THE PARTIAL VOLUMETRIC BEHAVIOR OF THE METHANE - N BUTANE - DECANE SYSTEM

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Abstract

The volumetric behavior of the methane - n butane - decane system was experimentally investigated at seven temperatures in the interval 100° to 460°F. at pressures up to 10,000 pounds per square inch absolute. The apparatus and methods employed in the investigation are discussed.

The experimental data, which were taken at random pressures and arbitrarily chosen compositions of the system, were graphically interpolated to a uniform series of pressures and a systematic distribution of compositions. The results are presented in tabular form expressing the molal volume as a function of temperature, pressure, and composition for 1225 states of the system.

The partial molal volume of each component of the system was computed by graphical methods. The results are presented in tabular form in which the partial molal volumes of methane, n butane, and decane are expressed as functions of temperature, pressure, and composition for the same 1225 states of the system employed in the tabulation of molal volume.

A discussion of some applications of partial volumes in the thermodynamic treatment of multicomponent systems is given.

Introduction

The production, processing, and marketing of fluid hydrocarbon materials from naturally occurring deposits in underground reservoirs constitute the primary activities of the petroleum industry. To an ever increasing extent each of these activities demands more accurate and more detailed information concerning the properties of the raw materials as they occur in nature and of the products at each stage of the processing operations.

In 1927 the American Petroleum Institute initiated Project 37 entitled "The Fundamentals of Hydrocarbon Behavior" under the direction of Prof. W. N. Lacey at first and later under the joint direction of Professors Lacey and B. H. Sage of the Department of Chemical Engineering at the California Institute of Technology. The purpose of the Project is to supply the petroleum industry with basic data concerning the behavior of oil and gas under the conditions encountered in underground reservoirs.

In addition to studies of petroleum substances as they occur in nature, the Project has conducted an extensive investigation of the properties of the pure hydrocarbon components of petroleum. Up to the time of the present work the Project's studies of pure hydrocarbons involved only single-component and two-component systems. The results of these investigations are widely used as a basis for predicting the behavior of multicomponent systems.

It is realized that the extension of information obtained from the study of simple systems to predict the properties of more complex systems involves assumptions which should be experimentally tested. On March 1, 1941 an investigation was begun of the volumetric properties of a three-component system composed of methane, n butane, and decane. One of the primary objectives of this investigation is to determine, if possible, some empirical principles by which information concerning two-component systems might be used to predict the behavior of a three-component system.

Apparatus and Procedures

Details concerning the construction and operation of the experimental equipment used in this work have been published,¹ so only a brief discussion of the principal features will be included here. Figure (1) represents a schematic diagram of the apparatus.

Stainless steel chambers A and B indicated in Figure (1), with inside diameters of 2.5 inches and volumes of about 50 cubic inches each, are designed to contain fluids at pressures up to 20,000 pounds per square inch. The material to be studied is confined in A, the volume of space occupied by the material being varied by the injection or withdrawal of mercury into or from the chamber. The contents of A are stirred by a "squirrel cage" agitator inside the chamber and magnetically coupled to a rotating field generated outside the chamber. Chamber B serves as a volumetric reservoir for the mercury used to vary the effective volume of A. Energy for the displacement of mercury from B to A is obtained from compressed air. An electric probe C, actuated so as to move in a vertical direction by means of a motor-driven worm gear, permits the determination of the position of the mercury level in B. Chambers

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1 References are at the end of the paper.



- A Volumetric cell in which materials to be studied are enclosed.
- B Reservoir for mercury used to vary the effective volume of A.
- C Electric probe to determine the amount of mercury in the reservoir B.
- D Platinum resistance thermometer for measuring temperature of oil bath in which A is immersed.
- Note: Dashed lines enclose those portions of the apparatus immersed in thermostatically controlled oil baths.

Figure 1

A and B are immersed in separate thermostatically controlled oil baths. The temperature of the oil bath for A, which may be set at any value in the interval 100° to 500°F., is measured by a platinum resistance thermometer D in conjunction with a Mueller bridge, a modification of the familiar Wheatstone bridge. The temperature of the oil bath for B is automatically controlled within 0.1° of 120°F., an arbitrarily chosen temperature which can be maintained with little expenditure of power.

The pressure prevailing in B is transmitted by an oil-filled tube to the pressure balance, which consists of a beam balance provided with suitable weight hangers on knife edges so as to permit the measurement of the thrust exerted by a piston and cylinder arrangement actuated by the pressure transmitted from B.

The greatly differing volatilities of the three substances studied in this investigation necessitated the development of different techniques in handling each substance in order to prepare quantitatively the desired mixtures. The materials to be studied are transferred to chamber A in the order of increasing volatility.

Liquid decane, which has a vapor pressure somewhat less than that of water, is drawn through the sample port into the evacuated chamber A from a glass ampoule. The chamber valve is then closed and residual decane left in the connecting lines is drawn back by chilling the ampoule. The difference in weights of the ampoule before and after transferring the sample of decane represents the amount transferred.

n Butane, which has a vapor pressure of about 40 pounds per

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square inch at room temperature, is vaporized into A from a steel bomb connected to the sample port. After closing the valve to A, the residual n butane in the connecting lines is condensed back into the steel bomb by chilling it with liquid air. The bomb is weighed before and after this process to determine the amount of n butane transferred to A.

Methane is a gas of such low density (about one-half that of air at room temperature and pressure) that a fairly high pressure and, consequently, a rather heavily constructed bomb would be required to contain a reasonably large quantity of the substance in a volume small enough to be weighed with convenience by an ordinary analytical balance. Moreover, methane is sufficiently volatile to make difficult a satisfactorily quantitative recovery of residual methane in the connecting lines by chilling the primary container in the manner employed with decane and n butane. Because of these properties of methane, an isochoric gas burette designed to operate at pressures up to 5000 pounds per square inch is used to measure the quantity of methane injected into A. The connecting line joining the burette to A consists of two concentric tubes with rapidly flowing oil in the annular space between the tubes. The circulating oil is obtained from the thermostatically controlled oil bath in which the gas burette is immersed. The amount of methane transferred from the burette to the volumetric chamber A is determined from measurements of the total pressure of the gas in the burette before and after the transfer. The relation between the change in the amount of methane in the burette and the change of gas pressure in the burette

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was obtained from a step-wise calibration of the burette by using a steel bomb to weigh relatively small samples of methane withdrawn through the sample port and noting the change in burette pressure associated with each withdrawal.

Materials

Vacuum techniques are used throughout in preparing the pure materials and their mixtures. The sources and purity of the materials used are described in several of the reprints of papers describing the work leading up to the present investigation (see appendix at the end of this paper). It is believed that the methane and n butane used in the present work did not contain more than 0.05 mole per cent hydrocarbon impurity. However, measurements of specific gravity, refractive index, and optical dispersion indicate that the decane used in this work consisted of a mixture of paraffinic hydrocarbon isomers comprising ten carbon atoms per molecule with n decane predominating.

Experimental Accuracy

The experimental operations are, in principle, directed toward the measurement of four fundamental quantities: weight, temperature, pressure, and volume.

All measurements of weight are referred directly or as nearly directly as possible to a set of stainless steel weights which have been calibrated in terms of a 1-gram gold weight and a 100-gram gold weight, both of the latter having been certified by the National Bureau of Standards at Washington, D. C. The buoyant effects of the atmosphere were taken into account when performing the calibration.

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A Christian Becker analytical balance with a capacity of about two kilograms and a sensitivity of about 1.0 milligram per scale division is used in weighing ampoules and bombs containing samples. The method of substitution is employed in all weighings. That is, the calibrated weights and the object to be weighed are placed upon the same pan of the balance while an ordinary set of laborabory weights serves as a targueight on the other pan. Changes through addition or withdrawal of material in the sample containers are measured by compensating adjustments with the calibrated weights leaving the tare weights undisturbed. This method of weighing eliminates errors arising from inequalities in the arms of the balance and from changes in the "rest point" of the balance as a consequence of variable load. In general, the weight of material used in the volumetric apparatus lies within the range of 10 to 100 grams. It is estimated that the weighing and transfer techniques permit the quantitative injection of material into the volumetric chamber with less than 10 milligrams uncertainty in the weight. Hence, it is believed that the total weight of a mixture is known with an uncertainty less than 0.1 per cent, and the weight fraction of a component of a mixture is known with an uncertainty less than 0.001. It is of interest to note that when these uncertainties are expressed in molal units the uniform uncertainties in the weights of the components result, in some instances, in an almost ten-fold greater uncertainty in the mole fraction of methane compared to the uncertainty in the mole fraction of decane.

The electrical resistance of pure platinum has been accurately

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measured as a function of temperature, and the Callendar formula². an empirical relation between the temperature and the electrical resistance of pure platinum, was adopted in 1927 as the basis for the International Temperature Scale throughout the interval of temperature from 0° to 660°C. A platinum resistance thermometer, consisting of a resistance element constructed of highest purity, hard drawn, annealed platinum wire 0.004 inch in diameter sealed in a pyrex glass tube filled with helium is used to measure the temperature of the oil bath in which the volumetric chamber A is immersed. A similar instrument certified by the National Eureau of Standards was used to calibrate the laboratory thermometer at 100°, 220°, 340°, and 460°F. By using the Callendar formula as an interpolation function the resistance of the laboratory thermometer at any temperature within the range of the calibration is obtained. A change of 0.02 ohm in the resistance of the thermometer corresponds approximately to a change of 1.0°F. in its temperature. The Mueller bridge and galvanometer used to measure the resistance of the thermometer are capable of detecting a change of 0.0001 ohm. The electrical current passing through the resistance element of the thermometer is of the order of 0.2 milliamperes. Since the total resistance of the thermometer is only about 10 ohms, the electrical energy dissipated in the resistance element may be assumed to have a negligle effect upon its temperature. The sensitivity of the thermometric apparatus exceeds that of the automatic thermal control equipment. Hence, although the instantaneous local temperatures in the oil bath may be measurable within a few hundredths of a degree, it is estimated that the uncertainty in the mean temperature of the entire oil bath is of the order of 0.1°F.

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A carefully constructed piston and cylinder combined with a suitable force measuring device, such as a balanced beam with knife edges supporting adjustable decades of weights, provides a very satisfactory means for measuring high pressures. Piston pressure balances are free from some of the defects characteristic of Bourdon pressure guages, i.e., non-linearity, hysteresis, and "creep". Bridgeman³ made an extensive study of piston pressure balances and verified that they can be made to perform with a linear response with less than 0.01 per cent uncertainty at pressures ranging from less than atmospheric to several hundred times greater than atmospheric pressure.

The piston of the pressure balance used in the present work has a diameter of about 0.125 inch and was ground and polished to a radial clearance of about 0.00005 inch with respect to the cylinder in which works. A light machine oil (No. 10 S.A.E.) is used as a pressure transmitting fluid and lubricant in the cylinder. At a pressure of 10,000 pounds per square inch the seepage of oil between the piston and the cylinder is about one drop per minute. A small electric motor with a worm-reduction gear slowly rotates the cylinder of the pressure balance while it is in operation thus eliminating static friction between the piston and the cylinder. The decades of weights used in connection with the beam balance for measuring the thrust of the piston were carefully constructed to be within 0.01 per cent of the correct weight ratios. The calibrated stainless steel weights, mentioned previously in regard to sample weighing, were employed in adjusting the weights used with the pressure balance.

Although it is feasible to compute an absolute calibration of the

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pressure balance on the basis of the dimensions and weights of its parts, it is much simpler to calibrate it empirically using a mercury manometer for pressures up to 3 or 4 atmospheres and using Bridgeman's ³ accurate evaluation of the vapor pressure of pure carbon dioxide at 0°C. (505.56 lb./sq.in. abs.) as a fixed reference point in the higher pressure range.

The absolute pressure of a fluid at the input to the pressure balance is given by the following simple relationship:

 $p = p + as + b \tag{1}$

where

p = absolute pressure

p_a = barometric pressure of the atmosphere
s = scale reading of the pressure balance
a,b = empirically evaluated constants of the
pressure balance.

The barometric pressure enters into equation (1) because the exterior surface of the pressure-balance piston is exposed to the atmosphere.

The pressure in the volumetric chamber A (Figure 1) is related in a rather complicated manner to the pressure indicated by the pressure balance, so that a number of terms must be added to equation (1) to obtain the correct pressure in A. First, there is an appreciable difference in elevation and, consequently, a difference in pressure between the ends of the oil-filled tube connecting the pressure balance to chamber B. Second, at elevated pressures the density of air becomes sufficient to produce a significant vertical pressure gradient above the mercury surface in B. Third, account must be taken of the

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difference in elevation and density of mercury in A and B. Fourth, the fugacity of mercury at the higher temperatures and pressures (Poynting effect 4) becomes sufficiently great to require correcting the pressure in A for the effective vapor pressure of mercury. This last correction is applied with the assumption that mercury and hydrocarbons are not appreciably miscible within the ranges of temperature and pressure involved in this work and that, therefore, the effective vapor pressure of mercury exerts its influence independently of the nature of the hydrocarbons present. Equation (1) then takes the following form:

 $p = p_{\alpha} + as + b + c + d + e - f$ (2)

in which the first four symbols on the right have the same meanings as in equation (1) while the additional terms are

- c = pressure difference between ends of oil line from pressure balance to chamber B.
- d = pressure difference due.to gravitational pressure
 gradient in the compressed air above the mercury
 surface in B.
- e = pressure difference due to difference in density and elevation of mercury in A and B.

f = vapor pressure of mercury in A.

The evaluation of the additional terms in equation (2) is straightforward but tedious. The result is intended to represent the pressure exerted by the hydrocarbon sample at the mercury-hydrocarbon interface in A. No account is taken of the gravitational pressure gradient in the sample of hydrocarbon being studied.

The sensitivity of the pressure balance is such as to permit the detection of pressure changes smaller than 0.1 pound per square inch

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in the volumetric chamber A, and it is estimated that the absolute pressure is indicated with an uncertainty of about 0.05 per cent at pressures above 200 pounds per square inch and with an uncertainty less than 0.1 pound per square inch at pressures below 200 pounds per square inch.

Experience has shown that the precise measurement of volume at high pressures is the most difficult operation to perform with the apparatus shown in Figure 1. The motor-driven micrometer probe C enters the chamber B through a high-pressure packing gland and terminates in a sharp-pointed electric contact. The electric contact is connected to the grid of a vacuum tube electronic valve, the cathode side of the electronic valve being connected to the chamber B. The electronic valve actuates a magnetic relay which operates an indicator light. The electrical characteristics of the grid circuit of the electronic valve are adjustable, and it was found that an open-circuit potential difference of 70 volts between the electric contact and the mercury surface and a closed-circuit current of about 0.2 milliamperes provides satisfactorily reproducible performance of the electroic contact.

The driving motor for the probe is equipped with a revolution counter which serves to indicate the position of the probe. One revolution of the motor shaft corresponds to a vertical motion of about 0.001 inch in the probe. The range of the probe is about 5 inches, the power to the driving motor being automatically disconnected at the extreme ends of the range so as to prevent damage to the equipment. In the vicinity of the mercury surface the motor shaft is

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turned by hand. Vibrations from the agitator motors distributed about the apparatus produce small ripples on the mercury surface which cause the indicator light of the probe to flicker rapidly on and off when the electric contact is within a few thousandths of an inch of the mercury surface. An experienced operator can judge the character of the clicks emitted by the magnetic relay actuating the flickering indicator light so as to obtain reproducible settings of the probe with an uncertainty of about 0.0003 inch, that is, with an uncertainty of about one-third of a revolution of the motor shaft which drives the probe. Backlash in the driving mechanism of the probe is taken into account by making all measurements, including the calibration of the volumetric apparatus, with the probe moving downward.

In general, the minimum volume occupied in A by a sample of material under investigation corresponds approximately to a one-inch displacement of the mercury level in B. From the foregoing information it might be inferred that, provided proper account is made of the thermo- and piezo-volumetric properties of the chambers A and B and the mercury therein, it should be possible to measure the volume of the material under consideration with an uncertainty of about 0.03 per cent. However, in practice such has not been the case. The chemical action of compressed air on the mercury in B results in a gradual change in the surface properties of the mercury so that the surface film which clings to the walls of the chamber becomes suffithick after about two or three weeks to require cleaning up the chamber and repurifying the mercury. For this reason the apparatus is periodically overhauled with a frequency which is estimated to

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avoid errors greater than 0.5 per cent in the measurement of the minimum volume of a sample. The use of a relatively inert gas, such as nitrogen, has been proposed in place of air in order to reduce the troublesome deterioration of the mercury surface in B, but the requisite man-hours for revamping the compressor system to this purpose have not, at the present writing, become available.

The principle employed in the measurement of volume consists in using chamber B to measure the amount of mercury displaced from chamber A by the material under investigation.

The volumetric calibration of the apparatus proceeds as follows. Chamber B is isolated from chamber A by freezing with dry ice a solid plug of mercury in a short length of the tube connecting the two chambers. Using known increments of mercury (weighed with the aforementioned calibrated stainless steel weights), the readings of the revolution counter on the motor shaft which drives the electric probe are correlated with the amount of mercury in chamber B. This calibration is repeated for a number of pressures covering the range of experimental interest. Hence, the amount of mercury in B is known as an empirical function of the revolution counter reading and the pressure. The frozen plug of mercury in the tube connecting the two chambers is then permitted to thaw and the volumetric properties of chamber A are determined by completely filling it with mercury from B and noting the revolution counter readings as a function of pressure. These measurements are repeated with chamber A at various temperatures covering the range of experimental interest. These measurements establish the "no sample", or "zero volume" behavior of the apparatus. The volume occupied by a sample of material in

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chamber A may then be determined by difference from the "no sample" characteristics of the apparatus.

In computing the volume of mercury displaced by a sample of material in chamber A at the temperature and pressure prevailing in A, the Smithsonian Tables for the specific volume of mercury as a function of temperature at atmospheric pressure and the data of Smith and Keyes ⁵ concerning the compressibility of mercury are used.

As a consequence of the foregoing considerations, the expression for the specific volume of the material under investigation takes the following form:

$$\mathbf{v} = \frac{\mathbf{v}_{H_g}}{\mathbf{m}} \left[\mathbf{k}_1 (\mathbf{N} - \mathbf{N}_0) + \mathbf{k}_2 \, \mathbf{N} \mathbf{p} + \mathbf{k}_3 \, \mathbf{p} + \mathbf{k}_4 \, \right] \tag{3}$$

in which k_1 , k_2 , k_3 , and k_4 are empirically determined constants of the apparatus and

V = specific volume of sample.

 V_{Hg} = specific volume of mercury at the pressure and temperature in chamber A.

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m = weight of sample.

N = revolution counter reading with sample in A. N_Q = revolution counter reading with no sample in A. p = pressure in chamber B.

As was mentioned earlier, volume is the most difficulty and without a doubt the least accurately measured of the four quantities (weight, temperature, pressure, and volume) determined by the apparatus and procedures which have been described. It is believed that by conscientiously adhering to a routine maintenance schedule involving frequent overhauling of the volumetric equipment, the uncertainty in the volume measurements were kept for the most part to within 0.2 per cent,

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and only rarely did the uncertainty become as great as 0.5 per cent.

The Investigation of the Methane - n Butane - Decane System

Before proceeding further with this dissertation it might be well to point out that the word system is here used in two difference senses. In thermodynamics the term system is applied to the contents of a region of space enclosed by suitably defined boundaries, the contents of the enclosed region being treated in a manner which regards them as distinguished from everything which may be present in the space exterior to that region. In this paper, system is also used to designate a group of substances which are studied with the objective of determining the synthetic and analytic properties of the group. However, so far as the writer is aware, the use of system in two different senses involves no serious ambiguities in practice.

The methane - n butane - decane system was selected for study because it is, perhaps, the simplest system of relatively pure substances which might be expected to exhibit properties resembling those observed in naturally occurring oil and gas mixtures. A rough correspondence can be made between the components of the methane n butane - decane system and some of the familiar constituents of petroleum. Methane is the principal ingredient of natural gas. n Butane is an important part of the "rock gas" commonly used in rural districts for heating and cooking. Decane resembles to some degree a rather thin fuel oil which is the residue left after the more volatile fuel constituents and the heavier lubricant fractions have been removed.

In approaching the study of the methane - n butane - decane

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system it was decided at the outset that graphical methods would be employed to correlate the data. This decision was made because no equation of state is known which, in the present case, would be satisfactory in regard either to accuracy or computational convenience in representing the date throughout the ranges of the variables involved in this work. An alternative technique based upon the construction of numerical difference tables was investigated and rejected because it requires for satisfactory results experimental data whose distribution with respect to temperature and composition is too dense to be economically feasible of attainment.

The adoption of graphical methods to correlate the data places a definite restriction upon the laboratory procedure in gathering the experimental data. For the purpose of this work the construction of graphs involves the determination of lines on two-dimensional surfaces. If one dimension of a surface is used to represent values of a dependent variable, we are left with only one dimension for representing variations of the independent variables. It is, therefore, desirable to restrict the experimental observations on the behavior of the system in such a way as to permit the simultaneous variation of only two variables, all others being fixed at constant values during measurements of a series of equilibrium states distributed in such a way as to establish the relation between the two chosen variables. This process is repeated in a systematic fashion for a series of values of each "fixed" variable. The equilibrium behavior of the system is then graphically described by families of curves which may be regarded as contour maps of a surface representing

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the locus of equilibrium states in a thermodynamic "phase space".

In the present work it is convenient to regard volume as the dependent variable while pressure, temperature, and the mole fractions of any two of the components of the system are treated as independent variables. The "fixed" variable are chosen to be those requiring the most time and effort to change and re-establish equilibrium in the system. Thus, a change in the composition of the system requires about one man-day for each component which is changed. A large variation in temperature entails a wait of about three hours to regain equilibrium. Only 20 minutes are required for the attainment of equilibrium in the system after changing the volume and pressure. Hence, the primary data from the laboratory consist of isothermal measurements on mixtures of fixed composition, the observed states of the system being chosen so as to establish the pressure-volume relationship at each temperature and composition studied.

The volumetric properties of pure methane ⁶ and n butane 7 as well as of mixtures of these substances ⁸ have been experimentally investigated throughout the ranges of pressure and temperature of interest to the present work. The volumetric behavior of decane was determined in connection with a study of the methane - decane system ⁹. Corresponding data concerning the n butane - decane system have recently been published ¹⁰. The investigation of threecomponent mixtures of these substances is still in process, and up to the present writing 13 mixtures have been studied. Data concerning 5 of the mixtures have been published.

Figure 2 represents a three-component molal composition diagram in which the distribution of experimentally studied three-component

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Three-component molal composition diagram showing the distribution of experimentally studied mixtures.

mixtures is shown. It will be noted that the experimental points in the diagram lie on straight lines radiating from the apex of the triangle. The points were chosen to lie in that manner as a concession to the previously discussed limitations of graphical methods for correlating data. By so choosing the experimental points, it is a simple matter graphically to correlate the isothemal, isobaric volumetric behavior as functions of the mole fraction of methane for the series of mixtures. The lines radiating from the apex of the triangle represent loci of constant molal ratio of n butane to decane. Four such lines were arbitrarily chosen for investigation. Their terminal points on the n butane - decane border of the diagram correspond in composition to 0.1787, 0.4631, 0.6617, and 0.8358 mole fraction n butane, respectively.

Although the experimental investigation of these series of mixtures is not yet completed, it is believed that sufficient data have been gathered to permit a reasonably satisfactory treatment of the single-phase region at the higher pressures. For the most part the area in which the data are sparse involves the two-phase region, and it is proposed to avoid the consideration of the twophase region in this paper.

The first objective of this thesis is to obtain by graphical interpolation of the experimental data the volumetric behavior of the system for a systematic distribution of mixtures covering in a more or less uniform fashion the entire area of the three-component molal composition diagram. In Figure 3 the distribution of the graphically interpolated mixtures is shown. Five straight lines

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Figure 3

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Three-component molal composition diagram showing the distribution of mixtures obtained by graphical interpolation of the experimental results. The points, a b c d e, along the baseline of the triangle are chosen to be at 10, 25, 50, 75, and 90 mole per cent n butane, respectively. A similar spacing holds for the indicated points along the sides of the triangle. The interpolations were carried out so as to obtain the volumetric behavior of those mixtures corresponding to each concurrence of three lines in the above diagram. radiating from each corner of the diagram are drawn so as to terminate at the 10, 25, 50, 75, and 90 mole per cent points on each side of the triangle. The concurrent intersections of three lines locates an interpolated three-component mixture. The composition of these interpolated mixtures are recorded in Table I under the heading "Threecomponent Systems".

In order to facilitate the identification of a mixture the following nomenclature is used. The lines which terminate on the n butane decane border of the diagram in Figure 2 are labeled with lower case letters a, b, c, d, and e. Arabic numerals 1, 2, 3, 4, and 5 designate those lines terminating on the methane - n butane border of the diagram while Roman numerals I, II, III, IV, and V indicate the remaining group of lines which terminate on the methane - decane border. An interpolated point in the interior of the diagram is identified by the three lines concurrent at that point. Thus, for example, we have the point a I 3 in the lower left corner of the diagram, or the point c III 3 in the middle of the diagram.

The kind of pattern chosen for distributing the interpolated compositions was dictated by the second objective of this thesis, which is to evaluate the partial molal volume of each component of the syste. However, discussion of this topic will be deferred to a later section of this paper.

The graphical procedures by which the experimental data were interpolated to the desired compositions of the system are straight forward and uninspiring. Large scale plots (50 x .75 cm.) on millimeter cross section graph paper were prepared describing the isothermal,

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isobaric relations between the molal volume and the mole fraction of methane for various constant mole ratios of n butane and decane. From these plots, others were made showing the isothermal, isobaric relations between molal volume and mole fraction n butane for fixed mole ratios of methane and decane. Corresponding plots relating molal volume and mole fraction decane for constant mole ratios of methane and n butane were also constructed. Plots were thus prepared for each of the 3 components at 5 pressures and 7 temperatures of the system. Hence, 105 plots were involved in the interpolation of the volumetric data to the desired distribution of compositions shown in Figure 3.

Strictly speaking, only one-third of the plots were essential to the determination of the required volumetric data, because the plots with respect to the mole fraction of any one of the components could have been used to determine the molal volumes for all of the interpolated threecomponent mixtures. This is apparent from the fact that the lines radiating from any one corner of the composition diagram (Figure 3) pass through all of the points representing interpolated three-component mixtures. However, by having prepared the plots in the manner indicated, the internal consistency of the interpolated data is greatly increased because the relations between molal volume and composition are "smoothed" with respect to mole fraction of each of the three components. The probable accuracy of the results is correspondingly increased. Moreover, it was known in regard to the subsequent evaluation of the partial volumes of the components of this system that all of the plots which had been prepared would be of value.

The results of the volumetric interpolation are recorded in

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Table II. Each page of the table corresponds to a different pressure of the system; i.e., to 2000, 4000, 6000, 8000, and 10,000 pounds per square inch, absolute. The data are tabulated in seven colums, one column for each experimentally studied temperature. The data are also arranged in groups corresponding to systems of one, two, and three components. The blank spaces which occur in the tabulations at 2000 and 4000 pounds per square inch correspond to states of the system which fall in the two-phase region. The maximum two-phase pressure of this system lies between 5000 and 6000 pounds per square inch.

The data concerning the one-component and two-component systems do not represent essentially new information, for these data may be obtained from the previously mentioned publications, a slight amount of effort being required to interpolate the published data to the particular states chosen for this paper. The information concerning the oneand two-component systems is included here as a matter of convenience to those who may find applications for these data, and because but little extra effort is required to present them since these data were necessarily obtained in carrying out the interpolations in regard to the three-component systems.

The tabulations concerning the three-component systems represent new information not obtainable from current publications.

The accuracy of the results recorded in Table II is estimated to be comparable to the accuracy of the experimental data from which the results were derived. In the discussion of experimental accuracy it was indicated that the measurement of volume involved the greatest sources of error, the estimated uncertainty being about 0.2 per cent,

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for the most part, with a possible occasional error of 0.5 per cent for the states of maximum compression of the system. The graphical procedures employed in performing the interpolation of the data are believed to have been carried out with sufficient care to have avoided the introduction of additional uncertainties greater than 0.1 per cent into the results. In fact, the graphical interpolations involved a process of "smoothing" the data so as to improve the consistency of the variations of volume with respect to pressure, temperature, and composition. It therefore seems likely that the graphical operations augmented rather than decreased the probable accuracy of the results. Contrary to the accepted practice in scientific literature in which the reported number of significant figures is customarily restricted to that which is just sufficient to represent the data within the estimated accuracy of the final results, the data in Table II are recorded in the greater part with one more significant figure than is warranted by the estimated accuracy of the results. This procedure in recording the data is in accord with the usual engineering practice of carrying out absurdly precise calculations based upon very bad data, and then applying a suitable "safety factor" to the result. The writer hastens to add that he does not wish to imply that the data herein presented are very bad.

As an aid to the reader who may wish a general picture of the behavior of the methane - n butane - decane system, several diagrams have been prepared illustrating the effects of varying composition and pressure upon the volumetric and phase behavior of the system at 220°F. Figure 4 is a three-component molal composition diagram show-

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Three-component molal composition diagram showing isobaric loci of bubble-point states at 220°F.

ing isobaric loci of bubble-point states of the system for 1000 poundper-square-inch intervals of pressure at 220°F. It will be noticed that at the lower pressures the mole fraction of methane, i.e., the "solubility" of methane, in the bubble-point liquid tends to remain relatively constant as the relative proportions of n butane and decame are varied. The curves at 2000 pounds per square inch and higher turn up and back so as to terminate at both ends on the methane - decame border of the diagram. The curves shown in the diagram are incomplete. The portions of the curves not shown represent dew-point loci at constant pressure and temperature. At the present writing, data for the establishment of the dew-point loci are still in process of being gathered by the laboratory.

Figures 5, 6, and 7 represent "cross section" views of the system at 220°F. taken along the three median lines of the triangular composition diagram. In each of these figures the isobaric variation of the molal volume is shown as a function of the mole fraction of one component, the other two components being fixed in equimolal proportions to each other. Since the median lines intersect at the midpoint of the triangle, we find that the three diagrams in Figures 5, 6, and 7 have one set of points in common, namely those points at a mole fraction of 0.333 will be found in each diagram to have the same values for the molal volume at corresponding pressures. The boundaries of the two-phase region and the isobaric curves crossing the two-phase region, shown as dashed lines, should be regarded as being only qualitatively established.

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Figure 5

Isobaric relations between molal volume and mole fraction methane at 220°F. for mixtures represented by the line from point c to the angle apex designated as methane in Figure 3. These mixtures contain equimolal proportions of n butane and decane. The dashed lines indicate information not yet well established by the available experimental data.



Figure 6

Isobaric relations between molal volume and mole fraction n butane at 220°F. for mixtures represented by the line from point III to the angle apex designated as n butane in Figure 3. These mixtures contain equimolal proportions of methane and decane. The bubble-point locus is not yet well determined by the available experimental data.



Figure 7

Isobaric relations between molal volume and mole fraction decane at 220°F. for mixtures represented by the line from point 3 to the angle apex designated as decane in Figure 3. These mixtures contain equimolal proportions of methane and n butane. The bubble-point locus is not yet well determined by the available experimental data.

The Partial Molal Volumes of Methane, n Butane, and Decane

G. N. Lewis ¹² has defined a thermodynamic concept which is of great value in the treatment of multicomponent systems. It is the concept of a partial molal quantity, defined in the following way:

$$\overline{\mathbf{G}}_{\mathbf{k}} = \left(\frac{\partial \mathbf{G}}{\partial \mathbf{m}_{\mathbf{k}}}\right)_{\mathbf{p}, \mathbf{T}, \mathbf{m}_{\mathbf{i}}}$$
(4)

where

 \underline{G} = any extensive property of the system, m_k = number of moles of component k, Subscripts p,T,m₁ signify that pressure, temperature, and the mole numbers of all the components except component k are constant.

The symbol \overline{G}_k represents the partial molal value of the property \underline{G} for component k. Although the property \underline{G} is extensive in character, its partial molal values for the various components of a system are intensive properties of the system. For a definition of extensive and intensive properties of a system, see R. C. Tolman, Phys. Rev. 2, 234 (1917).

Several methods for evaluating partial molal quantities are described in Lewis and Randall "Thermodynamics", the most useful of which, so far as graphical techniques are concerned, is the method of intercepts ¹³. (See the appendix of this thesis for a discussion of the method of intercepts.)

A straight hairline groove about 0.001 inch in width and about 30 inches long was ruled on a strip of clear lucite, a methyl methacrylate polymer which is dimensionally stable to a high degree.

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The lucite strip is about one-eighth inch thick, 4 inches wide, and 36 inches long. With the ruled side of the strip turned face downward and obliquely illuminated, a well defined black line is clearly visible. This device provides a convenient means of setting a tangent line at any desired point of a curve drawn on graph paper and thereby permitting the intercepts of that tangent with the coordinate lines of the graph to be read.

With the use of the above described device the partial molal volumes of the components of the methane - n butane - decane system were evaluated by applying the method of tangent intercepts to each of the previously mentioned 105 plots of the isobaric, isothermal variation of molal volume with respect to the mole fraction of each component. The "raw" data obtained from the tangent intercepts are likely to be rather rough because, in those cases for which the point of tangency to the curve is far removed from the point of intersection of the tangent with the coordinate axis, a relatively minor irregularity in the curve will produce a very large uncertainty in the position of the intercept. It is estimated that, in general, the uncertainty in the partial molal volume for a component of a mixture is linearly proportional to the total mole fraction of the other components in that mixture. Thus, for example, the uncertainty in the partial molal volume of methane in mixtures containing more than 90 mole per cent methane is of the same magnitude as the uncertainty in the primary volumetric data and may be of the order of 0.002 cubic foot per pound mole. On the other hand, the uncertainty in the partial molal volume of methane in mixtures containing less

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than 10 mole per cent methane may be from 10 to 100 times larger than that for the above example, the magnitude of the uncertainty being largely dependent upon the sharpness of curvature in the isobaric, isothermal relation between molal volume and mole fraction methane in the region under consideration.

In order to improve the internal consistency of the data and, possibly, to increase their probable accuracy, the results of the foregoing graphical computations were plotted and graphically correlated with respect to variations in the pressure, temperature, and composition of the system. The results obtained from this process of "smoothing" the data are recorded in Tables III, IV, and V, which present, respectively, the partial molal volumes of methane, n butane, and decane for the same states of the systems recorded in Tables I and II. Partial molal volumes for a few of the states at 2000 pounds per square inch have been omitted from the tabulations even though volumetric data for these states are given. These data are omitted because the graphical uncertainties in their evaluation were obviously so large as to make the information almost worthless.

Several tests may be applied to evaluate the internal consistency of the data. The most direct test which may be applied is to reverse the process of deriving the partial molal volumes by recombining them in their respective mole fractional proportions and to compare the result with the molal volume of the system at the particular state in question. The following relationship should hold:

$$\nabla = \mathbf{n}_{1}\overline{\nabla}_{1} + \mathbf{n}_{4}\overline{\nabla}_{4} + \mathbf{n}_{10}\overline{\nabla}_{10}$$
 (5)

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The operation indicated by equation (5) was applied to the data in Tables III, IV, and V and the results were compared with the molal volumes recorded in Table II. In more than 90 per cent of the cases the agreement is within 0.005 cubic foot per pound mole while the majority of the remaining cases agree within 0.010 cubic foot per pound mole. Isolated instances in which the discrepancies are larger were investigated by referring back to the graphs from which the data were derived. In the more extreme instances of disagreement, attempts were made to adjust the values of the partial molal volumes, the graphs of the primary data being used as guides in estimating the permissible limits of adjustment. However, the available time remaining before the formal presentation of this work did not permit a very thorough "working over" of the data.

Another test of the consistency of the data which might have been applied is that corresponding to the Gibbs - Duhem equation:

$$\mathbf{n}_{1} \frac{\partial \overline{\mathbf{v}}_{1}}{\partial \mathbf{n}_{k}} + \mathbf{n}_{4} \frac{\partial \overline{\mathbf{v}}_{4}}{\partial \mathbf{n}_{k}} + \mathbf{n}_{10} \frac{\partial \overline{\mathbf{v}}_{10}}{\partial \mathbf{n}_{k}} = 0 \qquad (6)$$

This equation, however, requires the evaluation of partial derivatives of the partial molal volumes, a time consuming and difficult task to perform with reasonable accuracy. Moreover, the interpretation of the results of applying equation (6) is not so obvious as that of equation (5). The writer has employed the Gibbs - Duhem equation to check the internal consistency of partial volumetric data for a twocomponent system ¹⁴. He does not feel that the test is entirely satisfactory because difficulties are encountered in deciding whether

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those discrepancies which are observed are attributable to inconsistencies in the primary data or to uncertainties in the process of differentiating the partial volumes. The foregoing reasons are considered sufficient to justify rejecting the application of equation (6) as a test of the data herein presented.

The expression of the probable error or uncertainty in terms of percentages is not always meaningful in the case of partial volumes because in some instances the partial volume of a component may vary continuously from positive to negative values so that at some state of the system that component will have a zero partial volume (See Table V, 2000 lb./sq.in, 460° F., system e V 3). The per cent uncertainty in a zero-valued partial volume is infinite, and a statement to that effect gives no useful information whatsoever concerning the absolute accuracy of the datum. Keeping in mind the comments in a previous paragraph concerning the variable character of the uncertainties associated with partial volumes, it is estimated that the probable error in the reported values of partial molal volumes in Tables III, IV, and V ranges from 0.002 to 0.200 cubic foot per pound mole, the largest uncertainties being associated with those mixtures containing the least amount of the component in question.

The general behavior of the partial molal volumes of methane, n butane, and decane as functions of the composition of the system is shown in Figures 8 to 16, inclusive. The same temperature, 220°F., and the same median lines crossing the three-component composition diagram are used for these figures as were used in Figures 5, 6, and 7 when describing the molal volume of the system. The order in which

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Isobaric relations at 220°F. between the partial molal volume of methane and the mole fraction of methane for mixtures represented by the line from point c to the angle apex designated as methane in Figure 3. The bubble-point locus is not yet well established by the available experimental data.



Isobaric relations at 220°F. between the partial molal volume of methane and the mole fraction of n butane for mixtures represented by the line from point III to the angle apex designated as n butane in Figure 3.



Isobaric relations at $220^{\circ}F$. between the partial molal volume of methane and the mole fraction of decane for mixtures represented by the line from point 3 to the angle apex designated as decane in Figure 3.



Isobaric relations at 220° F. between the partial molal volume of n butane and the mole fraction of methane for mixtures represented by the line from point c to the angle apex designated as methane in Figure 3.



Isobaric relations at 220°F. between the partial molal volume of n butane and the mole fraction of n butane for mixtures represented by the line from point III to the angle apex designated as n butane in Figure 3.



Figure 13

Isobaric relations at 220°F. between the partial molal volume of n butane and the mole fraction of decane for mixtures represented by the line from point 3 to the angle apex designated as decane in Figure 3.



Isobaric relations at 220°F. between the partial molal volume of decane and the mole fraction of methane for mixtures represented by the line from point c to the angle apex designated as methane in Figure 3.



Figure 15

Isobaric relations at 220°F. between the partial molal volume of decane and the mole fraction of n butane for mixtures represented by the line from point III to the angle apex designated as n butane in Figure 3.



Isobaric relations at 220°F. between the partial molal volume of decane and the mole fraction of decane for mixtures represented by the line from point 3 to the angle apex designated as decane in Figure 3.

Figures 8 to 16 are presented is as follows. The first three figures depict the partial molal volume of methane as isobaric, isothermal functions of the mole fractions of methane, n butane, and decane, respectively. The next three figures present corresponding information with regard to the partial molal volume of n butane, and in a similar manner the last three figures describe the partial molal volumetric behavior of decane. Information concerning the two-phase region and bubble-point states of the system has been established only qualitatively at the present writing.

It will be noticed in Figure 8 that the slope of the curves is zero as they terminate at the right hand border of the diagram. This behavior is in accord with the requirements of the Gibbs - Duhem equation. The right hand border of the diagram corresponds to a value of unity for the mole fraction of methane and zero for the other two components. Referring to equation (6) we see that under these conditions the derivative of \overline{V}_1 with respect to n_1 must be zero provided the derivatives of \overline{V}_4 and \overline{V}_{10} with respect to n_1 are finite. Similar conclusions regarding the curves in Figures 12 and 16 also hold.

In Figures 8, 12, and 16 the left hand border of each diagram represents the state of zero concentration for the component whose partial volume is shown. The terminal points of the curves, as they approach this border, represent the limit values of the partial volume of the component as the concentration of that component approaches zero. It may be said (with a smile) that the points of intersection of the curves with the left boundary in each of these diagrams represents the partial volumetric behavior of a component

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when there isn't any of that component present.

In general, the partial volume decreases with increasing pressure in a manner analogous to the behavior of volume. However, in Figures 11, 14, and 16 we see that in relatively large regions the partial volume increases as the pressure is increased.

All the foregoing diagrams depicting the partial volumetric behavior of the system are confined to one temperature, 220° F. To give an indication of the manner in which partial volumes behave with respect to changes in temperature, Figures 17, 18, and 19 are presented. Three points (b I 2, b IV 5, and e V 3), widely spaced from one another in respect to composition, were arbitrarily chosen, and the isobaric relations to variations in temperature are shown with regard to the partial molal volumes of methane, n butane, and decame for the three respective points. That the behaviors of these partial volumes are not simple is apparent, for in some cases the partial volume increases and in other cases decreases with rising temperature. In fact, in Figure 19 we see the partial volume of decame behaving in a manner completely opposite to that encountered in the case of volume, i.e., the partial volume increases with increasing pressure and decreases with increasing temperature.

It will be noted in the tabulations of the partial volumes that in some instances the partial volume of a component may assume negative values. This represents a rather curious behavior of the system. The total volume of a mixture is expressed in terms of the mole numbers and partial molal volumes of the components by the following equation:

$$\underline{\mathbf{v}} = \mathbf{m}_{1}\overline{\mathbf{v}}_{1} + \mathbf{m}_{4}\overline{\mathbf{v}}_{4} + \mathbf{m}_{10}\overline{\mathbf{v}}_{10}$$
(7)





Influence of temperature and pressure upon the partial molal volume of methane for the mixture corresponding to system b I 2, the mole fractions of the components in this mixture being 0.0769 methane, 0.2308 n butane, and 0.6923 decane.



Influence of temperature and pressure upon the partial molal volume of n butane for the mixture corresponding to system b IV 5, the mole fractions of the components of this mixture being 0.6923 methane, 0.0769 n butane, and 0.2308 decane.



Figure 19

Influence of temperature and pressure upon the partial molal volume of decane for the mixture corresponding to system e V 3, the mole fractions of the components of this mixture being 0.4737 methane, 0.4737 n butane, and 0.0562 decane. It is apparent from the above equation that, if the partial volume of any component is negative, the total volume of the mixture will decrease at constant pressure and temperature when the amount of that component is increased while holding the amounts of the other components fixed. An analogous statement holds also for the case in which two of the components have negative partial volumes. It is, of course, impossible for all of the components simultaneously to have negative partial volumes.

Applications of Partial Molal Volumes

To the petroleum production technologist the most important practical application of partial volumetric data is indicated by equation (7). Given sufficient information concerning the partial volumetric behavior of the components of petroleum under the conditions encountered in practice, the petroleum engineer may use these data to compute the volumetric properties of oil and gas mixtures at the temperatures and pressures characteristic of natural petroleum reservoirs. Such information is of great value in estimating the magnitudes of subsurface oil reserves, the relative amounts of the liquid and gas phases which may be present, the size and nature of the surface installations (pumping plants, refineries and other processing plants, storage and distribution facilities) required efficiently to exploit the reserves, and the duration of economic productivity to be anticipated.

In addition to being a function of pressure and temperature, the partial volumetric behavior of a substance depends also upon

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the relative amounts and kinds of other substances present. From this it might be inferred that nothing is gained in actuality by resorting to the complicated subterfuge of analyzing the volumetric properties of mixtures in terms of the partial volumes of the components, since all possible mixtures of substances would have to be experimentally studied before completely reliable information regarding partial volumes could be obtained. Rigorously speaking. this discouraging inference is true. However, from a practical viewpoint, the situation is not so bad. The concept of partial volumes permits, in effect, the quantitative evaluation of the individual contribution of each component to the total volumetric properties of a mixture. By experimentally investigating the volumetric behavior of a finite number of systems comprising representative examples of the various kinds of situations encountered in practice, it is postulated that the mass of data so obtained, if resolved into the partial volumetric behaviors of the components of the systems involved, will permit the development of the general behavior of the individual components so that the volumetric properties of any system composed of these components may be computed with satisfactory accuracy for all states falling within the range of practical interest.

A certain amount of partial volumetric data is already available in the published literature ^{14, 15, 16, 17}, these data being obtained almost entirely from studies of two-component systems. The present investigation, so far as the writer is aware, represents the first reasonably comprehensive volumetric study of a three-component system

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throughout relatively large ranges of pressure and temperature. It is hoped that the results herein presented will materially assist in the extension and improvement of the practical applications of partial volumes to the treatment of multicomponent systems.

To the petroleum refinery technologist the applications of partial volumetric data assume more erudite and complex forms than that which was discussed in connection with production engineering. One of the more important economic factors which must be considered in the development of refinery processes is the efficient use of thermal energy in bringing about the desired physical and chemical changes in the materials handled. It is desirable, therefore, in performing detailed thermodynamic analyses of processes, that the enthalpy change associated with a change in the state of a component be subject to precise calculation. As an illustration of the use of partial volumes to this purpose, a general procedure for computing the enthalpy change associated with the transfer of a component from the liquid phase to the gas phase of a heterogeneous multicomponent system at equilibrium will be demonstrated.

The condition of thermodynamic equilibrium in a heterogeneous system requires that the fugacity of any component of the system be the same in all phases. Thus, for component \propto ,

$$f_{\alpha g} = f_{\alpha l} \tag{8}$$

For an infinitesimal equilibrium change in the state of the system,

$$df_{ag} = df_{ag} \tag{9}$$

Regarding temperature, pressure, and the mole numbers of the components as independent variables, we may express any infinitesimal change in

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the fugacity of a component in an r-component system as follows:

$$\alpha f_{\alpha} = \left(\frac{\partial f_{\alpha}}{\partial T}\right)_{P,m} dT + \left(\frac{\partial f_{\alpha}}{\partial P}\right)_{T,m} dP + \sum_{k=1}^{r} \left(\frac{\partial f_{\alpha}}{\partial m_{k}}\right) dm_{k}$$
(10)

However,

$$\left(\frac{\partial f_{\alpha}}{\partial T}\right)_{P,m} = f_{\alpha} \frac{H_{\alpha}^{*} - H_{\alpha}}{RT^{2}}$$
 (11)

and, by definition

$$\left(\frac{\partial f\alpha}{\partial P}\right)_{T,m} = f\alpha \frac{V_{\alpha}}{RT}$$
 (12)

Moreover, with the restraint on the partial derivatives implied by the subscript m_i , it may be shown that

$$\left(\frac{\partial f_{\alpha}}{\partial m_{k}}\right)_{T, P, m_{i}} = (1 - n_{k}) \left(\frac{\partial f_{\alpha}}{\partial n_{k}}\right)_{T, P, n_{i}} dn_{k}$$
 (13)

Hence, equation (10) becomes

$$df_{\alpha} = \frac{f_{\alpha}}{R\tau^{2}} \left(H^{*} - H_{\alpha} + \tau \overline{V}_{\alpha} \right) + \sum_{k=1}^{\infty} (1 - n_{k}) \left(\frac{\partial f_{\alpha}}{\partial n_{k}} \right) dn_{k}$$
(14)

Substitution of equation (14) into equation (9) with a rearrangement

$$H_{ag} - H_{ae} = T \left(\frac{V_{ag}}{J_{ae}} - \frac{V_{ae}}{J_{ae}} \right) \left[\frac{dP}{dT} \right] + \frac{RT^{2}}{f_{a}} \sum_{k=1}^{r} \left(1 - y_{k} \right) \left(\frac{\partial f_{ag}}{\partial y_{k}} \right) \frac{dy_{k}}{dT} \\ - \frac{RT^{2}}{f_{a}} \sum_{k=1}^{r} \left(1 - \chi_{k} \right) \left(\frac{\partial f_{ae}}{\partial \chi_{k}} \right) \frac{d\chi_{k}}{dT} \\ T, P, y_{i}^{i}$$

$$(15)$$

Equation (15) is a perfectly general expression relating the desired enthalpy change for component α with measurable or calculable quantities, provided the partial volumetric properties of component α are known. We are free to choose in any manner we please the path of equilibrium changes of state along which to evaluate the differential ratios $\frac{dp}{dT}$, $\frac{dy_k}{dT}$, and $\frac{dx_k}{dT}$ in equation (15). It is possible to choose paths which simplify the calculations. For example, suppose we choose a path for changes in the state of the system such that the composition of the liquid phase is fixed. The second summation in equation (15) then vanishes and we are left with

$$H_{ag} - H_{ae} = T \left(\overline{V}_{ag} - \overline{V}_{ae} \right) \left[\frac{dP}{dT} \right]_{x} + \frac{2T^{2}}{f\alpha} \sum_{k=1}^{2} \left(\frac{J}{Sy_{k}} \right) \left(\frac{df_{ag}}{Sy_{k}} \right) \left[\frac{dg_{k}}{dT} \right]_{x} \quad (16)$$

Similarly, we may choose to fix the composition of the gas phase, in which case we have

$$Hag - Hae = T \left(Vag - Vae \right) \left[\frac{dP}{dT} \right]_{y} - \frac{2T^{2}}{fa} \sum_{k=1}^{2} \left(1 - X_{k} \right) \left(\frac{\partial fae}{\partial x_{k}} \right) \left[\frac{dX_{k}}{dT} \right]_{y}$$
(17)

In the case of a one-component system, equation (15) reduces to

$$H_q - He = T \left(V_q - V_e \right) \frac{dP}{dT}$$
 (18)

which is the familiar Clapeyron equation.

In the foregoing discussion it is assumed that the fugacity of component \varkappa is known or can be calculated. A method of computing the fugacity of a substance will be described. The fugacity of a component of a mixture may be considered as defined by the following expression:

$$\mathcal{RT}\left(\frac{\partial \mathcal{L}_{n}f_{\alpha}}{\partial p}\right)_{T,n} = \left(\frac{\partial F_{\alpha}}{\partial p}\right)_{T,n} = \vec{V}_{\alpha}$$
(19)

with the auxiliary condition that in the gaseous state,

$$\lim_{p^{\star} \to 0} \left(\frac{f \alpha^{\star}}{n_{\alpha} p^{\star}} \right) = 1$$
(20)

The integration of equation (19) with respect to pressure at constant temperature yields

$$\operatorname{RT}\ln\frac{f_{x}}{f_{x}^{*}} = \overline{F}_{x} - \overline{F}_{x}^{*} = \int_{p*}^{p} \overline{V}_{x} dp \qquad (21)$$

Between finite, non-zero limits of integration equation (21) is well behaved. However, as the lower limit of integration p* approaches zero, $\frac{1}{f_{\infty}^*}$, -F*, and \overline{V}_{∞} all tend toward infinity. The resolution of this difficulty in equation (21) is accomplished by applying the condition (20) and by transforming the integrand in equation (21) in the following manner. Let the partial residual volume of a component be defined as follows:

$$\overline{V_{\alpha}} = \frac{RI}{p} - \overline{V_{\alpha}}$$
(22)

Both from theoretical considerations (Van der Waals equation and the Beattie - Bridgeman equation of state) and from experimental observations it is known that $\overline{V}_{\mathcal{C}}$ remains finite as the pressure approaches zero. Substitution of equation (22) into equation (21) yields

$$RT \ln \frac{f_{\alpha} p^{*}}{f_{\alpha}^{*} p} = -\int_{p^{*}} \overline{V}_{\alpha} dp \qquad (23)$$

Suppose, now, the lower limit of integration approaches zero. Then, by the condition (20), we have

$$\frac{\mathbf{f}_{\alpha}^{*}}{\mathbf{p}_{\alpha}^{*}} = \mathbf{n}_{\alpha}$$

Hence

$$RT \ln \frac{f_{\alpha}}{n_{\alpha}p} = -\int \frac{V}{V_{\alpha}} dp \qquad (24)$$

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This is the desired relationship which, from a knowledge of the partial volumetric behavior of a substance, permits the fugacity of that substance to be computed.

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Nomenclature

- f fugacity
- G any molal property of a system
- H molal enthalpy
- m mole number
- n mole fraction
- p absolute pressure
- R universal gas constant
- T absolute temperature
- V molal volume
- V residual molal volume
- x molal composition of the liquid phase
- y molal composition of the gas phase

Subscripts & Superscripts

- 1 indicates methane
- 4 indicates n butane
- 10 indicates decane
- a indicates any component
- g indicates the gas phase
- i indicates all components except component k.
- k indicates component k
- ℓ indicates the liquid phase
- * indicates a highly attenuated (low pressure) state at which the perfect gas equation and the laws of ideal mixtures may be assumed to hold to any desired degree of accuracy.

Notes:

A bar under a symbol indicates the total value of an extensive property.

A bar over a symbol indicates the partial molal value of a property.

Subscripts on parentheses designate quantities held constant during partial differentiation.

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=40×

	Mole	Mole	Mole	Average
	Fraction	Fraction	Fraction	Molecular
	Methane	n Butane	Decane	Weight
System	One-compone	ent Systems		
Methane n Butane Decane	1.000	1.000	-	16.042 58.12 142.28
	Two-compone	nt Systems		
a	-	0.1000	0.9000	133.86
b		0.2500	0.7500	121.24
c		0.5000	0.5000	100.20
d		0.7500	0.2500	79.16
e		0.9000	0.1000	66.54
I II IV V	0.1000 0.2500 0.5000 0.7500 0.9000	-	0.9000 0.7500 0.5000 0.2500 0.1000	129.65 110.72 79.16 47.60 28.67
1 2 3 4 5	0.1000 0.2500 0.5000 0.7500 0.9000	0.9000 0.7500 0.5000 0.2500 0.1000	- - -	53.91 47.60 37.08 26.56 20.25
	Three-compo	nent Systems		
a I 3	0.0909	0.0909	0.8182	123.15
a II 4	0.2308	0.0769	0.6923	106.67
a III 5	0.4737	0.0526	0.4737	78.05
b I 2	0.0769	0.2308	0.6923	113.15
b II 3	0.2000	0.2000	0.6000	100.20
b III 4	0.4285	0.1429	0.4286	76.15
b IV 5	0.6923	0.0769	0.2308	48.41
c I l	0.0526	0.4737	0.4737	95.77
c II 2	0.1428	0.4286	0.4286	88.18
c III 3	0.3334	0.3333	0.3333	72.15
c IV 4	0.6000	0.2000	0.2000	49.71
c V 5	0.8182	0.0909	0.0909	31.34
d II 1	0.0769	0.6923	0.2308	74.31
d III 2	0.2000	0.6000	0.2000	66.54
d IV 3	0.4285	0.4286	0.1429	52.11
d V 4	0.6923	0.2308	0.0769	35.46
e III l	0.0909	0.8182	0.0909	61.95
e IV 2	0.2308	0.6923	0.0769	54.88
e V 3	0.4737	0.4737	0.0526	42.62

TABLE II MOLAL VOLUME *

2000 lb./sq.in. abs.

	100°F	160°F	220°F	280°F	3400F	400°F	4600F
System		One-com	ponent Sys	toms			
Methane n Butane Decane	2.561 1.601 3.122	3.029 1.703 3.222	3.464 1.825 3.329	3.874 1.984 3.446	4.270 2.200 3.580	4.650 2.510 3.735	5.022 2.938 3.905
		Two-com	ponent Syst	tems			
a b c d e	2.966 2.735 2.350 1.980 1.757	3.060 2.822 2.441 2.072 1.851	3.162 2.920 2.536 2.176 1.966	3.281 3.040 2.652 2.297 2.105	3.416 3.180 2.800 2.454 2.288	3.570 3.335 2.970 2.650 2.533	3.746 3.511 3.156 2.896 2.850
I II III IV	2.890 2.552 -	2.997 2.659 -	3.102 2.765 -	3.212 2.876 -	3.345 3.017 -	3.497 3.173 -	3.671 3. <u>3</u> 50 -
V	-	-	-	~	-	-	4.665
1 2 3 4 5	1.540 1.458 1.381 1.697 2.190	1.650 1.588 1.624 2.231 2.740	1.787 1.765 2.007 2.800 3.233	1.968 2.037 2.523 3.334 3.686	2.235 2.419 3.116 3.828 4.119	2.640 2.947 3.687 4.286 4.524	3.150 3.535 4.215 4.709 4.911
		Three-co	mponent Sy	ystems			
a I 3 a II 4 a III 5	2.771 2.477	2.867 2.574 -	2.971 2.683 -	3.087 2.802 -	3.217 2.941	3.373 3.100	3.545 3.272
bI2 bII3 bIII4 bIV5	2.588 2.357 1.938	2.677 2.450 -	2.777 2.557 -	2.898 2.682 - -	3.035	3.191 2.985 _	3.363 3.168 -
c I l c II 2 c III 3 c IV 4 c V 5	2.272 2.141 1.868 -	2.362 2.229 1.967	2.461 2.334 2.086	2.577 2.457 2.239 -	2.726 2.605 2.431	2.900 2.792 2.698	3.095 3.016 3.052
d II 1 d III 2 d IV 3 d V 4	1.895 1.766 1.552	1.988 1.862 1.681	2.097 1.980 1.848	2.223 2.125 2.096	2.390 2.324 2.488 -	2.611 2.612 2.942 -	2.894 2.973 3.497 4.372
0 III 1 0 IV 2 0 V 3	1.680 1.573 1.435	1.780 1.684 1.606	1.900 1.833 1.905	2.052 2.035 2.335	2.265 2.320 2.842	2.559 2.702 3.430	2.949 3.238 3.985

* Expressed as cu. ft. / 1b. mole.

	100 ⁰ F	160°F	2200F	2800F	3400F	400°F	460°F
System		One-com	onent Syst	toms			
Methane	1.360	1.585	1.808	2.023	2.233	2.435	2.631
n Butane	1.557	1.637	1.727	1.829	1.947	2.090	2.253
Decáne	3.083	3.169	3.265	3.370	3.482	3.601	3.733
		Two-comp	onent Syst	tems			
a	2.926	3.005	3.096	3.198	3.314	3.437	3.567
b	2.695	2.773	2.854	2.952	3.065	3.191	3.322
c	2.314	2.388	2.471	2.567	2.677	2.796	2.926
d	1.936	2.014	2.101	2.198	2.309	2.431	2.557
e	1.709	1.790	1.876	1.977	2.093	2.224	2.365
I II III IV V	2.850 2.509 1.951	2.932 2.590 2.035 - -	3.028 2.680 2.127 -	3.130 2.780 2.230 -	3.240 2.885 2.350 - 2.096	3.359 2.993 2.483 2.200 2.295	3.476 3.104 2.627 2.405 2.492
1	1.492	1.575	1.669	1.778	1.906	2.055	2.225
2	1.398	1.485	1.591	1.715	1.862	2.032	2.221
3	1.263	1.377	1.517	1.685	1.880	2.095	2.317
4	1.216	1.389	1.591	1.810	2.036	2.260	2.483
5	1.260	1.482	1.708	1.933	2.154	2.370	3.578
		Three-co	omponent Sy	rstems			
a I 3	2.730	2.812	2.902	°3.002	3.112	3.232	3.353
a II 4	2.430	2.515	2.603	2.698	2.807	2.920	3.035
a III 5	1.927	2.009	2.100	2.205	2.319	2.453	2.604
b I 2	2.552	2.627	2.712	2.807	2.917	3.039	3.162
b II 3	2.315	2.396	2.483	2.576	2.683	2.805	2.927
b III 4	1.888	1.972	2.064	2.163	2.276	2.407	2.568
b IV 5	1.451	1.547	1.665	1.806	1.970	2.161	2.392
c I l	2.231	2.311	2.395	2.489	2.598	2.718	2.853
c II 2	2.092	2.176	2.261	2.357	2.466	2.590	2.732
c III 3	1.816	1.898	1.991	2.092	2.207	2.338	2.506
c IV 4	1.460	1.550	1.656	1.780	1.932	2.127	2.371
c V 5	1.274	1.445	1.625	1.824	2.028	2.244	2.463
d II 1	1.849	1.930	2.020	2.120	2.232	2.364	2.498
d III 2	1.716	1.800	1.893	1.998	2.117	2.260	2.413
d IV 3	1.488	1.572	1.678	1.805	1.949	2.113	2.330
d V 4	1.280	1.416	1.568	1.747	1.955	2.173	2.410
0 III 1	1.631	1.714	1.805	1.910	2.031	2.170	2.323
0 IV 2	1.521	1.603	1.700	1.815	1.954	2.111	2.282
0 V 3	1.343	1.441	1.565	1.714	1.883	2.080	2.305

	100°F	160°F	2200F	280°F	3400F	400°F	460°F
System		One-com	ponent Sys	tems			
Methane	1.069	1.202	1.337	1.473	1.610	1.743	1.876
n Butane	1.523	1.590	1.663	1.744	1.830	1.929	2.041
Decane	3.048	3.127	3.214	3.306	3.403	3.507	3.620
		Two-com	ponent Syst	tems			
a	2.894	2.966	3.043	3.134	3.233	3.335	3.447
b	2.663	2.725	2.801	2.890	2.988	3.086	3.193
c	2.279	2.345	2.420	2.504	2.592	2.691	2.785
d	1.900	1.968	2.047	2.132	2.220	2.311	2.404
e	1.675	1.741	1.819	1.902	1.987	2.082	2.182
I	2.813	2.891	2.973	3.061	3.160	3.260	3.365
II	2.470	2.544	2.624	2.710	2.801	2.900	2.998
III	1.916	1.988	2.064	2.147	2.240	2.338	2.444
IV	1.389	1.465	1.550	1.650	1.760	1.876	1.998
V	1.141	1.246	1.363	1.487	1.618	1.751	1.890
1	1.454	1.520	1.600	1.682	1.774	1.872	1.981
2	1.352	1.424	1.505	1.592	1.692	1.797	1.910
3	1.200	1.283	1.375	1.478	1.595	1.720	1.846
4	1.090	1.193	1.310	1.438	1.570	1.708	1.845
5	1.064	1.182	1.311	1.449	1.586	1.724	1.861
		Three-co	mponent Sy	ystems			
a I 3	2.694	2.770	2.848	2.936	3.030	3.127	3.227
a II 4	2.394	2.468	2.548	2.632	2.722	2.817	2.913
a III 5	1.890	1.960	2.040	2.123	2.214	2.312	2.418
b I 2	2.511	2.582	2.656	2.741	2.836	2.933	3.034
b II 3	2.275	2.346	2.425	2.505	2.598	2.694	2.791
b III 4	1.850	1.920	2.000	2.086	2.175	2.274	2.378
b IV 5	1.397	1.469	1.555	1.646	1.750	1.870	2.002
c I l	2.200	2.267	2.340	2.422	2.510	2.607	2.708
c II 2	2.063	2.128	2.202	2.284	2.375	2.469	2.573
c III 3	1.776	1.848	1.924	2.010	2.103	2.200	2.305
c IV 4	1.409	1.480	1.560	1.650	1.750	1.870	2.008
c V 5	1.158	1.256	1.364	1.480	1.609	1.748	1.885
d II 1	1.816	1.882	1.957	2.042	2.130	2.226	2.325
d III 2	1.682	1.744	1.819	1.904	2.000	2.098	2.205
d IV 3	1.435	1.508	1.588	1.678	1.776	1.891	2.017
d V 4	1.198	1.285	1.386	1.495	1.616	1.748	1.885
e III l	1.598	1.663	1.739	1.824	1.914	2.012	2.117
e IV 2	1.480	1.548	1.622	1.709	1.807	1.908	2.021
e V 3	1.282	1.359	1.447	1.543	1.653	1.773	1.901

	100°F	1600F	2200F	280°F	450°F	400°F	460°F
System		One-com	ponent Sys	tems			
Methane	0.943	1.033	1.127	1.223	1.321	1.419	1.517
n Butane	1.497	1.552	1.616	1.683	1.755	1.833	1.918
Decane	3.015	3.091	3.170	3.251	3.336	3.431	3.532
		Two-com	ponent Syst	toms		a	
a	2.861	2.931	3.004	3.081	3.163	3.255	3.360
b	2.631	2.695	2.761	2.837	2.919	3.007	3.106
c	2.250	2.310	2.376	2.452	2.532	2.613	2.695
d	1.872	1.934	2.007	2.075	2.151	2.225	2.307
e	1.649	1.710	1.776	1.843	1.915	1.990	2.076
I	2.784	2.855	2.930	3.011	3.094	3.183	3.278
II	2.442	2.510	2.580	2.657	2.736	2.821	2.910
III	1.886	1.950	2.016	2.088	2.166	2.246	2.330
IV	1.349	1.411	1.482	1.559	1.635	1.720	1.811
V	1.068	1.146	1.228	1.315	1.406	1.498	1.591
1	1.425	1.483	1.547	1.618	1.690	1.767	1.850
2	1.319	1.380	1.447	1.520	1.593	1.675	1.755
3	1.158	1.224	1.298	1.374	1.457	1.543	1.635
4	1.023	1.098	1.183	1.272	1.365	1.460	1.560
5	0.965	1.049	1.140	1.235	1.330	1.430	1.530
		Three-co	omponent Sy	ystems			
a I 3	2.665	2.735	2.805	2.882	2.962	3.052	3.145
a II 4	2.365	2.430	2.501	2.579	2.656	2.738	2.825
a III 5	1.863	1.926	1.991	2.064	2.139	2.217	2.305
b I 2	2.480	2.546	2.616	2.690	2.769	2.853	2.948
b II 3	2.243	2.312	2.383	2.457	2.533	2.613	2.700
b III 4	1.823	1.885	1.952	2.025	2.098	2.180	2.268
b IV 5	1.357	1.417	1.486	1.558	1.637	1.722	1.813
c I l	2.167	2.230	2.298	2.373	2.451	2.534	2.615
c II 2	2.028	2.092	2.163	2.236	2.313	2.396	2.477
c III 3	1.746	1.810	1.877	1.952	2.025	2.106	2.191
c IV 4	1.371	1.432	1.500	1.571	1.649	1.732	1.818
c V 5	1.098	1.170	1.250	1.333	1.420	1.512	1.607
d II 1	1.783	1.846	1.916	1.986	2.062	2.143	2.225
d III 2	1.646	1.710	1.775	1.850	1.927	2.007	2.085
d IV 3	1.401	1.465	1.530	1.610	1.688	1.769	1.848
d V 4	1.148	1.215	1.290	1.372	1.457	1.548	1.640
0 III 1	1.566	1.627	1.695	1.765	1.838	1.917	1.995
0 IV 2	1.444	1.507	1.572	1.645	1.723	1.800	1.878
0 V 3	1.245	1.311	1.381	1.456	1.534	1.619	1.707

10,000 lb./sq.in. abs.

	100°F	160°F	220°F	280°F	340°F	4000F	460°F
System		One-com	ponent Sys	tem			
Methane	0.869	0.936	1.008	1.082	1.158	1.234	1.312
n Butane	1.473	1.523	1.579	1.636	1.696	1.763	1.835
Decane	2.985	3.056	3.127	3.201	3.281	3.368	3.463
		Two-com	ponent Sys	toms			
a	2.833	2.900	2.965	3.040	3.114	3.196	3.287
b	2.603	2.665	2.728	2.796	2.869	2.948	3.032
c	2.223	2.283	2.345	2.410	2.475	2.550	2.625
d	1.848	1.904	1.969	2.034	2.100	2.166	2.234
e	1.624	1.677	1.738	1.803	1.868	1.932	1.996
I	2.756	2.823	2.892	2.966	3.041	3.122	3.200
II	2.415	2.476	2.545	2.615	2.686	2.759	2.827
III	1.856	1.914	1.975	2.041	2.110	2.178	2.241
IV	1.312	1.369	1.424	1.485	1.552	1.627	1.705
V	1.017	1.081	1.147	1.215	1.283	1.355	1.431
1 ·	1.398	1.453	1.506	1.564	1.626	1.691	1.761
2	1.292	1.348	1.405	1.464	1.526	1.588	1.657
3	1.127	1.183	1.245	1.306	1.370	1.439	1.511
4	0.976	1.039	1.104	1.173	1.246	1.318	1.392
5	0.904	0.970	1.040	1.113	1.186	1.260	1.338
		Three-co	omponent Sy	ystems			
a I 3	2.636	2.703	2.772	* 2.840	2.913	2.991	3.073
a II 4	2.341	2.400	2.470	2.539	2.610	2.682	2.752
a III 5	1.832	1.891	1.953	2.019	2.086	2.153	2.218
b I 2	2.458	2.517	2.582	2.651	2.720	2.798	2.878
b II 3	2.225	2.282	2.348	2.417	2.487	2.558	2.632
b III 4	1.792	1.853	1.917	1.983	2.047	2.112	2.181
b IV 5	1.318	1.378	1.437	1.500	1.564	1.634	1.708
c I l	2.144	2.202	2.263	2.326	2.393	2.468	2.547
c II 2	2.008	2.065	2.127	2.190	2.255	2.328	2.405
c III 3	1.718	1.778	1.840	1.902	1.967	2.036	2.107
c IV 4	1.336	1.395	1.450	1.518	1.580	1.648	1.722
c V 5	1.050	1.112	1.177	1.246	1.310	1.381	1.460
d II 1	1.755	1.814	1.877	1.941	2.010	2.077	2.145
d III 2	1.625	1.675	1.737	1.800	1.867	1.933	2.002
d IV 3	1.378	1.430	1.487	1.550	1.613	1.680	1.750
d V 4	1.108	1.168	1.230	1.294	1.359	1.428	1.509
e III 1	1.544	1.593	1.655	1.717	1.780	1.845	1.915
e IV 2	1.422	1.471	1.532	1.592	1.653	1.720	1.790
e V 3	1.220	1.272	1.332	1.395	1.454	1.522	1.600

TABLE III PARTIAL MOLAL VOLUME OF METHANE *

2000 lb./sq.in. abs.

	100°F.	160°F.	220°F.	280°F	3400F	400°F	460°F
System		One-compo	ment Syste)ms	-21		
Methane n Butane Decane	2.561 1.000 0.828	3.029 1.150 0.902	3.464 1.415 1.000	3.874 1.820 1.110	4.270 2.460 1.230	4.650 3.500 1.360	5.022 4.800 1.510
		Two-compo	ment Syste	ms			
a b c d e	0.829 0.830 0.845 0.875 0.875	0.905 0.910 0.932 0.980 1.054	1.003 1.017 1.050 1.129 1.245	1.120 1.147 1.200 1.340 1.560	1.250 1.291 1.378 1.630 2.020	1.392 1.458 1.625 2.063 2.690	1.556 1.652 1.950 2.720 3.645
I II TTT	0.841	0.922 0.971	1.025	1.147 1.239	1.282	1.440 1.628	1.625 1.870
IV	-	-		-	ati		-
A	-	-	-	e5	-	8	-
1 2 3 4 5	1.020 1.080 1.430 2.386 2.550	1.190 1.336 2.105 3.120 3.045	1.500 1.791 3.148 3.627 3.487	2.030 2.710 4.130 4.025 3.887	2.847 3.824 4.697 4.390 4.281	3.982 4.903 5.100 4.750 4.658	5.232 5.625 5.439 5.100 5.030
		Three-con	ponent Sys	toms			
a I 3 a II 4 a III 5	0.839 0.868 -	0.923 0.977	1.022 1.108	1.150 1.274 -	1.300 1.474	1.480 1.732	1.690 2.050 -
bI2 bII3 bIII4 bIV5	0.840 0.876	0.928 0.983 -	1.033 1.141 -	1.159 1.315 -	1.300 1.516 -	1.472 1.764 -	1.700 2.143 -
c I 1 c II 2 c III 3 c IV 4 c V 5	0.850 0.866 0.935	0.942 0.975 1.094 - -	1.068 1.110 1.317	1.223 1.295 1.663	1.405 1.508 2.180	1.680 1.860 2.910	2.079 2.442 3.875 -
d II 1 d III 2 d IV 3 d V 4	0.900 0.945 1.085	1.003 1.070 1.343 -	1.165 1.288 1.860	1.402 1.628 2.500 -	1.740 2.098 3.650 -	2.290 2.900 4.400 -	3.075 3.875 5.298
⊖ III 1 ⊖ IV 2 ⊖ V 3	0.956 1.013 1.272	1.100 1.205 1.674	1.330 1.570 3.000	1.706 2.126 3.707	2.295 3.040 4.600	3.100 4.010 5.200	4.200 5.250 5.525

* Expressed as cu. ft. / 16. mole.

TABLE III (Cont.) PARTIAL MOLAL VOLUME OF METHANE

	100 ⁰ F.	160°F.	220°F	280°F	340°F	400°F.	460°F.
System		One-comp	onent Syst	tems			
Methanə	1.360	1.585	1.808	2.023	2.233	2.435	2.631
n Butanə	0.895	0.995	1.134	1.310	1.511	1.712	1.884
Dəcanə	0.755	0.815	0.887	0.973	1.079	1.143	0.978
		Two-comp	onent Syst	tems			
ය. C d ල	0.768 0.793 0.840 0.870 0.885	0.829 0.856 0.907 0.948 0.973	0.898 0.925 0.982 1.052 1.097	0.989 1.020 1.082 1.185 1.255	1.085 1.110 1.188 1.347 1.450	1.162 1.210 1.337 1.550 1.668	1.085 1.260 1.552 1.800 1.865
I II III IV V	0.775 0.812 0.876 - -	0.840 0.880 0.958 - -	0.912 0.960 1.063 -	1.000 1.058 1.207	1.100 1.170 1.404 - 2.200	1.183 1.300 1.563 2.139 2.403	1.138 1.407 1.880 2.388 2.609
1	0.900	1.002	1.154	1.340	1.570	1.815	2.050
2	0.931	1.050	1.221	1.448	1.721	2.020	2.310
3	1.065	1.249	1.485	1.778	2.076	2.362	2.610
4	1.239	1.500	1.754	1.997	2.230	2.448	2.648
5	1.320	1.567	1.800	2.018	2.235	2.438	2.636
		Three-co	mponent Sj	rstoms			
aI3	0.782	0.848	0.923	1.020	1.121	1.208	1.188
aII4	0.813	0.880	0.965	1.073	1.184	1.300	1.365
aIII5	0.870	0.938	1.035	1.177	1.344	1.540	1.750
b I 2	0.795	0.860	0.935	1.029	1.129	1.242	1.325
b II 3	0.808	0.875	0.958	1.058	1.174	1.322	1.478
b III 4	0.850	0.925	1.032	1.180	1.360	1.580	1.864
b IV 5	1.000	1.205	1.420	1.650	1.895	2.150	2.407
c I l	0.843	0.910	0.988	1.093	1.198	1.352	1.570
c II 2	0.850	0.918	1.000	1.112	1.228	1.392	1.620
c III 3	0.878	0.960	1.067	1.190	1.352	1.564	1.840
c IV 4	0.990	1.134	1.303	1.518	1.782	2.090	2.396
c V 5	1.207	1.470	1.730	1.975	2.215	2.425	2.619
d II 1	0.870	0.949	1.054	1.192	1.362	1.570	1.835
d III 2	0.877	0.960	1.080	1.230	1.415	1.640	1.920
d IV 3	0.938	1.060	1.216	1.420	1.660	1.927	2.210
d V 4	1.134	1.368	1.610	1.875	2.150	2.395	2.596
e III l	0.890	0.981	1.105	1.268	1.470	1.704	1.955
e IV 2	0.922	1.015	1.152	1.335	1.560	1.831	2.144
e V 3	1.003	1.180	1.392	1.636	1.912	2.206	2.493

TABLE III (Cont.) PARTIAL MOLAL VOLUME OF METHANE

6000 lb.sq.in. abs.

	100oF.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	1.069	1.202	1.337	1.473	1.610	1.743	1.876
n Butane	0.827	0.920	1.035	1.152	1.270	1.363	1.426
Decane	0.704	0.760	0.822	0.896	0.968	1.013	0.902
		Two-comp	onent Syst	oms			
a	0.730	0.793	0.861	0.933	1.002	1.048	0.990
b	0.752	0.813	0.880	0.949	1.024	1.095	1.123
c	0.790	0.857	0.925	0.997	1.080	1.172	1.292
d	0.810	0.864	0.932	1.016	1.117	1.231	1.359
e	0.824	0.891	0.970	1.069	1.180	1.307	1.435
I	0.736	0.781	0.842	0.912	0.989	1.051	1.028
II	0.770	0.822	0.885	0.960	1.048	1.138	1.223
III	0.832	0.900	0.980	1.040	1.178	1.307	1.450
IV	0.892	0.988	1.100	1.224	1.368	1.522	1.668
V	1.028	1.162	1.304	1.447	1.586	1.725	1.865
1	0.830	0.928	1.028	1.144	1.272	1.385	1.488
2	0.846	0.941	1.048	1.161	1.310	1.458	1.605
3	0.935	1.044	1.173	1.321	1.478	1.634	1.798
4	1.018	1.146	1.284	1.434	1.580	1.722	1.867
5	1.058	1.188	1.328	1.466	1.603	1.740	1.873
		Three-co	mponent Sy	stems			
a I 3	0.749	0.807	0.871	0.943	1.018	1.080	1.078
a II 4	0.771	0.833	0.906	0.993	1.082	1.160	1.213
a III 5	0.821	0.873	0.956	1.054	1.178	1.310	1.439
bI2	0.759	0.821	0.892	0.968	1.040	1.105	1.153
bII3	0.763	0.830	0.907	0.992	1.087	1.175	1.248
bIII4	0.815	0.867	0.945	1.039	1.153	1.282	1.428
bIV5	0.900	1.000	1.118	1.244	1.385	1.540	1.680
c I l	0.800	0.856	0.920	0.996	1.079	1.179	1.294
c II 2	0.803	0.870	0.939	1.018	1.100	1.198	1.324
c III 3	0.830	0.883	0.970	1.061	1.167	1.288	1.413
c IV 4	0.894	0.981	1.085	1.200	1.337	1.490	1.671
c V 5	1.000	1.130	1.274	1.420	1.564	1.700	1.833
d II 1	0.818	0.856	0.909	0.983	1.088	1.228	1.405
d III 2	0.812	0.872	0.948	1.044	1.159	1.298	1.445
d IV 3	0.850	0.948	1.052	1.172	1.300	1.443	1.608
d V 4	0.965	1.082	1.221	1.368	1.520	1.669	1.818
e III l	0.828	0.883	0.964	1.066	1.189	1.331	1.480
e IV 2	0.859	0.913	0.998	1.107	1.240	1.390	1.546
e V 3	0.900	1.000	1.119	1.254	1.396	1.548	1.772

TABLE III (Cont.) PARTIAL MOLAL VOLUME OF METHANE

	100 ⁰ F.	160°F.	220 ⁰ F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	0.943	1.033	1.126	1.223	1.321	1.419	1.517
n Butanø	0.780	0.861	0.943	1.036	1.114	1.183	1.233
Decane	0.682	0.732	0.791	0.857	0.913	0.938	0.929
		Two-comp	onent Syst	ems			
a	0.700	0.760	0.823	0.889	0.950	0.981	0.930
b	0.721	0.781	0.847	0.911	0.975	1.026	1.030
c	0.741	0.801	0.869	0.936	1.004	1.080	1.162
d	0.747	0.792	0.847	0.911	0.990	1.084	1.190
e	0.751	0.811	0.880	0.962	1.056	1.152	1.240
I	0.714	0.753	0.803	0.870	0.934	0.978	0.936
II	0.740	0.790	0.844	0.907	0.968	1.027	1.079
III	0.791	0.850	0.912	0.979	1.054	1.138	1.227
IV	0.829	0.898	0.978	1.066	1.158	1.250	1.341
V	0.916	1.004	1.099	1.196	1.295	1.392	1.507
1	0.781	0.863	0.944	1.037	1.120	1.198	1.245
2	0.803	0.875	0.951	1.040	1.123	1.219	1.308
3	0.859	0.943	1.033	1.119	1.229	1.331	1.441
4	0.903	0.993	1.095	1.195	1.294	1.400	1.500
5	0.937	1.026	1.120	1.217	1.315	1.417	1.515
		Three-co	mponent Sy	stems			
a I 3	0.720	0.769	0.825	0.889	0.953	1.011	1.016
a II 4	0.738	0.797	0.865	0.935	1.007	1.068	1.095
a III 5	0.780	0.829	0.891	0.968	1.047	1.132	1.215
bI2	0.720	0.784	0.853	0.920	0.986	1.047	1.080
bII3	0.726	0.794	0.863	0.941	1.013	1.082	1.139
bIII4	0.770	0.824	0.884	0.953	1.029	1.112	1.203
bIV5	0.838	0.905	0.988	1.075	1.172	1.270	1.360
c I l	0.759	0.810	0.868	0.932	1.002	1.076	1.152
c II 2	0.760	0.814	0.875	0.939	1.010	1.084	1.170
c III 3	0.778	0.831	0.893	0.968	1.042	1.129	1.221
c IV 4	0.824	0.895	0.972	1.058	1.150	1.245	1.345
c V 5	0.907	0.994	1.083	1.183	1.284	1.383	1.474
d II 1	0.775	0.810	0.859	0.920	0.994	1.083	1.187
d III 2	0.766	0.821	0.888	0.961	1.044	1.137	1.231
d IV 3	0.810	0.880	0.950	1.026	1.109	1.197	1.292
d V 4	0.887	0.968	1.059	1.158	1.262	1.364	1.463
e III l	0.790	0.840	0.900	0.968	1.049	1.141	1.238
e IV 2	0.806	0.857	0.921	0.998	1.080	1.171	1.262
e V 3	0.840	0.913	0.992	1.081	1.179	1.284	1.395
10,000 lb./sq.in.abs.

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	0.869	0.936	1.008	1.082	1.158	1.234	1.312
n Butane	0.740	0.809	0.878	0.943	1.000	1.054	1.098
Decane	0.661	0.710	0.762	0.827	0.886	0.903	0.800
		Two-comp	onent Syst	ems			
a	0.675	0.730	0.790	0.851	0.906	0.935	0.880
b	0.693	0.754	0.815	0.872	0.925	0.966	0.954
c	0.701	0.763	0.822	0.878	0.935	0.987	1.038
d	0.695	0.732	0.783	0.841	0.906	0.976	1.040
e	0.700	0.758	0.816	0.877	0.943	1.008	1.067
I	0.704	0.735	0.782	0.846	0.899	0.925	0.879
II	0.712	0.764	0.818	0.868	0.922	0.970	1.003
III	0.753	0.801	0.856	0.915	0.980	1.043	1.116'
IV	0.782	0.840	0.900	0.961	1.032	1.113	1.198
V	0.847	0.917	0.990	1.065	1.134	1.208	1.282
1	0.739	0.816	0.883	0.952	1.017	1.068	1.117
2	0.773	0.825	0.898	0.960	1.023	1.098	1.160
3	0.805	0.865	0.934	1.010	1.089	1.185	1.252
4	0.839	0.910	0.987	1.060	1.141	1.209	1.285
5	0.865	0.929	1.003	1.077	1.156	1.230	1.308
		Three-co	mponent Sy	atems			
a I 3	0.700	0.747	0.797	0.854	0.912	0.962	0.966
a II 4	0.710	0.762	0.825	0.889	0.946	0.984	0.995
a III 5	0.740	0.783	0.837	0.896	0.960	1.034	1.102
bI2	0.691	0.751	0.814	0.877	0.941	0.994	1.019
bII3	0.696	0.760	0.823	0.887	0.947	0.997	1.029
bIII4	0.733	0.782	0.833	0.894	0.959	1.028	1.102
bIV5	0.790	0.844	0.909	0.977	1.051	1.130	1.200
c/I l	0.709	0.768	0.825	0.885	0.940	0.995	1.055
c II 2	0.719	0.772	0.829	0.888	0.946	1.001	1.060
c III 3	0.736	0.780	0.834	0.892	0.957	1.025	1.096
c IV 4	0.786	0.840	0.901	0.964	1.032	1.105	1.175
c V 5	0.837	0.909	0.978	1.052	1.124	1.200	1.279
d II 1	0.730	0.763	0.807	0.860	0.919	0.986	1.052
d III 2	0.738	0.781	0.832	0.888	0.947	1.007	1.076
d IV 3	0.774	0.835	0.892	0.950	1.008	1.067	1.128
d V 4	0.818	0.884	0.953	1.026	1.103	1.186	1.255
⊖ III l	0.758	0.798	0.847	0.898	0.958	1.020	1.085
⊖ IV 2	0.763	0.811	0.861	0.916	0.977	1.043	1.118
⊖ V 3	0.794	0.852	0.918	0.983	1.054	1.132	1.218

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TABLE IV PARTIAL MOLAL VOLUME OF n BUTANE *

2000 lb./sq.in. abs.

	100°F.	160°F.	220°F	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	toms		,	
Methane n Butane Decane	-1.253 1.601 1.561	0.316 1.703 1.616	1.305 1.825 1.696	2.240 1.984 1.805	2.920 2.200 1.949	3.503 2.510 2.100	4.020 2.938 2.310
		Two-comp	onent Syst	tems			
a b c d e	1.570 1.580 1.592 1.600 1.601	1.630 1.643 1.684 1.702 1.703	1.711 1.730 1.791 1.821 1.823	1.825 1.847 1.910 1.969 1.982	1.970 1.992 2.067 2.150 2.190	2.130 2.172 2.260 2.386 2.478	2.348 2.403 2.513 2.718 2.880
I II III	1.530 1.458	1.610 1.570	1.710	1.820 1.850 -	1.970 2.020	2.120 2.205	2.310 2.400
IV V	-	-	8	-	-		-
1 2 3 4 - 5	1.600 1.584 1.335 -0.346 -1.034	1.698 1.668 1.143 -0.440 -0.100	1.816 1.755 0.865 0.318 0.880	1.959 1.812 0.917 1.297 1.884	2.170 1.950 1.536 2.100 2.600	2.490 2.293 2.272 2.895 3.285	2.919 2.838 2.991 3.535 3.841
		Three-co	mponent Sy	ystems			
a I 3 a II 4 a III 5	1.540 1.478 -	1.622 1.590 -	1.720 1.715 -	1.835 1.861 -	1.978 2.031 -	2.133 2.225	2.330 2.460
bI2 bII3 bIII4 bIV5	1.560 1.532 1.450	1.649 1.622 - -	1.744 1.740 -	1.858 1.880 -	2.000 2.050	2.170 2.265 -	2.390 2.537 - -
c I l c II 2 c III 3 c IV 4 c V 5	1.597 1.600 1.580	1.690 1.685 1.682	1.793 1.795 1.797	1.913 1.928 1.965	2.062 2.103 2.200 -	2.272 2.350 2.505 -	2.573 2.682 2.960
d II 1 d III 2 d IV 3 d V 4	1.600 1.600 1.520	1.700 1.702 1.625	1.825 1.825 1.775	1.970 1.984 1.950	2.170 2.200 2.165 -	2.448 2.510 2.460	2.847 2.938 2.878 -
e III 1 e IV 2 e V`3	1.601 1.597 1.474	1.703 1.695 1.060	1.825 1.820 0.950	1.984 1.980 1.088	2.200 2.160 1.550	2.510 2.470 2.150	2.938 2.915 2.968

* Expressed as cu, ft. / 16, mole.

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	0.500	0.530	0.750	1.130	1.520	1.940	2.390
n Butane	1.557	1.637	1.727	1.828	1.947	2.090	2.253
Decane	1.519	1.569	1.638	1.720	1.819	1.940	2.073
		Two-comp	onent Syst	ems			
a	1.528	1.581	1.652	1.740	1.836	1.956	2.089
b	1.538	1.602	1.678	1.767	1.864	1.980	2.111
c	1.552	1.628	1.713	1.808	1.913	2.030	2.160
d	1.555	1.636	1.726	1.826	1.940	2.072	2.214
e	1.557	1.637	1.727	1.828	1.946	2.088	2.245
I II III IV V	1.520 1.510 1.460 -	1.570 1.570 1.555 - -	1.640 1.650 1.668	1.730 1.750 1.785 - -	1.836 1.868 1.912 1.688	1.970 2.011 2.060 2.020 1.972	2.125 2.188 2.218 2.260 2.315
1	1.555	1.635	1.723	1.826	1.942	2.080	2.242
2	1.553	1.629	1.708	1.804	1.918	2.038	2.188
3	1.460	1.505	1.546	1.594	1.684	1.827	2.021
4	1.147	1.090	1.125	1.240	1.440	1.700	1.988
5	0.728	0.713	0.874	1.163	1.457	1.752	2.046
		Three-co	mponent Sy	stems			
a I 3	1.532	1.585	1.659	1.752	1.858	1.986	2.143
a II 4	1.515	1.585	1.679	1.764	1.884	2.025	2.216
a III 5	1.500	1.585	1.680	1.790	1.920	2.050	2.220
b I 2	1.548	1.610	1.688	1.781	1.890	2.015	2.171
b II 3	1.531	1.612	1.695	1.790	1.908	2.050	2.240
b III 4	1.545	1.620	1.711	1.812	1.940	2.070	2.240
b IV 5	1.440	1.380	1.425	1.559	1.720	1.930	2.160
c I l	1.556	1.631	1.720	1.818	1.930	2.048	2.184
c II 2	1.552	1.635	1.725	1.825	1.938	2.080	2.245
c III 3	1.575	1.652	1.746	1.836	1.980	2.125	2.280
c IV 4	1.535	1.580	1.650	1.735	1.855	2.000	2.200
c V 5	1.238	1.150	1.090	1.175	1.420	1.750	2.166
d II 1	1.557	1.638	1.730	1.830	1.950	2.090	2.250
d III 2	1.567	1.651	1.738	1.842	1.970	2.129	2.260
d IV 3	1.565	1.635	1.740	1.870	2.000	2.120	2.225
d V 4	1.393	1.354	1.388	1.458	1.620	1.800	2.075
e III 1	1.560	1.638	1.727	1.835	1.952	2.093	2.252
e IV 2	1.559	1.638	1.726	1.827	1.948	2.098	2.235
e V 3	1.527	1.568	1.641	1.734	1.834	1.954	2.117

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
Systems		One-comp	onent Syst	oms			
Methane	0.948	0.940	1.030	1.180	1.360	1.562	1.789
n Butane	1.523	1.590	1.663	1.744	1.830	1.928	2.041
Decane	1.482	1.528	1.591	1.660	1.740	1.825	1.924
		Two-comp	onent Syst	ems			
a	1.491	1.542	1.606	1.679	1.758	1.843	1.941
b	1.503	1.561	1.629	1.702	1.783	1.871	1.966
c	1.518	1.584	1.656	1.731	1.815	1.910	2.004
d	1.523	1.590	1.663	1.743	1.829	1.926	2.032
e	1.523	1.590	1.663	1.744	1.830	1.928	2.038
I	1.482	1.530	1.597	1.668	1.750	1.835	1.935
II	1.480	1.535	1.603	1.679	1.762	1.851	1.949
III	1.470	1.538	1.612	1.690	1.777	1.880	1.968
IV	1.427	1.484	1.547	1.620	1.717	1.858	1.978
V	1.298	1.332	1.372	1.461	1.480	1.737	1.914
1	1.523	1.588	1.662	1.742	1.828	1.926	2.037
2	1.520	1.585	1.657	1.735	1.823	1.914	2.012
3	1.464	1.519	1.574	1.634	1.710	1.804	1.895
4	1.303	1.331	1.386	1.447	1.540	1.665	1.784
5	1.115	1.123	1.182	1.292	1.429	1.588	1.754
		Three-co	mponent Sy	stems			
a I 3	1.508	1.548	1.603	• 1.672	1.753	1.848	1.960
a II 4	1.496	1.561	1.630	1.704	1.786	1.882	2.007
a III 5	1.473	1.543	1.620	1.702	1.790	1.883	1.980
bI2	1.518	1.572	1.633	1.705	1.784	1.873	1.973
bII3	1.525	1.580	1.643	1.720	1.808	1.906	2.022
bIII4	1.503	1.570	1.647	1.736	1.828	1.932	2.042
bIV5	1.474	1.519	1.580	1.662	1.768	1.898	2.040
c I l	1.515	1.587	1.668	1.755	1.841	1.930	2.016
c II 2	1.531	1.595	1.667	1.748	1.833	1.930	2.034
c III 3	1.535	1.601	1.676	1.758	1.850	1.948	2.052
c IV 4	1.508	1.559	1.626	1.709	1.810	1.923	2.046
c V 5	1.363	1.397	1.447	1.515	1.607	1.733	1.900
d II 1	1.527	1.599	1.676	1.760	1.846	1.940	2.039
d III 2	1.540	1.597	1.671	1.753	1.847	1.945	2.051
d IV 3	1.540	1.594	1.662	1.750	1.851	1.948	2.035
d V 4	1.440	1.479	1.528	1.589	1.669	1.766	1.896
⊖ III 1	1.528	1.595	1.670	1.751	1.836	1.934	2.045
⊖ IV 2	1.530	1.594	1.670	1.750	1.842	1.938	2.035
⊖ V 3	1.504	1.552	1.614	1.689	1.773	1.865	1.958

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
Systems	2	One-comp	onent Syst	oms			
Methane	1.161	1.156	1.224	1.316	1.422	1.533	1.636
n Butane	1.497	1.552	1.616	1.683	1.755	1.833	1.918
Decane	1.450	1.494	1.548	1.608	1.675	1.744	1.824
		Two-comp	onent Syst	ems			
a	1.460	1.509	1.565	1.626	1.694	1.764	1.845
b	1.475	1.529	1.588	1.651	1.720	1.793	1.875
c	1.491	1.548	1.611	1.677	1.749	1.826	1.910
d	1.497	1.552	1.616	1.683	1.755	1.833	1.918
e	1.497	1.552	1.616	1.683	1.755	1.833	1.918
I	1.466	1.507	1.558	1.613	1.668	1.753	1.842
II	1.482	1.522	1.570	1.621	1.688	1.768	1.865
III	1.500	1.535	1.578	1.626	1.691	1.778	1.882
IV	1.476	1.508	1.547	1.595	1.660	1.741	1.850
V	1.390	1.413	1.450	1.500	1.571	1.660	1.773
1	1.496	1.551	1.614	1.682	1.753	1.830	1.916
2	1.490	1.548	1.611	1.681	1.751	1.826	1.903
3	1.452	1.505	1.562	1.622	1.684	1.755	1.828
4	1.378	1.415	1.447	1.502	1.576	1.640	1.732
5	1.220	1.260	1.320	1.397	1.470	1.562	1.658
		Three-co	mponent Sy	stems			
a I 3	1.489	1.525	1.569	1.623	1.689	1.764	1.848
a II 4	1.475	1.532	1.593	1.655	1.721	1.791	1.873
a III 5	1.455	1.517	1.582	1.650	1.721	1.793	1.868
bI2	1.489	1.537	1.592	1.650	1.716	1.792	1.875
bII3	1.488	1.539	1.596	1.660	1.733	1.817	1.913
bIII4	1.472	1.537	1.600	1.676	1.755	1.837	1.921
bIV5	1.467	1.512	1.568	1.634	1.705	1.782	1.860
c I 1	1.491	1.553	1.624	1.696	1.772	1.843	1.910
c II 2	1.504	1.561	1.624	1.690	1.765	1.845	1.928
c III 3	1.505	1.562	1.627	1.698	1.775	1.856	1.937
c IV 4	1.486	1.537	1.598	1.667	1.748	1.840	1.925
c V 5	1.400	1.441	1.491	1.550	1.623	1.707	1.806
d II 1	1.500	1.563	1.632	1.702	1.773	1.845	1.917
d III 2	1.513	1.566	1.626	1.695	1.769	1.850	1.932
d IV 3	1.502	1.554	1.616	1.690	1.770	1.851	1.923
d V 4	1.448	1.494	1.546	1.604	1.672	1.747	1.825
0 III 1	1.498	1.557	1.623	1.691	1.763	1.838	1.919
0 IV 2	1.500	1.559	1.623	1.691	1.762	1.836	1.912
0 V 3	1.478	1.528	1.590	1.657	1.729	1.803	1.876

10,000 lb./sq.in.abs.

	100°F.	160°F.	2200F.	280°F.	340°F.	400°F.	460°F.
Systems		One-comp	onent Syst	ems			
Methane	1.202	1.231	1.297	1.365	1.441	1.517	1.572
n Butane	1.473	1.523	1.579	1.636	1.696	1.763	1.835
Decane	1.423	1.464	1.510	1.564	1.619	1.679	1.748
		Two-comp	onent Syst	oms			
a	1.435	1.480	1.528	1.585	1.643	1.703	1.772
b	1.451	1.501	1.552	1.612	1.670	1.733	1.801
c	1.467	1.520	1.575	1.634	1.693	1.759	1.829
d	1.472	1.523	1.579	1.636	1.696	1.763	1.835
e	1.473	1.523	1.579	1.636	1.696	1.763	1.835
I II IV V	1.432 1.449 1.461 1.427 1.332	1.476 1.495 1.514 1.481 1.373	1.528 1.550 1.574 1.540 1.436	1.583 1.610 1.633 1.600 1.500	1.638 1.662 1.687 1.653 1.562	1.699 1.724 1.746 1.712 1.623	1.767 1.790 1.806 1.769 1.678
1	1.475	1.523	1.575	1.635	1.693	1.760	1.832
2	1.470	1.522	1.573	1.632	1.692	1.757	1.823
3	1.442	1.500	1.541	1.593	1.650	1.708	1.769
4	1.400	1.427	1.463	1.513	1.575	1.640	1.710
5	1.255	1.327	1.380	1.430	1.491	1.544	1.605
		Three-co	mponent Sy	stems			
a I 3	1.473	1.506	1.548	1.596	1.654	1.721	1.797
a II 4	1.460	1.512	1.566	1.622	1.683	1.748	1.823
a III 5	1.440	1.495	1.553	1.613	1.677	1.742	1.810
b I 2	1.465	1.507	1.555	1.611	1.671	1.739	1.818
b II 3	1.460	1.506	1.558	1.613	1.679	1.750	1.831
b III 4	1.448	1.508	1.569	1.635	1.700	1.770	1.838
b IV 5	1.452	1.495	1.548	1.603	1.662	1.727	1.788
c I l	1.470	1.524	1.582	1.646	1.713	1.775	1.834
c II 2	1.476	1.525	1.580	1.639	1.703	1.769	1.838
c III 3	1.475	1.525	1.580	1.639	1.705	1.774	1.846
c IV 4	1.465	1.512	1.565	1.626	1.691	1.759	1.825
c V 5	1.405	1.449	1.502	1.557	1.621	1.691	1.772
d II 1	1.471	1.528	1.589	1.654	1.719	1.783	1.844
d III 2 .	1.489	1.538	1.593	1.653	1.720	1.787	1.852
d IV 3	1.478	1.522	1.577	1.640	1.712	1.783	1.847
d V 4	1.434	1.476	1.524	1.576	1.635	1.697	1.763
e III l	1.473	1.527	1.587	1.648	1.708	1.770	1.840
e IV 2	1.473	1.526	1.583	1.642	1.704	1.769	1.834
e V 3	1.459	1.507	1.562	1.624	1.687	1.744	1.798

2000 lb./sq.in. abs.

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		On⊖-comj	ponent Sys	tems			
Methane n Butane Decane	-10.5 3.267 3.122	-9.00 3.272 3.222	-6.00 3.272 3.329	-3.00 3.224 3.446	-0.40 3.005 3.580	0.65 2.345 3.735	1.45 1.407 3.905
		Two-com	ponent Sys	toms			
a b c d e	3.122 3.120 3.110 3.075 3.124	3.222 3.218 3.190 3.158 3.187	3.328 3.322 3.288 3.240 3.231	3.444 3.438 3.402 3.318 3.248	3.576 3.568 3.535 3.384 3.173	3.730 3.721 3.670 3.448 2.945	3.900 3.898 3.795 3.420 2.590
I II III IV V	3.121 3.120 - -	3.221 3.220 - -	3.327 3.320 - -	3.441 3.431 - -	3.570 3.552 -	3.713 3.680 - -	3.875 3.812 -
1 2 3 4 5	3.160 2.940 2.220 - -	3.150 2.750 0.825 - -	3.020 2.380 -0.160 -	2.720 1.665 -2.102 -	2.180 0.544 -1.930 - -	1.250 -0.830 -1.090 -	-0.400 -2.000 0.600 -
		Three-co	omponent S	ystems			
a I 3 a II 4 a III 5	3.118 3.113 -	3.220 3.210 -	3.327 3.310	3.438 3.413	3.569 3.532 -	3.725 3.671 -	3.900 3.770
bI2 bII3 bIII4 bIV5	3.115 3.107 3.073	3.221 3.203 -	3.311 3.303 -	3.429 3.425 -	3.563 3.540 -	3.707 3.646 -	3.867 3.728 -
c I l c II 2 c III 3 c IV 4 c V 5	3.107 3.092 3.048	3.190 3.177 3.128	3.290 3.270 3.150	3.398 3.372 3.120	3.510 3.480 3.040 -	3.630 3.550 2.850	3.757 3.540 2.430
d II 1 d III 2 d IV 3 d V 4	3.078 3.053 2.850 -	3.140 3.092 2.640	3.208 3.093 2.165 -	3.260 3.020 1.400	3.278 2.882 0.350	3.240 2.625 0.250	3.069 2.151 -0.456
e III 1 e IV 2 e V 3	3.090 2.983 2.513	3.125 2.915 1.750	3.110 2.710 0.460	3.012 2.330 -1.210	2.789 1.760 -1.350	2.380 0.900 -1.000	1.800 -0.400 0.000

* Expressed as cu. ft. / 16. mole.

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	-1.100	-0.260	0.120	0.300	0.510	0.930	1.490
n Butane	3.147	3.217	3.297	3.380	3.429	3.409	3.308
Decane	3.083	3.168	3.265	3.370	3.482	3.601	3.734
		Two-comp	onent Syst	ems			
a b c d	3.083 3.081 3.069 3.045 3.079	3.168 3.163 3.143 3.121 3.158	3.264 3.253 3.230 3.211 3.240	3.368 3.360 3.322 3.300 3.322	3.479 3.470 3.431 3.388 3.398	3.600 3.592 3.558 3.480 3.435	3.733 3.730 3.697 3.576 3.420
I II III IV V	3.078 3.077 3.024	3.168 3.157 3.109 - -	3.261 3.255 3.180 - -	3.368 3.360 3.251 - -	3.480 3.466 3.310 1.150	3.598 3.570 3.362 2.386 1.382	3.723 3.666 3.372 2.456 1.876
1	3.102	3.160	3.242	3.319	3.360	3.350	3.250
2	3.000	3.021	3.038	3.043	3.040	3.024	3.000
3	2.600	2.500	2.338	2.062	1.691	1.473	1.898
4	1.840	1.450	0.874	0.538	0.627	0.996	1.400
5	0.870	0.552	0.350	0.300	0.500	0.910	1.400
		Three-co	mponent Sy	stoms			
a I 3	3.080	3.163	3.260	3.367	3.476	3.592	3.718
a II 4	3.082	3.164	3.260	3.357	3.459	3.560	3.663
a III 5	3.042	3.120	3.197	3.277	3.357	3.419	3.403
bI2	3.078	3.158	3.250	3•348	3.468	3.592	3.732
bII3	3.071	3.156	3.260	3•358	3.468	3.568	3.646
bIII4	3.049	3.122	3.197	3•273	3.352	3.430	3.431
bIV5	2.750	2.597	2.469	2•374	2.321	2.325	2.400
c I l	3.064	3.136	3.220	3.318	3.420	3.544	3.668
c II 2	3.062	3.137	3.211	3.306	3.394	3.493	3.608
c III 3	3.041	3.112	3.182	3.251	3.308	3.348	3.357
c IV 4	2.815	2.771	2.700	2.591	2.450	2.360	2.468
c V 5	1.783	1.520	1.290	1.109	1.027	1.100	1.570
d II 1	3.054	3.120	3.195	3.288	3.380	3.463	3.532
d III 2	3.042	3.090	3.142	3.202	3.260	3.319	3.371
d IV 3	2.908	2.921	2.911	2.851	2.750	2.701	2.768
d V 4	2.274	2.028	1.677	1.300	1.150	1.329	1.740
e III 1	3.067	3.130	3.207	3.290	3.359	3.390	3.365
e IV 2	3.018	3.051	3.082	3.113	3.132	3.150	3.152
e V 3	2.783	2.696	2.576	2.418	2.217	2.048	2.270

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			
Methane	1.500	1.342	1.325	1.400	1.537	1.738	1.965
n Butane	3.086	3.178	3.278	3.382	3.477	3.534	3.499
Decane	3.048	3.127	3.214	3.306	3.403	3.507	3.620
		Two-comp	onent Syst	oms			
a	3.046	3.125	3.207	3.301	3.398	3.503	3.617
b	3.043	3.121	3.197	3.290	3.386	3.492	3.610
c	3.032	3.102	3.176	3.259	3.354	3.461	3.577
d	3.007	3.084	3.163	3.252	3.344	3.426	3.515
e	3.033	3.117	3.204	3.297	3.388	3.454	3.477
I	3.044	3.124	3.209	3.304	3.400	3.504	3.615
II	3.038	3.118	3.203	3.297	3.396	3.493	3.582
III	2.998	3.075	3.152	3.232	3.310	3.383	3.442
IV	2.925	2.919	2.919	2.923	2.935	2.950	2.973
V	2.165	1.996	1.900	1.870	1.908	1.987	2.113
1	3.050	3.131	3.219	3.308	3.394	3.450	3.444
2	2.980	3.029	2.981	3.138	3.195,	3.258	3.321
3	2.768	2.712	2.657	2.622	2.628	2.685	2.819
4	2.282	2.151	2.050	2.009	2.030	2.098	2.200
5	1.845	1.692	1.629	1.640	1.711	1.842	2.023
		Three-co	mponent Sy	stoms			
a I 3	3.043	3.124	3.207	3.295	3•393	3.498	3.607
a II 4	3.040	3.118	3.201	3.289	3•382	3.476	3.571
a III 5	3.007	3.081	3.159	3.243	3•328	3.401	3.448
bI2	2.043	3.116	3.195	3.287	3.382	3.486	3.600
bII3	3.032	3.110	3.191	3.282	3.378	3.473	3.560
bIII4	3.022	3.092	3.169	3.244	3.325	3.397	3.447
bIV5	2.865	2.863	2.866	2.871	2.880	2.895	2.917
c I l	3.035	3.100	3.178	3.263	3.358	3.460	3.563
c II 2	3.027	3.092	3.168	3.251	3.341	3.435	3.534
c III 3	3.000	3.070	3.150	3.223	3.295	3.361	3.425
c IV 4	2.868	2.885	2.903	2.925	2.950	2.980	3.013
c V 5	2.442	2.290	2.181	2.124	2.128	2.190	2.298
d II 1	3.012	3.083	3.166	3.252	3.344	3.428	3.506
d III 2	3.010	3.066	3.130	3.203	3.284	3.366	3.444
d IV 3	2.931	2.960	2.995	3.035	3.081	3.128	3.179
d V 4	2.608	2.543	2.461	2.373	2.335	2.405	2.543
0 III 1	3.028	3.087	3.155	3.237	3.323	3.410	3.478
0 IV 2	3.002	3.055	3.112	3.173	3.239	3.300	3.358
0 V 3	2.825	2.838	2.832	2.820	2.815	2.860	2.993

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	;ems			
Methane	1.947	1.879	1.860	1.878	1.922	2.000	2.093
n Butane	3.066	3.159	3.260	3.362	3.454	3.509	3.499
Decane	3.015	3.091	3.170	3.251	3.336	3.431	3.532
		Two-comp	onent Syst	ems			
a	3.013	3.088	3.166	3.245	3.328	3.427	3.528
b	3.010	3.082	3.154	3.233	3.315	3.415	3.518
c	3.000	3.062	3.131	3.203	3.292	3.386	3.488
d.	2.976	3.048	3.125	3.208	3.288	3.373	3.456
e	2.998	3.081	3.169	3.265	3.349	3.415	3.460
I	3.013	3.090	3.169	3.251	3.335	3.428	3.529
II	3.008	3.080	3.160	3.245	3.333	3.423	3.506
III	2.978	3.047	3.121	3.197	3.276	3.354	3.427
IV	2.902	2.944	2.989	3.035	3.088	3.147	3.207
V	2.436	2.388	2.370	2.378	2.400	2.440	2.497
1	3.019	3.101	3.190	3.293	3.389	3.461	3.470
2	2.948	3.008	3.073	3.157	3.245	3.325	3.378
3	2.810	2.819	2.832	2.851	2.876	2.918	2.970
4	2.535	2.495	2.469	2.453	2.448	2.454	2.473
5	2.228	2.171	2.147	2.143	2.159	2.184	2.228
	*	Three-co	mponent Sy	stems			
a I 3	3.018	3.087	3.161	3.241	3.328	3.422	3.518
a II 4	3.010	3.085	3.160	3.240	3.323	3.407	3.493
a III 5	2.988	3.061	3.134	3.213	3.296	3.374	3.440
b I 2	3.016	3.081	3.153	3.233	3.322	3.415	3.516
b II 3	3.005	3.076	3.152	3.234	3.320	3.406	3.492
b III 4	2.994	3.063	3.136	3.214	3.294	3.365	3.425
b IV 5	2.895	2.918	2.950	2.989	3.037	3.092	3.162
c I l	3.009	3.069	3.136	3.211	3.298	3.391	3.490
c II 2	3.002	3.065	3.135	3.212	3.292	3.377	3.471
c III 3	2.967	3.039	3.113	3.189	3.267	3.350	3.432
c IV 4	2.903	2.941	2.978	3.017	3.060	3.103	3.148
c V 5	2.630	2.560	2.518	2.502	2.511	2.548	2.603
d II 1	2.980	3.052	3.128	3.212	3.298	3.379	3.448
d III 2	2.985	3.049	3.116	3.191	3.270	3.350	3.433
d IV 3	2.917	2.977	3.037	3.097	3.158	3.214	3.267
d V 4	2.744	2.711	2.693	2.687	2.696	2.725	2.783
e III 1	3.000	3.063	3.135	3.213	3.296	3.382	3.464
e IV 2	2.970	3.034	3.105	3.183	3.269	3.352	3.405
e V 3	2.863	2.877	2.892	2.923	2.972	3.058	3.186

10,000 lb./sq.in. abs.

	100°F.	160°F.	220°F.	280°F.	340°F.	400°F.	460°F.
System		One-comp	onent Syst	ems			36
Methane	2.216	2.189	2.173	2.175	2.194	2.229	2.298
n Butane	3.052	3.142	3.244	3.348	3.433	3.486	3.489
Decane	2.985	3.056	3.127	3.201	3.281	3.368	3.463
		Two-comp	onent Syst	ems			
a	2.984	3.054	3.125	3.198	3.276	3.363	3.459
b	2.980	3.050	3.116	3.190	3.265	3.348	3.446
c	2.968	3.027	3.094	3.165	3.241	3.320	3.418
d	2.945	3.013	3.087	3.165	3.247	3.329	3.409
e	2.966	3.050	3.136	3.234	3.318	3.392	3.442
I	2.983	3.054	3.125	3.202	3.282	3.366	3.458
II	2.978	3.045	3.120	3.195	3.275	3.352	3.434
III	2.956	3.020	3.093	3.166	3.238	3.312	3.383
IV	2.882	2.950	3.016	3.079	3.139	3.195	3.246
V	2.563	2.551	2.550	2.561	2.600	2.668	2.778
1	2.992	3.082	3.179	3.271	3.359	3.420	3.452
2	2.940	3.004	3.072	3.146	3.221	3.298	3.371
3	2.887	2.878	2.872	2.881	2.917	3.009	3.148
4	2.649	2.616	2.584	2.569	2.566	2.605	2.750
5	2.409	2.382	2.361	2.349	2.341	2.368	2.470
		Three-co	mponent Sy	stoms			
a I 3	2.992	3.055	3.125	3.198	3.276	3.359	3.448
a II 4	2.983	3.050	3.120	3.195	3.272	3.355	3.438
a III 5	2.965	3.035	3.107	3.180	3.256	3.324	3.382
bI2	2.987	3.047	3.114	3.188	3.268	3.355	3.447
bII3	2.987	3.050	3.117	3.190	3.269	3.351	3.430
bIII4	2.961	3.030	3.101	3.178	3.255	3.325	3.385
bIV5	2.906	2.941	2.982	3.030	3.089	3.155	3.230
c I l	2.986	3.043	3.103	3.173	3.248	3.332	3.421
c II 2	2.988	3.040	3.103	3.172	3.248	3.330	3.418
c III 3	2.945	3.015	3.087	3.162	3.239	3.317	3.399
c IV 4	2.875	2.930	2.990	3.053	3.119	3.187	3.254
c V 5	2.698	2.670	2.660	2.670	2.700	2.742	2.802
d II 1	2.953	3.023	3.096	3.176	3.258	3.335	3.406
d III 2	2.966	3.024	3.088	3.159	3.234	3.314	3.398
d IV 3	2.889	2.961	3.033	3.103	3.171	3.227	3.273
d V 4	2.840	2.833	2.835	2.848	2.873	2.911	2.963
e III l	2.978	3.043	3.115	3.191	3.277	3.359	3.429
e IV 2	2.948	3.011	3.078	3.150	3.231	3.312	3.383
e V 3	2.892	2.908	2.928	2.961	3.019	3.110	3.243

Appendix

Evaluation of Partial Molal Volumes by the Method of Tangent

The defining expression for the partial molal value of a property may be developed into a form which lends itself to a simple geometrical interpretation and provides a convenient graphical mode of evaluating partial molal volumes. The procedure is as

follows: $\overline{G}_{k} = \left(\frac{\partial G}{\partial m_{k}}\right)_{p,T,m_{i}}$ = (JmG) $= G + m \left(\frac{\partial G}{\partial m_k} \right)$ $= G + m \left(\frac{\partial G}{\partial n_k} \right)_{T.P.M.} ($ $= G + (I - n_k) \left(\frac{\partial G}{\partial n_k} \right)_{T_1}$

The geometrical interpretation of this last expression is illustrated in Figure 20 in which G is taken to be the molal volume of the system. Let the curve ABC represent the isothermal, isobaric molal volume as a function of the mole fraction of component k with the restriction that the relative mole ratios of all the components except component k are fixed. Let the straight line EBD represent the tangent to the curve at point B. Then point D, the intercept of the tangent with the ordinate corresponding to a mole fraction of unity for component k,



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represents the partial molal volume of component k at the state represented by point B on the curve. An elementary application of analytical geometry suffices to demonstrate that volumetric value represented by point D satisfies the requirements of equation (25).

In the case of a two-component system it is easily shown from considerations of symmetry that point E of the diagram in Figure 20 represents the partial molal volume of the second component of the system.

Figure 21 shows how the method of intercepts may be applied to indicate simultaneously the partial molal volumes of all three of the components of a three-component system. In this Figure the curved surface ABC represents the isothermal. isobaric molal volume as a function of the composition of the system. The plane surface DEF is tangent to the curved surface at point P. The intercepts D, E, and F of the tangent plane with the indicated coordinate lines represent the partial molal volumes of methane, n butane, and decane, respectively. It is apparent from a consideration of Figure 21 why the kind of pattern used in distributing the interpolated threecomponent mixtures shown in Figure 3 was chosen. The lines radiating from the corners of the triangular composition diagram represent variations in the composition of the system which exactly satisfy the restraints with respect to composition imposed by the definition of partial molal volumes, i.e., fixed mole ratios among all components of the system with the exception of one component.

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