## THE PRESSURE- VOLUME- TEMPERATURE RELATIONS FOR THE METHANE- DECANE SYSTEM IN THE LIQUID AND TWO-PHASE REGIONS

Thesis by

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### Introduction

In the petroleum industry the prediction of the behavior of crude oil, natural gas, and the various petroleum derivatives is desirable in the development of processes to be used by the industry and in control of the present methods of production and refining. Results obtained by the use of simplified relationships such as the perfect gas law and the law of ideal solutions (1) are often greatly in error. Hence it is desirable to obtain experimental results describing the behavior of these hydrocarbons.

The problem of establishing the gas-liquid equilibrium relations for natural gas, crude oil, gasoline, and other multicomponent hydrocarbon mixtures is a complex one. An approach to the solution of the problem is made by the study of the equilibrium behavior of the simpler hydrocarbon systems under conditions similar to those encountered in actual practice.

The methane-decane system here studied is an additional member of a series for which P-V-T relations have been established. Pressures up to 4500 lbs. per sq. in. and temperatures from 70°F. to 250°F. were employed. Measurements of specific volume in the liquid and two-phase regions were made and the partial volumes for each component in the liquid phase were calculated. Equilibrium constants for methane at bubble point were also calculated. The partial volumes and equilibrium constants were compared with those for similar binary systems consisting of methane and a second paraffinic hydrocarbon.

Two types of apparatus have been developed for the measurement of the P-V-T relations in hydrocarbon systems. The first is the glass P-V-T apparatus described by Young (2), Bahlke and Kay (3), and Cummings, Stones and Volante (4). The second type is the steel P-V-T apparatus such as described by Sage, Webster and Lacey (5). The latter apparatus with a few minor changes was employed in the present study.

The advantages of the steel P-V-T apparatus as compared with glass apparatus lie in the facts that a much larger pressure range may be employed and a larger sample permits more accurate determination of the composition of the system.

On the other hand the disadvantages lie in the fact that the sample cannot be visually observed to determine the phase boundaries as can be done with the glass apparatus. Further, the cost of large samples of a valuable hydrocarbon is a drawback.

#### MATERIALS

The methane here used was obtained from the Buttonwillow field in California and originally contained 0.1 per cent ethane and heavier hydrocarbons and 0.3 per cent carbon diaxide. The amount of nitrogen and other non-condensable gases contained was negligible as indicated by a careful combustion analysis on the samples. The methane was further purified before addition to the system by passing through calcium chloride, activated chargoal, ascarite and sodium hydroxide at a pressure of 400-500 lbs. per sq. in. The methane thus prepared was believed to contain less than 0.2 per cent impurities.

The decane was purchased as chemically pure n-decane from the Eastman Kodak Company. It was further purified in a fractionating column and then distilled into a steel bomb for storage.

A diagram of the purification apparatus is shown in Figure 1. The glass fractionating column, (T), was surrounded by a silvered

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vacuum jacket, (C). Around the jacket was wound a 100 watt heater and the whole jacket was then covered with 85% magnesia heat insulation. The flask, (A), containing the decane to be purified, was attached to the column by a ground glass joint, (B). To insure a vacuum tight seal. mercury was poured into a cup surrounding the seal. Around the tube. (D), leading from the top of the column a 100 watt heater was wound and the tube was insulated with 85% magnesia. The heater on tube, (D), served to prevent the decane from condensing until it reached the total condenser. (E). From here the condensed material dropped through drip indicators. (F) and (G), and returned to the top of the column to supply the reflux. Volatile impurities were pumped off at the drip indicator, (F). Pressure in the system was indicated by manometer, (L), and the rate at which noncondensables were drawn off was indicated by the rate of fall of the mercury level in manometer (M) when stopcock (S) was closed. The vacuum header, (P), was attached to a mercury vapor pump and a Cenco Hivac pump. Traps (N) and (N') were immersed in solid carbon dioxide and acetone to condense out heavy materials in the gas pumped off and thus protect the vacuum pumps. The storage bomb was attached at the brass block (K). into which the tube from the drip indicator, (H), was sealed with sodium silicate. After refluxing for a sufficient time, the liquid decane was drawn into the evacuated bomb by opening stopcock (J). The bomb was immersed in a solid carbon dioxide-acetone mixture during this time. Reflux was maintained in the column during this period at a ratio of about 4 parts of reflux to 1 part of product. After the middle fraction had been distilled over, the stopcock, (J), was closed and while the contents of the bomb remained frozen, it was evacuated for a period of 20 minutes.

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Fig. I. Diagram of the decane purification apparatus.

For purifying decame the apparatus was operated at a pressure of about 3-6 mm. of mercury. The main impurities removed were air and methane. Any heavier hydrocarbons contained by the decame remained in flask (A).

The decane obtained from the purification column exhibited a density of 0.7213 grams per cc. at 100°F. This value differs appreciably from that of 0.7166 given by Doss (6). It possessed a viscosity of 6.59 millipoises at 100°F. as compared with 7.83 millipoises for n-decane given by Doss. As several isomeric decanes possess density values greater than that for the present material, it was decided that the material was a mixture of isomeric decanes rather than pure n-decane.

### APPARATUS AND METHOD

The apparatus has been described by Sage. Webster and Lacey (5). However, it is desirable to describe it briefly again in connection with this work.

Figure 2 is a schematic diagram of the apparatus employed. The steel variable volume cell, A, had an inside diameter of 2 inches and an inside height of 11 inches. The volume of the cell which was occupied by the sample could be varied by addition or withdrawal of mercury through valve, B, in the bottom of the cell. The volume of the space above the mercury sample was determined by the height of the mercury surface. This was measured by means of an electrical contact, E, mounted on a hollow rod, C, which extended up through the mercury. The rod, C, entered the cell through a packing gland, D, in the bottom of the cell. Rod, C, was threaded and engaged a nut, F, which was driven by 5 worm gear, G. A counter was mounted on the worm gear and it was

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Fig. 2. Diagram of the steel P-V-T equilibrium

cell.

thus possible to determine the height of the mercury by the counter reading. The top of the cell was removable. The seal was made with a thin copper gasket so that the top of the cell could be removed and replaced without changing the volume of the cell.

The cell was bored and lapped to a true cylinder whose diameter varied by less than 0.0002 inch.

On the bottom of the contact rod was mounted a plunger. H, of the same diameter as rod, C. The plunger moved in a cylinder filled with mercury and acted as a compensator so that a change in volume caused by withdrawal of the contact rod from the cell was exactly compensated for by injection of mercury from the compensator.

The cell was calibrated at a given counter reading by removing the top of the cell and weighing in crystal oil until the oil level came very close to the top of the cell. The crystal oil used was a mixture of hydrocarbons refined from a non-waxy crude. It had a narrow boiling point range and exhibited an average molecular weight of about 340. The top was then replaced and a curve of pressure versus counter reading determined. The amount of air which was trapped in the top of the cell was estimated to be 1 or 2 cc. By going to high pressures the air was forced into solution in the crystal oil. Since the amount of air (0.002 g.) was small compared with the amount of crystal oil (40 g. or larger) and the partial specific volume of air in crystal oil is small, the effect of the dissolved air was negligible. The isotherm of pressure versus counter reading was extrapolated to atmospheric pressure at which pressure the specific volume of the crystal oil was known. Thus the volume of the cell at a given mercury height was determined. Knowing the pitch of the accurately machined thread on the rod, C, it was then possible to calculate the volume of the cell as a linear function of the

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counter reading. It was found that the position of the mercury surface could be determined with an accuracy of better than 0.001 inch. This corresponds to a volume of 0.003 cubic inch in volumes from 3 to 30 cubic inches.

The effect of pressure upon the calibration of the instrument was determined by maintaining the mercury surface at a fixed height as measured by an electrical contact fastened to the top of the cell and noting the change in counter reading with increase in pressure. It was found that the maximum pressure correction was less than 0.05% in going from atmospheric to 3000 lb. per sq. in. at the maximum volume of the apparatus.

The effect of temperature upon the volume of the cell, A, was taken into account by calibration at different temperatures. The maximum error in volume determination for the samples is believed to be less than 0.2 per cent.

The pressure was measured by means of a specially designed fluid pressure balance which used oil as a working fluid. The pressure was transmitted through the mercury-oil trap indicated in Figure 2. The trap was provided with an electrical contact so that the mercury-oil interface could be maintained at a constant height.

The balance was equipped with two rotating plungers. Using the small plunger, pressures from 0 to 6000 lbs. per sq. in. could be measured by 0.11b. per sq. in. steps. Using the large plunger, pressures from 0 to 600 lbs. per sq. in by 0.01 lb. per sq. in. steps could be measured. The balance was equipped with a lifting mechanism similar to that found in the better grades of analytical balances. The force from the plungers was transmitted through a series of knife edges to a

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beam at the end of which could be suspended a series of weights. The balance beams were designed to possess a maximum deflection of less than 0.001 inch in a length of 14 inches.

The balance was sensitive to pressure changes of 0.05 lb. per sq. in. at a pressure of 3000 lbs. per sq. in. It was calibrated against the vapor pressure of carbon dioxide at 32°F. using a technique similar to that of Bridgeman (7). At 32°F. the vapor pressure of carbon dioxide was taken as 505.56 lbs. per sq. in.

In calculating pressures from the measurements made, correction for the oil and mercury heads in the connecting lines and cell was made. For these reasons it is believed that the pressure measurements reported were accurate within 1 lb. per sq. in.

The temperature of the cell was maintained by an oil bath which could be controlled by a thermostat at a predetermined value. The bath was heated by an external continuous heater, a differential heater where the cell block passed out of the thermostat bath and a small intermittent heater which maintained the temperature on the control point. The oil bath temperature was measured by a Mueller bridge circuit using a platinum resistance thermometer in the bath. The thermometer was calibrated against a Bureau of Standards platinum resistance thermometer. The thermostat control circuit consisted of a Mueller shunted Wheatstone bridge using a nickel resistance thermometer in the bath. A high sensitivity galvanometer in the circuit actuated a photo electric relay circuit which controlled the intermittent heater.

The temperature of the cell was measured by means of a thermocouple inserted in a hole drilled in the cell block. The thermocouple

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was calibrated in place against a Bureau of Standards platinum resistance thermometer. A White potentiometer was used to measure the thermocouple potentials.

The temperature of the cell could be measured by this method within 0.02°F. The temperature gradients in the oil bath were less than 0.05°F. Thus it is believed that the temperature measurements were in error by less than 0.1°F.

Agitation to hasten the attainment of equilibrium within the bomb was supplied by four uniform vertical rods mounted on a ring and driven by a bevel gear on a shaft which extended through a packing gland in the side of the cell. It was judged that equilibrium was attained when changes of volume with time at constant temperature and pressure were no longer measurable.

The bomb could be evacuated by means of a mercury vapor pump and a Cenco Hivac pump in series.

The decane was added to the evacuated cell by forcing the decane from the heated sample bomb through valve P, in the top of the cell. The amount of decane added was determined by measuring the volume of the liquid at 100°F. as function of pressure and extrapolating to atmospheric pressure. From the known density of the decane at atmospheric pressure, the weight of decane added could be determined.

The methane was added through a second valve (S) in the top of the cell. Connected to the valve by a steam jacketed line was a thermostated reservoir. The steam jacketed line was always maintained at the same steam pressure. Methane was pumped into the reservoir until the reservoir pressure was higher than the cell pressure and then the connecting valve was opened allowing methane to flow into the cell. The weight of methane added for a given change in pressure in the

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reservoir was determined by running a calibration in which the methane at a given initial pressure was run over into the evacuated equilibrium cell where an isotherm was run on the methane. Thus the weight of methane added could be calculated from a knowledge of the P-V-T relations for methane. From a knowledge of the initial and final pressures for each addition, the calibration was complete. The reservoir had previously been calibrated by withdrawal into a thermostated mercury buret.

It is believed that composition as determined by the above methods of addition was accurate within 0.2%.

### EXPERIMENTAL RESULTS

Isotherms at 70°F., 100°F., 160°F., 220°F., and 250°F. were obtained with a range in pressure of 0 to 4500 lbs. per sq. in. for seven mixtures of methane and decane ranging in composition from 0 to 15 weight per cent methane. Specific volumes were calculated at these temperatures for the liquid region and for the two-phase region for values up to about four times the bubble point specific volume. The results are shown in Table I.

The partial specific volumes for methane and decane in the liquid phase were determined from isothermal plots of specific volume versus composition according to the method of Lewis and Randall (S). The partial volumes are represented by the intercepts, on the axes of ordinates, of the tangent to the specific volume curve at any given composition. They were smoothed against pressure, combustion and temperature until consistent within 0.3%. The smoothed partial volumes are given in Tables II and III. It is believed these values are

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accurate within 0.5%. Equilibrium constants were calculated for the methane in the bubble point liquid on the assumption that the gas phase present was pure methane. Thus  $K_1 = \frac{Y_1}{X_1} = \frac{1}{X_1}$ . The results are shown in Table III.

In order to aid in the visualization of the behavior of the system, several diagrams have been prepared. Figure 3 shows the isothermal pressure-volume curves for a mixture containing 12.18 weight per cent of methane. The bubble point curve shows a reversal of slope at a pressure of about 3060 lbs. per sq. in. This is the point of maximum pressure at which two phases can exist for a system of this composition. Because of the great difference in the molecular weight between methane and decane, the critical state was not reached for the compositions in the range of pressures and temperatures here given.

In Figure 4 are represented isothermal curves of bubble point composition versus pressure. The rapid increase in curvature of the saturated liquid lines at higher pressures is expected as the critical region is approached.

Figure 5 shows specific volume of the system as a function of composition at 160°F. Figure 6 presents the isothermal relation between the equilibrium constant and pressure. The systems observed did not reach the critical state. This is evident since at the critical point for any system KP = P (or in other words the equilibrium constant equals one) and both phases become continuously identical. KP was plotted instead of K since it reduces the variation in the quantities plotted.

The isobaric relation in the liquid phase between partial specific volume and composition for methane and for decane for a temperature of 160°F. is shown in Figure 7. Figure 8 indicates the relation in the liquid phase between the partial specific volume of decane and pressure for systems of constant composition at a temperature of 160°F. The system exhibits a positive isothermal compressibility in the bubble point region for the higher compositions of methane.

### CORRELATIONS

It is of interest to ascertain the effect of chemical nature of the other component upon the partial specific volume of methane in the liquid phase for binary systems of methane and another paraffin hydrocarbon. Figure 9 represents a plot of partial specific volume of methane in the liquid phase at 100°F. and a pressure of 3000 lbs. per sq. in. versus molecular weight of the other paraffin hydrocarbon in binary systems of methane and ethane, propane, n-butane, n-pentane, n-hexane and decane. For the pure methane system and the methaneethane system the points taken were above the critical temperatures of the system so that the phase present is merely a matter of definition. This fact is indicated by dotted lines up to the molecular weight of propane.

The data for methane and the methane-ethane system were obtained from a system studied in this laboratory but as yet unpublished. The data for the other binary systems were obtained from studies by Sage, Hicks and Lacey (9). It was decided that the curves for constant weight per cent methane should run through the points corresponding to the molecular weights of ethane, n-butane, n-pentane and decane. These data were more precise than those for propane and n-hexane. The data for propane were given to two significant figures and represented work on a variable mass, variable composition system. The data for n-hexane did not represent as complete a study as did the rest of the data. Figure 10 represents a correlation of the equilibrium constants for methane in a binary system versus molecular weight of the less volatile paraffinic hydrocarbon. Data for the methane were obtained from a similar correlation by Sage and Lacey (10). The data agree rather well with those predicted in the paper. Significant deviations from the points occur at pressures above 1000 lbs. per sq. in. in the region of the molecular weight of hexane.

At the higher pressures it was decided to draw the curves under the points corresponding to the molecular weight of decane as the pressures are approaching the critical pressures of the system where the equilibrium constant for decane is 1 instead of 0. Hence it is believed that the constants for methane calculated on the assumption that the decane in the gas phase is negligible are too high in this region. -15-TANDE 1. SPECIFIC VOLUMES OF ANTIPALE OF ANTI-

TANLY I. SPECIPIC VILLENS OF FLATORS S. C. S. SALAR

|       |                        |                      |                    | Wei,dt Per        | . ont Methene                     | AS Follows -       | 200 - 10 - 10 - 20 - 20 - 20 - 20 - 20 - |                   |
|-------|------------------------|----------------------|--------------------|-------------------|-----------------------------------|--------------------|--|-------------------|
| Temp. | Pressure<br>Lb./sq.in. | 0                    | 1.174              | 1.830             | 5. 7                              | 11.35              | 12.18                                    | 14.45             |
| 70    | Absolute               |                      | (406) <sup>a</sup> | (443)             | (1245)                            | (2496)             | (2635)                                   | (3025)            |
| 70    | Bubble Point           | 0,02181 <sup>b</sup> | 0.02221            | 0.02234           | 0.02306                           | 0.02476            | 1,02501                                  | 0.02554           |
|       | .250                   | 0.02178              | 0.03120            | 0.0337?           |                                   |                    |  |                   |
|       | 500                    | 0.02175              | 0.02219            | 1.02233           | 0 <b>.0427</b> 2                  |                    |  |                   |
|       | 750                    | 0.02171              | 0.02215            | 0.02227           | 0.03095                           | 0.95650            | 0.05988                                  |                   |
|       | 1000                   | 0.02167              | 0,02210            | 0.02232           | 0.02538                           | 0.04407            | .04619                                   | 0.05293           |
|       | 1250                   | 0.02164              | 0.02206            | 0.02218           | .023-6                            | .03692             | 0.03868                                  | 0.04337           |
|       | 15-10                  | 0.02160              | 0.02:03            | 0.02215           | 0.0230                            | . 35.35            | 0.03401                                  | 0.03671           |
|       | 1750                   | 0,02157              | 0.02199            | 0.02210           | 0.02294                           | 0.0.9.0            | 0.03065                                  | 0.03060           |
|       | 2000                   | 0.02153              | 0.02195            | .02707            | 0.02389                           | 00475              | 02545                                    | 0.02753           |
|       | 2500                   | 0.02146              | 0.02187            | 0.001/9           | 0.02278                           |                    | 02487                                    | 0.02559           |
|       | 3000                   | 0,02140              | 0.02179            | .02192            | . 92. 58                          |                    | 0.02469                                  | 0.02537           |
|       | 3500                   | 0.02132              | 0.02171            | 0.02186           | 0.02.6                            | 0,02400            | 0.02454                                  | 0.02521           |
|       | 4000                   |                      |                    |                   |                                   | 004.77             | 0.0244.3                                 | 0.02505           |
|       | 4500                   | · · ·                |                    |                   |                                   |                    |  |                   |
| 100   | Rubble Point           | 0.02223              | (428)<br>0.02264   | (469)<br>0.02275  | (1350)<br>0.02354                 | ( 606)<br>. 22528  | (12 <b>754</b> )<br>, 12556              | (3156)<br>0.02614 |
|       | 250                    | 0.02217              | 0.0331.            | 0,03548           |                                   |                    |  | • •               |
|       | 500                    | 0.02213              | 0.02.63            | o. 02 <b>274</b>  |                                   | 10.0               |  |                   |
|       | 750                    | 0,02208              | 0.02257            | . 00067           | 0.03045                           | . 4.77             | 0,06369                                  |                   |
|       | 1000                   | 0.02204              | 0.02252            |                   | (1°68)                            | 0.046-1            | .04963                                   | 0.05681           |
|       | 1250                   | 0.02200              | 0.02247            |                   | .x41                              |                    | 0.04146                                  | 0.04672           |
|       | 1500                   | 0.02196              | 0.02243            | 0.32750           | 0.02350                           |                    | 0.03610                                  | 0.04039           |
|       | 1750                   | .02192               | 0.02237            | 0.00246           | . 1040                            | . 3 1              | .03248                                   | 0.03599           |
|       | 2000                   | 0.02168              | 0.02233            | 0.02241           | . 17 نغد 17                       | . 0969             | .02994                                   | 0.03301           |
|       | 2500                   | 0.02180              | 0.02224            | 0.027 <b>3</b> 2  | 0.0055                            | . 17569            | .02666                                   | 0.02917           |
|       | 3000                   | 0.02172              | 0.02214            | 0.02224           | 0.01315                           | 0.02513            | 0.02542                                  | 0.02663           |
|       | 3500                   | 0.02163              | 0,02205            | .02214            | 0.00300                           | 0. 2496            | 0.02515                                  | 0.02600           |
|       | 4000                   |                      |                    |                   |                                   | .0248              | 0,02510                                  | 0.02580           |
|       | 4500                   |                      | H -                | ••                |                                   |                    | . 12495                                  | 0.02559           |
| 160   |                        |                      | (475)              | (518)             | (14.0)                            | (~93)              | (:94C)                                   | (3324)            |
|       | Bubble Point           | 0.07310              | 0.00 <b>35</b> 2   | . ".46            | .)*446                            | .02645             | 0.02678                                  | 0.02751           |
|       | 250                    | 0.02302              | 0.93794            | A. 52 /B          | ÷                                 |                    |  |                   |
|       | 500                    | 1.02294              | 0.02351            | .0:416            | . 050 4                           |                    |  |                   |
|       | 750                    | 0.02288              | 0.02344            | . 3 356           |                                   |                    | 07117                                    |                   |
|       | 1000                   | 0.02282              | 0.02336            | J. 12 <b>34</b> 8 | .02968                            | • 1997 P.          | 0.05571                                  | .06461            |
|       | 1250                   | 0.02277              | .02529             | 40.0P             | 0.02621                           | . /1416            | 0.04640                                  | 0.05326           |
|       | 1500                   | 0.02272              | 0.02325            | 0.02333           | 0.02445                           | . 13842            | .04047                                   | 0.04587           |
|       | 1750                   | 0.02267              | 0.02316            | 0.02526           |                                   | 0.00448            | 0.03630                                  | 0.04072           |
|       | 3000                   | 0.02261              | 0.02310            | 0.00321           | 0.024.30                          | 3163               | 0.03322                                  | 0.03704           |
|       | 2500                   | 0.02251              | 0,02298            | 9(ئۇ ل            | 0.02415                           | . 02776            | . 2906                                   | 0.03208           |
|       | 3000                   | 0.02241              | 0.02287            | 0.02297           | 07398                             | .02629             | 0.07674                                  | 0.02883           |
|       | 3500                   |                      | 0. 22:07           | ),02286           | 0.00.983                          | •026Cm             | 0,42644                                  | 0.02740           |
|       | 4000                   |                      |                    |                   |                                   | . 00580            | 0.0262:                                  | 0.02712           |
|       | 4500                   |                      |                    |                   |                                   |                    | .0.06 5                                  | .02685            |
| 220   |                        |                      | (521)              | (565)             | (1589)                            | (2896)             | (3040)                                   | (3400)            |
|       | Bubble Point           | 0.02403              | 0.02452            | 0.02465           | .)2548                            |                    | . 12815                                  | 0.02913           |
|       | 250                    | 1,02394              | 0.04112            | 0.04280           | 1997 - 1997<br>1997 - 1997 - 1997 |                    |  |                   |
|       | 500                    | 0,02386              | 0,03454            | 0.02638           | 0.05454                           |                    |  |                   |
|       | 750                    | 0.02378              | 0.02443            |                   | . A 100                           |                    | .OF '9"                                  |                   |
|       | 1000                   | .023/1               | 0.02433            | 0.02440           | -03.0c                            |                    | .06265                                   | . 77235           |
|       | 1500                   | 0.02.65              | 0.02415            | 0.430             | 0.0049                            |                    |  | .05938            |
|       | 1750                   | 0.02348              | 0.02408            | 0.02418           |                                   | 1.5775             | (  |                   |
|       | 2000                   | 0.02341              | 0.02399            | 1.92410           | .025.53                           |                    |  | and the second    |
|       | 2500                   | 0.02328              | 0.02384            | 0.0: 396          | . 42514                           | . 3003             | .0.4146                                  | 0.450.3           |
|       | 3000                   | 0.02316              | 0.02370            | 0.02387           | .02495                            | .02768             | .02833                                   | 0.03179           |
|       | 3500                   | 0.00303              | 0.02356            | 0 <b>.0236</b> 8  | .02476                            | . 2735             | .02785                                   | .0: -0:2          |
|       | 4000                   |                      |                    |                   |                                   | ר ולניו            | .02751                                   | 0.07867           |
|       | 4500                   |                      | × -                |                   |                                   | .02677             | .00726                                   | . 1975            |
| 260   |                        |                      | 154-1              | 1 K. 17           | 110.00                            | 100000             | g (200)                                  | a spar            |
| 750   | Bubble Point           | 0.2457               | .00503             | (599)             | (1630)                            | (19994)<br>(19994) | (264.0)<br>02904                         | (.400)            |
|       | 250                    | .02447               |                    |                   |                                   |                    |  |                   |
|       | 500                    | 0.02436              |                    | .02746            |                                   |                    |  | - 1947<br>- 1947  |
|       | 750                    | 0.02426              |                    | .0.25.07          | .04.52                            | 0.05.44            |  |                   |
|       | 1 200                  | 0.02416              | 0.02487            | 0.02495           | . 334.27                          | . 0156             | . 26579                                  | .07601            |
|       | 1250                   |                      | .02476             |                   | • O. 1989                         | . 21 %             | .05435                                   | 6. 6013           |
|       | 1500                   | 7.02398              |                    | 0.03476           | .0779                             |                    | .04695                                   | .05.352           |
|       | 1750                   | 0.02390              | 0.02456            | 0.02466           | 0.07600                           | .03943             | . 4170                                   | .04723            |
|       | 2000                   | 0.02382              | 0,03447            | .02457            | 1.02540                           | . 35.1             | · .//3788                                | .04~73            |
|       | 250C                   | 0.02368              | .024.79            | 439               | . 12566                           | . 31/1             |  | 0.0.641           |
|       | 3000                   | 0.02354              | 0.02413            | 0.02422           | .02545                            |                    | .0.9.%                                   | 0.03244           |
|       | 3500                   | 0.00341              | 0.0:399            | 0,024.54          | . #15.14                          | . 0805             | 1964                                     | •(:2000           |
|       | 40 X                   | ÷ •                  |                    |                   |                                   | . 472              | • 27                                     | . 547             |
|       | 45.43                  |                      | 1212               |                   | A (5)                             |                    | · 19-4                                   | ·                 |

\* Figures in parentheses are built of wild searches in smalls per surge burg. I have

b Specific volume, cubic fact mer bound.

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# TABLE II. PARTIAL SPECIFIC VOLUMES OF METHANE IN THE LIQUID PHASE OF THE METHANE-DECANE SYSTEM

|               |                                    |        | Weight Per Cent Methane as Follows |        |        |              |        |  |  |
|---------------|------------------------------------|--------|------------------------------------|--------|--------|--------------|--------|--|--|
| Temp.<br>° F. | Pressure<br>Lb./sq.in.<br>Absolute | 0      | 4                                  | 8      | 10     | 12.5         | 15     |  |  |
| 70            | Bubble Point                       | 0.0502 | 0.0519                             | 0.0533 | 0.0539 | 0.0546       | 0.0554 |  |  |
|               | 500                                | 0.0495 |                                    |        |        |              |        |  |  |
|               | 1000                               | 0.0488 | 0.0518                             | ·      |        |              |        |  |  |
|               | 1500                               | 0.0482 | 0.0508                             |        |        |              |        |  |  |
|               | 2000                               | 0.0477 | 0.0499                             | 0.0529 |        |              |        |  |  |
|               | 2500                               | 0.0472 | 0.0492                             | 0.0517 | 0.0532 |              |        |  |  |
|               | 3000                               | 0.0468 | 0.0486                             | 0.0506 | 0.0519 | 0.0536       |        |  |  |
|               | 3500                               | 0.0464 | 0.0479                             | 0.0497 | 0.0508 | 0.0522       | 0.0538 |  |  |
|               | 4000                               | 0.0460 | 0.0473                             | 0.0489 | 0.0498 | 0.0509       | 0.0520 |  |  |
|               | 4500                               | 0.0456 | 0.0468                             | 0.0482 | 0.0488 | 0.0496       | 0.0503 |  |  |
|               |                                    |        |                                    |        |        |              |        |  |  |
| 100           | Bubble Point                       | 0.0524 | 0.0547                             | 0.0569 | 0.0579 | 0.0592       | 0.0603 |  |  |
|               | 500                                | 0.0517 |                                    |        |        |              |        |  |  |
|               | 1000                               | 0.0510 |                                    |        |        |              |        |  |  |
|               | 1500                               | 0.0503 | 0.0535                             |        |        |              |        |  |  |
|               | 2000                               | 0.0497 | 0.0524                             | 0.0568 |        |              |        |  |  |
|               | 2500                               | 0.0491 | 0.0515                             | 0.0548 | 0.0572 |              |        |  |  |
|               | 3000                               | 0.0485 | 0.0507                             | 0.0531 | 0.0551 | 0.0584       |        |  |  |
|               | 3500                               | 0.0479 | 0.0499                             | 0.0519 | 0.0534 | 0.0555       | 0.0587 |  |  |
|               | 4000                               | 0.0473 | 0.0491                             | 0.0509 | 0.0521 | 0.0536       | 0.0560 |  |  |
|               | 4500                               | 0.0467 | 0.0484                             | 0.0501 | 0.0510 | 0.0521       | 0.0536 |  |  |
|               |                                    |        |                                    |        |        |              |        |  |  |
| 160           | Bubble Point                       | 0.0575 | 0.0598                             | 0.0626 | 0.0650 | 0.0685       | 0.0724 |  |  |
|               | 500                                | 0.0563 |                                    |        |        |              |        |  |  |
|               | 1000                               | 0.0552 |                                    |        |        |              |        |  |  |
|               | 1500                               | 0.0541 | 0.0589                             |        |        |              |        |  |  |
|               | 2000                               | 0.0531 | 0.0574                             |        |        |              |        |  |  |
|               | 2500                               | 0.0521 | 0.0561                             | 0.0610 |        |              |        |  |  |
|               | 3000                               | 0.0512 | 0.0548                             | 0.0592 | 0.0626 | 0.0684       |        |  |  |
|               | 3500                               | 0.0504 | 0.0536                             | 0.0575 | 0,0603 | 0.0649       | 0.0706 |  |  |
|               | 4000                               | 0.0497 | 0.0525                             | 0.0560 | 0.0582 | 0.0617       | 0.0662 |  |  |
|               | 4500                               | 0.0490 | 0.0515                             | 0.0545 | 0.0562 | 0.0587       | 0.0621 |  |  |
|               |                                    |        |                                    |        |        |              |        |  |  |
| 220           | Bubble Point                       | 0.0621 | 0.0657                             | 0.0700 | 0.0725 | 0.0765       | 0.0835 |  |  |
|               | 500                                | 0.0607 |                                    |        |        |              |        |  |  |
|               | 1000                               | 0.0595 |                                    |        |        |              | 1      |  |  |
|               | 1500                               | 0.0583 | 0.0650                             |        |        |              |        |  |  |
|               | 2000                               | 0.0571 | 0.0633                             |        |        |              |        |  |  |
|               | 2500                               | 0.0559 | 0.0616                             | 0.0688 |        |              |        |  |  |
|               | 3000                               | 0.0548 | 0.0601                             | 0.0663 | 0.0703 |              |        |  |  |
|               | 3500                               | 0.0537 | 0.0585                             | 0.0640 | 0.0675 | 0.0735       | 0.0834 |  |  |
|               | 4000                               | 0.0526 | 0.0570                             | 0.0618 | 0.0650 | 0.0702       | 0.0770 |  |  |
|               | 4500                               | 0.0516 | 0.0556                             | 0.0598 | 0.0627 | 0.0672       | 0.0725 |  |  |
|               | - 1                                |        |                                    |        |        |              |        |  |  |
| 250           | Bubble Point                       | 0.0647 | 0.0679                             | 0.0732 | 0.0763 | 0.0815       | 0.0898 |  |  |
|               | 500                                | 0.0632 | ·                                  |        |        | · <u>-</u> - |        |  |  |
|               | 1000                               | 0.0618 |                                    |        |        |              |        |  |  |
|               | 1500                               | 0.0605 | 0.0673                             |        |        |              |        |  |  |
|               | 2000                               | 0.0593 | 0.0655                             |        |        |              |        |  |  |
|               | 2500                               | 0.0580 | 0.0637                             | 0.0722 |        |              |        |  |  |
|               | 3000                               | 0.0568 | 0.0619                             | 0.0697 | 0.0745 |              |        |  |  |
|               | 3500                               | 0.0555 | 0.0602                             | 0.0673 | 0.0718 | 0.0784       | 0.0896 |  |  |
|               | 4000                               | 0.054? | 0.0586                             | 0.0650 | 0.0690 | 0.0749       | 0.0830 |  |  |
| 1/4 52        | 4500                               | 0.0529 | 0.0571                             | 0.0627 | 0.0663 | 0.0713       | 0.0770 |  |  |
| 10 g 10 g     |                                    |        |                                    |        |        |              |        |  |  |

## TABLE III. PARTIAL SPECIFIC WOLLIMES OF DECAME IN THE LIQUID PHASE OF THE METHAME-DECAME SYSTEM

|               |  | 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - |                      | Weight Per Cent Methane as Follows |         |         |         |  |  |
|---------------|--|---|----------------------|------------------------------------|---------|---------|---------|--|--|
|               | Temp.<br>°F.                                 | Pressure<br>Lb./sq.in.<br>Absolute  | 4                    | 8                                  | 10      | 12.5    | 15      |  |  |
|               | 70   | Bubble Point  | 0.02153 <sup>a</sup> | 0.02121                            | 0.02104 | 0.02082 | 0.02045 |  |  |
|               |  | 500   |                      |                                    |         |         | 1       |  |  |
|               |  | 1000  | 0.02153              |                                    |         |         |         |  |  |
|               |  | 1500  | 0.02146              |                                    |         |         |         |  |  |
|               |  | 5000  | 0.02139              | 0.02120                            |         |         |         |  |  |
|               |  | 2500  | 0.02134              | 0.02118                            | 0.02104 |         |         |  |  |
| · · · · ·     |  | 3000  | 0.02129              | 0.02115                            | 0.02104 | 0.02087 |         |  |  |
| See Section 5 | ener al la                                   | 3500  | 0.02124              | 0.02112                            | 0.02103 | 0.05090 | 0.02057 |  |  |
|               |  | 4000  | 0.02119              | 0.02107                            | 0.02099 | 0.02089 | 0.02067 |  |  |
|               |  | <b>45</b> 00  | 0.02114              | 0.02101                            | 0.02094 | 0.02084 | 0.02069 |  |  |
|               | 100  | Bubble Point  | 0.02192              | 0.02157                            | 0.02137 | 0.02098 | 0.02029 |  |  |
|               |  | 500   |                      |                                    |         |         |         |  |  |
|               |  | 1000  |                      |                                    |         |         |         |  |  |
|               |  | 1500  | 0.02186              |                                    |         |         |         |  |  |
|               |  | 5000  | 0.02179              | 0.02157                            | ·       |         |         |  |  |
|               |  | 2500  | 0.02172              | 0.02155                            | 0.02138 |         | '       |  |  |
|               |  | 3000  | 0.02164              | 0.02153                            | 0.02140 | 0.02104 |         |  |  |
|               |  | 3500  | 0.02158              | 0.02150                            | 0.02140 | 0.02118 | 0.02069 |  |  |
|               |  | 4000  | 0.02153              | 0.02146                            | 0.02140 | 0.02124 | 0.02097 |  |  |
|               |  | 4500  | 0.02148              | 0.02142                            | 0.02138 | 0.02126 | 0.02102 |  |  |
|               |  | ×   |                      |                                    |         |         |         |  |  |
|               | 160  | Bubble Point  | 0.02262              | 0.02214                            | 0.02180 | 0.02120 | 0.01984 |  |  |
|               |  | 500   |                      |                                    |         |         |         |  |  |
|               |  | 1000  |                      |                                    |         |         |         |  |  |
|               |  | 1500  | 0.02257              |                                    |         |         |         |  |  |
|               | С. ж. с. | 2000  | 0.02249              | '                                  |         |         |         |  |  |
|               |  | 2500  | 0.02241              | 0.02213                            |         |         |         |  |  |
|               | 41 (*  | 3000  | 0.02232              | 0.02210                            | 0.02182 | 0.02120 |         |  |  |
|               |  | 3500  | 0.02224              | 0.02205                            | 0.02183 | 0.02143 | 0.01997 |  |  |
|               |  | 4000  | 0.02216              | 0.02198                            | 0.02181 | 0.02154 | 0.02085 |  |  |
|               |  | <b>450</b> 0  | 0.02207              | 0.02189                            | 0.02177 | 0.02156 | 0.02104 |  |  |
|               | 220  | Bubble Point  | 0.02342              | 0.02270                            | 0.02215 | 0.02123 | 0.02004 |  |  |
|               |  | 500   |                      |                                    |         |         |         |  |  |
|               |  | 1000  |                      |                                    |         |         |         |  |  |
|               |  | 1500  | 0.02337              |                                    |         |         |         |  |  |
|               |  | 2000  | 0.02326              |                                    |         |         |         |  |  |
|               |  | 2500  | 0.02315              | 0.02269                            |         |         |         |  |  |
|               |  | 3000  | 0.02303              | 0.02267                            | 0.02227 |         |         |  |  |
|               |  | 3500  | 0.02290              | 0.02262                            | 0.02228 | 0.02149 |         |  |  |
|               |  | 4000  | 0.02282              | 0.02256                            | 0.02224 | 0.02168 | 0.02066 |  |  |
|               |  | 4500  | 0.02275              | 0.02249                            | 0.02220 | 0.02177 | 0.02083 |  |  |

a Partial specific volume, cubic feet per pound.

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Fig. 3. Isothermal pressure volume curves for a methanedecane mixture containing 12.18 weight per cent methane.



Fig. 4. Bubble point composition versus pressure for the methane-decane system.



Fig. 5. Specific volume of the methane-decane system as a function of composition at 160°F.



Fig. 6. Pressure times the equilibrium constant as a function of pressure for the methane-decane system.











Fig. 9. Partial specific volume of methane at 100°F. and 3000 lbs. per sq. in. as a function of molecular weight of the less volatile constituent for binary systems of methane and a second paraffinic hydrocarbon.





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