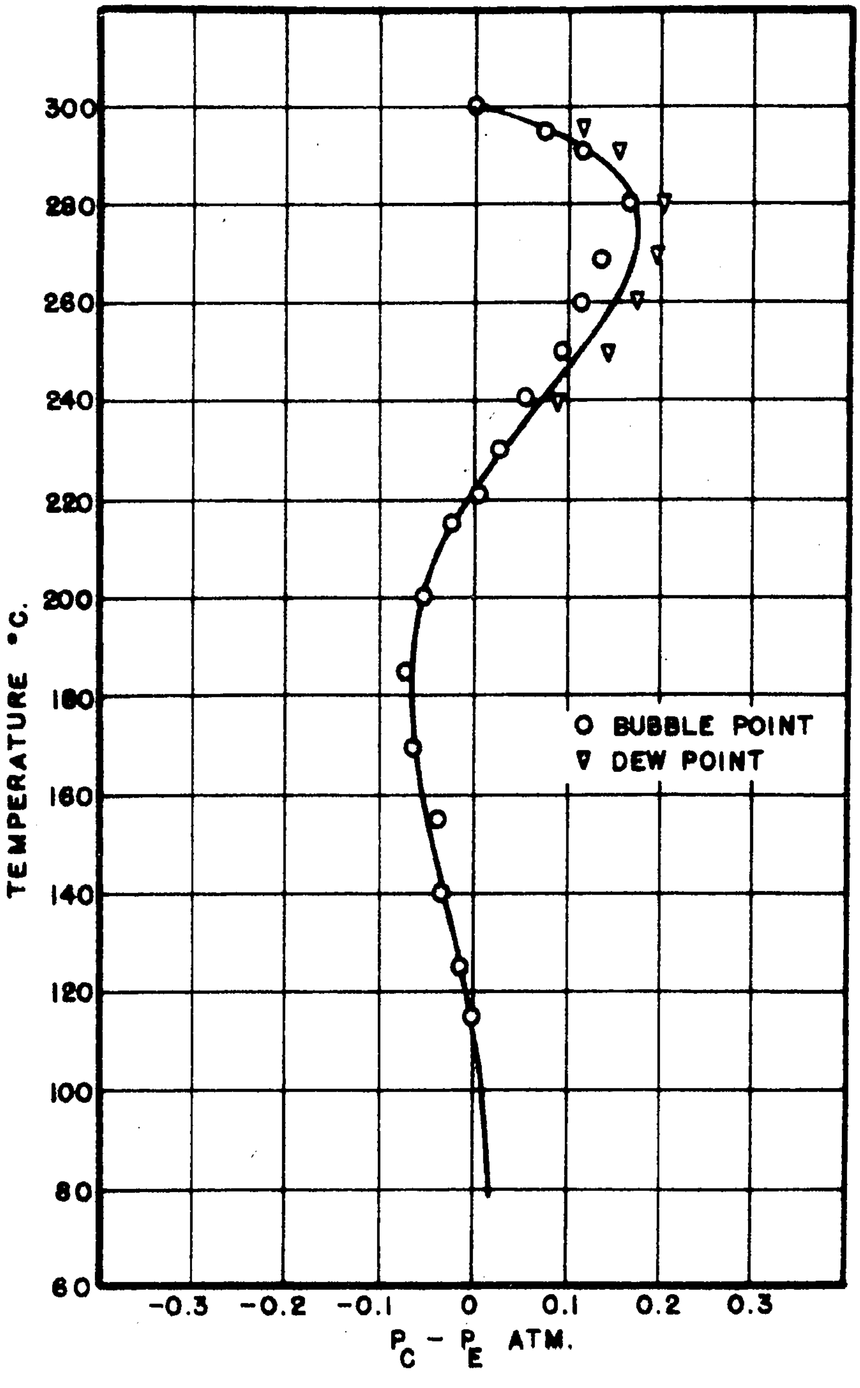


FIGURE 30, VAPOR PRESSURE DEVIATION CURVE FOR 2,3,3-TRIMETHYLPENTANE

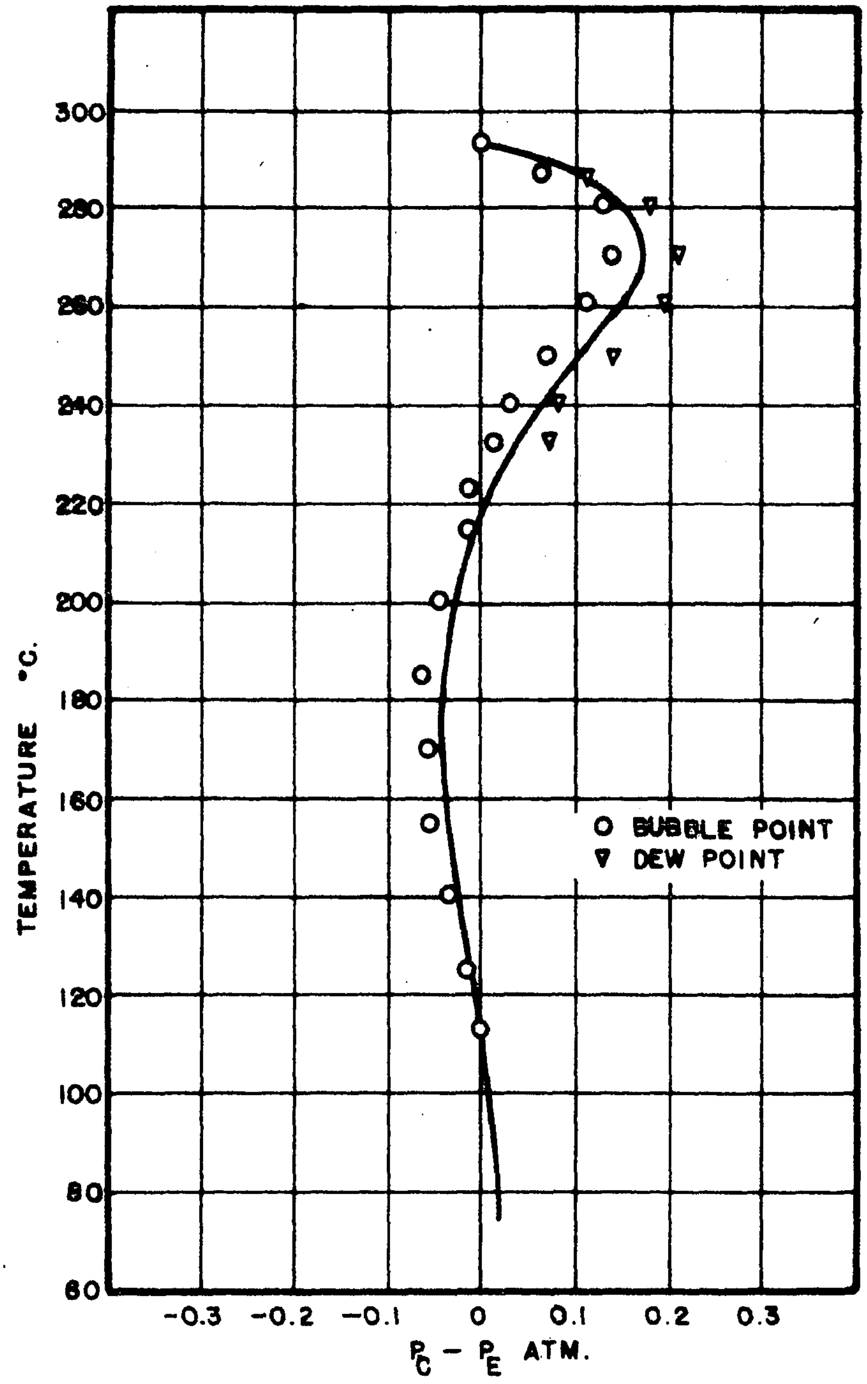


FIGURE 31, VAPOR PRESSURE DEVIATION CURVE FOR 2,3,4-TRIMETHYLPENTANE

TABLE 2

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of n-Heptane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
98.42	0.000	1.000	-----	-----
100.00	-0.004	1.050	0.608	-----
110.00	-0.015	1.391	0.598	-----
120.00	-0.025	1.811	0.588	-----
130.00	-0.035	2.323	0.578	-----
140.00	-0.045	2.941	0.567	-----
150.00	-0.055	3.681	0.556	-----
160.00	-0.061	4.553	0.544	-----
170.00	-0.065	5.576	0.531	-----
180.00	-0.063	6.765	0.517	-----
190.00	-0.055	8.135	0.503	-----
200.00	-0.035	9.701	0.488	0.042
210.00	0.006	11.472	0.472	0.047
220.00	0.066	13.467	0.455	0.052
230.00	0.130	15.725	0.436	0.060
240.00	0.167	18.290	0.415	0.072
250.00	0.179	21.186	0.385	0.094
260.00	0.145	24.449	0.335	0.135
266.85	0.000	27.002	0.232 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.58932 - 1705.34/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 3

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2-Methylhexane

			Saturated Density	
Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Liquid gm/cc	Vapor gm/cc
90.05	0.000	1.000	0.606	-----
100.00	-0.015	1.337	0.598	-----
110.00	-0.027	1.751	0.590	-----
120.00	-0.039	2.257	0.582	-----
130.00	-0.050	2.868	0.572	-----
140.00	-0.059	3.599	0.562	-----
150.00	-0.064	4.463	0.552	-----
160.00	-0.065	5.477	0.540	-----
170.00	-0.052	6.648	0.528	-----
180.00	-0.026	7.995	0.513	-----
190.00	0.010	9.540	0.499	-----
200.00	0.050	11.306	0.484	-----
210.00	0.090	13.310	0.467	-----
220.00	0.123	15.602	0.447	0.058
230.00	0.146	18.181	0.422	0.075
240.00	0.151	21.079	0.392	0.096
250.00	0.115	24.342	0.350	0.129
257.15	0.000	26.971	0.238	Critical

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.54120 - 1649.45/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 4

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 3-Methylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
91.85	0.000	1.000	-----	-----
100.00	-0.015	1.271	0.622	-----
110.00	-0.030	1.671	0.612	-----
120.00	-0.045	2.159	0.602	-----
130.00	-0.057	2.808	0.592	-----
140.00	-0.066	3.447	0.582	-----
150.00	-0.070	4.275	0.572	-----
160.00	-0.066	5.245	0.561	-----
170.00	-0.057	6.374	0.550	-----
180.00	-0.041	7.680	0.538	-----
190.00	-0.018	9.180	0.524	-----
200.00	0.015	10.889	0.508	-----
210.00	0.056	12.828	0.489	0.048
220.00	0.116	15.006	0.468	0.058
230.00	0.175	17.460	0.445	0.071
240.00	0.197	20.246	0.418	0.089
250.00	0.180	23.385	0.386	0.119
260.00	0.081	26.939	0.313	0.183
262.04	0.000	27.767	0.248	Critical

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.53958 - 1657.04/(t^{o}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 5

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 3-Ethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
93.47	0.000	1.000	-----	-----
100.00	-0.005	1.205	0.620	-----
110.00	-0.016	1.583	0.610	-----
120.00	-0.027	2.046	0.599	-----
130.00	-0.038	2.607	0.588	-----
140.00	-0.046	3.277	0.578	-----
150.00	-0.051	4.071	0.568	-----
160.00	-0.053	5.003	0.557	-----
170.00	-0.050	6.090	0.545	-----
180.00	-0.039	7.343	0.533	-----
190.00	-0.010	8.772	0.520	-----
200.00	0.030	10.400	0.506	-----
210.00	0.072	12.253	0.490	-----
220.00	0.115	14.352	0.473	0.053
230.00	0.148	16.725	0.453	0.065
240.00	0.165	19.352	0.429	0.079
250.00	0.161	22.391	0.398	0.100
260.00	0.125	25.735	0.353	0.134
265.00	0.075	27.564	0.314	0.170
267.42	0.000	28.530	0.241 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.52268 - 1658.19/(t^{o}C. + 273.17)$$

and pressure deviation.

TABLE 6

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 2,2-Dimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
79.20	0.000	1.000	-----	-----
90.00	-0.011	1.367	0.612	-----
100.00	-0.021	1.791	0.602	-----
110.00	-0.031	2.310	0.591	-----
120.00	-0.040	2.936	0.581	-----
130.00	-0.046	3.683	0.570	-----
140.00	-0.048	4.565	0.560	-----
150.00	-0.045	5.598	0.548	-----
160.00	-0.036	6.798	0.537	-----
170.00	-0.024	8.185	0.524	-----
180.00	-0.002	9.771	0.511	-----
190.00	0.038	11.564	0.496	-----
200.00	0.096	13.584	0.478	-----
210.00	0.149	15.924	0.457	0.063
220.00	0.168	18.474	0.431	0.078
230.00	0.161	21.401	0.400	0.100
240.00	0.110	24.688	0.355	0.133
247.29	0.000	27.367	0.241 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.45009 - 1568.08/(t^{o}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 7

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 2,3-Dimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
89.78	0.000	1.000	-----	-----
90.00	-0.001	1.007	0.661	-----
100.00	-0.017	1.344	0.650	-----
110.00	-0.031	1.757	0.638	-----
120.00	-0.044	2.259	0.626	-----
130.00	-0.052	2.859	0.614	-----
140.00	-0.058	3.574	0.604	-----
150.00	-0.063	4.421	0.592	-----
160.00	-0.062	5.411	0.580	-----
170.00	-0.056	6.561	0.568	-----
180.00	-0.043	7.885	0.556	-----
190.00	-0.020	9.398	0.541	-----
200.00	0.020	11.110	0.526	0.042
210.00	0.069	13.048	0.508	0.051
220.00	0.119	15.240	0.489	0.062
230.00	0.158	17.706	0.469	0.076
240.00	0.176	20.484	0.444	0.095
250.00	0.165	23.595	0.412	0.121
260.00	0.099	27.085	0.360	0.168
264.14	0.000	28.700	0.262 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.49262 - 1630.60/(t^\circ\text{C.} + 273.17)$$

and pressure deviation.

TABLE 8

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,4-Dimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
80.50	0.000	1.000	-----	-----
90.00	-0.017	1.327	0.611	-----
100.00	-0.033	1.747	0.602	-----
110.00	-0.047	2.260	0.592	-----
120.00	-0.060	2.879	0.582	-----
130.00	-0.071	3.619	0.572	-----
140.00	-0.080	4.497	0.560	-----
150.00	-0.085	5.527	0.548	-----
160.00	-0.084	6.724	0.534	-----
170.00	-0.070	8.100	0.520	-----
180.00	-0.035	9.665	0.504	0.037
190.00	0.025	11.433	0.489	0.044
200.00	0.081	13.452	0.472	0.052
210.00	0.130	15.745	0.451	0.064
220.00	0.160	18.342	0.427	0.079
230.00	0.163	21.268	0.398	0.100
240.00	0.100	24.584	0.256	0.136
246.58	0.000	27.009	0.240 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.47991 - 1584.41/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 9

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 3,3-Dimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
86.06	0.000	1.000	0.622	-----
90.00	-0.004	1.121	0.618	-----
100.00	-0.010	1.474	0.608	-----
110.00	-0.016	1.908	0.598	-----
120.00	-0.025	2.438	0.588	-----
130.00	-0.031	3.072	0.577	-----
140.00	-0.034	3.823	0.565	-----
150.00	-0.031	4.704	0.554	-----
160.00	-0.023	5.730	0.542	-----
170.00	-0.006	6.914	0.529	-----
180.00	0.021	8.270	0.516	-----
190.00	0.065	9.809	0.502	-----
200.00	0.110	11.562	0.488	-----
210.00	0.155	14.546	0.474	-----
220.00	0.195	15.784	0.458	0.058
230.00	0.225	18.298	0.438	0.071
240.00	0.235	21.126	0.414	0.088
250.00	0.211	24.261	0.382	0.112
260.00	0.125	27.783	0.328	0.160
263.19	0.000	29.073	0.242 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.43153 - 1591.94/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 10

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,2,3-Trimethylbutane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
80.88	0.000	1.000	-----	-----
90.00	-0.010	1.299	-----	-----
100.00	-0.019	1.698	0.630	-----
110.00	-0.030	2.187	0.618	-----
120.00	-0.042	2.778	0.605	-----
130.00	-0.054	3.483	0.592	-----
140.00	-0.059	4.311	0.580	-----
150.00	-0.058	5.276	0.467	-----
160.00	-0.050	6.394	0.554	-----
170.00	-0.030	7.676	0.542	-----
180.00	0.000	9.138	0.529	-----
190.00	0.039	10.799	0.515	-----
200.00	0.090	12.672	0.500	0.046
210.00	0.145	14.782	0.484	0.056
220.00	0.180	17.167	0.464	0.068
230.00	0.201	19.839	0.442	0.083
240.00	0.203	22.819	0.412	0.104
250.00	0.165	26.142	0.362	0.139
257.96	0.000	29.146	0.252	Critical

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.39299 - 1555.34/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 11

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

n-Octane

			Saturated Density	
Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Liquid gm/cc	Vapor gm/cc
125.66	0.000	1.000	-----	-----
130.00	-0.006	1.128	0.608	-----
140.00	-0.021	1.471	0.599	-----
150.00	-0.034	1.886	0.590	-----
160.00	-0.046	2.384	0.580	-----
170.00	-0.056	2.976	0.569	-----
180.00	-0.062	3.674	0.558	-----
190.00	-0.066	4.494	0.546	-----
200.00	-0.068	5.449	0.534	-----
210.00	-0.064	6.550	0.512	-----
220.00	-0.050	7.810	0.509	-----
230.00	-0.023	9.241	0.495	0.040
240.00	0.011	10.865	0.479	0.045
250.00	0.055	12.697	0.460	0.053
260.00	0.091	14.771	0.438	0.064
270.00	0.120	17.104	0.411	0.079
280.00	0.129	19.727	0.378	0.100
290.00	0.110	22.664	0.332	0.135
295.59	0.000	24.537	0.232 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.65176 - 1855.26/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 12

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2-Methylheptane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
117.65	0.000	1.000	-----	-----
120.00	-0.004	1.070	0.614	-----
130.00	-0.015	1.399	0.604	-----
140.00	-0.028	1.803	0.594	-----
150.00	-0.042	2.292	0.583	-----
160.00	-0.055	2.876	0.572	-----
170.00	-0.064	3.565	0.560	-----
180.00	-0.069	4.373	0.549	-----
190.00	-0.068	5.312	0.536	-----
200.00	-0.063	6.399	0.524	-----
210.00	-0.047	7.643	0.511	-----
220.00	-0.024	9.064	0.496	-----
230.00	0.005	10.679	0.481	0.047
240.00	0.041	12.504	0.462	0.054
250.00	0.081	14.558	0.441	0.064
260.00	0.112	16.873	0.417	0.078
270.00	0.125	19.475	0.386	0.099
280.00	0.088	22.412	0.342	0.133
286.41	0.000	24.517	0.234 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.60725 - 1800.61/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 13

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 3-Methylheptane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
118.92	0.000	1.000	-----	-----
120.00	-0.002	1.032	0.620	-----
130.00	-0.010	1.348	0.612	-----
140.00	-0.021	1.738	0.603	-----
150.00	-0.038	2.215	0.594	-----
160.00	-0.045	2.776	0.584	-----
170.00	-0.052	3.443	0.573	-----
180.00	-0.055	4.225	0.562	-----
190.00	-0.055	5.137	0.550	-----
200.00	-0.052	6.194	0.538	-----
210.00	-0.041	7.407	0.525	-----
220.00	-0.020	8.789	0.512	-----
230.00	0.005	10.362	0.498	-----
240.00	0.040	12.136	0.482	0.054
250.00	0.086	14.127	0.462	0.064
260.00	0.120	16.375	0.440	0.078
270.00	0.139	18.900	0.413	0.096
280.00	0.115	21.746	0.376	0.124
285.00	0.081	23.302	0.350	0.147
290.45	0.000	25.127	0.246 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.60063 - 1803.86/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 14

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 4-Methylheptane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
117.71	0.000	1.000	-----	-----
120.00	-0.002	1.066	-----	-----
130.00	-0.010	1.391	0.614	-----
140.00	-0.021	1.792	0.604	-----
150.00	-0.029	2.274	0.594	-----
160.00	-0.046	2.860	0.582	-----
170.00	-0.057	3.548	0.572	-----
180.00	-0.064	4.355	0.560	-----
190.00	-0.065	5.292	0.548	-----
200.00	-0.061	6.375	0.534	-----
210.00	-0.051	7.620	0.520	-----
220.00	-0.032	9.037	0.504	-----
230.00	-0.004	10.646	0.488	0.044
240.00	0.028	12.465	0.472	0.050
250.00	0.065	14.511	0.451	0.060
260.00	0.100	16.810	0.428	0.074
270.00	0.119	19.391	0.399	0.096
280.00	0.100	22.294	0.360	0.126
288.52	0.000	25.087	0.240 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.60194 - 1798.81/(t^{\circ}C. + 273.17)$$

and pressure deviation.

TABLE 15

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 3-Ethylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
118.53	0.000	1.000	-----	-----
120.00	-0.001	1.041	0.632	-----
130.00	-0.012	1.363	0.622	-----
140.00	-0.025	1.757	0.612	-----
150.00	-0.037	2.232	0.602	-----
160.00	-0.045	2.796	0.592	-----
170.00	-0.054	3.467	0.582	-----
180.00	-0.058	4.253	0.572	-----
190.00	-0.060	5.170	0.561	-----
200.00	-0.055	6.237	0.549	-----
210.00	-0.046	7.443	0.536	-----
220.00	-0.028	8.829	0.524	0.042
230.00	-0.004	10.404	0.510	0.046
240.00	0.028	12.180	0.493	0.052
250.00	0.067	14.177	0.474	0.063
260.00	0.109	16.415	0.453	0.077
270.00	0.135	18.928	0.426	0.095
280.00	0.122	21.758	0.391	0.124
290.00	0.050	24.940	0.326	0.180
292.27	0.000	25.738	0.251 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.59076 - 1798.20/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 16

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,2-Dimethylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
106.84	0.000	1.000	-----	-----
110.00	-0.001	1.091	-----	-----
120.00	-0.010	1.427	0.608	-----
130.00	-0.020	1.839	0.597	-----
140.00	-0.031	2.338	0.586	-----
150.00	-0.040	2.934	0.574	-----
160.00	-0.046	3.637	0.564	-----
170.00	-0.047	4.460	0.552	-----
180.00	-0.045	5.420	0.539	-----
190.00	-0.039	6.530	0.526	-----
200.00	-0.025	7.801	0.512	-----
210.00	0.000	9.246	0.498	-----
220.00	0.029	10.888	0.482	0.050
230.00	0.060	12.744	0.465	0.054
240.00	0.096	14.830	0.445	0.063
250.00	0.122	17.175	0.421	0.078
260.00	0.133	19.802	0.391	0.100
270.00	0.096	22.759	0.348	0.136
275.00	0.041	24.385	0.300	0.180
276.65	0.000	24.961	0.239 Critical	

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.52412 - 1719.21/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 17

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,3-Dimethylhexane

	Pressure	Vapor	Saturated Density	
Temperature °C.	Deviation Atm.	Pressure* Atm.	Liquid gm/cc	Vapor gm/cc
115.61	0.000	1.000	-----	-----
120.00	-0.010	1.134	0.626	-----
130.00	-0.020	1.475	0.616	-----
140.00	-0.028	1.887	0.606	-----
150.00	-0.035	2.383	0.597	-----
160.00	-0.045	2.979	0.587	-----
170.00	-0.050	3.679	0.576	-----
180.00	-0.051	4.498	0.565	-----
190.00	-0.050	5.452	0.554	-----
200.00	-0.043	6.552	0.542	-----
210.00	-0.031	7.812	0.529	-----
220.00	-0.014	9.250	0.514	-----
230.00	0.022	10.866	0.500	0.046
240.00	0.065	12.688	0.483	0.052
250.00	0.110	14.738	0.464	0.064
260.00	0.144	17.045	0.440	0.077
270.00	0.154	19.637	0.413	0.095
280.00	0.125	22.548	0.376	0.122
285.00	0.090	24.133	0.345	0.167
290.27	0.000	25.938	0.244	Critical

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.56126 - 1773.33/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 18

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,4-Dimethylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
109.43	0.000	1.000	0.604	-----
110.00	-0.004	1.020	0.602	-----
120.00	-0.010	1.335	0.596	-----
130.00	-0.020	1.725	0.588	-----
140.00	-0.032	2.200	0.579	-----
150.00	-0.044	2.771	0.570	-----
160.00	-0.055	3.445	0.560	-----
170.00	-0.061	4.236	0.550	-----
180.00	-0.063	5.158	0.540	-----
190.00	-0.059	6.224	0.528	-----
200.00	-0.047	7.446	0.514	-----
210.00	-0.026	8.840	0.502	-----
220.00	0.009	10.417	0.488	0.043
230.00	0.050	12.199	0.472	0.052
240.00	0.090	14.212	0.454	0.063
250.00	0.123	16.477	0.432	0.078
260.00	0.140	19.020	0.406	0.098
270.00	0.127	21.871	0.370	0.126
280.30	0.000	25.229	0.242 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.54094 - 1737.36/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 19

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,5-Dimethylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
109.10	0.000	1.000	-----	-----
110.00	-0.001	1.026	-----	-----
120.00	-0.014	1.352	0.606	-----
130.00	-0.025	1.748	0.596	-----
140.00	-0.035	2.227	0.586	-----
150.00	-0.042	2.799	0.574	-----
160.00	-0.046	3.478	0.562	-----
170.00	-0.050	4.280	0.550	-----
180.00	-0.049	5.214	0.538	-----
190.00	-0.043	6.295	0.524	-----
200.00	-0.034	7.542	0.510	-----
210.00	-0.019	8.967	0.495	-----
220.00	0.007	10.582	0.480	0.044
230.00	0.045	12.402	0.462	0.052
240.00	0.087	14.452	0.442	0.063
250.00	0.119	16.763	0.419	0.078
260.00	0.131	19.362	0.391	0.099
270.00	0.098	22.291	0.346	0.131
276.84	0.000	24.542	0.237	Critical

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.55744 - 1742.17/(t^{o}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 20

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 3,3-Dimethylhexane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
111.97	0.000	1.000	-----	-----
120.00	-0.010	1.246	0.632	-----
130.00	-0.019	1.609	0.624	-----
140.00	-0.027	2.049	0.615	-----
150.00	-0.036	2.577	0.606	-----
160.00	-0.041	3.201	0.596	-----
170.00	-0.045	3.937	0.587	-----
180.00	-0.045	4.793	0.577	-----
190.00	-0.043	5.787	0.566	-----
200.00	-0.037	6.931	0.555	-----
210.00	-0.024	8.234	0.543	-----
220.00	-0.002	9.712	0.530	0.043
230.00	0.029	11.378	0.514	0.050
240.00	0.066	13.250	0.495	0.058
250.00	0.110	15.344	0.474	0.070
260.00	0.134	17.700	0.450	0.087
270.00	0.149	20.324	0.422	0.108
280.00	0.125	23.261	0.384	0.120
288.80	0.000	26.187	0.258 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.50672 - 1735.72/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 21

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 3,4-Dimethylhexane

Temperature	Pressure Deviation	Vapor Pressure*	Saturated Density	
$^{\circ}$C.	Atm.	Atm.	Liquid gm/cc	Vapor gm/cc
117.72	0.000	1.000	-----	-----
120.00	-0.002	1.065	-----	-----
130.00	-0.009	1.385	0.635	-----
140.00	-0.019	1.779	0.623	-----
150.00	-0.028	2.253	0.611	-----
160.00	-0.038	2.721	0.598	-----
170.00	-0.045	3.490	0.586	-----
180.00	-0.049	4.274	0.574	-----
190.00	-0.046	5.182	0.562	-----
200.00	-0.041	6.234	0.550	-----
210.00	-0.031	7.439	0.538	-----
220.00	-0.013	8.812	0.524	-----
230.00	0.012	10.367	0.508	0.044
240.00	0.050	12.115	0.491	0.050
250.00	0.100	14.071	0.474	0.058
260.00	0.135	16.280	0.454	0.068
270.00	0.150	18.760	0.431	0.084
280.00	0.140	21.534	0.400	0.107
290.00	0.084	24.628	0.348	0.146
295.63	0.000	26.569	0.245 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.55388 - 1780.07/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 22

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2-Methyl-3-ethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
115.65	0.000	1.000	-----	-----
120.00	-0.005	1.127	-----	-----
130.00	-0.014	1.464	0.635	-----
140.00	-0.025	1.876	0.624	-----
150.00	-0.036	2.371	0.613	-----
160.00	-0.045	2.959	0.602	-----
170.00	-0.050	3.650	0.590	-----
180.00	-0.051	4.458	0.580	-----
190.00	-0.050	5.398	0.569	-----
200.00	-0.046	6.482	0.558	-----
210.00	-0.036	7.724	0.546	-----
220.00	-0.018	9.134	0.532	0.040
230.00	0.011	10.751	0.518	0.046
240.00	0.052	12.514	0.501	0.054
250.00	0.101	14.517	0.483	0.064
260.00	0.137	16.773	0.462	0.077
270.00	0.150	19.305	0.438	0.095
280.00	0.133	22.137	0.406	0.122
290.00	0.064	25.308	0.350	0.172
293.87	0.000	26.651	0.258 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.53619 - 1763.76/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 23

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 3-Methyl-3-ethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
118.26	0.000	1.000	-----	-----
120.00	-0.001	1.072	0.646	-----
130.00	-0.008	1.360	0.636	-----
140.00	-0.016	1.740	0.628	-----
150.00	-0.026	2.199	0.618	-----
160.00	-0.035	2.745	0.609	-----
170.00	-0.040	3.386	0.599	-----
180.00	-0.040	4.134	0.589	-----
190.00	-0.036	5.001	0.578	-----
200.00	-0.030	6.003	0.566	-----
210.00	-0.019	7.150	0.554	-----
220.00	0.000	8.452	0.540	-----
230.00	0.029	9.921	0.525	-----
240.00	0.060	11.580	0.510	0.045
250.00	0.095	13.439	0.493	0.054
260.00	0.129	15.521	0.474	0.064
270.00	0.160	17.838	0.453	0.076
280.00	0.174	20.421	0.429	0.093
290.00	0.160	23.294	0.395	0.119
300.00	0.091	26.498	0.331	0.152
303.36	0.000	27.706	0.251 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.49320 - 1758.77/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 24

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,2,3-Trimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
109.84	0.000	1.000	-----	-----
120.00	-0.009	1.313	0.636	-----
130.00	-0.017	1.689	0.626	-----
140.00	-0.027	2.145	0.616	-----
150.00	-0.037	2.691	0.606	-----
160.00	-0.045	3.335	0.595	-----
170.00	-0.051	4.091	0.585	-----
180.00	-0.053	4.968	0.575	-----
190.00	-0.049	5.978	0.564	-----
200.00	-0.032	7.129	0.552	-----
210.00	-0.020	8.451	0.540	-----
220.00	0.005	9.942	0.526	0.044
230.00	0.040	11.618	0.512	0.051
240.00	0.078	13.501	0.496	0.060
250.00	0.115	15.610	0.478	0.070
260.00	0.146	17.964	0.455	0.084
270.00	0.160	20.589	0.426	0.104
280.00	0.131	23.525	0.388	0.134
290.00	0.020	26.824	0.299	0.220
290.28	0.000	26.937	0.262 Critical	

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.46647 - 1710.70/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 25

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES of 2,2,4-Trimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
99.24	0.000	1.000	-----	-----
100.00	-0.012	1.033	-----	-----
110.00	-0.025	1.328	0.616	-----
120.00	-0.040	1.758	0.607	-----
130.00	-0.053	2.239	0.596	-----
140.00	-0.064	2.813	0.586	-----
150.00	-0.068	3.488	0.574	-----
160.00	-0.070	4.282	0.563	-----
170.00	-0.068	5.207	0.550	-----
180.00	-0.062	6.277	0.538	-----
190.00	-0.049	7.504	0.524	-----
200.00	-0.022	8.895	0.510	-----
210.00	0.024	10.462	0.494	-----
220.00	0.080	12.228	0.477	0.053
230.00	0.124	14.231	0.458	0.062
240.00	0.152	16.490	0.436	0.075
250.00	0.160	19.025	0.409	0.093
260.00	0.136	21.863	0.373	0.121
270.74	0.000	25.340	0.243	Critical

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.45216 - 1658.03/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 26

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,3,3-Trimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
114.76	0.000	1.000	-----	-----
120.00	-0.005	1.152	0.643	-----
130.00	-0.017	1.492	0.633	-----
140.00	-0.030	1.904	0.623	-----
150.00	-0.044	2.398	0.612	-----
160.00	-0.057	2.983	0.602	-----
170.00	-0.066	3.667	0.592	-----
180.00	-0.070	4.462	0.582	-----
190.00	-0.066	5.377	0.572	-----
200.00	-0.054	6.425	0.560	-----
210.00	-0.034	7.619	0.548	-----
220.00	-0.006	8.972	0.535	-----
230.00	0.031	10.499	0.521	-----
240.00	0.072	12.217	0.506	0.050
250.00	0.116	14.140	0.490	0.058
260.00	0.151	16.296	0.470	0.069
270.00	0.171	18.705	0.445	0.082
280.00	0.175	21.379	0.420	0.100
290.00	0.132	24.366	0.384	0.128
295.00	0.083	25.990	0.351	0.152
300.34	0.000	27.833	0.251	Critical

* Calculated by means of equation

$$\log P\ (\text{Atm.}) = 4.46422 - 1731.80/(t^{o}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 27

VAPOR PRESSURE, SATURATED LIQUID, AND VAPOR DENSITIES

of 2,3,4-Trimethylpentane

Temperature °C.	Pressure Deviation Atm.	Vapor Pressure* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
113.47	0.000	1.000	-----	-----
120.00	-0.009	1.197	0.640	-----
130.00	-0.018	1.548	0.630	-----
140.00	-0.023	1.970	0.620	-----
150.00	-0.030	2.480	0.610	-----
160.00	-0.040	3.089	0.599	-----
170.00	-0.045	3.804	0.587	-----
180.00	-0.044	4.634	0.576	-----
190.00	-0.038	5.595	0.564	-----
200.00	-0.027	6.701	0.551	-----
210.00	-0.011	7.965	0.538	-----
220.00	0.010	9.403	0.524	-----
230.00	0.029	11.036	0.508	0.044
240.00	0.065	12.567	0.492	0.053
250.00	0.105	14.905	0.473	0.060
260.00	0.150	17.183	0.451	0.074
270.00	0.174	19.735	0.426	0.091
280.00	0.150	22.604	0.392	0.116
290.00	0.066	25.816	0.330	0.165
293.19	0.000	26.941	0.248	Critical

* Calculated by means of equation

$$\log P \text{ (Atm.)} = 4.50775 - 1742.87/(t^{\circ}\text{C.} + 273.17)$$

and pressure deviation.

TABLE 28

SUMMARY OF

VAPOR PRESSURE EQUATION CONSTANTS

Name of Compound	A	B
n-Heptane	4.58932	-1705.34
2-Methylhexane	4.54120	-1649.45
3-Methylhexane	4.53958	-1657.04
3-Ethylpentane	4.52268	-1658.19
2,2-Dimethylpentane	4.45009	-1568.08
2,3-Dimethylpentane	4.49262	-1630.60
2,4-Dimethylpentane	4.47991	-1584.41
3,3-Dimethylpentane	4.43153	-1591.94
2,2,3-Trimethylbutane	4.39299	-1555.34
n-Octane	4.65176	-1855.26
2-Methylheptane	4.60725	-1800.61
3-Methylheptane	4.60063	-1803.86
4-Methylheptane	4.60194	-1798.81
3-Ethylhexane	4.59076	-1798.20
2,2-Dimethylhexane	4.52412	-1719.21
2,3-Dimethylhexane	4.56126	-1773.33
2,4-Dimethylhexane	4.54094	-1737.36
2,5-Dimethylhexane	4.55744	-1742.17
3,3-Dimethylhexane	4.50672	-1735.72
3,4-Dimethylhexane	4.55388	-1780.07
2-Methyl-3-ethylpentane	4.53619	-1763.76
3-Methyl-3-ethylpentane	4.49320	-1758.77
2,2,3-Trimethylpentane	4.46647	-1710.70
2,2,4-Trimethylpentane	4.45216	-1658.03
2,3,3-Trimethylpentane	4.46422	-1731.80
2,3,4-Trimethylpentane	4.50775	-1742.87

TABLE 29

CRITICAL CONSTANTS FOR THE HEPTANES AND OCTANES

Name of Compound	Temperature °C.	Pressure atm.	Density gm/cc.
n-Heptane	266.85	27.002	0.232
2-Methylhexane	257.15	26.971	0.238
3-Methylhexane	262.04	27.767	0.248
3-Ethylpentane	267.42	28.530	0.241
2,2-Dimethylpentane	247.29	27.367	0.241
2,3-Dimethylpentane	264.14	28.700	0.262
2,4-Dimethylpentane	246.58	27.009	0.240
3,3-Dimethylpentane	263.19	29.073	0.242
2,2,3-Trimethylbutane	257.96	29.146	0.252
n-Octane	295.59	24.537	0.232
2-Methylheptane	286.41	24.517	0.234
3-Methylheptane	290.45	25.127	0.246
4-Methylheptane	288.52	25.087	0.240
3-Ethylhexane	292.27	25.738	0.251
2,2-Dimethylhexane	276.65	24.961	0.239
2,3-Dimethylhexane	290.27	25.938	0.244
2,4-Dimethylhexane	280.30	25.229	0.242
2,5-Dimethylhexane	276.84	24.542	0.237
3,3-Dimethylhexane	288.80	26.187	0.258
3,4-Dimethylhexane	295.63	26.569	0.245
2-Methyl-3-ethylpentane	293.87	26.651	0.258
3-Methyl-3-ethylpentane	303.36	27.706	0.251
2,2,3-Trimethylpentane	290.28	26.937	0.262
2,2,4-Trimethylpentane	270.74	25.340	0.244
2,3,3-Trimethylpentane	300.34	27.833	0.251
2,3,4-Trimethylpentane	293.19	26.941	0.248

TABLE 30

COMPARISON OF DATA FROM THIS STUDY WITH KAY AND WARZEL (11).

for 2,2,4-Trimethylpentane

			Saturated Density			
	Vapor Pressure		Liquid		Vapor	
Temp. °C.	Found Atm.	K & W Atm.	Found Atm.	K & W Atm.	Found Atm.	K & W Atm.
110.00	1.328	-----	0.616	-----	-----	-----
120.00	1.758	1.736	0.607	0.603	-----	-----
130.00	2.239	-----	0.596	-----	-----	-----
140.00	2.813	2.783	0.586	0.582	-----	-----
150.00	3.488	-----	0.574	-----	-----	-----
160.00	4.282	4.253	0.563	0.560	-----	-----
170.00	5.207	-----	0.550	-----	-----	-----
180.00	6.277	6.245	0.538	0.536	-----	-----
190.00	7.504	7.479	0.524	0.523	-----	-----
200.00	8.895	8.867	0.510	0.509	-----	-----
210.00	10.462	10.452	0.494	0.493	-----	-----
220.00	12,228	12.238	0.477	0.476	0.053	0.050
230.00	14.231	14.249	0.458	0.457	0.062	0.061
240.00	16.490	16.500	0.436	0.435	0.075	0.075
250.00	19.025	19.022	0.409	0.408	0.093	0.093
260.00	21.863	21.873	0.373	0.372	0.121	0.120
265.00	------	------	0.349	-----	0.141	-----
270.00	25.340	25.308	0.243	0.243	0.243	0.243 CP

CP - Critical Point

CORRELATION OF CRITICAL TEMPERATURE AND PRESSURE OF PURE SUBSTANCES

THEORY

The critical temperature of a pure compound may be defined as the maximum temperature at which the liquid and vapor may coexist. The vapor pressure at this temperature is termed the critical pressure. According to kinetic theory of the liquid state the potential energy of attraction between molecules is counterbalanced to some extent by the kinetic energy of the molecules. The latter tends to separate randomly all portions of the liquid. Vapor pressure is caused by the fact that some of the liquid molecules have sufficiently high kinetic energy to break away from the strong cohesive force fields of the liquid. As the temperature is raised on a liquid system the kinetic energy of the molecules increases but the temperature has little effect on the cohesive forces. The temperature at which the average molecular kinetic energy becomes equal to the negative potential energy of attraction is termed the critical temperature. Any reliable method for predicting critical constants should be based upon this kinetic hypothesis but because there is no general method to calculate accurately the potential energy of attraction between molecules, any accurate theoretical prediction of critical constants is not likely at present. Simplification in the calculation of the potential energy, such as assuming the inverse power relationship of intermolecular forces with distance, are not of much value in real systems.

EMPIRICAL EQUATIONS FOR CRITICAL TEMPERATURE AND PRESSURE

The equations that have been proposed for the estimation of the critical temperature and pressure are strictly empirical. Reid and Sherwood (15) have tested a number of these equations by comparing the calculated values with experimentally determined values and have presented the results in terms of the deviation of calculated from experimental. A brief summary of the methods recommemded by Reid and Sherwood is of interest in helping to discover the variables upon which T_c (critical temperature) and P_c (critical pressure) depend.

For the prediction of the critical temperature, Vowles (22), Riedel (16), and Lydersen (12) have proposed the simple equation

$$T_c = T_B / \theta \qquad (1)$$

where T_c and T_B are the critical temperature and the standard boiling point Temperature in ^{o}K. and θ is a constant different for each compound but which may be calculated by summing atomic and structural constants which represent the component parts of the molecule. The values of these constants for a given component differ with the author.

Thodos (20,21) evaluated the van der Waal constants a and b from structural considerations for saturated and unsaturated aliphatic hydrocarbons and proposed that the critical temperature be calculated using these constants in the equation

$$T_c = 8a/27\,R\,b \tag{2}$$

where T_c = critical temperature °K.

R = gas constant, 82.06 cm^3-atm/°K,g-mole.

a = van der Waal's constant $(cm^3/g\text{-mole})^2$atm.

b = van der Waal's constant cm^3/g-mole.

By the methods based on equation (1) the average deviation of the calsulated from the experimental value is about 1.4%; by equation (2) it is of the order of 1%.

In the prediction of the critical pressure there is a much greater diversity in the form of the empirical equation proposed.

Riedel (16) and Lydersen (12) have developed the following equation:

$$P_c(\text{atm}) = \frac{M}{(\phi + 0.33)^2} \tag{3}$$

where M = molecular weight

ϕ = an additive constant determined from molecular structure

Vowles (22) correlated the critical pressure in atmospheres with the critical temperature T_c in °K and an additive function γ by the following equation

$$P_c^{\alpha} = \frac{T_c}{\gamma} \tag{4}$$

where the exponent α depends on the homologous family.

Herzog (1) used the equation

$$\log P\,(\text{atm}) = A + B \log P_{ch} \tag{5}$$

where A and B are constants for a particular family of substances and P_{ch} is the parachor of the compound.

Thodos (20,21) proposed the equation

$$P_c = \frac{a}{27\ b^2} \qquad (6)$$

where a and b are estimated van der Waal constants.

Compared with the equation for estimating the critical temperature, those representing the critical pressure are subject to much greater uncertainty. The errors in the calculated values may run as high as 10 to 15% for relatively simple non-polar compounds but usually are of the order of 3 to 4%.

The reason for the relatively large error in the calculated values of T_c and P_c, it would seem, is due to the failure to discover the form of the function for the effect of molecular structure on intermolecular forces. This is manifested indirectly by the fact that none of the equations proposed for the critical temperature and pressure contain terms which can distinguish differences in molecular structure of isomeric compounds.

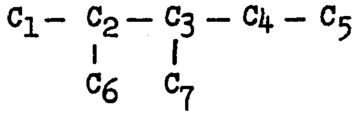
WIENER'S CHARACTERIZATION OF MOLECULAR STRUCTURE

The Path Number and the Polarity Number

In a study of the relation between the standard boiling and the molecular structure, Wiener proposed, in 1947, a method of characterizing isomeric compounds, which appears to have real promise as a method for correlating critical constants. According to Wiener (23) the boiling points of the paraffins may be expressed by the linear equation

$$t_B = a\,w + b\,p + c \qquad (7)$$

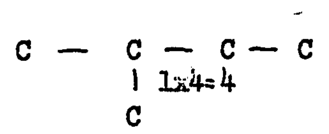
where a, b and c are constants for a given isomeric group and p and w are structural variables. The polarity number p is the number of pairs of carbon atoms which are separated by three carbon-carbon bonds. For example, for 2,3-Dimethylpentane



$$\begin{array}{ccccccccc} C_1 & - & C_2 & - & C_3 & - & C_4 & - & C_5 \\ & & | & & | & & & & \\ & & C_6 & & C_7 & & & & \end{array}$$

the pairs of carbon atoms three bonds apart are C_1C_4, C_1C_7, C_2C_5, C_4C_6, C_5C_7, and C_6C_7. The polarity number of the compound is therefore, $p = 6$.

The path number w, is equal to the sum of the distances between any two carbon atoms in the molecule, in terms of the carbon-carbon bonds. The path number is calculated by multiplying the number of carbon atoms on one side of any bond by those on the other side and determining the sum of these quantities for all bonds. To illustrate, consider 2-Methylbutane. The skeleton equation is



$$\begin{array}{ccccccc} & (1x4=4) & & (2x3=6) & & (1x4=4) & \\ C & - & C & - & C & - & C \\ & & | \; 1x4=4 & & & & \\ & & C & & & & \end{array}$$

and the path number is $w = 4 + 6 + 4 + 4 = 18$

According to Wiener (23), the path number indicates the compactness of the molecule. As the compactness increases, that is, as w decreases, the boiling point decreases. The polarity number is considered as a semi-quantitative measure of intra-molecular attractive forces transmitted through the carbon chain.

In the application of the concepts of the path number and polarity number to the correlation of the standard boiling points of the compounds of the paraffin series, it was found more convenient to modify equation (7) to read

$$\Delta t = a\,\Delta w + b\,\Delta p$$

where $\Delta t = t_o - t_B$, $\Delta w = w_o - w$ and $\Delta p = p_o - p$. in this form the boiling points of the branched isomers were referred to the boiling points of the normal paraffins which, throughout the series, have been more intensively and accurately determined and correlated. Using this equation with the value of $a = 98/n^2$ and $b = 5.5$, where n = number of carbon atoms, Wiener was able to calculate the standard boiling point of 94 pure paraffin hydrocarbons with an average deviation between calculated and observed values of less than one degree.

ESTIMATION OF THE CRITICAL TEMPERATURE AND PRESSURE OF ISOMERS

The Wiener numbers make it possible to express differences in molecular structure in a quantitive manner. Their application to the correlation of critical temperatures and pressures of the a model, Wiener's correlation of the standard boiling points of the hydrocarbons and employing the ratio of the Wiener path numbers of the isomeric compound to the normal compound w_i/w_n, a plot was prepared in which the logarithm of $\left[(T_{Rbp})_n - (T_{Rbp})_i\right]$ was plotted against the logarithm of $(1 - w_i/w_n)$. $(T_{Rbp})_n$ and $(T_{Rbp})_i$ are the reduced standard boiling points of the normal and isomeric compounds, respectively. The result is shown in Figure 32, a linear relation is indicated with only a slight scattering of the data. The equation for this line was found to be

$$\log \left[(T_{Rbp})_n - (T_{Rbp})_i\right] = -0.75463 + 1.52669 \log (1 - w_i/w_n) \quad (9)$$

Critical temperatures calculated by means of equation (9) are compared with the experimental values in Table 31. For the isomeric hexanes (8), heptanes and octanes, a total of 28 isomeric compounds, the calculated critical temperatures agree with the experimental values with an average deviation of 0.55°K. or 0.1 percent and a maximum deviation of 2.17°K. or 0.38 percent.

From a study of the critical pressure data it was found that, $(P_{cn} - P_{ci})$, the difference between the critical pressure of the n-compound and iso-compound, varied linearly with the difference between the reduced boiling point of the n- and iso-compound, when the polarity ratio P_i/P_n remained the same. A plot of the data points is shown in Figure 33. These relations have been expressed analytically by the empirical equation using

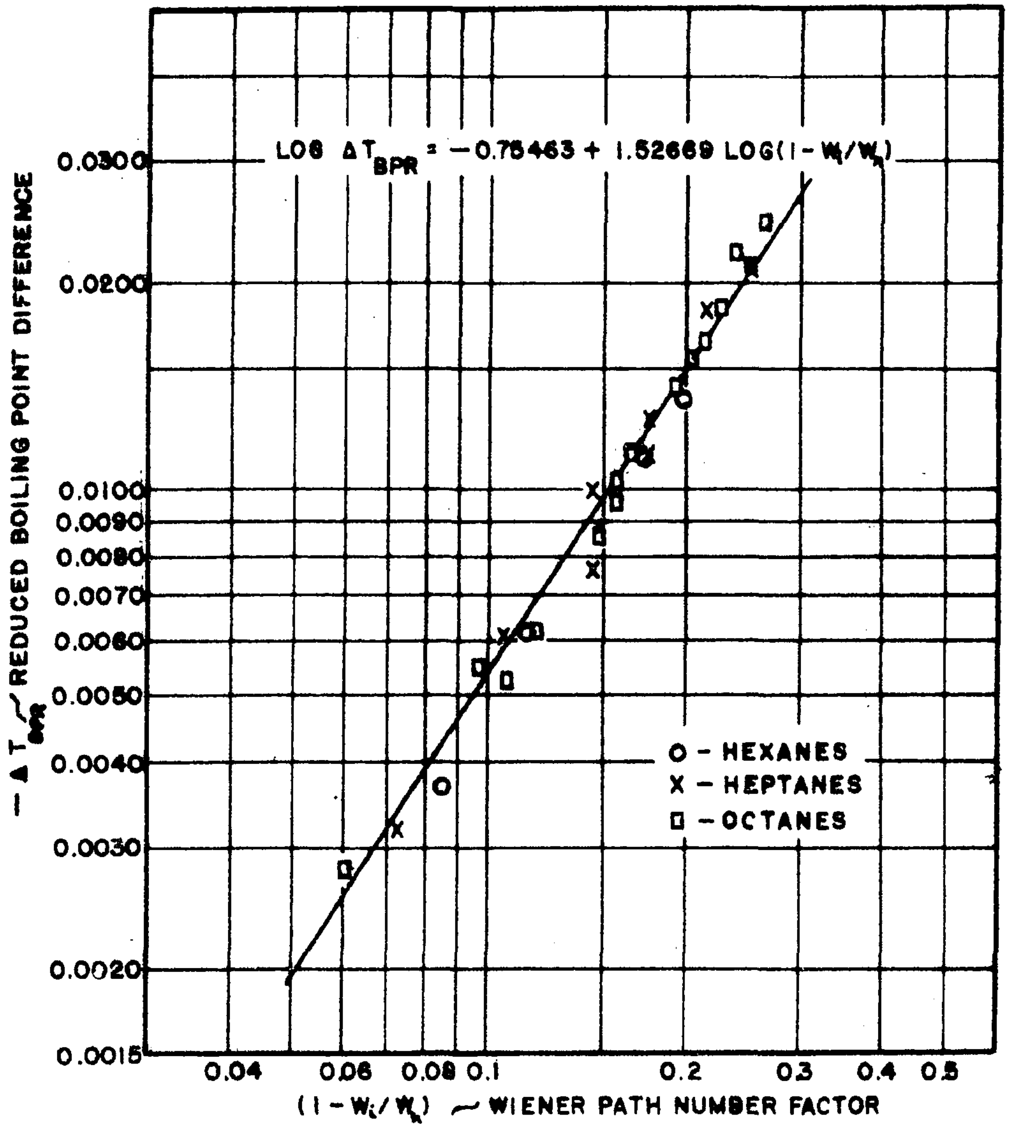


FIGURE 32, REDUCED BOILING POINT DIFFERENCE AS A FUNCTION OF WIENER PATH NO. RATIO

TABLE 31

COMPARISON OF PREDICTED VALUES OF CRITICAL TEMPERATURES TO EXPERIMENTAL VALUES

Name of Compound	Path Number Ratio	Critical Temperatures			
		Calc.* °K.	Exp. °K.	Dev. °K.	%Dev.
n-Hexane	1.000	------	507.87	-----	----
2-Methylpentane	0.914	498.41	498.07	0.34	0.07
3-Methylpentane	0.885	504.65	504.37	0.28	0.06
2,2-Dimethylbutane	0.800	490.67	489.37	1.30	0.26
2,3-Dimethylbutane	0.829	500.79	500.27	0.52	0.10
n-Heptane	1.0000	------	540.02	-----	----
2-Methylhexane	0.9286	530.25	530.32	-0.07	0.01
3-Methylhexane	0.8929	534.98	535.21	-0.23	0.04
3-Ethylpentane	0.8571	539.91	540.59	-0.68	0.13
2,2-Dimethylpentane	0.8241	521.49	520.46	1.03	0.20
2,3-Dimethylpentane	0.8241	537.15	537.31	-0.16	0.02
2,4-Dimethylpentane	0.8571	520.79	519.75	1.04	0.20
3,3-Dimethylpentane	0.7857	535.13	536.36	-1.23	0.23
2,2,3-Trimethylbutane	0.7500	530.89	531.12	-0.23	0.04
n-Octane	1.0000	------	568.76	-----	----
2-Methylheptane	0.9405	559.27	559.58	-0.31	0.06
3-Methylheptane	0.9048	563.12	563.63	-0.51	0.09
4-Methylheptane	0.8929	562.09	561.69	0.40	0.07
3-Ethylhexane	0.8571	565.88	565.44	0.44	0.08
2,2-Dimethylhexane	0.8452	549.94	549.82	0.12	0.02
2,3-Dimethylhexane	0.8333	563.61	563.44	0.17	0.03
2,4-Dimethylhexane	0.8452	552.73	553.47	-0.74	0.13
2,5-Dimethylhexane	0.8809	550.50	550.01	0.49	0.09
3,3-Dimethylhexane	0.7976	561.59	561.97	-0.38	0.07
3,4-Dimethylhexane	0.8095	568.83	568.80	0.03	0.00
2-Methyl-3-ethylpentane	0.7976	566.96	567.04	-0.08	0.01
3-Methyl-3-ethylpentane	0.7619	574.36	576.53	-2.17	0.38
2,2,3-Trimethylpentane	0.7500	563.25	563.45	-0.02	0.04
2,2,4-Trimethylpentane	0.7857	544.14	543.91	0.23	0.04
2,3,3-Trimethylpentane	0.7381	571.83	573.51	-1.68	0.29
2,3,4-Trimethylpentane	0.7738	566.09	566.36	-0.27	0.05
			Average	0.55	0.10

* Critical temperature calculated from the equation:

$$\log.\left[(T_{Rbp})_n - (T_{Rbp})_i\right] = -0.75463 + 1.52669 \ \log(1 - w_i/w_n)$$

where,

T_{Rbp} = reduced boiling point
w = Wiener Path Number
Subscripts - i = isomer and n = normal

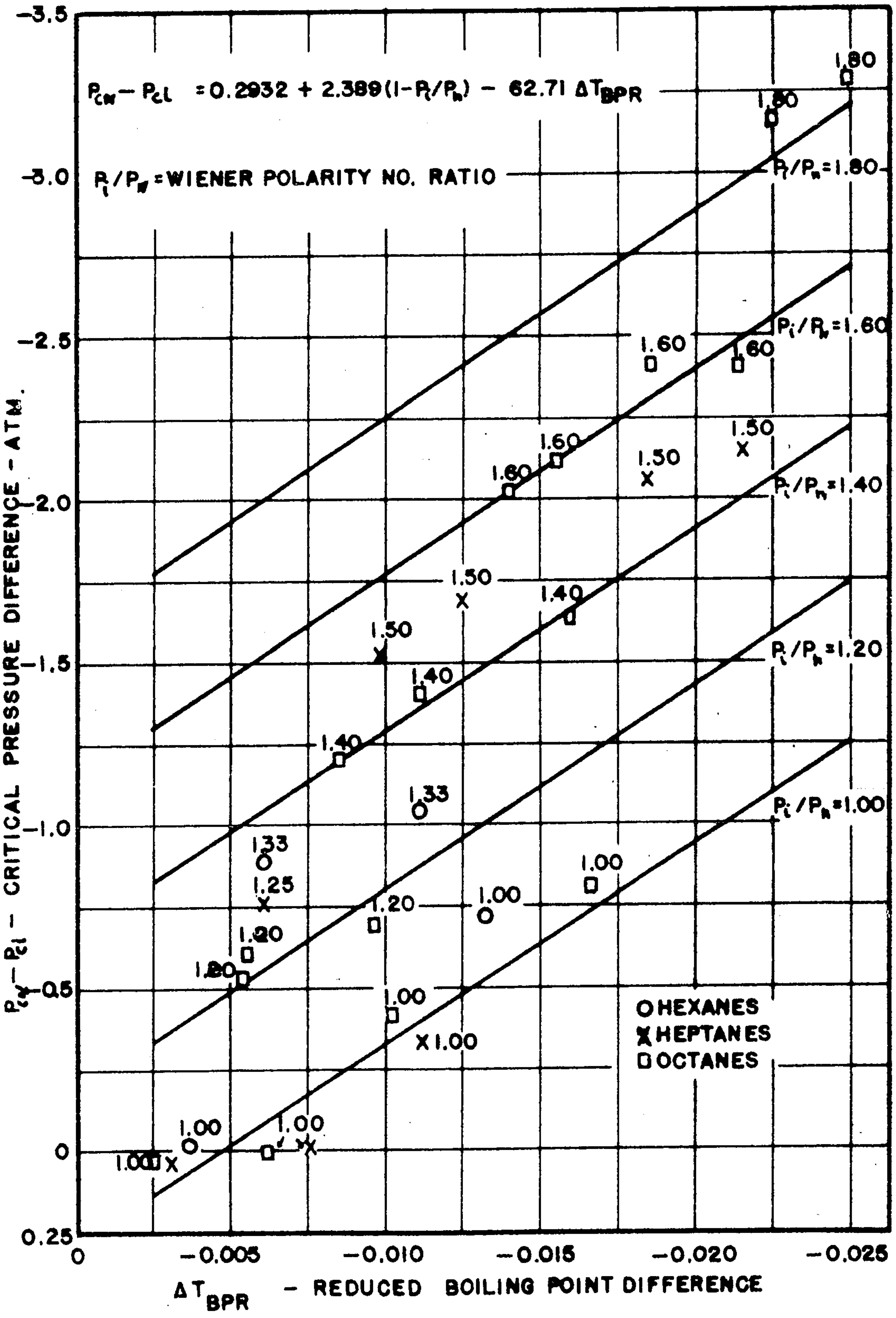


FIGURE 33, CRITICAL PRESSURE CORRELATION the method of least mean squares for the evaluation of the constants of the equation.

$$P_{cn} - P_{ci} = 0.2932 + 2.389(1 - P_i/P_n) - 62.71\,\Delta T_{Rbp} \qquad (10)$$

Table 32 shows a comparison to the calculated with the experimental values of the critical pressure. As will be noted, the average deviation of the calculated from the experimental values is 0.091 atmospheres or 0.33 percent while the maximum deviation amounts to 0.31 atm. or 1.14 percent.

TABLE 32

COMPARISON OF PREDICTED VALUES OF CRITICAL PRESSURES TO EXPERIMENTAL VALUES

Name of Compound	Polarity Number Ratio	Calc.* Atm.	Critical Pressures Exp. Atm.	Dev. Atm.	%Dev.
n-Hexane	1.000	-----	29.94	-----	----
2-Methylpentane	1.000	29.91	29.95	-0.04	0.13
3-Methylpentane	1.333	30.85	30.83	0.02	0.07
2,2-Dimethylbutane	1.000	30.59	30.67	0.08	0.25
2,3-Dimethylbutane	1.333	31.19	30.99	0.20	0.64
n-Heptane	1.000	-----	27.00	-----	----
2-Methylhexane	1.000	26.90	26.97	-0.07	0.25
3-Methylhexane	1.250	27.67	27.77	-0.10	0.35
3-Ethylpentane	1.500	28.47	28.53	-0.06	0.22
2,2-Dimethylpentane	1.000	27.49	27.37	0.12	0.43
2,3-Dimethylpentane	1.500	28.68	28.70	-0.02	0.07
2,4-Dimethylpentane	1.000	27.27	27.01	0.26	0.98
3,3-Dimethylpentane	1.500	28.96	29.07	-0.12	0.40
2,2,3-Trimethylbutane	1.500	29.23	29.15	0.09	0.30
n-Octane	1.000	-----	24.54	-----	----
2-Methylheptane	1.000	24.39	24.52	-0.12	0.50
3-Methylheptane	1.200	25.03	25.13	-0.10	0.39
4-Methylheptane	1.200	25.08	25.09	-0.01	0.01
3-Ethylhexane	1.400	25.76	25.74	0.03	0.10
2,2-Dimethylhexane	1.000	24.88	24.96	-0.08	0.31
2,3-Dimethylhexane	1.400	25.91	25.94	-0.02	0.09
2,4-Dimethylhexane	1.200	25.29	25.23	0.06	0.23
2,5-Dimethylhexane	1.000	24.67	24.54	0.13	0.53
3,3-Dimethylhexane	1.400	26.16	26.19	-0.02	0.08
3,4-Dimethylhexane	1.600	26.56	26.57	-0.01	0.05
2-Methyl-3-ethylpentane	1.600	26.64	26.65	-0.01	0.03
3-Methyl-3-ethylpentane	1.800	27.39	27.70	-0.31	1.14
2,2,3-Trimethylpentane	1.600	27.01	26.94	0.07	0.26
2,2,4-Trimethylpentane	1.000	25.30	25.34	-0.04	0.17
2,3,3-Trimethylpentane	1.800	27.58	27.83	-0.25	0.89
2,3,4-Trimethylpentane	1.600	26.82	26.94	-0.12	0.47
			Average	0.09	0.33

* Critical pressure calculated from the equation

$$P_{cn} - P_{ci} = 0.2932 + 2.389(1 - p_i/p_n) - 62.71\,\Delta T_{Rbp}$$

where
P = pressure in atm.
p = Wiener polarity number
ΔT_{Rbp} = reduced boiling point difference

and subscripts n, i, and c refer to normal, isomer, and critical, respectively.

VAPOR PRESSURE CORRELATION

The vapor pressure data for each hydrocarbon have been represented by the standard vapor pressure equation $\log P = A + B/T$ supplemented with a deviation curve of T versus $(P_{calc} - P_{exp})$. If the temperature is expressed as reduced temperature, the curves are brought close together and, in the limit, should coincide to form a common deviation curve in accord with the theorem of corresponding states. Figure 34 shows the reduced temperature-pressure deviation curves for all of the isomeric heptanes. Figure 35 is the same for n-octane and 2,3,3-trimethylpentane. The deviation curves of all other isomeric octanes lie in between these two curves as limits. Since the maximum difference between the individual curves is about 0.1 atmosphere, the average error that would be introduced into the estimation of the vapor pressure, if an average deviation curve were drawn to represent the heptanes and octanes, would be less than 0.05 atm. over the temperature range from the standard boiling point to the critical point.

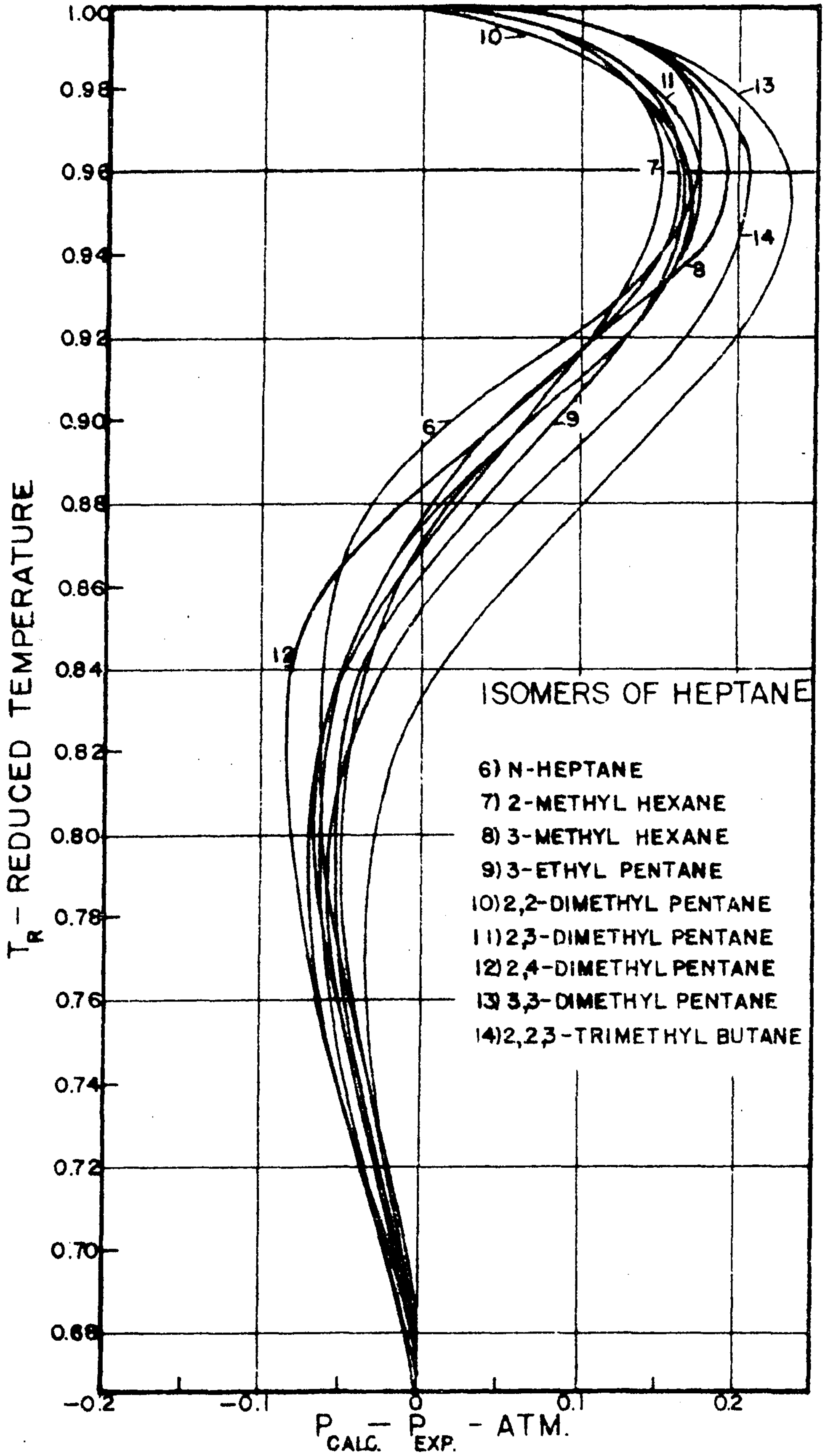


FIG.34, VAPOR PRESSURE DEVIATION - REDUCED TEMPERATURE

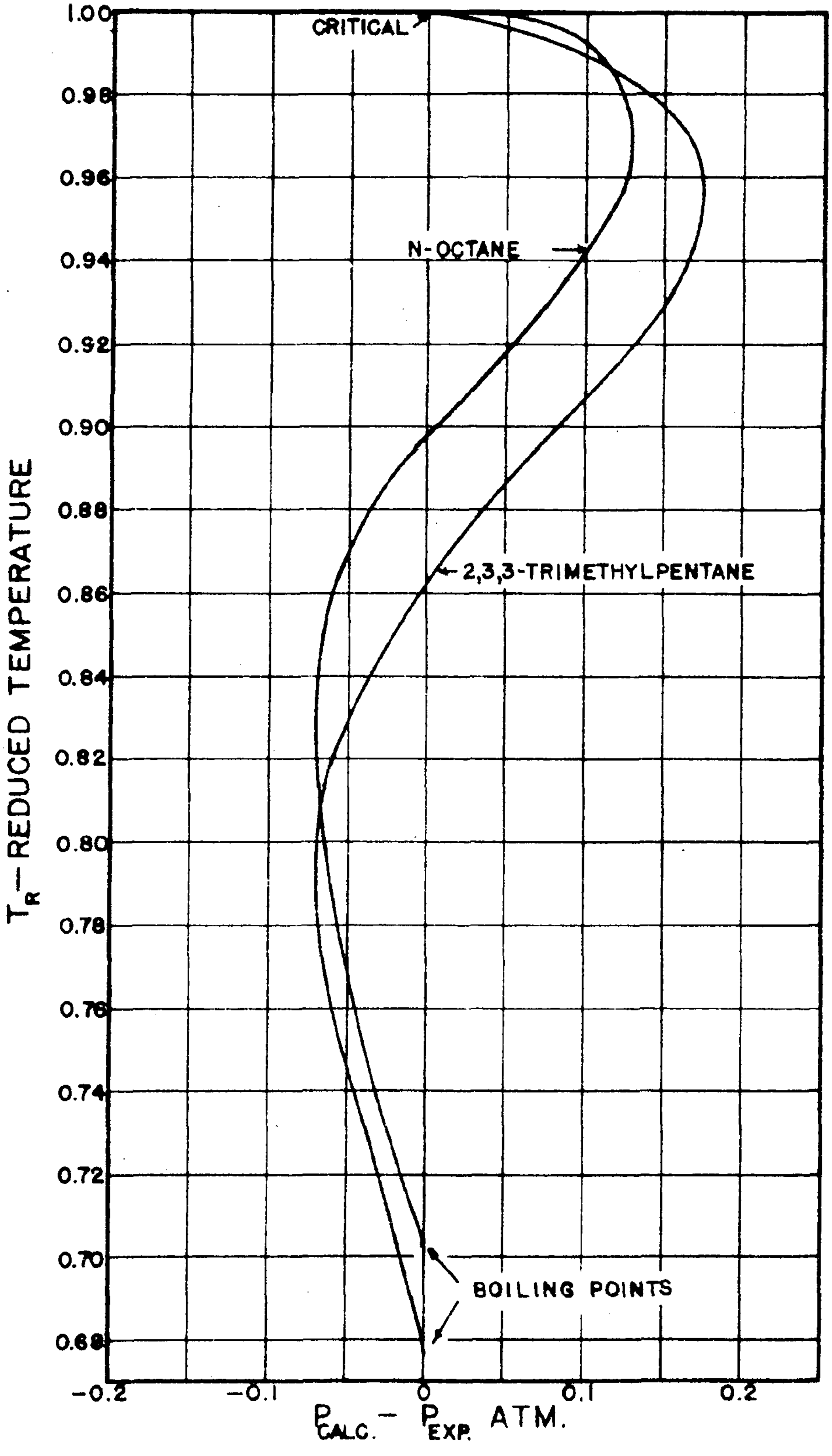


FIG. 35, VAPOR PRESSURE DEVIATION - REDUCED TEMPERATURE

APPENDIX I

EXPERIMENTAL DATA

The treatment of experimental data is shown, by example, in Table 32; two bubble points and a dew point determination are given for n-heptane. Explainations of the entries in Table 32 are given below (Numerals refer to equipment in Figure 1, page 5).

"Gage Temperature"

The temperature used to calculate the temperature correction for the dead-weight piston gage.

"True Gage Pressure"

The pressure which was exerted at the base of the piston of the dead-weight piston gage, 16, Figure 1. An example calculation is shown in Appendix II, ("Pressure Gage Calibration").

"Barometric Pressure"

The barometric pressure measured with a wall barometer, corrected to standard gravity and temperature.

"Hg Head Room Zone"

Since the differential mercury head between the back leg of the compressor block 4, and the top of the mercury in the experimental tube was at two different temperatures (room temperature and the temperature in the heating bath), the mercury head was calculated in two parts; "Hg Head Room Zone" and "Hg Head Hot Zone." The room zone was taken as the difference in mercury height from the back leg to the top of the mercury in the outer jacket at 19.

The level in the back leg was calculated from a knowledge of the mercury height in the experimental tube and back leg when the tube was loaded, the height of the mercury in the tube at the given pressure, and the volume ratio between the experimental tube and the back leg.

"Hg Head Hot Zone"

This head was calculated from the mercury height from the level in the outer jacket 19 to the top of the mercury meniscus, and the specific gravity of mercury at the temperature measured by the platinum resistance thermometer 3.

"Oil Head"

The oil head was calculated from a measure of the oil level in the reservoir of the piston gage 15, to the base of the piston, and the specific gravity of the oil. The level of the piston was maintained at a set level by means of an electronic relay arrangement.

"Hg Vapor Pressure"

It was assumed that the mercury and hydrocarbon were completely immiscible and the pressure exerted by the vapor, with both liquids present, was the sum of the hydrocarbon and mercury vapor pressures. Therefore, the mercury vapor pressure was subtracted from the pressure gage reading.

"Sample Liquid Head"

In the case of bubble points, a head due to the liquid sample was present and was calculated from the sample mass and the tube cross sectional area.

"Ball Head"

The head due to the steel stirring ball.

"Capillarity"

Calculated as the mercury depression in a 2 mm bore tube containing a hydrocarbon; for vapors the capillarity for mercury-pentane vapors was used and for liquids mercury-octane liquid.

"Vapor Pressure"

The vapor pressure, at the dew point or bubble point, was calculated by summing the pressure values just described. As may be seen in Figure 1, the pressure measured at the base of the piston, the sum of the weights and barometric pressure, was opposed by a differential mercury leg, an oil leg, a gas leg (negligible), the sample head, capillarity, the ball head, and the vapor pressure of the hydrocarbon and mercury. The only unknown pressure was the vapor pressure of the hydrocarbon; calculated by subtracting the pressure heads from the pressure gage weights and barometric pressure.

"Sample Temperature"

The sample temperature was determined by measuring the resistance of the platinum coil and then calculating the temperature from the calibration values.

"Sample Length"and "Sample Volume"

The sample length, the distance from the tube tip to the top of the meniscus, and the height of the mercury meniscus were measured with a cathetometer, measuring to 0.05 mm. The volume was calculated from the sample length, meniscus height and temperature, as described in Appendix II ("Calibration of Experimental Tubes").

"Density"

The density of the sample was determined from the sample volume and the mass of the sample. The mass of the sample had previously been determined from the volume of the sample at room temperature and the density of the sample at that temperature (19).

Tables 33 through 58 give the experimentally determined dew point pressures and temperatures, saturated vapor densities, bubble point pressures and temperatures, and saturated liquid densities. The "Observed Pressure" is the experimentally determined pressure. The "Pressure Deviation" is the deviation of the calculated pressure minus the observed pressure, where $P_{calc} = A + B/T$. The "Saturated Densities" are the densities determined for either the saturated vapor or liquid; the saturated liquid densities were determined at the bubble points and the saturated vapor densities were determined at the dew points.

Tables 59 through 83 give the data used for "P-V Isotherms", which were used to determine the vapor pressure of the hydrocarbons with relation to the bubble points and dew points. The "length" refers to the sample length which could have been used to calculate the volumes, but because all the values are at the same temperature, the length represents the volume.

TABLE 33

SAMPLE DATA POINTS

n-Heptane

Type of Point	Dew Point	Bubble Point	Bubble Point
Gage Temp., ^{o}C.	32.2	32.2	28.9
True Gage Press., Psi	227.46	231.86	118.23
Barometric Press., Psi	14.362	14.362	14.411
Hg. Head Room Zone, Psi	-4.255	-4.279	-4.450
Hg. Head Hot Zone, Psi	-3.164	-6.438	-6.400
Oil Head, Psi	-0.148	-0.148	-0.148
Hg. Vapor Press., Psi	-0.844	-0.844	-0.242
Sample Liquid Head, Psi	0.000	-0.018	-0.018
Ball Head, Psi	-0.006	-0.006	-0.006
Capillarity, Psi	-0.080	-0.080	-0.101
Vapor Pressure, Psi	233.33	234.41	121.27
Sample Temperature*	230.65	230.65	190.44
Sample Length, mm.	209.85	33.35	29.50
Height of Meniscus, mm.	0.40	0.45	0.70
Vol. of Sample, cc.**	0.63837	0.09065	0.07896
Sample Mass, g.	0.03944	0.03944	0.03944
Density, gm/cc	0.0618	0.4351	0.4995

* Platinum Resistance Thermometer # 770041

** Experimental Tube B.

TABLE 34

EXPERIMENTAL DATA
n-Heptane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
147.87	3.585	-0.125	0.5596	------
152.79	3.987	-0.134	0.5532	------
166.10	5.231	-0.136	0.5398	------
173.63	6.046	-0.123	0.5248	------
190.44	8.251	-0.105	0.4995	------
199.45	9.646	-0.073	0.4867	------
206.52	10.866	-0.046	0.4772	------
206.52	10.830	-0.010	------	0.0446
210.00	11.470	0.007	------	0.0476
210.00	11.528	-0.051	0.4710	------
216.57	12.759	0.040	------	0.0490
216.71	12.841	-0.012	0.4602	------
230.65	15.875	0.139	------	0.0618
230.65	15.948	0.046	0.4351	------
240.36	18.396	0.161	------	0.0747
240.37	18.453	0.104	0.4113	------
251.88	21.781	0.166	------	0.0994
251.88	21.824	0.123	0.3784	------
256.32	23.196	0.171	------	0.1133
256.34	23.251	0.122	0.3599	------
266.85	27.002	0.000	0.2242 Critical	

The points below were considered to deviate too greatly from those above to be used for the vapor pressure determination.

108.48	1.406	-0.085	0.6030	------
124.47	2.101	-0.103	0.5880	------
154.82	4.176	-0.151	0.5547	------
139.27	2.969	-0.121	0.5753	------
154.50	4.145	-0.147	0.5567	------
249.54	21.038	0.186	------	0.0936
249.54	21.099	0.125	0.3870	------

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc.}\ (\text{Atm.}) = A + B/T(^{\circ}K)$$

A = 4.58932
B = -1705.34

TABLE 35

EXPERIMENTAL DATA

2-Methylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
98.78	1.311	-0.033	0.6015	------
109.62	1.759	-0.052	0.5898	------
119.43	2.254	-0.067	0.5822	------
124.16	2.518	-0.064	0.5749	------
130.89	2.946	-0.069	0.5701	------
135.33	3.263	-0.076	0.5655	------
145.66	4.100	-0.092	0.5596	------
155.02	4.992	-0.105	0.5242	------
179.01	7.882	-0.058	0.5153	------
199.10	11.173	0.011	0.4838	------
209.63	13.279	0.049	0.4682	------
217.18	14.954	0.091	0.4520	------
217.38	14.943	0.149	------	0.0545
217.39	15.011	0.084	0.4517	------
217.43	15.045	0.059	------	------
225.83	17.103	0.103	0.4320	------
225.76	17.079	0.109	------	------
229.41	18.042	0.123	------	------
229.51	18.025	0.168	------	0.0754
229.51	18.094	0.099	0.4244	------
237.66	20.371	0.152	------	0.0920
237.66	20.402	0.121	0.4026	------
244.58	22.537	0.131	0.3767	------
244.47	22.477	0.222	------	0.1063
249.10	24.027	0.126	------	0.1260
249.10	24.045	0.108	0.3550	------
257.15	26.971	0.000	Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{o}K)$$

A = 4.54120
B = -1649.45

TABLE 36

EXPERIMENTAL DATA
3-Methylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
105.40	1.542	-0.088	0.6569	------
124.12	2.454	-0.117	0.5980	------
139.94	3.506	-0.130	0.5793	------
149.37	4.286	-0.137	0.5716	------
158.30	5.133	-0.131	0.5654	------
167.72	6.165	-0.123	0.5514	------
184.81	8.444	-0.099	0.5332	------
198.88	10.750	-0.053	0.5098	------
210.00	12.891	-0.007	0.4875	------
210.00	12.820	0.064	------	0.0481
218.51	14.743	0.029	0.4729	------
218.51	14.662	0.110	------	0.0577
234.12	18.648	0.108	0.4230	------
234.12	18.559	0.197	------	0.0786
243.84	21.454	0.150	0.4076	------
243.84	21.398	0.206	------	0.0976
252.00	24.087	0.143	0.3768	------
252.00	24.051	0.179	------	0.1269
262.04	27.767	0.000	Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (°K)}$$

$A = 4.53958$
$B = -1657.04$

TABLE 37

EXPERIMENTAL DATA
3-Ethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
100.61	1.232	-0.012	------	------
106.11	1.430	-0.015	------	------
125.49	2.341	-0.033	0.5934	------
135.34	2.952	-0.044	0.5822	------
144.80	3.651	-0.058	0.5726	------
154.75	4.500	-0.057	0.5623	------
166.60	5.725	-0.074	0.5485	------
174.37	6.639	-0.069	0.5406	------
184.58	8.006	-0.059	0.5254	------
194.58	9.544	-0.046	0.5131	------
217.02	13.730	0.072	------	0.0506
217.08	13.790	0.045	0.4795	------
223.81	15.281	0.071	0.4618	------
225.13	15.528	0.139	------	0.0585
225.16	15.583	0.091	0.4659	------
228.71	16.423	0.124	------	0.0626
228.79	16.477	0.091	0.4537	------
229.84	16.720	0.113	0.4525	------
239.20	19.203	0.133	0.4284	------
239.25	19.188	0.162	------	0.0781
249.72	22.305	0.162	------	0.0990
249.80	22.363	0.125	0.3990	------
256.06	24.386	0.131	0.3760	------
263.29	27.000	0.020	0.3381	------
267.42	28.530	0.000	0.2452	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}\text{K})$$

$A = 4.52268$

$B = -1658.19$

TABLE 38

EXPERIMENTAL DATA
2,2-Dimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
89.12	1.374	-0.050	0.6226	------
109.03	2.296	-0.071	0.5924	------
125.03	3.335	-0.083	0.5750	------
139.92	4.598	-0.089	0.5596	------
162.45	7.161	-0.074	0.5296	------
178.02	9.469	-0.038	0.5055	------
189.75	11.558	-0.004	0.4843	------
199.61	13.545	0.050	0.4792	------
209.95	15.856	0.163	------	0.0638
209.95	15.904	0.115	0.4571	------
216.88	17.670	0.123	0.4369	------
216.90	17.623	0.175	------	0.0737
216.88	17.612	0.181	------	0.0735
216.88	17.689	0.104	0.4355	------
230.30	21.479	0.175	------	0.1005
230.30	21.527	0.127	0.3980	------
240.61	24.878	0.128	------	0.1363
240.61	24.922	0.074	0.3524	------
247.29	27.367	0.000	0.2407	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{o}K)$$

$A = 4.45009$
$B = -1568.08$

TABLE 39

EXPERIMENTAL DATA
2,3-Dimethylpentane

			Saturated Density	
Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Liquid gm/cc	Vapor gm/cc
99.97	1.491	-0.165	0.6418	------
109.66	1.883	-0.172	0.6310	------
109.69	1.871	-0.139	0.6374	------
124.96	2.658	-0.164	0.6201	------
124.96	2.663	-0.169	0.6141	------
140.22	3.714	-0.181	0.6036	------
154.71	4.985	-0.179	0.5867	------
168.06	6.438	-0.171	0.5695	------
183.58	8.506	-0.138	0.5507	------
198.17	10.768	0.025	------	0.0419
198.17	10.887	-0.094	0.5288	------
210.00	13.041	0.076	------	0.0495
210.00	13.163	-0.046	0.5084	------
220.08	15.254	0.123	------	0.0627
220.09	15.371	0.006	0.4896	------
230.12	17.732	0.163	------	0.0767
230.12	17.856	0.039	0.4685	------
240.08	20.498	0.185	------	0.0949
240.08	20.588	0.095	0.4445	------
249.91	23.554	0.177	------	0.1197
249.91	23.625	0.106	0.4124	------
259.04	26.724	0.116	------	0.1597
259.04	26.775	0.065	0.3672	------
264.14	28.700	0.000	0.2556	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.49262$
$B = -1630.60$

TABLE 40

EXPERIMENTAL DATA
2,4-Dimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
94.45	1.536	-0.057	0.6126	------
109.88	2.284	-0.078	0.5923	------
120.53	2.954	-0.100	0.5810	------
135.38	4.111	-0.113	0.5671	------
148.16	5.369	-0.128	0.5511	------
163.29	7.204	-0.128	0.5293	------
177.88	9.364	-0.091	0.5068	------
189.70	11.343	0.057	------	0.0424
189.70	11.421	-0.021	0.4905	------
199.45	13.310	0.107	------	0.0512
199.43	13.376	0.032	0.4721	------
210.01	15.734	0.143	------	0.0637
210.01	15.793	0.084	0.4493	------
216.30	17.286	0.193	------	0.0721
216.14	17.262	0.190	------	0.0721
216.14	17.354	0.098	0.4356	------
220.97	18.575	0.197	------	0.0802
220.97	18.660	0.112	0.4252	------
231.44	21.687	0.193	------	0.1034
231.44	21.753	0.127	0.3925	------
239.88	24.521	0.122	------	0.1349
239.88	24.566	0.077	0.3573	------
246.58	27.009	0.000	0.2357 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}\text{K})$$

$A = 4.47991$
$B = -1584.41$

TABLE 41

EXPERIMENTAL DATA
3,3-Dimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
87.86	1.069	-0.017	0.6246	------
101.23	1.528	-0.016	0.6048	------
110.10	1.919	-0.022	0.5980	------
124.56	2.720	-0.035	0.5824	------
140.43	3.866	-0.042	0.5666	------
155.81	5.290	-0.035	0.5500	------
164.92	6.318	-0.041	0.5317	------
174.41	7.519	-0.024	0.5250	------
189.37	9.747	0.021	0.5042	------
204.74	12.525	0.078	0.4820	------
217.36	15.201	0.152	------	------
217.43	15.156	0.213	------	------
217.65	15.265	0.156	------	0.0561
217.64	15.286	0.233	0.4599	------
224.17	16.800	0.207	------	0.0630
224.18	16.828	0.182	0.4478	------
235.59	19.824	0.243	------	0.0801
235.53	19.830	0.220	0.4246	------
241.36	21.474	0.281	------	0.0904
241.36	21.516	0.239	0.4083	------
244.73	22.539	0.249	------	0.0976
244.74	22.567	0.224	0.3996	------
250.72	24.468	0.240	------	0.1149
250.72	24.496	0.212	0.3786	------
253.49	25.422	0.213	------	0.1230
253.46	25.444	0.180	0.3541	------
257.63	26.890	0.174	------	0.1414
257.64	26.919	0.149	0.3423	------
261.61	28.409	0.083	0.3073	------
261.61	28.399	0.093	------	0.1743
263.19	29.073	0.000	0.2408 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

A = 4.43153
B = -1591.94

TABLE 42

EXPERIMENTAL DATA
2,2,3-Trimethylbutane

Temperature ^{o}C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
109.14	2.158	-0.046	0.6182	------
109.81	2.187	-0.040	0.6169	------
125.32	3.142	-0.053	0.6032	------
140.45	4.359	-0.068	0.5873	------
155.06	5.832	-0.066	0.5592	------
155.36	5.861	-0.061	0.5618	------
166.15	7.173	-0.051	0.5436	------
173.52	8.169	-0.022	0.5343	------
186.38	10.180	0.018	0.5207	------
198.50	12.394	0.063	0.5114	------
198.50	12.371	0.086	------	0.0452
199.56	12.595	0.075	0.4969	------
208.13	14.386	0.114	0.4858	------
217.16	16.482	0.110	0.4741	------
217.15	16.475	0.153	0.4693	------
217.19	16.443	0.191	------	0.0643
217.91	16.639	0.178	------	0.0648
224.49	18.343	0.177	0.4505	------
224.67	18.349	0.217	------	0.0750
232.13	20.418	0.230	------	0.0865
240.56	23.006	0.189	0.4101	------
240.56	22.968	0.227	------	0.1062
244.79	24.362	0.192	0.4100	------
244.81	24.342	0.218	------	0.1174
249.81	26.087	0.152	0.3718	------
249.79	26.047	0.151	------	0.1391
254.63	27.846	0.076	0.3389	------
254.62	27.813	0.116	------	0.1657
257.96	29.146	0.000	Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T(^{o}K)$$

$A = 4.39299$
$B = -1555.34$

TABLE 43

EXPERIMENTAL DATA
n-Octane

Temperature $^\circ$C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
139.82	1.506	-0.062	0.5977	------
155.18	2.176	-0.064	0.5849	------
155.54	2.199	-0.089	0.5819	------
167.73	2.849	-0.070	0.5718	------
167.76	2.895	-0.114	------	------
183.90	3.998	-0.083	0.5525	------
199.29	5.396	-0.088	0.5376	------
208.90	6.443	-0.086	0.5262	------
217.64	7.554	-0.111	------	------
223.33	8.275	-0.051	0.5047	------
237.33	10.386	0.027	------	0.0422
237.33	10.435	-0.022	0.4815	------
239.99	10.850	0.024	------	0.0466
239.99	10.900	-0.026	0.4797	------
254.30	13.545	0.084	------	0.0577
254.31	13.608	0.021	0.4503	------
260.74	14.920	0.108	------	0.0650
260.74	15.005	0.023	0.4322	------
259.94	14.820	0.029	0.4310	------
268.82	16.798	0.134	------	0.0761
268.82	16.875	0.057	0.4130	------
279.76	19.650	0.139	------	0.0987
279.76	19.703	0.086	0.3794	------
290.40	22.779	0.118	------	0.1375
290.40	22.806	0.091	0.3313	------
295.59	24.537	0.000	0.2279 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^\circ\text{K})$$

$A = 4.65176$
$B = -1855.26$

TABLE 44

EXPERIMENTAL DATA
2-Methylheptane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
124.95	1.229	-0.014	0.6084	------
140.01	1.809	-0.034	0.5931	------
154.87	2.568	-0.053	0.5786	------
170.12	3.576	-0.066	0.5575	------
184.97	4.829	-0.076	0.5424	------
200.01	6.404	-0.067	0.5238	------
210.03	7.657	-0.057	0.5104	------
220.01	9.080	-0.039	0.4968	------
230.05	10.704	-0.012	0.4820	------
240.00	12.480	0.065	------	0.0535
240.00	12.527	0.018	0.4607	------
249.97	14.518	0.115	------	0.0641
249.97	14.576	0.057	0.4389	------
260.19	16.906	0.127	------	0.0782
260.19	16.947	0.086	0.4164	------
270.06	19.474	0.142	------	0.0986
270.06	19.513	0.103	0.3856	------
280.01	22.402	0.101	------	0.1326
280.01	22.430	0.073	0.3429	------
286.41	24.517	0.000	0.2342	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}\text{K})$$

$A = 4.60725$

$B = -1800.61$

TABLE 45

EXPERIMENTAL DATA
3-Methylheptane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
125.67	1.204	-0.008	0.6154	------
139.99	1.740	-0.024	0.6026	------
155.00	2.482	-0.040	0.5870	------
170.06	3.447	-0.052	0.5734	------
183.84	4.562	-0.059	0.5583	------
199.89	6.188	-0.058	0.5376	------
215.41	8.136	-0.034	0.5184	------
226.10	9.731	-0.012	0.5021	------
232.85	10.857	0.003	0.4913	------
240.03	12.126	0.056	------	0.0540
240.03	12.150	0.032	0.4817	------
249.98	14.115	0.094	------	0.0649
249.98	14.138	0.071	0.4608	------
260.06	16.375	0.135	------	0.0776
260.06	16.397	0.113	0.4393	------
269.68	18.804	0.149	------	0.0947
269.68	18.821	0.132	0.4137	------
279.73	21.653	0.129	------	0.1226
279.73	21.667	0.115	0.3780	------
285.53	23.474	0.074	------	0.1501
285.53	23.475	0.073	0.3460	------
290.45	25.127	0.000	0.2463 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (°K)}$$

$A = 4.60063$
$B = -1803.86$

TABLE 46

EXPERIMENTAL DATA
4-Methylheptane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
125.04	1.232	-0.017	0.6190	------
140.02	1.809	-0.037	0.6040	------
154.49	2.542	-0.054	0.5897	------
170.03	3.559	-0.066	0.5700	------
185.01	4.816	-0.074	0.5528	------
199.98	6.388	-0.076	0.5345	------
214.97	8.312	-0.053	0.5134	------
225.03	9.835	-0.033	0.4958	------
233.95	11.304	0.042	------	0.0467
233.95	11.356	-0.010	0.4801	------
240.09	12.454	0.056	------	0.0504
240.09	12.499	0.011	0.4710	------
250.04	14.480	0.105	------	0.0627
250.04	14.545	0.040	0.4501	------
260.04	16.790	0.130	------	0.0758
260.04	16.841	0.079	0.4283	------
269.97	19.337	0.165	------	0.0945
269.97	19.399	0.103	0.3990	------
279.97	22.269	0.115	------	0.1253
279.97	22.296	0.088	0.3588	------
283.62	23.423	0.087	------	0.1420
283.62	23.453	0.057	0.3388	------
288.52	25.087	0.000	0.2414	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (°K)}$$

$A = 4.60194$
$B = -1798.81$

TABLE 47

EXPERIMENTAL DATA
3-Ethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
125.01	1.197	-0.009	0.6254	------
139.63	1.740	-0.023	0.6116	------
154.96	2.504	-0.046	0.5986	------
170.04	3.476	-0.060	0.5832	------
184.98	4.699	-0.066	0.5713	------
200.01	6.247	-0.074	0.5448	------
214.98	8.121	-0.047	0.5303	------
225.11	9.593	0.000	------	0.0426
225.11	9.625	-0.032	0.5160	------
231.99	10.723	0.019	------	0.0492
231.99	10.756	-0.014	0.5046	------
240.00	12.175	0.033	------	0.0520
240.00	12.192	0.016	0.4833	------
249.99	14.168	0.074	------	0.0632
249.99	14.185	0.057	0.4741	------
260.18	16.451	0.116	------	0.0789
260.18	16.474	0.093	0.4543	------
270.00	18.917	0.146	------	0.0950
270.00	18.945	0.118	0.4263	------
279.97	21.745	0.126	------	0.1215
279.97	21.765	0.106	0.3901	------
287.37	24.059	0.083	------	0.1550
287.37	24.076	0.066	0.3553	------
292.27	25.738	0.000	0.2457 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}\text{K})$$

$A = 4.59076$
$B = -1798.20$

TABLE 48

EXPERIMENTAL DATA
2,2-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
120.11	1.445	-0.024	0.6074	------
134.78	2.080	-0.039	0.5910	------
149.68	2.930	-0.057	0.5742	------
155.12	3.297	-0.061	0.5705	------
167.77	4.284	-0.066	0.5547	------
179.93	5.429	-0.061	0.5380	------
189.85	6.526	-0.053	0.5257	------
200.24	7.862	-0.053	0.5123	------
209.90	9.258	-0.028	0.4955	------
216.96	10.357	0.029	------	0.0439
216.99	10.414	-0.023	0.4872	------
232.63	13.253	0.086	------	0.0555
232.65	13.325	0.018	0.4586	------
240.18	14.858	0.109	------	0.0647
240.16	14.927	0.035	0.4288	------
253.91	18.148	0.148	------	0.0864
253.92	18.218	0.081	0.4099	------
261.07	20.071	0.162	------	0.1033
261.07	20.137	0.096	0.3870	------
265.28	21.302	0.138	------	0.1174
265.28	21.359	0.081	0.3710	------
271.13	23.102	0.101	------	0.1415
271.13	23.140	0.063	0.3414	------
276.65	24.961	0.000	0.2375 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.52412$

$B = -1719.21$

TABLE 49

EXPERIMENTAL DATA
2,3-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
125.36	1.304	-0.011	0.6219	------
139.35	1.854	-0.024	0.6054	------
155.04	2.671	-0.041	0.5883	------
168.01	3.532	-0.051	0.5774	------
183.46	4.816	-0.055	0.5606	------
199.22	6.483	-0.066	0.5459	------
216.96	8.839	-0.065	0.5185	------
227.11	10.353	0.047	------	0.0424
227.11	10.448	-0.057	0.5039	------
236.47	11.998	0.072	------	0.0483
236.47	12.097	-0.027	0.4901	------
239.99	12.762	-0.011	0.4825	------
239.98	12.681	0.067	------	0.0522
250.30	14.800	0.115	------	0.0623
250.30	14.903	0.012	0.4602	------
260.63	17.182	0.163	------	0.0787
260.63	17.295	0.050	0.4384	------
268.90	19.318	0.174	------	0.0931
268.90	19.424	0.068	0.4130	------
279.28	22.318	0.137	------	0.1196
279.28	22.396	0.059	0.3769	------
284.98	24.109	0.107	------	0.1451
284.98	24.165	0.051	0.3466	------
290.27	25.938	0.000	0.2391	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.56126$

$B = -1773.33$

TABLE 50

EXPERIMENTAL DATA
2,4-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
109.32	1.003	-0.006	0.6052	------
124.37	1.505	-0.024	0.5947	------
139.60	2.190	-0.042	0.5806	------
155.05	3.106	-0.063	0.5665	------
167.32	4.020	-0.070	0.5522	------
179.62	5.129	-0.072	0.5406	------
189.17	6.149	-0.079	0.5273	------
202.11	7.754	-0.061	0.5137	------
216.70	9.864	0.007	------	0.0417
216.70	9.914	-0.043	0.4939	------
229.30	12.058	0.056	------	0.0523
229.30	12.116	-0.002	0.4695	------
240.02	14.201	0.105	------	0.0626
240.02	14.277	0.029	0.4507	------
253.80	17.402	0.139	------	0.0828
253.80	17.471	0.070	0.4225	------
260.27	19.085	0.148	------	0.1003
260.27	19.130	0.103	0.4040	------
269.31	21.662	0.131	------	0.1208
269.31	21.697	0.096	0.3730	------
274.69	23.313	0.117	------	0.1433
274.69	23.360	0.070	0.3445	------
280.30	25.229	0.000	0.2408 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.54094$

$B = -1737.36$

TABLE 51

EXPERIMENTAL DATA
2,5-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
125.29	1.561	-0.029	0.6004	------
139.60	2.216	-0.044	0.5857	------
154.86	3.132	-0.061	0.5690	------
184.40	5.685	-0.062	0.5322	------
199.28	7.458	-0.046	0.5128	------
215.03	9.733	0.014	------	0.0414
215.03	9.773	-0.026	0.4887	------
225.34	11.500	0.053	------	0.0477
225.34	11.550	0.003	0.4705	------
235.07	13.380	0.097	------	0.0576
235.07	13.437	0.040	0.4510	------
240.01	14.424	0.117	------	0.0625
240.01	14.487	0.054	0.4426	------
250.11	16.758	0.151	------	0.0786
250.11	16.808	0.101	0.4179	------
260.27	19.407	0.160	------	0.0982
260.24	19.456	0.103	0.3906	------
270.32	22.358	0.128	------	0.1322
270.32	22.418	0.068	0.3460	------
276.84	24.542	0.000	0.2342	Critical

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.55744$

$B = -1742.17$

TABLE 52

EXPERIMENTAL DATA
3,3-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
125.34	1.430	-0.014	0.6276	------
139.82	2.042	-0.029	0.6128	------
154.96	2.877	-0.042	0.5987	------
170.06	3.946	-0.050	0.5882	------
183.87	5.167	-0.050	0.5737	------
198.98	6.812	-0.043	0.5547	------
214.05	8.794	0.001	------	0.0390
214.05	8.833	-0.038	0.5333	------
222.05	10.006	0.035	------	0.0463
222.05	10.050	-0.009	0.5248	------
230.62	11.471	0.048	------	0.0494
230.62	11.513	0.006	0.5133	------
240.00	13.225	0.091	------	0.0596
240.00	13.281	0.035	0.4929	------
250.30	15.399	0.122	------	0.0712
250.30	15.437	0.084	0.4739	------
260.68	17.836	0.169	------	0.0884
260.68	17.883	0.122	0.4494	------
270.02	20.318	0.161	------	0.1068
270.02	20.347	0.132	0.4226	------
279.12	22.976	0.142	------	0.1354
279.12	22.999	0.119	0.3870	------
284.91	24.842	0.078	------	0.1682
284.91	24.859	0.061	0.3516	------
288.80	26.187	0.000	0.2568 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T(^{\circ}K)$$

$A = 4.50672$
$B = -1735.72$

TABLE 53

EXPERIMENTAL DATA
3,4-Dimethylhexane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
125.71	1.238	-0.004	0.6312	------
139.74	1.768	-0.019	0.6254	------
155.13	2.537	-0.038	0.6037	------
169.91	3.489	-0.050	0.5840	------
185.01	4.721	-0.057	0.5667	------
199.48	6.187	-0.053	0.5505	------
214.58	8.062	-0.039	0.5340	------
224.88	9.559	-0.013	0.5152	------
231.34	10.562	0.044	------	0.0420
231.34	10.621	-0.015	0.5068	------
239.97	12.079	0.080	------	0.0493
239.97	12.148	0.011	0.4909	------
250.07	14.055	0.131	------	0.0584
250.07	14.130	0.056	0.4741	------
260.26	16.330	0.146	------	0.0695
260.26	16.399	0.077	0.4510	------
269.47	18.595	0.176	------	0.0844
269.47	18.660	0.111	0.4330	------
279.30	21.300	0.171	------	0.1048
279.31	21.358	0.113	0.4023	------
289.47	24.452	0.101	------	0.1423
289.47	24.500	0.053	0.3538	------
295.63	26.569	0.000	0.2401 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.55388$
$B = -1780.07$

TABLE 54

EXPERIMENTAL DATA
2-Methyl-3-ethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
124.98	1.289	-0.012	0.6362	------
139.63	1.862	-0.028	0.6249	------
154.81	2.646	-0.045	0.6048	------
168.40	3.540	-0.057	0.5918	------
183.95	4.822	-0.060	0.5752	------
199.71	6.467	-0.064	0.5569	------
214.95	8.387	-0.015	------	0.0374
214.95	8.412	-0.040	0.5351	------
221.22	9.301	0.002	------	0.0408
221.22	9.334	-0.031	0.5270	------
230.06	10.719	0.029	------	0.0458
230.06	10.753	-0.005	0.5159	------
240.03	12.494	0.078	------	0.0536
240.03	12.540	0.032	0.5002	------
249.99	14.496	0.120	------	0.0652
249.99	14.541	0.075	0.4816	------
260.14	16.782	0.162	------	0.0777
260.14	16.837	0.107	0.4599	------
269.27	19.094	0.166	------	0.0928
269.27	19.131	0.129	0.4382	------
280.02	22.126	0.150	------	0.1202
280.02	22.133	0.143	0.4046	------
280.03	22.135	0.147	------	0.1199
280.04	22.164	0.118	0.4053	------
286.82	24.244	0.109	------	0.1469
286.82	24.273	0.080	0.3750	------
293.87	26.651	0.000	0.2575 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.53619$
$B = -1763.76$

TABLE 55

EXPERIMENTAL DATA
3-Methyl-3-ethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
124.98	1.196	-0.005	0.6416	------
139.39	1.716	-0.017	0.6285	------
154.95	2.459	-0.032	0.6145	------
170.24	3.402	-0.039	0.5968	------
184.90	4.546	-0.041	0.5828	------
199.87	5.995	-0.036	0.5707	------
215.30	7.825	-0.015	0.5493	------
221.03	8.603	-0.005	0.5386	------
230.18	9.962	0.017	0.5250	------
239.93	11.545	0.082	------	0.0461
239.93	11.581	0.046	0.5119	------
250.53	13.514	0.127	------	0.0548
250.53	13.565	0.076	0.4927	------
260.85	15.683	0.157	------	0.0650
260.85	15.719	0.121	0.4739	------
270.39	17.897	0.198	------	0.0776
270.39	17.942	0.153	0.4515	------
279.84	20.355	0.196	------	0.0929
279.84	20.383	0.168	0.4289	------
289.14	23.010	0.187	------	0.1158
289.14	23.037	0.160	0.3986	------
295.41	24.986	0.129	------	0.1388
295.41	25.024	0.091	0.3691	------
303.36	27.706	0.000	0.2512 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{o}K)$$

$A = 4.49320$
$B = -1758.77$

TABLE 56

EXPERIMENTAL DATA
2,2,3-Trimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density	
			Liquid gm/cc	Vapor gm/cc
125.69	1.521	-0.016	0.6307	------
139.40	2.118	-0.020	0.6167	------
154.84	2.991	-0.042	0.6007	------
170.16	4.126	-0.073	0.5868	------
184.71	5.425	-0.051	0.5710	------
199.18	7.037	-0.042	0.5529	------
215.17	9.179	0.012	------	0.0419
215.17	9.204	-0.013	0.5296	------
224.50	10.654	0.038	------	0.0469
224.50	10.680	0.012	0.5197	------
230.87	11.747	0.070	------	0.0509
230.87	11.784	0.033	0.5120	------
240.02	13.467	0.117	------	0.0594
240.02	13.519	0.065	0.4973	------
250.06	15.582	0.157	------	0.0718
250.06	15.638	0.101	0.4777	------
260.02	17.942	0.173	------	0.0849
260.02	17.986	0.129	0.4550	------
269.99	20.557	0.189	------	0.1053
269.99	20.595	0.151	0.4316	------
278.97	23.191	0.152	------	0.1299
278.97	23.209	0.134	0.3937	------
286.76	25.691	0.089	------	0.1706
286.76	25.706	0.074	0.3518	------
290.28	26.937	0.000	0.2607 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc}\ (\text{Atm.}) = A + B/T\ (^{\circ}K)$$

$A = 4.46647$
$B = -1710.70$

TABLE 57

EXPERIMENTAL DATA
2,2,4-Trimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
110.01	1.413	-0.079	0.6154	------
110.81	1.398	-0.036	0.6192	------
124.42	1.976	-0.062	0.6061	------
124.81	2.030	-0.098	0.5960	------
139.78	2.803	-0.067	0.5894	------
139.86	2.855	-0.114	0.5813	------
154.37	3.804	-0.054	0.5740	------
154.86	3.915	-0.126	0.5692	------
154.36	3.818	-0.068	0.5740	------
166.54	4.909	-0.107	0.5609	------
166.97	4.953	-0.110	0.5609	------
166.74	4.941	-0.120	0.5522	------
183.88	6.755	-0.080	0.5333	------
199.03	8.781	-0.054	0.5103	------
216.41	11.443	0.185	------	0.0521
216.41	11.620	0.008	0.4835	------
216.38	11.624	-0.001	0.4825	------
220.66	12.329	0.107	------	0.0519
220.66	12.413	0.023	0.4764	------
230.62	14.353	0.136	------	0.0618
230.62	14.427	0.062	0.4583	------
240.10	16.502	0.164	------	0.0753
240.10	16.565	0.101	0.4349	------
249.60	18.921	0.157	------	0.0919
249.60	18.964	0.114	0.4107	------
251.94	19.522	0.187	------	0.0980
251.94	19.599	0.110	0.3798	------
258.86	21.488	0.176	------	0.1172
258.86	21.562	0.102	0.3772	------
265.10	23.392	0.152	------	0.1410
265.10	23.485	0.059	0.3463	------
270.74	25.340	0.000	0.2429 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (}^{\circ}\text{K)}$$

A = 4.45216
B = -1658.03

TABLE 58

EXPERIMENTAL DATA
2,3,3-Trimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Saturated Density Vapor gm/cc
125.02	1.315	-0.012	0.6377	------
140.02	1.908	-0.033	0.6223	------
155.23	2.680	-0.039	0.6052	------
169.98	3.666	-0.066	0.5925	------
185.00	4.908	-0.073	0.5757	------
199.98	6.423	-0.054	0.5610	------
215.03	8.285	-0.027	0.5396	------
220.31	9.012	0.001	0.5336	------
230.00	10.503	0.027	0.5219	------
240.04	12.206	0.090	------	0.0493
240.04	12.241	0.055	0.5052	------
249.98	14.111	0.142	------	0.0583
249.98	14.160	0.093	0.4904	------
259.95	16.259	0.177	------	0.0679
259.95	16.320	0.116	0.4679	------
269.25	18.493	0.192	------	0.1142
269.25	18.547	0.138	0.4480	------
280.22	21.413	0.203	------	0.1019
280.22	21.450	0.166	0.4189	------
290.38	24.462	0.153	------	0.1297
290.38	24.499	0.116	0.3824	------
294.98	25.952	0.114	------	0.1516
294.98	25.994	0.072	0.3543	------
300.34	27.833	0.000	0.2460 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (}^{\circ}\text{K)}$$

A = 4.46422
B = -1731.80

TABLE 59

EXPERIMENTAL DATA
2,3,4-Trimethylpentane

Temperature °C.	Observed Pressure Atm.	Pressure Deviation* Atm.	Saturated Density Liquid gm/cc	Vapor gm/cc
125.01	1.370	-0.019	0.6357	------
139.94	1.979	-0.034	0.6210	------
154.97	2.786	-0.051	0.6047	------
170.11	3.826	-0.059	0.5857	------
185.01	5.118	-0.062	0.5687	------
200.02	6.724	-0.048	0.5517	------
215.08	8.685	-0.013	0.5294	------
222.50	9.824	-0.017	0.5194	------
231.90	11.332	0.071	------	0.0445
231.90	11.393	0.010	0.5070	------
240.00	12.843	0.080	------	0.0505
240.00	12.895	0.028	0.4907	------
250.00	14.870	0.140	------	0.0622
250.00	14.943	0.067	0.4730	------
260.97	17.378	0.193	------	0.0754
260.97	17.460	0.111	0.4484	------
270.06	19.715	0.210	------	0.0913
270.06	19.790	0.135	0.4255	------
280.06	22.593	0.179	------	0.1162
280.06	22.645	0.127	0.3911	------
287.46	24.949	0.111	------	0.1468
287.46	24.999	0.061	0.3539	------
293.19	26.941	0.000	0.2511 Critical	

* Pressure deviation obtained by subtracting the observed pressure from the pressure calculated by the following equation:

$$\log P_{calc} \text{ (Atm.)} = A + B/T \text{ (}^{\circ}\text{K)}$$

$A = 4.50775$
$B = -1742.87$

TABLE 60

PRESSURE-VOLUME ISOTHERM

n-Heptane

t = 210.005°C.

Pressure psia.	Length* mm.
168.61	270.90 Dew Point
168.65	210.50
168.59	155.10
168.62	103.00
168.81	60.20
169.44	31.10 Bubble Point

* Length represents volume.

TABLE 61

PRESSURE-VOLUME ISOTHERM

2-Methylhexane

t = 217.44°C.

Pressure psia.	Length* mm.
220.02	235.75 Dew Point
220.10	209.85
219.98	180.85
220.39	148.60
220.45	99.50
220.80	64.80
220.82	38.40
221.14	34.55 Bubble Point

* Length represents volume.

TABLE 62

PRESSURE-VOLUME ISOTHERM

3-Methylhexane

t = 210.00°C.

Pressure psia.	Length* mm.	
188.434	273.65	Dew Point
188.450	263.80	
188.485	243.50	
188.545	193.50	
188.613	144.00	
188.724	97.30	
188.941	55.80	
189.468	30.70	Bubble Point

* Length represents volume.

TABLE 63

PRESSURE-VOLUME ISOTHERM

3-Ethylpentane

t = 217.25°C.

Pressure psia.	Length* mm.	
202.317	243.60	Dew Point
202.287	210.50	
202.370	187.90	
202.418	137.00	
202.543	90.40	
202.641	69.05	
202.788	50.40	
203.094	29.35	Bubble Point

* Length represents volume.

TABLE 64

PRESSURE-VOLUME ISOTHERM

2,2-Dimethylpentane

t = 209.95°C.

Pressure psia.	Length* mm.	
233.051	221.30	Dew Point
233.194	175.00	
233.309	127.80	
233.434	80.95	
233.691	41.30	
233.761	34.40	Bubble Point

* Length represents volume.

TABLE 65

PRESSURE-VOLUME ISOTHERM

2,3-Dimethylpentane

t = 210.00°C.

Pressure psia.	Length* mm.	
191.66	241.30	Dew Point
191.73	217.65	
191.83	169.50	
191.96	123.60	
192.10	77.60	
192.67	44.90	
192.81	35.70	
193.45	28.65	Bubble Point

* Length represents volume.

TABLE 66

PRESSURE-VOLUME ISOTHERM

2,4-Dimethylpentane

t = 210.01°C.

Pressure psia.	Length* mm.
231.23	172.35 Dew Point
231.47	167.85
231.49	159.95
231.48	132.45
231.60	85.75
231.87	46.75
232.10	27.95 Bubble Point

TABLE 67

PRESSURE-VOLUME ISOTHERM

3,3-Dimethylpentane

t = 241.36°C.

Pressure psia.	Length* mm.
315.98	133.20 Dew Point
316.12	125.98
316.22	105.39
316.29	84.11
316.38	63.35
316.59	35.73
316.56	32.89
316.59	32.71 Bubble Point

* Length represents volume.

TABLE 68

PRESSURE-VOLUME ISOTHERM

n-Octane

t = 239.99°C.

Pressure psia.	Length* mm.	
159.47	282.05	Dew Point
159.65	247.15	
159.73	198.10	
159.65	140.80	
159.71	90.20	
159.91	46.90	
160.20	31.10	Bubble Point

* Length represents volume.

TABLE 69

PRESSURE-VOLUME ISOTHERM

2-Methylheptane

t = 240.00°C.

Pressure psia.	Length* mm.	
183.42	247.20	Dew Point
183.53	223.95	
183.70	179.20	
183.76	129.05	
183.83	79.15	
183.90	55.75	
184.10	32.35	Bubble Point

* Length represents volume.

TABLE 70

PRESSURE-VOLUME ISOTHERM

3-Methylheptane

t = 240.03°C.

Pressure psia.	Length* mm.	
178.21	299.15	Dew Point
178.32	280.95	
178.45	234.30	
178.47	182.00	
178.48	128.80	
178.45	74.30	
178.46	58.65	
178.55	36.50	Bubble Point

* Length represents volume.

TABLE 71

PRESSURE-VOLUME ISOTHERM

4-Methylheptane

t = 240.09°C.

Pressure psia.	Length* mm.	
183.03	276.15	Dew Point
183.16	256.15	
183.28	208.80	
183.32	157.20	
183.39	107.15	
183.51	60.25	
183.69	33.20	Bubble Point

* Length represents volume.

TABLE 72

PRESSURE-VOLUME ISOTHERM

3-Ethylhexane

t = 240.00°C.

Pressure psia.	Length* mm.
178.93	244.50 Dew Point
178.97	219.50
178.99	167.20
178.99	113.50
178.99	62.70
179.18	29.30 Bubble Point

* Length represents volume.

TABLE 73

PRESSURE-VOLUME ISOTHERM

2,2-Dimethylhexane

t = 240.17°C.

Pressure psia.	Length* mm.
218.36	206.55 Dew Point
218.47	173.70
218.51	122.45
218.52	123.35
218.69	76.85
218.80	56.95
219.37	34.65 Bubble Point

* Length represents volume.

TABLE 74

PRESSURE-VOLUME ISOTHERM

2,3-Dimethylhexane

t = 239.99°C.

Pressure psia.	Length* mm.	
186.36	243.35	Dew Point
186.36	206.30	
186.45	157.85	
186.59	111.30	
186.83	70.90	
187.27	40.80	
187.55	30.00	Bubble Point

* Length represents volume.

TABLE 75

PRESSURE-VOLUME ISOTHERM

2,4-Dimethylhexane

t = 240.02°C.

Pressure psia.	Length* mm.	
208.70	209.20	Dew Point
208.91	192.25	
208.96	141.20	
209.14	97.35	
209.36	55.10	
209.43	43.65	
209.82	31.90	Bubble Point

* Length represents volume.

TABLE 76

PRESSURE-VOLUME ISOTHERM

2,5-Dimethylhexane

t = 240.01°C.

Pressure psia.	Length* mm.
211.97	195.70 Dew Point
212.16	178.35
212.33	134.10
212.43	85.60
212.64	44.25
212.90	31.15 Bubble Point

* Length represents volume.

TABLE 77

PRESSURE-VOLUME ISOTHERM

3,3-Dimethylhexane

t = 240.00°C.

Pressure psia.	Length* mm.
194.36	199.80 Dew Point
194.53	181.90
194.61	132.80
194.66	81.75
194.83	37.40
195.18	27.10 Bubble Point

* Length represents volume.

TABLE 78

PRESSURE-VOLUME ISOTHERM

3,4-Dimethylhexane

t = 239.97°C.

Pressure psia.	Length* mm.	
177.52	257.25	Dew Point
177.67	238.10	
177.90	196.60	
177.98	147.50	
178.05	98.30	
178.20	52.40	
178.52	29.55	Bubble Point

* Length represents volume.

TABLE 79

PRESSURE-VOLUME ISOTHERM

2-Methyl-3-ethylpentane

t = 240.03°C.

Pressure psia.	Length* mm.	
183.61	232.65	Dew Point
183.80	216.15	
184.03	174.40	
184.02	120.55	
184.08	70.00	
184.15	47.00	
184.29	27.90	Bubble Point

* Length represents volume.

TABLE 80

PRESSURE-VOLUME ISOTHERM

3-Methyl-3-ethylpentane

t = 239.93°C.

Pressure psia.	Length* mm.	
169.67	273.95	Dew Point
169.83	255.70	
169.99	208.15	
170.01	156.05	
170.01	102.00	
170.07	51.90	
170.20	28.40	Bubble Point

* Length represents volume.

TABLE 81

PRESSURE-VOLUME ISOTHERM

2,2,3-Trimethylpentane

t = 240.02°C.

Pressure psia.	Length* mm.	
197.91	237.20	Dew Point
198.11	219.20	
198.31	176.45	
198.44	130.20	
198.48	78.60	
198.65	33.95	
198.68	31.25	Bubble Point

* Length represents volume.

TABLE 82

PRESSURE-VOLUME ISOTHERM

2,2,4-Trimethylpentane

t = 240.10°C.

Pressure psia.	Length* mm.
242.51	155.55 Dew Point
242.62	136.00
242.73	88.75
242.99	49.00
243.44	30.35 Bubble Point

* Length represents volume.

TABLE 83

PRESSURE-VOLUME ISOTHERM

2,3,3-Trimethylpentane

t = 240.04°C.

Pressure psia.	Length* mm.
179.39	293.10 Dew Point
179.37	270.35
179.61	224.60
179.64	172.49
179.67	120.40
179.73	70.30
179.90	32.30 Bubble Point

* Length represents volume.

TABLE 84

PRESSURE-VOLUME ISOTHERM

2,3,4-Trimethylpentane

t = 240.00°C.

Pressure psia.	Length* mm.	
188.74	277.10	Dew Point
188.71	248.70	
188.94	207.60	
189.00	157.30	
189.09	108.55	
189.22	61.70	
189.30	48.80	
189.51	32.20	Bubble Point

* Length represents volume.

APPENDIX II

CALIBRATIONS

CALIBRATION OF EXPERIMENTAL TUBES

The experimental tubes were calibrated by measuring the volume of mercury in a given length of tube.

The clean, dry tube was weighed on an analytical balance, and then mounted in a vertical position and the tube was partially filled with mercury by means of a fine capillary. The distance from the tube tip to the top of the mercury meniscus and the height of the mercury meniscus were measured with the aid of a cathetometer, reading to 0.05 mm. The tube containing the mercury was weighed, the tube remounted, more mercury added to the tube, remeasured and reweighed. This procedure was repeated several times. From a knowledge of the specific volume of mercury at the temperature of the length measurement, and the weight of the mercury, the volume of mercury was calculated for each length measurement. The volume change from one set of readings to the next per unit length was calculated, from which the average change in volume per unit length was calculated. Since the average volume per unit length is the cross sectional area of a tube, the tube diameter was calculated from this value. The volume occupied by the compliment of the meniscus was taken as the difference in volume of a cylinder of diameter D and height h and a spherical segment of one base of diameter D and height h; h is the height of the meniscus and D is the tube diameter. Therefore, the volume of the compliment of the meniscus was calculated from the equation:

$$V = \pi h(D^2/8 - h^2/6) \qquad (1)$$

The volume of the compliment of the meniscus was calculated for each volume determination and added to the volume of the mercury, thereby, giving the total volume of the tube for any given length. it was assumed that the volume to length relationship was linear, giving an equation of the type:

$$V = a + bL \qquad (2)$$

where, V is the volume in cc., a and b are constants and L is the length from the tube tip to the point for which the volume is desired, in mm. The values of the constants were determined by the least mean squares technique.

Tables 84, 85, and 86 present the data for the three tubes used. The data given are temperature, length, volume and the deviation of the volume calculated from the equation and the experimental volume. Also, the volume of the compliment of the meniscus for several different meniscus heights and the derived equation are given for each tube.

From an analysis of the deviations of the calculated and determined volumes, it was decided that no correction to the equation was necessary.

Volume Calculation

The volume of the hydrocarbons was calculated in the following manner:

1) The volume was calculated from equation (2) by using the length from the tube tip to the top of the mercury meniscus.

2) The volume of the compliment of the meniscus was added to the volume calculated from equation (2). The volume of the compliment was calculated from equation (1).

3) The ball volume was subtracted from the volume, or a modified volume equation was used which took the ball volume into account.

4) The volume of the tube was corrected for temperature by using the volumetric coefficient of expansion for pyrex.

Example Volume Calculation

Tube A , $L = 25.25$ mm., $h = 0.50$ mm., $t = 200^\circ$C., and $d = 0.20187$

1) $V = 0.003200\,(25.25) - 0.0011918 = 0.09774$ cc.

2) $V_c = (0.050)\pi\left[(0.20187)^2/8 - (0.05)^2/6\right] \quad 0.00073$

3) Ball volume $= 0.03095$, $V_{30^\circ} = 0.06752$

4) $V_{200^\circ} = 0.06752 + 0.06752 \times 24 \times 10^{-7} \times (200 - 30) = 0.06755$

$$V_{200^\circ} = 0.06755 \text{ cc.}$$

TABLE 85

CALIBRATION DATA

EXPERIMENTAL TUBE A

Temperature °C.	Length mm.	Volume cc.	Deviation* cc.
28.7	29.25	0.08193	-0.00024
28.8	41.90	0.12208	0.00008
27.8	54.75	0.16329	-0.00001
27.8	70.35	0.21321	-0.00001
27.8	89.05	0.27296	0.00008
28.0	104.75	0.32327	0.00001
29.4	121.20	0.37600	-0.00008
29.8	145.15	0.45250	0.00006
30.3	181.50	0.56901	-0.00013
29.7	196.40	0.61651	0.00005
29.8	238.80	0.75254	-0.00030
29.4	257.90	0.81357	-0.00021
29.2	272.35	0.85947	0.00013
29.1	298.20	0.94245	-0.00013
29.2	327.30	1.03534	0.00010
25.6	39.00	0.11287	0.00001
28.7	117.35	0.36381	-0.00021
26.1	165.80	0.51884	-0.00020
25.6	218.60	0.68806	-0.00046
24.6	274.40	0.86646	-0.00030
26.1	318.35	1.00678	0.00002
25.8	101.90	0.31445	-0.00029
25.6	170.10	0.53284	-0.00044
25.6	264.70	0.83475	0.00037
24.6	342.35	1.08331	0.00029
26.5	28.90	0.07997	-0.00059
26.6	207.30	0.65198	-0.00054
26.6	348.85	1.10414	0.00036
26.6	294.00	0.92920	-0.00032
	Average Absolute Deviation		0.00021

Volume of Compliment of Meniscus

h, mm.	0.40	0.50	0.60	0.70	0.80
v, cc.	0.00061	0.00073	0.00085	0.00094	0.00101

* deviation is $V_{calc} - V_{exp}$, where V_{calc} is from the equation

$$V = 0.003200\ L - 0.0011918$$

Where L is in mm. and V is in cc.   Tube Diameter = 2.0187 mm.

TABLE 86

CALIBRATION DATA

EXPERIMENTAL TUBE B

Temperature °C.	Length mm.	Volume cc.	Deviation* cc.
28.6	50.35	0.14443	0.00036
28.2	62.15	0.18115	0.00024
28.0	85.15	0.25317	-0.00044
25.6	111.75	0.33551	-0.00026
29.5	130.65	0.39475	-0.00087
27.2	166.70	0.50558	0.00012
28.0	241.95	0.73845	0.00068
27.6	301.90	0.92538	-0.00029
27.5	320.95	0.98424	-0.00005
27.2	24.75	0.06540	-0.00003
28.3	57.90	0.16825	-0.00004
27.0	86.65	0.25739	0.00000
28.3	116.50	0.34981	0.00017
27.5	191.50	0.58217	0.00046
27.0	224.95	0.68619	0.00021
27.9	265.25	0.81147	-0.00006
26.9	305.20	0.93562	-0.00029
		Average Absolute Deviation	0.00027

Volume of Compliment of Meniscus

h, mm.	0.40	0.50	0.60	0.70	0.80
v, cc.	0.00059	0.00071	0.00082	0.00091	0.00098

* deviation is $V_{calc} - V_{exp}$, where V_{calc} is from the equation

$$V = 0.003102\ L - 0.01140$$

Where L is in mm. and V is in cc.   Tube Diameter = 1.991 mm.

TABLE 87

CALIBRATION DATA

EXPERIMENTAL TUBE C

Temperature °C.	Length mm.	Volume cc.	Deviation* cc.
26.8	21.25	0.05272	0.00014
26.8	46.45	0.13087	0.00038
26.8	99.05	0.29505	-0.00016
27.3	132.65	0.39930	0.00012
26.8	156.40	0.47315	0.00016
27.0	200.25	0.61038	-0.00086
26.60	252.70	0.77280	0.00009
27.00	287.60	0.88117	0.00029
26.95	333.90	1.02547	0.00004
26.8	19.85	0.04865	-0.00015
26.8	40.60	0.11340	-0.00034
27.1	61.95	0.17940	0.00008
27.0	93.55	0.27769	0.00009
27.2	120.70	0.26236	-0.00012
26.5	144.30	0.43577	-0.00010
26.5	193.15	0.58779	-0.00015
25.9	226.70	0.69192	0.00009
25.9	336.30	1.03238	0.00059
	Average Absolute Deviation		0.00022

Volume of Compliment of Meniscus

h, mm.	0.40	0.50	0.60	0.70	0.80
v, cc.	0.00059	0.00071	0.00082	0.00091	0.00098

* deviation is $V_{calc} - V_{exp}$, where V_{calc} is from the equation

$$V = 0.003111\ L - 0.013255$$

Where L is in mm. and V is in cc.   Tube Diameter = 1.9902

PRESSURE GAGE CALIBRATION

A Star dead-weight pressure gage with piston No.55 was used for all pressure measurements above 45 pounds per square inch. The gage and piston were calibrated July 22, 1958, against the vapor pressure of carbon dioxide at 0.00°C., as given by Meyers and Van Dusen (13). The purpose of this calibration was to determine the effective area of the piston.

A carbon dioxide sample was degassed and loaded into the experimental tube in a manner similar to that used for the hydrocarbons (apparatus shown in Figure 4). Commercial Dry Ice, the source of carbon dioxide, was allowed to vaporize through a drying tube which contained phosphorus pentoxide; the drying tube was connected to the loading apparatus. After the Dry Ice had vaporized sufficiently to flush the drying tube thoroughly, a valve to the high-vacuum manifold was opened. Carbon dioxide vapors were allowed to flush the loading apparatus for a few minutes, then a liquid nitrogen cold bath was placed around bulb D, and valve B was closed. When sufficient carbon-dioxide had been collected in bulb D, the valve from the drying tube was closed. The carbon dioxide was then alternately distilled between bulbs D and H in the same manner as that described in "Loading the Experimental Tube", page 12. Before each distillation, a small amount of carbon dioxide was condensed in the cold trap G and the experimental tube was flushed with carbon dioxide by condensing it in the tube and then pumping it off in trap G. After this process had been repeated six times, a small amount of carbon dioxide was condensed into the experimental tube and mercury was forced from reservoir K to fill the tube. The experimental tube was removed from the line, after the vacuum line had been returned to atmospheric pressure and the tube was placed in the compressor block. During placement of the experimental tube into the compressor block and until sufficient nitrogen pressure had been applied to balance the vapor pressure of CO_2 at room temperature, a specially constructed dewar flask, filled with liquid nitrogen, was held around the experimental tube. The dewar was then removed slowly so that the mercury would melt before the carbon dioxide, to avoid damage to the experimental tube by expansion of the carbon dioxide. A glass jacket was placed around the experimental tube and filled with clear commercial ice and a small amount of distilled water. The amount of water and ice was carefully adjusted until the temperature, as measured by the platinum resistance thermometer, was 0.00°C. The carbon dioxide vapor pressure was measured at several V/L ratios until the vapor pressure remained reasonably constant for several ratios.

Table 87, gives the vapor pressure measurements, the pressure gage area corrections, and the average area correction. It was assumed that the gage area correction was constant, thus giving a linear relationship between gage pressure and true pressure:

$$P_{true} = P_{gage} \times \text{(area correction factor)} \qquad (1)$$

TABLE 88

PRESSURE GAGE CALIBRATION

Star Piston No. 55

Temperature 0.00°C. ± 0.01°C.

Gage Temperature	26.8	26.7	26.7	26.5
Nominal Pressure	500.762	501.262	501.762	500.262
Temperature Corr.	0.036	0.037	0.037	0.040
Gage Pressure	500.798	501.299	501.799	500.302
Barometric Pressure	14.313	14.313	14.314	14.317
Gas Head	0.004	0.004	0.004	0.004
Mercury Heads	8.789	9.270	9.806	8.308
Oil Head	0.114	0.114	0.114	0.114
Ball Head	0.006	0.006	0.006	0.006
CO_2 Liquid Head	0.044	0.042	0.059	0.046
Apparent Vapor Pressure	506.162	506.184	506.132	506.149
Actual Vapor Pressure	505.502	505.502	505.502	505.502
Deviation	0.660	0.682	0.630	0.647
Area Correction Factor	0.99868	0.99864	0.00874	0.99871

Average Area Correction Factor (1 - 0.00131)

Pressure Gage Equation $P_{true} = P_{gage}$ (1- 0.00131)

Effective Piston Area at 30°C. = 0.12484 square inches

Approximate Deviation from Pressure Gage Equation ± 0.03 psi at 500 psi.

P_{true} is the pressure exerted on the piston and P_{gage} is the pressure which would be exerted on a 1/8 square inch piston at the same temperature.

Calibration of Pressure Gage Weights

The weights, used on the pressure balance were marked with a nominal pressure value to be used with a 1/8 square inch piston. The correction to be made on the nominal pressure value was found by weighing the weights, on an analytical balance, and calculating the pressure which would be measured by them on a 1/8 square piston. Table 88 gives the values of the weights and their corresponding pressure value.

Temperature Corrections

A temperature correction was used to correct the effect of expansion or contraction on the effective area of the piston. The temperatures were referred to 30°C.

Calculation of True Pressure

The true pressure was calculated from equation (1), the nominal pressure (as marked on the weights), the weight corrections, and the temperature correction. Calculation of pressure is shown by the example on the next page.

Example Calculation: Temperature 35°C.

Weights on Piston	Nominal Pressure	Correction
2K	100	-0.0296
2L	100	-0.0288
1A	10	-0.0026
1C	5	-0.0008
Spinner, Piston, and Can	10.40	0.0040
Small Weights in Can	1.52	0.0000
Sum	226.92	-0.0578

Nominal Pressure - Sum of Corrections	226.86 psi
Temperature Correction	-0.03 psi
Gage Pressure	226.83 psi

True Pressure = 226.83 (1 - 0.00131) = 226.83 - 0.30 psi = 226.53 psi

TABLE 89

PRESSURE GAGE WEIGHTS

Designation	Weight - Grams	Pressure on 1/8 sq. in.
1A	566.8403	10 - 0.0026 psi
1B	566.8498	10 - 0.0025
1C	283.4518	5 - 0.0008
1D	1133.6560	20 - 0.0056
1E	2834.192	50 - 0.0136
1F	2834.182	50 - 0.0144
1G	2834.212	50 - 0.0120
2K	5668.22	100 - 0.0296
2L	5668.30	100 - 0.0288
2M	5668.22	100 - 0.0293
2N	5668.15	100 - 0.0309
Piston	283.5498	5 0.0010
Spinner	283.5184	5 0.0040
Wt. Container (can)	22.6222	0.4 - 0.0010

Small weights correct as marked to four significant figures.

TEMPERATURE MEASUREMENT

Temperatures, except for four of the samples, were measured with a platinum resistance thermometer and a Mueller Bridge: Mueller Bridge #713926, Leeds and Northup model G-2, NBS file #1.1/113128; Platinum Resistance Thermometer #714136, R_0 = 25.5663 abs. ohm; Platinum Resistance Thermometer #770041, R_0 = 25.5530 abs. ohm. The Mueller Bridge and the platinum resistance thermometers were calibrated by the National Bureau of Standards. Tables of the calibrations are given by Hill (2). The initial resistances for the thermometers were checked and the bridge was checked with a standard resistance: these checks agreed with the original calibrations. Table 89 gives the number of the platinum resistance thermometer used for each sample or indicates that a thermocouple was used.

The copper-constantan thermocouple, which was used for four samples, was calibrated by comparison to platinum resistance thermometer #770041. Thermocouple temperatures were calculated from the emf-temperature data of I.C.T. 1,58 and the deviation of this temperature from that measured with the platinum resistance thermometer, was plotted as a correction curve. The correction was applied to the temperature measured with the thermocouple.

Tempersture, °C.	0.00	131.11	216.53	256.27	304.69
Correction, °C.	0.00	-0.35	0.542	-0.543	-0.55

TABLE 90

EQUIPMENT USED

Compound	Thermometer*	Exp. Tube	Sample Weight
n-Heptane	pt 770041	B	0.03944
2-Methylhexane	thermocouple	A	0.04382
3-Methlhexane	pt 770041	A	0.04154
3-Ethylpentane	thermocouple	A	0.03866
2,2-Dimethylpentane	pt 770041	B	0.04300
2,3-Dimethylpentane	pt 714136	C	0.03912
2,4-Dimethylpentane	pt 770041	A	0.03429
3,3-Dimethylpentane	thermocouple	A	0.03736
2,2,3-Trimethylbutane	thermocouple	A	0.03809
n-Octane	pt 770041	B	0.04019
2-Methylheptane	pt, 714136	A	0.04165
3-Methylheptane	pt 714136	C	0.04974
4-Methylheptane	pt 714136	A	0.04387
3-Ethylhexane	pt 714136	C	0.03907
2,2-Dimethylhexane	pt 714136	B	0.04067
2,3-Dimethylhexane	pt 714136	A	0.03999
2,4-Dimethylhexane	pt 714136	C	0.04008
2,5-Dimethylhexane	pt 714136	A	0.03832
3,3-Dimethylhexane	pt 714136	C	0.03647
3,4-Dimethylhexane	pt 714136	A	0.03998
2-Methyl-3-Ethylpentane	pt 714136	C	0.03826
3-Methyl-3-Ethylpentane	pt 714136	A	0.03981
2,2,3-Trimethylpentane	pt 714136	C	0.04323
2,2,4-Trimethylpentane	pt 714136	A	0.03654
2,3,3-Trimethylpentane	pt 714136	A	0.04559
2,3,4-Trimethylpentane	pt 714136	A	0.04413

* pt refers to platinum resistance thermometer.

APPENDIX III

EXAMPLE OF CORRELATIONS

EXAMPLE CALCULATION OF CRITICAL TEMPERATURE AND PRESSURE for 2,2,3,3-Tetramethylbutane

$$w_i = 58,\ w_n = 84,\ Pi = 9,\ Pn = 5$$

$$T_{bp} = 379.63^{\circ}K.\ (19)$$

Critical Temperature for 2,2,3,3-Tetramethylbutane

$$\log (1 - w_i/w_n) = \log (1 - 58/84) = -0.50934$$

$$\log \Delta T_{Rbp} = -0.75463 + 1.52669 \log (1 - w_i/w_n)$$

$$\log \Delta T_{Rbp} = -0.75463 + 1.52669 (-0.50934)$$

$$\Delta T_{Rbp} = 0.0294$$

$$(T_{Rbp})_i = (T_{Rbp})_n - \Delta T_{Rbp} = 0.7012 - 0.0294 = 0.6718$$

$$T_c = T_{bp}/(T_{Rbp})_i = 379.63/0.6718 = 565.1^{\circ}K \text{ or } \underline{291.9}^{\circ}C.$$

Critical Pressure for 2,2,3,3-Tetramethylbutane

$$(P_{cn} - P_{ci}) = 0.2932 + 2.389(1 - P_i/P_n) - 62.71 \Delta T_{Rbp}$$

$$(P_{cn} - P_{ci}) = 0.2932 + 2.389(1 - 1.800) - 62.71(0.0294)$$

$$(P_{cn} - P_{ci}) = 3.462$$

$$P_{ci} = P_{cn} - (P_{cn} - P_{ci}) = 24.54 \text{ atm} + 3.462 \text{ atm} = 28.00 \text{ atm}.$$

EXAMPLE VAPOR PRESSURE ESTIMATION for 2,2,3,3-Tetramethylbutane

The difference between the boiling point and the point at which the deviation curve is zero, other than the boiling point or critical, for n-Octane was observed to be 111.1°C., from this and the boiling point of the isomer, the point at which the deviation curve crosses the zero axes was calculated.

$$(T_o)_i = T_{bp} + 111.1^oC = 106.46 - 111.1 = 217.6^oC.$$

This temperature on a reduced scale is:

$$T_o/T_c = 490.8/565.1 = 0.8685$$

and the reduced boiling point is $T_{Rbp} = 0.6718$

The critical values as calculated are: $T_c = 565.1^oK.$ and $P_c = 28.00$ atm. From these critical values and the boiling point the constants of the vapor pressure equation were calculated to be:

$$A = 4.40938$$

$$B = -1673.93$$

The vapor pressure deviation curve was drawn utilizing the deviation curve of n-Octane, the critical temperature, the reduced boiling point and the estimated zero deviation temperature. It was also noted that when the reduced boiling point was low and therefore the point at which the deviation curve crosses the zero axes was low, The positive deviation just below the critical region was great. This observation was utilized in estimating the vapor pressure deviation curve for 2,2,3,3-Tetramethylbutane.

The estimated deviation curve for 2,2,3,3-Tetramethylbutane is shown on Figure 36 with the curve for n-Octane; the calculated vapor pressure data are shown in Table 90.

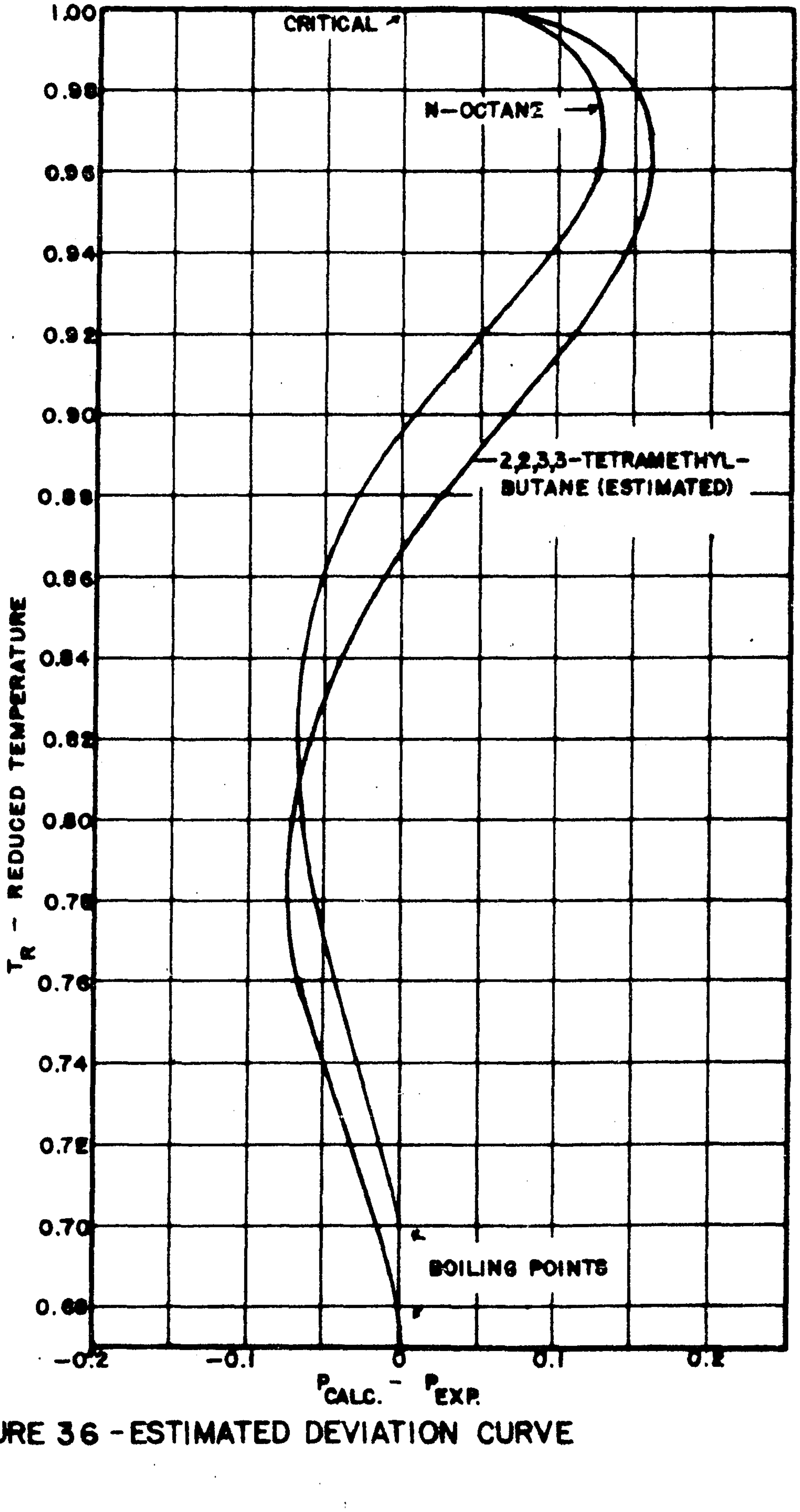


FIGURE 36 - ESTIMATED DEVIATION CURVE

TABLE 91

ESTIMATED VAPOR PRESSURE OF 2,2,3,3-TETRAMETHYLBUTANE*

Temperature		Calculated Pressure	Estimated Deviation	Estimated Pressure
T °K	T_r °K	Atm.	Atm.	Atm.
379.63	0.6718	1.000	0.00	1.00
383.17	0.6781	1.098	0.00	1.10
393.17	0.6958	1.419	-0.01	1.43
403.17	0.7135	1.809	-0.03	1.84
413.17	0.7312	2.280	-0.04	2.32
423.17	0.7488	2.842	-0.06	2.90
433.17	0.7666	3.508	-0.07	3.58
443.17	0.7842	4.288	-0.08	4.37
453.17	0.8019	5.195	-0.07	5.27
463.17	0.8196	6.242	-0.06	6.30
473.17	0.8373	7.442	-0.04	7.48
483.17	0.8550	8.809	-0.02	8.83
493.17	0.8727	10.355	0.01	10.36
503.17	0.8904	12.095	0.04	12.06
513.17	0.9081	14.042	0.09	13.95
523.17	0.9258	16.210	0.10	16.09
533.17	0.9435	18.612	0.15	18.46
543.17	0.9612	21.262	0.16	21.10
553.17	0.9789	24.172	0.15	24.02
565.09	1.0000 (Critical)	28.000	0.00	28.00

*Calculated pressure is found using the equation:

$$\text{Log } P = 4.40938 - 1673.93/T\ (^{\circ}K),\ P \text{ in atm.}$$

The constants of this equation have been evaluated from the critical and boiling points. The estimated pressure is found by subtracting the estimated pressure deviation from the calculated pressure.

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I, James Harvey Mc Micking, was born in Detroit, Michigan, August 5, 1929. I received my secondary-school education at Concordia High School, Fort Wayne, Indiana. I received my undergraduate training at Wayne State University, which granted me the Bachelor of Science in Chemical Engineering degree in 1953; I was granted the Master of Science degree by the same university in 1955. While earning the Master of Science degree, I was a graduate student assistant. I was an American Chemical Society Petroleum Research Fund Fellow for two years, a Shell Oil Company Fellow for one year, and a summer instructor in the Department of Chemical Engineering at The Ohio State University while completing the requirements for the Doctor of Philosophy degree.