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ON THE COMPUTATION OF THERMO-PHYSICAL PROPERTIES OF HYDROCARBON FUELS IN A HIGH PRESSURE OXIDIZING ENVIRONMENT

By

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ABSTRACT

Two methods have been presented for the evaluation of the composition of the different phases of hydrocarbon fuel-oxidizer system. The first method, assuming the vapor phase to consist of oxidizer only, gives the composition of the liquid phase. In the second method, a realistic approach that the liquid and vapor phases consist of the oxidizer and fuel both, a representation of the actual situation encountered in the combustion of the fuel droplet, has been adopted. The liquid and vapor phase compositions have been predicted and compared with experimental results for a number of systems. This technique is particularly useful for the systems for which no data other than the temperature and total pressure is available. The method for the evaluation of the interaction coefficient between the components of the system has also been presented.

NOMENCLATURE

A	=	Parameter of R-K equation.
a	=	Parameter of R-K equation.
a_i	=	Activity of component 'i'.
B	=	Parameter of R-K equation.
b	=	Parameter of R-K equation.
ΔE	=	Isothermal change in energy.
ΔF	=	Molar change in free energy.
$\Delta \bar{F}$	=	Partial molar change in free energy.
f	=	Fugacity of pure component.
$\hat{f}_i^L$	=	Fugacity of component 'i' in liquid phase.
$\hat{f}_i^V$	=	Fugacity of component 'i' in vapor phase.
ΔH	=	Change in enthalpy.
K_{ij}	=	The i-j interaction constant.
P	=	Pressure.
P_c	=	Critical pressure.
P_R	=	Reduced pressure.
P_v	=	Vapor pressure.
P_v^*	=	Corrected vapor pressure.
R	=	Gas constant.
T	=	Temperature.
T_c	=	Critical temperature.
T_R	=	Reduced temperature.
V	=	Molar volume.
$\bar{V}$	=	Partial molar volume.

NOMENCLATURE (CONTD.)

V_c = Critical volume.

V_R = Reduced volume.

x_i = Mole fraction of component 'i' in the liquid phase.

y_i = Mole fraction of component 'i' in the vapor phase.

z = Compressibility factor.

SUBSCRIPT

i = Component 'i'.

j = Component 'j'.

K = Component 'K'.

L = Liquid.

M = Mixture.

V = Vapor.

GREEK LETTERS

γ = Activity coefficient.

δ = Solubility parameter.

π = Isometric mixing pressure.

ω = Accentric factor.

Ω_a = Constant of R-K equation.

Ω_b = Constant of R-K equation.

Φ = Fugacity coefficient of pure component.

$\hat{\Phi}_i^L$ = Fugacity coefficient of component 'i' in the liquid phase.

$\hat{\Phi}_i^V$ = Fugacity coefficient of component 'i' in the vapor phase.

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I. INTRODUCTION

Many of the physical properties of hydrocarbon fuels such as the vapor pressure, heat of vaporization, specific heat, surface tension, etc. may change at high pressures in an oxidising atmosphere. There is very little knowledge as to what extent these properties change; especially in a high pressure environment. Furthermore, to what extent these property changes may influence the atomization, evaporation and combustion of hydrocarbon fuels in high pressure combustor is not at all clear.

The rates of vaporization of fuels are determined from the model theories of vaporization which make use of these properties. The heating up time of a fuel droplet in a combustor is a function of the specific heat of the fuel which further depends on the composition of the liquid phase. The atomization of the fuel also in a way involves the knowledge of liquid phase composition, since it depends on the surface tension of the fuel droplet. The rate of diffusion of the fuel vapor into the oxidiser is dependent upon the composition of the vapor immediately surrounding the droplet. In addition, the rate of evaporation is a function of the latent heat of vaporization which also may be a function of the liquid phase composition. In other words, the vapor-liquid equilibrium of the fuels (usually hydrocarbons) at high pressures in the presence of an oxidiser must be known.

It is worth noting that equilibrium may only be attained at the droplet surface and that there will be composition gradients throughout the droplet. However, in the evaporation and combustion study of fuels, the area of interest is mainly the surface of the droplet and, therefore, the knowledge of equilibrium compositions near the surface is vital.

There are many ways to study the vapour-liquid equilibrium. The most common and simple approach is to study the vapour liquid equilibrium behaviour in the laboratory with the help of some suitable equilibrium stills. The data thus obtained is of great significance in a number of chemical engineering operations, but, as is evident, resorting to laboratory experiments for the entire range of the composition is a difficult and time consuming process. Moreover, the mixtures of hydrocarbon fuels and oxidisers at high pressures are explosive and thus dangerous for the laboratory work. Thus, the development of short cut methods for the estimation of vapor-liquid equilibrium becomes essential. Methods which need none or very little experimental data to give the vapor-liquid equilibrium data are termed as the prediction or correlation methods. A considerable amount of work has been done in this field, but still the search of a foolproof method is on, so as to give results close to the experimental data.

In the present study, an extensive literature survey of correlation and prediction techniques used for vapor-liquid equilibrium calculations has been made. It may be pointed out that, whereas the domain of chemical engineering concerns itself mainly with the development of correlation and prediction techniques, mechanical engineering utilizes these techniques to study the changes in some of the physical properties. Thus, this survey has been made with a view to find the best techniques available and to utilize these, in particular, for the study of combustion. Normal octane and oxygen system is considered as the main example system and the problem of prediction of vapor-liquid equilibria has been approached in two ways. Firstly it is assumed that at equilibrium the vapor phase entirely consists of the oxidiser and the liquid phase consists of both the fuel and the oxidiser. In other words, the calculations are made only for the solubility of the gas in the solvent. The second approach gives the complete compositions of both the liquid and vapor phases of the mixture at the given temperature and total pressure of the mixture.

2. LITERATURE SURVEY

The literature on vapor-liquid equilibrium is quite voluminous and is beyond the scope of this review. However, an attempt has been made to provide a critical review of the prediction and correlation techniques for binary and multicomponent systems. The survey is divided into four sections.

1. Binary Systems a) Utilization of pure component properties.
   b) Utilization of mixture and pure component properties.
2. Multicomponent Systems.
3. Hydrocarbon Systems - Binary and Multicomponent Systems.
4. Solubility of gases in different solvents.

The main emphasis in this survey, in general, is on the correlation and prediction of vapor-liquid data for general binary systems and in particular for binary hydrocarbon systems (non-polar) at high pressures.

2.1 BINARY SYSTEMS

2.1.1. UTILIZATION OF PURE COMPONENT PROPERTIES

Vapor-liquid equilibria have been predicted using pure component properties based on molecular structure and also from those based on regular solution theory. Pierotti, Deal and Derr[1] have considered molecular structure as a basis for making quantitative estimates of activities in

mixtures of non-electrolytes. The Pierotti correlation deals directly with the limiting activity coefficients. The coefficients in this correlation refer to pure liquid solute as a standard reference i.e. with net differences between interaction of solute groups with the standard state environment made up of like molecules and the solvent environment made up of generally unlike molecules. As a result, the relation between activity coefficients in a given family of solution is somewhat complicated by a change from one solute to another in a standard state environment, even though the solvent environment in question remains fixed. Deal, Derr and Papadopoulos[2] suggest that this complication can be avoided by dealing with any suitable solvent environment as a reference state- that is, by dealing with the ratios of solute activity coefficients in one fixed environment to that in a second fixed environment.

The schemes of Pierotti, Deal and Derr and of Deal, Derr and Papadopoulos suggest that in any solvent environment the partial molal excess free energy of solutions of a solute molecule can be taken as the sum of the individual contribution from each of its structural groupings and that those contributions depend to some extent upon the numbers and kinds of structural groupings which make up the environment. Redlich, Derr and Pierotti[3]

and Papadopoulos and Derr[4] have taken a similar approach and developed a detailed 'group' interaction model for heat of solution which correlates heats of solution for hydrocarbon mixtures quite satisfactorily and which may prove useful in polar systems.

Wilson and Deal[5] consider a solution to be a mixture of structural groups. Activity coefficients for the groups in a solution are calculated from molecular activity coefficients and plotted against group concentrations. These group activity coefficients can be used to calculate the molecular activity coefficients for other systems containing the same structural groups. The 'solution of groups' model has been found to represent actual solutions with nearly quantitative results in several cases. Scheller[6] modified and extended the work of Wilson and Deal and developed the theory in terms of thermodynamics instead of empirical quantities.

The 'solution of groups' approach to liquid mixtures permits a wide range of estimates using very little data and has a number of practical uses. The approach is particularly useful in making estimates of phase equilibria for screening possible separation processes and for evaluating the general validity of individual experimental measurements. The approach is also useful in

estimating activity coefficients of compounds where experimental measurements are difficult; e.g. as in biological systems.

Gilmont[7] developed a method of correlating and predicting vapor-liquid equilibria by analyzing the changes in internal energy that occur during vaporization. The method uses the statistical theory of least squares with weighted factors to account for the difference in experimental precision due to change in composition. It is based on a two parameter equation which obeys Gibbs-Duhem equation and is therefore inherently thermodynamically consistent. For predicting the composition of vapor in equilibrium with a liquid mixture of two components, the information required includes field factors (given in the original paper) and properties of the pure components such as slope and intercept of the Othmer plot, parachor, and critical temperature and pressure.

Based on a regular solution theory, Finch and Winkle[8] presented a method for predicting the activity coefficient at infinite dilution of the components in binary systems. The basis of the method is Van Arkels[9] concept of internal pressure. They introduced an asymmetry constant K_A into the Scatchard-Hildebrand type of equations for activity coefficients, thereby bringing theory in

agreement with the experimental data. The asymmetry constant can be obtained from an empirical plot of K_A VS. $\left|\sqrt{I_{p_1}} - \sqrt{I_{p_2}}\right|$ *. I_{p_1} and I_{p_2} are the internal pressures of components 1 and 2 respectively. The final equations for activity coefficients are derived on the assumption that the excess entropy of mixing is zero and the vapor-phase behaves ideally. In spite of these assumptions, the empirical modification of Van Arkel's theory gave good reproduction of the experimental equilibrium data for a large number of binary systems.

2.1.2 UTILIZATION OF MIXTURE AND PURE COMPONENT PROPERTIES

Several methods (10, 11, 12, 13, 14, 15) have been reported in the literature for evaluating liquid activity coefficients, partial pressures and equilibrium vapor compositions from total pressure-liquid composition measurements. In general, these methods involve evaluation of either constants of equation representing the liquid activity coefficients or equilibrium vapor compositions directly by means of a step wise integration procedure. All the methods, however, involve the Gibbs-Duhem equation.

Levy (14) reviewed the numerous procedures proposed in the past and developed one for use with the

* This plot (in the paper) has been developed on purely empirical basis and once the absolute difference in the square root of internal pressure is known, K_A at that value can be obtained from the graph.

Margules equation of activity coefficients. Othmer and Rieciardi[10] derived a set of differential equations starting from the Gibbs-Duhem equation. The solution of the differential equations makes possible the prediction of vapor-composition from vapor-pressure or boiling point data. The differential equations, however, do not yield a direct mathematical solution. Methods of step wise integration and algebraic relations have been given in the original paper. Wehe and Coates[13] proposed a method for correlating activity coefficients. A procedure is outlined for predicting the entire composition in both the phases from the non-ideal vapor-pressures.

Carlson and Colburn[14] used the fact that from an isothermal measurement of total pressure-liquid composition curve, the Van Laar or Margules equation of activity coefficients may be employed to estimate equilibrium vapor-composition. Redlich and Kister[15] noticed that a knowledge of total pressure of a binary solution as a function of the liquid phase composition at constant temperature is sufficient for a complete description of vapor-liquid equilibria.

A digital computer method has been developed by Christian[16] for calculating the partial pressure of components in binary mixtures of non-electrolytes using total pressure-composition data. The constant temperature

and constant pressure Gibbs-Duhem equation has been applied with the assumption that the component in the vapor phase follows the ideal gas law. Ho et. al.[17] also proposed another computational method for binary non-electrolyte mixtures. The liquid activity coefficients are represented by the Redlich-Kister equation. The method of least squares was employed for the evaluation of constants of this equation. The equilibrium vapor compositions were also evaluated by means of step wise integration procedure.

Based on temperature-composition measurements, Othmer et. al.[18] derived a set of differential equations starting from the Gibbs-Duhem equation. The equations which represent isopiestic thermodynamic relationships between the mole fractions and temperature for binary systems, can be used for correlating and checking available data. The methods indicated for solution of these equations are useful in predicting vapor-phase mole fractions from the temperature and liquid phase compositions for the binary mixtures. Ellis and Jonah[19] developed thermodynamically consistent expressions for activity coefficients at infinite dilution. These involve the determination of the slopes of the boiling point-composition curve. A graphical procedure is presented for accurate measurement of these slopes.

Based on regular solution theory, Tassios and Van Winkle[20] developed an empirical method for the estimation of activity coefficients at infinite dilution. This method is applicable to binary systems consisting of solvent and individual members of a homologous series from existing data on two binary systems in the series.

It has long been realised, in the case of binary solutions at least, that the behavior of one component is coupled to that of the other through the Gibbs-Duhem equation and that the gross behavior of the solution (vapor pressure vs. composition) is thus uniquely dependent on the behavior of only one of its components. Several methods have been employed for the calculation of component behavior from gross-solution behavior. Ljunglin and Van Ness[21] have shown that the application of thermodynamic methods allows the calculation of vapor-liquid equilibria of binary systems from measurement of total pressure. They discussed techniques of handling non-constant temperature or pressure conditions as well as non-ideal vapor phase behavior.

The indirect methods involve first the calculation of the liquid phase activity coefficients and subsequent calculations of vapor compositions therefrom. These methods usually involve ascertaining which of selected solution

equations to the Gibbs-Duhem equation lead to the best fit to the experimental vapor-pressure data. They also involve determination of the parametric values producing the best fit. Barker[23] developed a procedure based on the assumption that the excess free energy can be represented as a polynomial function of composition. This assumption is equivalent to assuming that the Margules equations relate the activity coefficients to composition. Barker's method necessitates the assumption of the nature of molecular interactions. This deficiency has been recognised by Tao[24] who presented another indirect method. Tao's procedure involves calculation of activity coefficients essentially by integration of an equation resembling the coexistence equation.

Mixon et. al.[25] have proposed another indirect method for computing vapor-liquid equilibrium data from solution vapor-pressure measurements. The method involves the determination of excess Gibbs free energy by successive approximations to the solution vapor pressure, with activity coefficients obtained by differentiation of the free energy function. This method has the advantage over the earlier method in that it can also be applied to ternary and multicomponent systems.

Tao[26] proposed a numerical method which may produce precise phase equilibrium data from experimental

temperature-mole fraction and the pressure-mole fraction data. The method developed is based on rigorous material balance and thermodynamic considerations and can be programmed on a high speed digital computer.

2.2 MULTI-COMPONENT SYSTEMS

There is no general method for correlating or predicting vapor-liquid equilibria of a multicomponent system from the binary data. Data for numerous binary systems have been reported in the literature but the data for ternary and multicomponent systems are scarce. Thus, the advantage of predicting vapor-liquid equilibria in multicomponent systems from pure component and binary system data is obvious. Several methods based on the activity coefficient-composition correlation have been proposed for calculating vapor liquid equilibria of multicomponent systems. Usually vapor-liquid equilibria are calculated using liquid phase activity coefficients which are expressed either by Margules or Van Laar types of equations. Hildebrand's equation, which belongs to the Van Laar type and is based on the regular solution theory (27) has been used by many investigators and has given very successful results for many systems under certain conditions. It fails, however, to predict the vapor-liquid

equilibria for systems having molecules of large size differences. The thermodynamic properties of solutions of molecules of different size have been discussed in terms of Miller-Guggenheim [28, 29] or Flory-Huggins [30,31] theory. The utility of combining the Hildebrand and Miller-Guggenheim -Flory-Huggins theories for mixtures of molecules of unequal size have been successfully demonstrated recently. [32, 33, 34]

Black [35] modified the Van Laar equation and utilized it in the calculation of multicomponent vapor-liquid equilibria using the data of the pure components and of their binary mixtures. Chao and Hougen [36] proposed another modification to Van Laar's equation for ternary systems by neglecting the ternary constants and retained the rest of the parts of the equation in which only binary constants are involved. Unfortunately, the ternary equations are not consistent with the relevant binary systems. A fair prediction of ternary vapor-liquid equilibrium can, however, be made using Nagata's ternary equation [37] in which again the ternary constants are omitted.

Orye and Prausnitz [38] used Wilson's equation [39] for the estimation of liquid phase activity coefficients. Deshpande and Lu [40] developed a general method for extending binary data, using a minimum number of experimental

points by the application of Gibbs-Duhem equation.

Carlson and Colburn [12] extended the method of binary systems for predicting the ternary equilibrium data. Colburn and Schoenborn [41] claim that this method is unsatisfactory because it is not in agreement with the Gibbs-Duhem equation in a hypothetical case. However, they observed that this method does give satisfactory results for systems having at least one ideal binary mixture. Scheibel and Friedland [42] proposed a method based on interpolation of activity coefficients for ternary systems. This method requires data for three binary mixtures but gives results of very high accuracy.

Gilmont et. al. [43] presented a method in which activity coefficients are directly determined from relative volatility. In this case vapor-liquid equilibrium data can be correlated by a single equation without the knowledge of the total pressure data at constant temperature.

Edward et. al. [44] utilised the parameters determined from relative volatility data of binary systems defined by Gilmont et. al. [43] By plotting the relative volatility, they obtained a series of parameters which determine an analytical expression for activity coefficients of ternary systems. Equations for determining these parameters are generalized for use under constant pressure and constant temperature and have also been

extended to predict multicomponent equilibria. McDermott and Ellis[45] extended Barker's method[23] of fitting a binary correlating equation to the total pressure measurements for the isothermal vapor-liquid equilibrium. This method does not require a knowledge of binary data since the equivalent binary constants are determined directly from the ternary total pressure-composition measurements.

2.3 HYDROCARBON SYSTEMS

Hydrocarbon processing calculations deal with mixtures for which phase equilibria calculations must be made. Before 1932, the vapor-liquid equilibria phase distribution calculations for hydrocarbon systems were frequently made using vapor pressure data. During the past four decades the thermodynamic tools for such process engineering calculations have been improving gradually and new methods are available for estimating the temperature, pressure and composition effects on the vapor-liquid equilibria for hydrocarbon systems. Edmister and Ruby[46] have reviewed and discussed all the proposed correlations prior to 1955.

In the last two decades, the use of several different approaches such as the convergence pressure concept, equation of state, the application of the principle of the corresponding states etc. have been tried for

hydrocarbon systems. The applicability of each method of correlation, based on any of the above approaches, is restricted to certain systems and limited temperature and pressure conditions.

The use of convergence pressure for calculating vapor-liquid equilibrium was originated by Organick and Brown [47]. The convergence pressure has been defined for the equilibrium constant "K" of a given system, as the pressure on the critical locus on a plot of log K vs. log P for a given temperature. Organick and Brown developed a correlation for the equilibrium constants of hydrocarbon systems. Employing an empirical relationship based on the critical pressures for methane binary systems, the correlating pressure for any mixture of paraffin hydrocarbons, binary or complex, was defined in terms of three other variables; the equilibrium pressure, and functions of the equilibrium vapor composition and of the liquid phase compositions. The correlation was tested for many binary and complex experimental vapor-liquid equilibrium systems and the results were satisfactory within the limits of experimental uncertainty. Hadden [49] presented a practical working procedure for obtaining vapor-liquid equilibria in hydrocarbon systems from low pressures up to the convergence pressure. Hadden's correlation is applicable over

large temperature and pressure ranges and also correlations were presented for the equilibrium constant of non-hydrocarbon systems frequently occuring in hydrocarbon streams either as contaminates or as process materials.

Although the theory of corresponding states as originally stated by Van der Waals in 1881 applies only to pure substances, Salsburg and Kirkwood [50] and Scott [51] have provided a theoretical basis for extending it to multicomponent systems. Scott used the theory of corresponding states to deduce the properties of solutions from theoretically derived properties of the pure components. A characteristic of this theory is that it is useful only when the molecules are of the same size. Scott pointed out that in any corresponding states treatment, the entropy of mixing is not ideal either at constant pressure or at constant volume. Leland and Muller [52] suggested a method based on the theory of corresponding states to calculate hypothetical or pseudo-critical conditions for both liquid and vapor phases. These are then used to calculate reduced conditions at which thermodynamic properties of mixtures may be found. The generalized correlations for pure substances or an equation of state or tabulated properties of a pure substance chosen as a reference, are used to predict the thermodynamic properties. The advantage of this approach is that it does not require a knowledge of equation of state constants and their combination rules for

all components. Further, different equations of state for liquid and vapor phases or any number of different equations of state each fitted to various regions of the observed P-V-T properties of the reference substance can be used.

Leland et. al. (53) presented a correlation for the prediction of vapor-liquid equilibria of non-polar substances using the corresponding states principle. Properties of liquid and vapor mixtures were evaluated, even in the critical region, from either experimentally measured properties of closely related pure substances or from generalized tables of thermodynamic properties. They presented a derivation of an improved pseudo-critical expression applicable to liquids which may be approximated by simple spherical molecules and also suggested a way for a possible extension of the technique to more complex molecules. This approach avoids the extrapolation of liquid properties into regions where no liquid can exist. It is especially useful for systems in which an equation of state is not available for all of the components present and also avoids the difficulties in defining the combination rules for complicated equations of state.

The use of equations of state to predict the vapor-liquid equilibria of hydrocarbons is most common and, in fact, all the work done recently towards the computation

of equilibrium data at high pressures inevitably makes use of such an equation. For a wide variety of mixtures, there is no equation of state capable of describing accurately both vapor and liquid phases. In fact, the entire problem of phase equilibria at any pressure could be completely solved if such an equation of state were available. The most common equations of state used for the prediction of vapor-liquid equilibria are the Benedict-Webb-Rubin (B-W-R) equation [54] and the Redlich-Kwong (R-K) equation. [55] Yorizane and Masuoka [56] made a comparison of B-W-R, R-K, and H-B-M-S (Hirschfelder-Bueber-McGee-Sulton) equations of state* at high pressures from the standpoint of vapor-liquid equilibria. They pointed out that in two phase regions, the accuracy decreases in the order H-B-M-S equation, B-W-R equation and R-K equation. H-B-M-S equation is usually not used for quantitative vapor-liquid equilibrium calculations since this is a discontinuous equation. Since B-W-R equation involves the evaluation of eight constants, it is cumbersome to handle and not used commonly. The R-K equation is most commonly used because it has only two constants. Both of these can be evaluated from the critical data only.

In the period 1940 - 1952, extensive calculations for hydrocarbon mixtures were reported by Benedict, Webb and Rubin using their eight-constant equation of state.

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* See Appendix 1.

The proposed equation and the numerical values of its eight constants for pure components methane, ethane, propane and n-butane are presented in reference (54) while the equation extended to mixtures is presented in reference (57). The numerical values of constants for eight other hydrocarbons are presented in references (58) and (59) and reference (60) gives a comparison of the observed liquid-vapor equilibria for mixtures of these hydrocarbons with that predicted by the B-W-R equation. Schiller and Canjar (61) applied this equation to a binary mixture of nitrogen and carbon - monoxide, which have very similar molecular structures, and showed that it could satisfactorily predict the vapor-liquid equilibria for systems other than the hydrocarbons. Cullen and Kobe (62) investigated the possibility of a general application of this equation of state to binary systems. The general system chosen by them was that of carbon-dioxide and propane, which have molecules differing in size. However, the predicted results for this system were found to be far from satisfactory.

The results of the calculations of Benedict, Webb and Rubin are given in 276 large charts which have been published in a huge book (63) " which by virtue of its size alone is likely to become a monument to the history of applied thermodynamics". With the aid of some simplifying assumptions

Depriester[64] and also Edmister and Ruby[65] condensed these charts into a manageable form; these results are useful for estimating vapor-liquid equilibria for mixtures of light paraffinic and olefinic hydrocarbons. Calculations based on these charts are of the iterative, trial and error type, but they can be carried out very efficiently by an electronic computer.

Stotler and Benedict[66] suggested two modifications of the B-W-R equation of state. One modification was that the numerical value of one of the coefficients, C_o be changed at different temperature levels so that the low temperature vapor-pressure of the component concerned be adequately represented. However, no explanation was given as to why the coefficient C_o and not others should be adjusted. A need to fit an interaction constant was suggested as the second modification. However, Cullen and Kobe[62] who used this modified equation, obtained unsatisfactory results in the prediction of the compositions of propane-carbon-dioxide system. Lin and Naphtali[67] restudied the prediction of vapor-liquid equilibria with B-W-R equation of state. Further, the importance of the modifications suggested by Stotler and Benedict[66] was determined. They chose a tentative form of the modification of this equation and obtained satisfactory results for four systems.

Van Horn and Kobayashi[68] developed a correlational procedure to predict the vapor-liquid equilibrium behavior of light hydrocarbons in heavier hydrocarbon solvents at low temperatures and elevated pressures. This method, applicable to paraffinic as well as aromatic solvents, used the B-W-R equation of state to predict vapor-phase fugacities. Excellent agreement between the predicted and experimental data at low temperature has been reported.

The Redlich-Kwong equation of state[55] has been widely used in the last 20 years for the prediction of the fugacities and the compositions of both liquid and vapor phases of hydrocarbon mixtures. It is stated that the component fugacities of vapor obtained by using the R-K equation are almost, if not quite, as good as those obtained from the complex B-W-R equation of state, though the accuracy decreases as the pressure approaches the mixture critical pressure. This equation, in its original form, was used with good results by Edmister[69], Prausnitz et. al.[70] and Edmister et. al.[71] to determine the fugacity coefficients for vapors. Prausnitz et. al.[70] while using the regular solution theory to calculate the vapor-liquid equilibria, discussed the effect of temperature on the solubility parameter used in the regular solution theory. They further suggested a method for the evaluation of the solubility parameter of the gaseous components whose temperatures are above their critical temperatures. Based on a three-parameter theory of corresponding states, Lyckman et. al.[72]

calculated the generalized liquid volumes and solubility parameters for regular solution application. These two parameters have been tabulated for reduced temperatures from 0.56 to 0.99 and may be used for non-polar or slightly polar liquids.

It has been customary to define a standard state for the prediction of vapor-liquid equilibria of hydrocarbons. Prausnitz [73] discussed in detail the various standard states used, with special emphasis on those used for the high pressure phase equilibria. Stiehl et. al. [74] used the R-K equation to determine the heats of condensation and enthalpies of saturated liquid hydrocarbon mixtures.

A method using the solubility parameter concept and certain aspects of the corresponding states theory, was proposed by Chao and Seader [75] to determine the equilibrium constants for hydrocarbon mixtures. The vapour phase component fugacity in this correlation was determined by using the R-K equation. Definite restrictions* of temperature ($800^{\circ}F$ to reduced temperature of 0.5) and pressure (up to about 3,000 psia) have been placed on this technique, but it is not stated to what extent these result from the use of R-K equation. The strength of the Chao-Seader correlation lies in its generality; that is, in its ability to predict vapor-liquid phase behavior, even at high pressures, in systems composed of paraffins, naphthenes and aromatics,

* Reference (100).

and including gases such as hydrogen, nitrogen, carbon dioxide and hydrogen sulfide at low concentrations. Shelton and Wood [76] presented a computer program for the Chao-Seader correlation for calculating the equilibrium constants. Their technique replaced all the then existing methods for performing flash calculations and the predicted equilibrium parameters were reported to be in good agreement with the experimental values.

Many attempts have been made to make the R-K equation more flexible by the introduction of a third parameter and also to obtain an improved representation of the near critical region. At the same time, the good behavior of the original equation at high pressures and at high temperatures was to be conserved. Wilson [77] applied the R-K equation simultaneously to the coexisting vapor and liquid phases with one set of constants in the manner of the B-W-R equation. He modified the original mixing rules of mixtures for this equation and further proposed [78] to make the constant Ω_a temperature dependent and to utilize $\Omega_b = 0.0867$ at all temperatures. Mixtures of carbon dioxide with light hydrocarbons exhibit unusual P-V-T behavior which can be attributed to the interaction effects between the carbon dioxide and hydrocarbon molecules. Conventional methods failed to give satisfactory results for the fugacity coefficients of these mixtures. Joffe and

Zudkevitch[79] introduced interaction coefficients into the constants of the R-K equation and the fugacity coefficient values for these mixtures derived from this modified equation gave quite satisfactory results. Zudkevitch and Kaufmann[80] evaluated the fugacity coefficients for hydrocarbon mixtures at high pressures, using the modified R-K equation. They demonstrated that the prediction of mixtures' phase behavior is simpler if only one set of constants is used.

Chueh and Prausnitz[81] presented a method for predicting the partial molar volumes in non-polar mixtures at high pressures. The molar volumes of saturated liquid mixtures were computed by extending to mixtures the corresponding states correlation of Lyckman et, al.[72] These mixture volumes were then used to calculate partial molar volumes with an expression based on a modification of the R-K equation. They suggested that the evaluation of constants Ω_a and Ω_b for a component be made from the saturated liquid and vapor-density data.

The thermodynamic analysis of vapor-liquid equilibria at high pressures, including the critical region, has been discussed by Chueh and Prausnitz[82]. Equations have been presented for reducing raw binary data to thermodynamically significant binary parameters and upon generalizing these equations to systems containing any number of components, the phase behavior of multicomponent mixtures

can be predicted without introducing any ternary (or higher) parameters. Robinson and Jacoby[83] and Esters and Tully[84] have also suggested modifications of the R-K equation but Chueh and Prausnitz's[81] modified form is the one commonly used.

Redlich and Dunlop[85] and Redlich et. al.[86] attempted to improve the R-K equation by adding a function of temperature and pressure to the compressibility factor computed by the old equation. Stringent conditions for this function could be formulated and the simplest suitable function resulted from a rather cumbersome comparison with observed data. The disadvantage was the complicated nature of the additional functions, although they contained only a single individual parameter in addition to the critical temperature and pressure. The purely technical difficulties in the extension of such an equation to mixtures and the derivation of fugacity coefficients are considerable. Very recently Redlich and Ngo[87] have presented another modification of this equation. The critical compressibility factor has been chosen as the third parameter and to improve the equation in the region around the critical point certain conditions are satisfied by the introduction of two functions of the reduced temperature and volume. The actual computation for the fugacity coefficients involve both algebraic and numerical integrations.

Recently Zudkevitch and Joffe[88] treated the parameters Ω_a and Ω_b of R-K equation as a function of temperature and applied the modified R-K equation to the calculation of phase equilibria in multicomponent systems. These parameters were obtained for each pure component from experimental vapor pressures and liquid densities with the help of Lyckman et. al.'s[89], generalized fugacity coefficient correlation for saturated vapors. Chang and Lu[90] also treated these parameters as temperature dependent and predicted the partial molal volumes of normal fluid mixtures. However, Chang and Lu did not use Lyckman's relation and instead set up an iterative procedure which involved the knowledge of liquid phase compressibility factor. Hsi and Lu[91] have extended this technique for the prediction of equilibrium compositions of binary and ternary systems in which the critical temperature of one of the components is less than the temperature of the mixture. Their method requires the knowledge of at least one experimental data point. Hsi and Lu assumed that these parameters Ω_a and Ω_b were unique for a component; that is, if these parameters were known for a component in one binary system, those values could be used for that component in any other binary system.

2.4 SOLUBILITY OF GASES IN SOLVENTS

The regular-solution equations do not take into account the volume changes on mixing and therefore require modification for the solutions of gases in liquids. The modified regular solution theory has been most commonly used to predict the solubility of gases in various hydrocarbon solvents. Prausnitz[92] modified the regular solution theory equations for the gas-liquid solutions. He considered a three step process : (a) Isothermal compression of the pure gas from its partial pressure and the pure liquid from its vapor pressure to the isometric mixing pressure. (b) Isothermal, isometric and isopiestic mixing at the isometric mixing pressure* and (c) Isothermal expansion of solution from the isometric mixing pressure to the equilibrium pressure. The resulting equations gave reasonable estimates of the solubilities of gases and also of the temperature coefficient of solubility. Shair and Prausnitz[93] presented a thermodynamic correlation for gas solubilities based on a two step process of condensing the gas isothermally to a hypothetical liquid at 1 atm and then dissolving this hypothetical liquid in the solvent. He also gave a semi-empirical method for correlating the solubilities of gases in polar solvents.

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* The isometric mixing pressure is the pressure at which gaseous solute and liquid solvent mix isothermally and isopiestically without change of volume.

Yen and McKetta[94] derived equations based on regular-solution theory for thermodynamic correlation of non-polar gas solubilities in polar liquids. They were also able to semiempirically correlate solubilities of non-polar gases in both polar and non-polar solvents. Lachowicz and Weale[95] also derived equations based on regular solution theory to predict gas solubility in non-polar liquids and the application of their equations to existing data resulted in useful correlations. Arai et. al.[96] modified the regular solution theory by introducing the excess entropy of mixing term and by using the temperature dependent solubility parameters. The excess entropy of mixing was estimated by the Flory-Huggins equation. The solubilities were also obtained as a by-product from the method of Hsi and Lu[91] for the prediction of vapor-liquid equilibria.

3. SOLUBILITY CALCULATIONS

In this section, it is proposed to study the solubility of an oxidiser into a hydrocarbon fuel at high pressure. Such a situation is most commonly encountered in high pressure combustion chambers such as those of liquid propellant rocket motors and diesel engines. At the pressures encountered in the above situations, some of the fuel is vaporised and some quantity of the oxidiser is absorbed in the liquid fuel at the equilibrium conditions. In this analysis it is assumed that the hydrocarbon fuel is present in the vapor phase in a negligible quantity and, for all practical purposes, the vapor phase consists of the pure oxidising component.

The situation to be considered is that for which the oxidising component in the combustion chamber is at the total pressure P and the hydrocarbon fuel is injected into the chamber. The partial pressure P_i of the oxidising component shall be the same as the total pressure P, since the vapor phase is assumed to consist of oxidiser only. The temperatures considered are such that they are always above the critical temperature of the oxidiser and below the critical temperature of the hydrocarbon fuel.

The problem of estimating the solubility of gases becomes a matter of estimating the activity coefficients of the solutes in the pressure of the solvents. Many theoretical

and empirical approaches have been proposed to find the solubility of the gases (92, 93, 96). All approaches are aimed at the prediction of the thermodynamic properties of solution using the pure component data and the minimum experimental data. No existing theory completely fulfils this aim, but various proposed theoretical treatments give good approximations in certain restricted areas. Most of the theoretical treatments are based on the Scatchard-Hildebrand theory of regular solutions which makes use of solubility parameters. Prausnitz (92) extended these equations to solutions of non-polar gases in non-polar liquids.

Prausnitz's method (92) utilizes certain experimental data and also a few graphs to evaluate some of the parameters required in the analysis. The aim of the present study is to avoid the use of any graphs and also to evaluate these parameters from the knowledge of critical properties of the components only. Prausnitz's equations have the restriction of being useful at low pressures whereas , the present study, after certain modifications, will render them useful even at high pressures of the order of several hundred atmospheres. Further,these equations would become useful for the quantitative work.

3.1 SOLUBILITY EQUATIONS

The regular solution equations assume that the excess entropy of mixing is zero i.e. the entropy of mixing is equal to that of an ideal solution and also that there are no chemical effects acting between the molecules, Further, it is assumed that there is no change in volume because of isothermal and isobaric mixing of components. On the basis of these assumptions, it has been shown (27) that for a binary solution :

$$RT \ln \gamma_i = V_i \phi_j^2 (\delta_i - \delta_j)^2 \qquad ---(3.1)$$

where γ = Activity coefficient

V = Molal liquid volume.

$$\phi_j = \frac{x_j V_j}{\sum_j x_j V_j}$$

δ = Solubility parameter $= \left(\frac{\Delta E}{V}\right)^{1/2}$

ΔE = Isothermal molar change in energy for a pure component in going from liquid to ideal gas state.

Equation (3.1) is not applicable to the gas-liquid solutions since:

(1) There is a change in enthalpy and entropy when a gas is dissolved in a liquid. Further, there is a large decrease in volume because the volume of the gaseous solute in the condensed phase is much smaller than that in the vapor phase. Thus equation (3.1) cannot be applied, as

such, for the calculation of the solubility of a gas in a liquid solvent.

(2) The solubility parameter as defined above has no meaning for a component above its critical temperature.

All these difficulties can be overcome (92) by considering the mixing process as an isothermal process in a series of three steps.

(a) In step one it is assumed that the pure gas is compressed isothermally from its partial pressure to the isometric mixing pressure (the pressure at which gaseous solute and liquid solvent mix isothermally and isopiestically without change of volume) and the pure liquid is compressed from its vapor-pressure to the isometric mixing pressure.

The molar free energy change for the isothermal compression of pure gas from its partial pressure to the isometric mixing pressure π is given by :

$$\Delta F_i^{(a)} = \int_{P_i}^{\pi} V_i \, dP$$

Since it is assumed that the gaseous component has a partial pressure P_i equal to the total pressure P of the system, therefore $\Delta F_i^{(a)} = \int_{P}^{\pi} V_i \, dP = RT \ln \frac{f_i(\pi)}{f_i(P)}$ ---(3.2)

(Note that the sub-script 'i' always refers to the gaseous solute).

(b) In the second step there is mixing of pure components at constant isometric pressure, temperature and volume.

Applying the regular solution equation (3.1) to the gas-liquid solution:

$$RT \ln \gamma_i = \overline{V}_i \phi_j^2 (\delta_i - \delta_j)^2 \quad \text{----(3.3)}$$

Note that for the gas-liquid solution, the molal liquid volume V_i is replaced by the partial molar volume $\overline{V}_i$.

The molar free energy change is given as :

$$\Delta \overline{F}_i = RT \ln a_i$$

where a_i is the activity of component 'i' defined as :

$$a_i = \gamma_i x_i$$

Therefore, the free energy change for the second step is given by :

$$\Delta \overline{F}_i^{(b)} = \overline{V}_i \phi_j^2 (\delta_i - \delta_j)^2 + RT \ln x_i \quad (3.4)$$

$\overline{V}_i$ is the partial molar volume of the gaseous solute at pressure π and mole fraction x_i.

Prausnitz[92] assumed that the partial molar volume of the solvent was the same as the molar volume of the pure component. In the present work, as will be seen later, the partial molar volumes of both the solute and the solvent are calculated by a method very recently suggested by Chueh and Prausnitz[81].

(c) Step three consists of the isothermal expansion of the solution from the isometric mixing pressure π to the equilibrium pressure P, the molar free energy change for this step is given by:

$$\Delta \overline{F}_i^{(c)} = \int_{\pi}^{P} \overline{V}_i \, dP \quad (3.5)$$

Prausnitz[92] assumed that the gas observes Lewis' fugacity rule at low pressure and since, in the present analysis, it has been assumed that the vapor phase consists of oxidiser only, therefore Prausnitz's assumption holds good for this analysis too. If the solubility is chosen such that the solution is in equilibrium with gas at pressure P, then the total free energy change for the gaseous component is zero.

Therefore $\Delta F_i^{(a)} + \Delta \bar{F}_i^{(b)} + \Delta \bar{F}_i^{(c)} = 0$ (3.6)

Substitution of equations (3.2), (3.4) and (3.5) into (3.6) gives :

$$RT \ln\left(\frac{f_i(P)}{x_i f_i(\pi)}\right) = \bar{V}_i \phi_j^2 (\delta_i - \delta_j)^2 - \int_P^\pi \bar{V}_i \, dP \quad \text{---(3.7)}$$

It is evident from equation (3.7) that to compute the solubility of a gas in a liquid, the partial molar volume and the isometric mixing pressure must be known.

These quantities along with the thermodynamic properties of pure gas and those of the pure solvent are sufficient to determine all other quantities in equation (3.7).

N-octane-oxygen system will be studied here, though this analysis can be applied to any hydrocarbon-oxidiser system. The basic difference in the present study and Prausnitz's work[92] is in the method of evaluation of the partial molar volume, the isometric mixing pressure and the solubility parameters. Thus, the method of evaluating

each of these shall be described in detail.

The reader is reminded that chemical engineering is concerned with the development of the various techniques for calculating the solubility of the gases in different solvents. This is because the solubility of gases plays an important part in extractive distillation or separation processes. In the petroleum industry, it is necessary to have the knowledge of the solubility of various fractions with different solvents, so as to be able to separate each fraction effectively. However, our purpose here is to select suitable techniques which will help us to study the various problems associated with the combustion of fuels.

3.2 PARTIAL MOLAR VOLUMES

Accurate measurements of partial molar volumes of gases in liquid solutions are very difficult to obtain and consequently experimental data for such binary systems are rare. For multicomponent systems there is no data at all. Prausnitz (92) correlated all available reliable data for partial molar volume in a generalised plot.

Knowing the reduced temperature and volume, one could find the partial molar volume of the gaseous component in a particular solvent. But this method is not suitable for quantitative work.

Very recently, Chueh and Prausnitz[81] developed a correlation from the Redlich-Kwong equation of state (55) for the partial molar volumes at the saturation conditions. This correlation gives the partial molar volume as a function of the composition, temperature and the molar volume of the liquid mixture. Pressure does not appear explicitly but is implicit in the volume which depends on the pressure.

For saturated molar volume of liquid mixtures, a correlation developed on the corresponding states principle by Lyckman et. al.[72] will be used. Lyckman et. al. slightly revised Pitzer's tables[97] for the saturated liquid volume of pure substances. The correlation of Lyckman et. al. gives better results at low reduced temperatures, when liquids have large molecular weight components. Further, this correlation has been generalised by accounting for a larger class of liquids and a larger temperature range. Pitzer's correlation is linear in accentric factor whereas that of Lyckman et.al. is a quadratic function of accentric factor; it has the form :

$$V_R \equiv \frac{V}{V_c} = V_R^{(0)} + \omega V_R^{(1)} + \omega^2 V_R^{(2)} \qquad (3.8)$$

where V_c is the critical volume and ω is the accentric factor,* The generalised functions $V_R^{(0)}$, $V_R^{(1)}$, and $V_R^{(2)}$ depend on reduced temperature and are tabulated for

---

* Accentric factor depends upon both the critical pressure and temperature and is defined as follows : $\omega = -\log P'_R - 1.0$ where P'_R represents the reduced vapor pressure at a reduced temperature of 0.7.

reduced temperatures from 0.56 to 0.995 (72). To facilitate calculations with computers, Chueh and Prausnitz (81) fitted the tabulated values to the following relation :

$$V_R^{(j)} \equiv \left(\frac{V}{V_c}\right)^{(j)} = a^{(j)} + b^{(j)} T_R + c^{(j)} T_R^2 + d^{(j)} T_R^3 + e^{(j)}/T_R + f^{(j)} \ln(1-T_R) \quad (3.9)$$

The constants $a^{(j)}$ to $f^{(j)}$ are given below for different values of j.

(j)	$a^{(j)}$	$b^{(j)}$	$c^{(j)}$	$d^{(j)}$	$e^{(j)}$	$f^{(j)}$
0	0.11917	0.009513	0.21091	-0.06922	0.07480	-0.084476
1	0.98465	-1.60378	1.82484	-0.61432	-0.34546	0.087037
2	-0.55314	-0.15793	-1.01610	+0.34095	0.46795	-0.239938

Equation (3.9) agrees with originally tabulated values within $\pm$ 1 in the fourth significant figure.

If the reduced temperature is less than 0.56, then a slightly different equation for the saturated liquid volume can be used (98).

$$V_R \equiv \frac{V}{V_c} = V_R^{(o)} + \omega V_R^{(1)} \quad (3.10)$$

where $V_R^{(o)} = 0.34037 + 0.009531 T_R + 0.1131 T_R^2$

$$V_R^{(1)} = -0.16262 + 0.20403 T_R - 0.64159 T_R^2 + 0.77987 T_R^3$$

For application to mixtures, mixing rules for the pseudocritical volume and temperature are necessary. Chueh and Prausnitz (81) proposed the following mixing rules, which are different from the previous pseudocritical rules(53,99),

in that the combination of mole fraction and volume fraction instead of mole fraction only is used in defining the critical temperature and accentric factor of the mixture. This change is necessitated due to the fact that because of small separation between the molecules, molecular size is a more important factor in the liquid phase than in the vapor phase.

$$V_{cM} = \sum_i x_i V_{ci}$$

$$T_{cM} = \sum_i \sum_j \phi_i \phi_j T_{cij}$$

$$\omega_M = \sum_i \phi_i \omega_i$$

$$\phi_K = \frac{x_K V_{cK}}{\sum_i x_i V_{ci}}$$

$$T_{cij} = \sqrt{T_{cii} T_{cjj}} (1 - K_{ij})$$

The binary constant K_{ij} represents the deviation from the geometric mean rule for T_{cij}. It is a constant characteristic of the i-j interaction; to a good approximation it is independent of the temperature, density and composition.* In general, K_{ij} must be obtained from some experimental information about the binary interaction, Best estimates of K_{ij} for 115 binary system are given in (98).

* See section (4.3).

Unfortunately there is no experimental information available about the binary interaction of the oxygen-n-octane system. Because of the explosive nature of the system, especially at high pressures, it has never been studied experimentally.Thus, in the absence of any information about the interaction of the components, K_{ij} is assumed as equal to zero. This might result in a lower value of the saturated molar volume at a given mole fraction than the value obtained by using the appropriate K_{ij} as is evident from carbon-dioxide-n-butane system studied before(81).

All the pure component constants, required for the analysis in section 3, have been taken from (100, 101). The saturated molar volume of the liquid mixture can be calculated provided the mole fractions of the components are known. As will be seen later, a value of the mole fraction of oxygen in the liquid phase is assumed and an iterative cycle is started till the mole fraction of oxygen at the equilibrium conditions is determined.

The saturated liquid volume of the mixture, as determined from equation 3.8, at 300°K is plotted against the mole fraction of oxygen as shown in figure 3.1. Figure 3.2 gives the variation of saturated liquid volume of the mixture with the total pressure.

Redlich and Kwong (55) gave the maximum deviations between the experimental and calculated compressibility

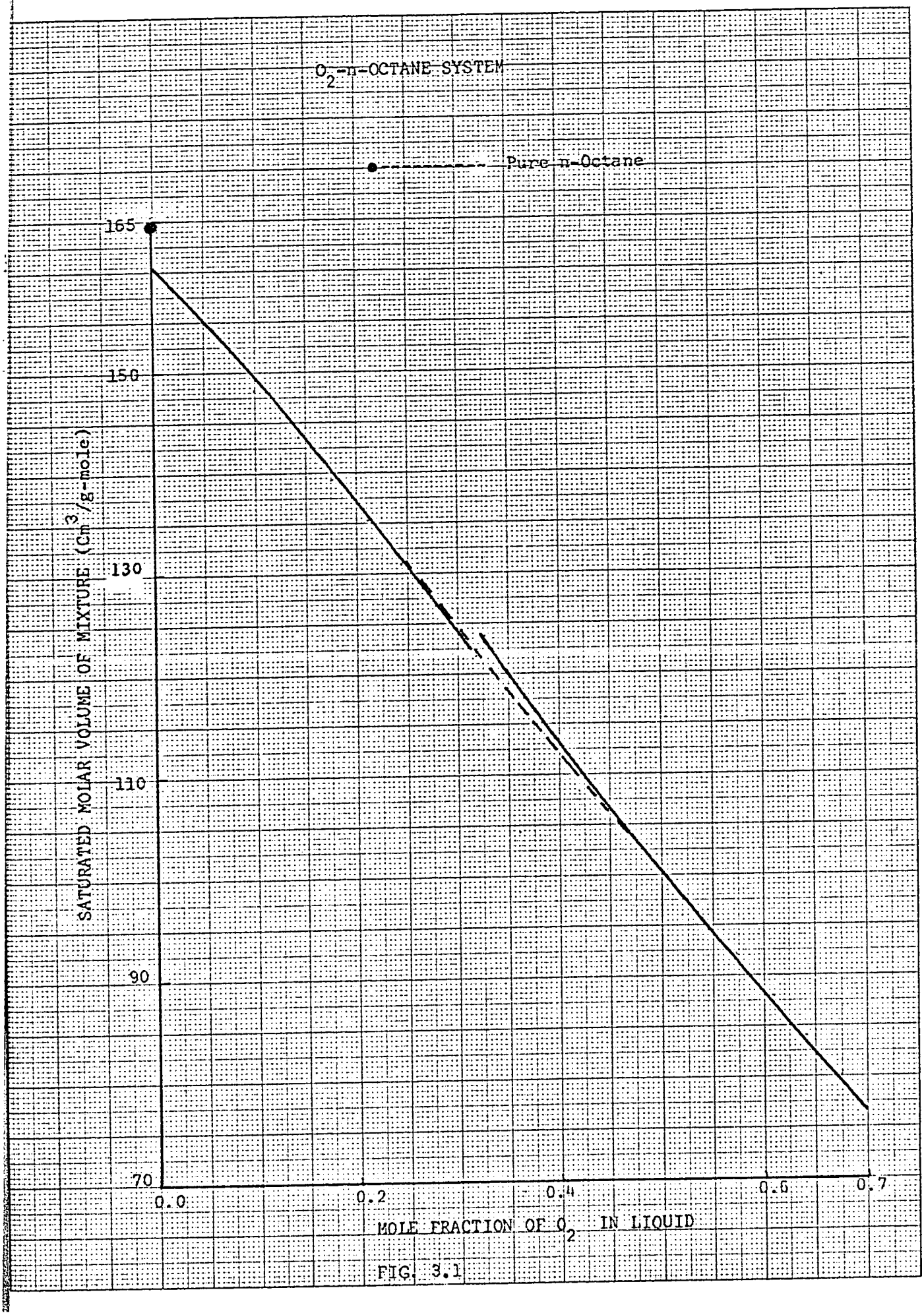
O_2-n-OCTANE SYSTEM
Pure n-Octane
165
150
130
110
90
70
SATURATED MOLAR VOLUME OF MIXTURE (Cm^3/g-mole)
0.0
0.2
0.4
0.6
0.7
MOLE FRACTION OF O_2 IN LIQUID

FIG. 3.1

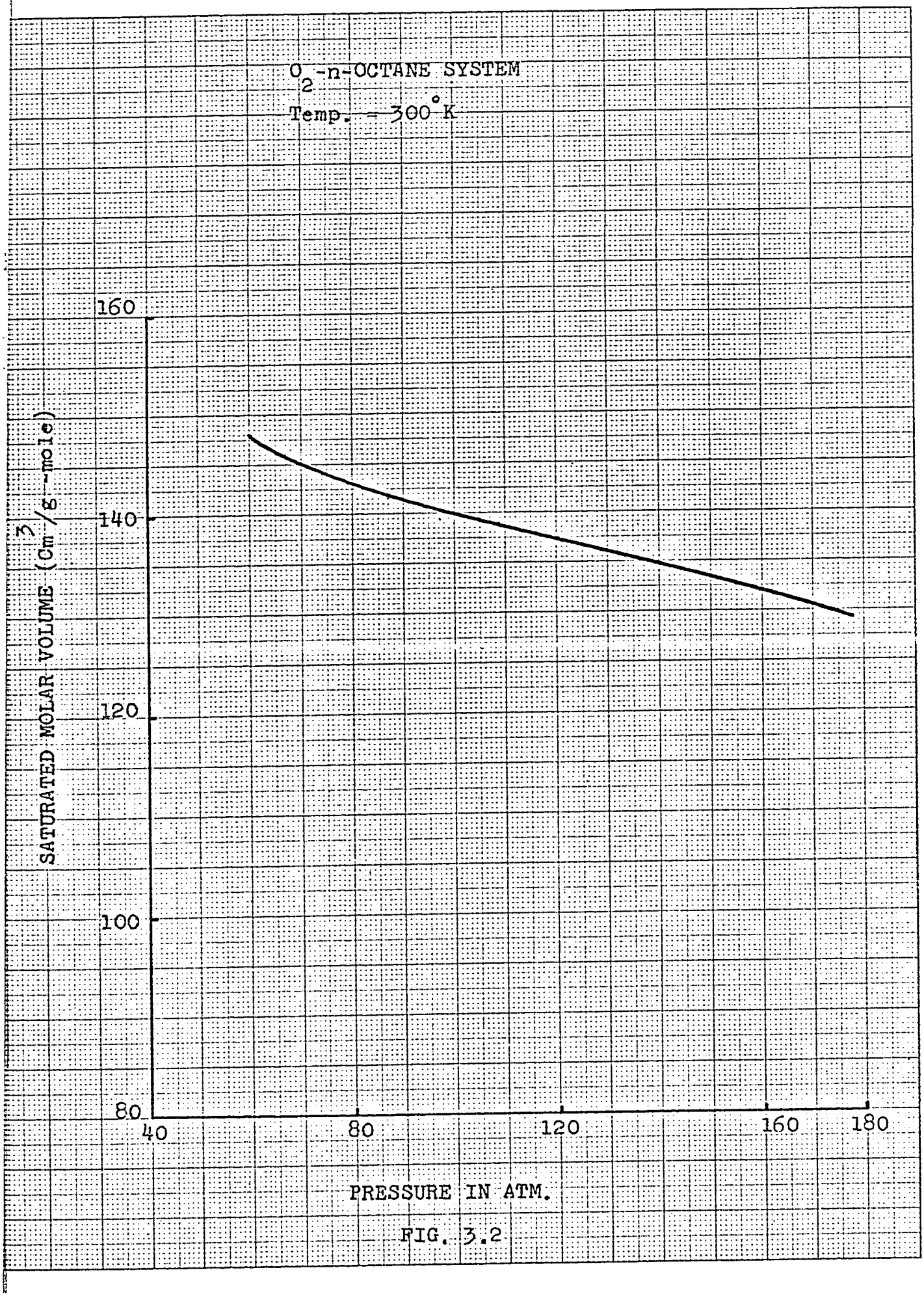
O_2-n-OCTANE SYSTEM
Temp. = 300° K
SATURATED MOLAR VOLUME (Cm^3/g-mole)
160
140
120
100
80
40
80
120
160
180
PRESSURE IN ATM.

FIG. 3.2

factors for a number of gases. For the sake of reference, a graph (Fig. 3.3) is reproduced on a large scale to show experimental and calculated compressibility factors for CO_2 and H_2. It can be seen that the R-K equation gives a very good reproduction of the experimental P-V-T data. Based on the R-K equation of state (55), Chueh and Prausnitz (81) derived the following equation for the partial molar volume of a component K.

$$\overline{V}_K = \frac{\frac{RT}{(V-b)}\left(1+\frac{b_K}{(V-b)}\right) - \frac{2(\sum_i x_i a_{Ki}) - \frac{a b_K}{(V+b)}}{V(V+b)T^{1/2}}}{\frac{RT}{(V-b)^2} - \frac{a}{T^{1/2}}\left(\frac{2V+b}{V^2(V+b)^2}\right)} \qquad (3.11)$$

The various constants in the above equation, as proposed by Chueh and Prausnitz, are given by :

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$b = \sum_i x_i b_i$$

$$a_{ii} = \frac{\Omega_a R^2 T_{cii}^{2.5}}{P_{cii}}$$

$$b_i = \frac{\Omega_b R T_{cii}}{P_{cii}}$$

$$a_{ij} = \frac{0.25(\Omega_{ai}+\Omega_{aj}) R T_{cij}^{1.5} (V_{ci}+V_{cj})}{0.291 - 0.04(\omega_i+\omega_j)}$$

The dimensionless constants Ω_a and Ω_b, are equal to 0.4278 and 0.0867 respectively, if the first and second isothermal derivatives of pressure with respect to volume are set

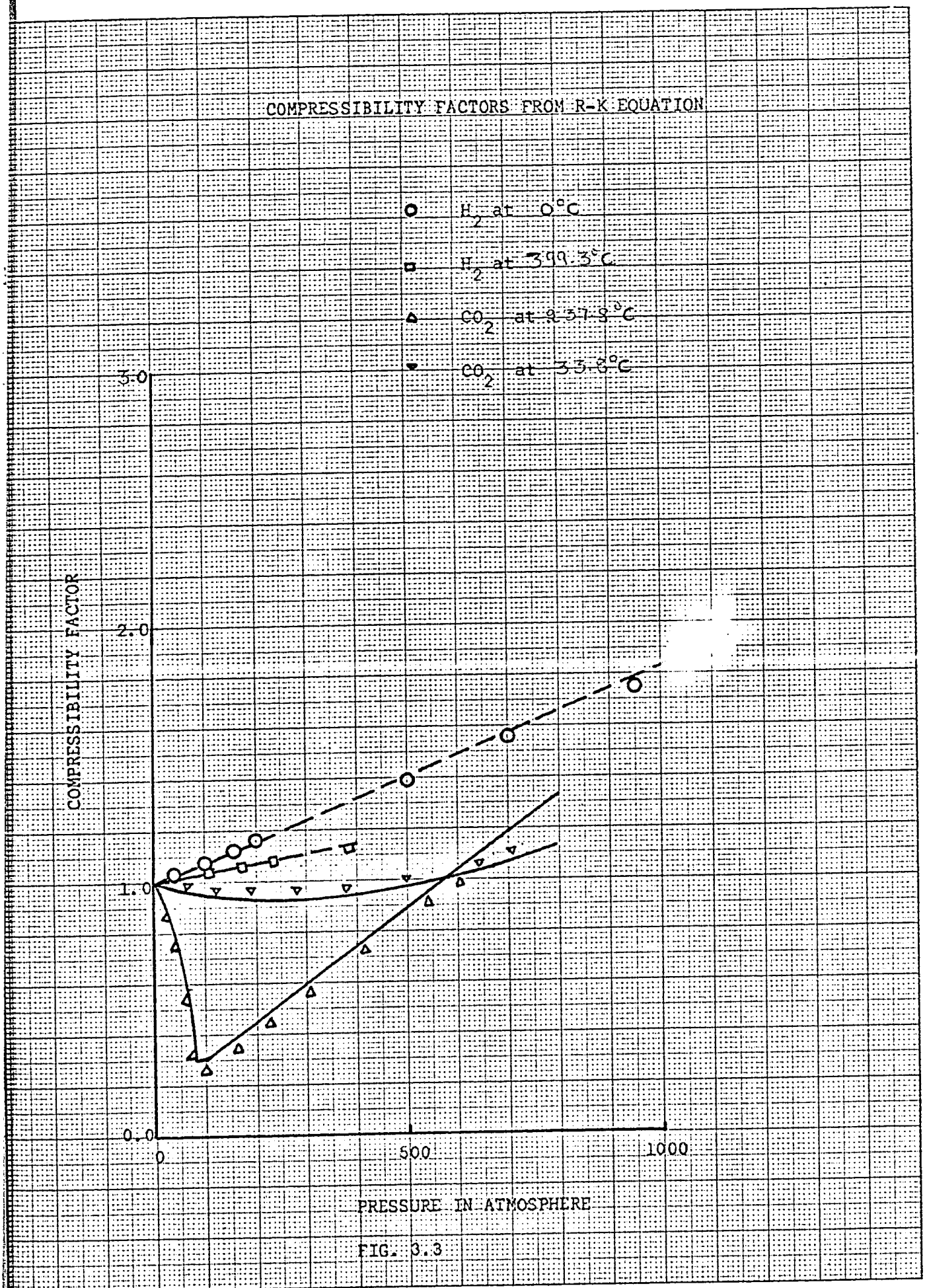
COMPRESSIBILITY FACTORS FROM R-K EQUATION
H2 at 0°C
H2 at 399.3°C
CO2 at 237.8°C
CO2 at 33.6°C
COMPRESSIBILITY FACTOR
3.0
2.0
1.0
0.0
0
500
1000
PRESSURE IN ATMOSPHERE

FIG. 3.3

equal to zero at the critical point. In other words, these values result by fitting the experimental data to critical region only. However, the critical region does not provide the best fit for a wide range of conditions. This is particularly true when the equation is applied to the liquid phase. Using these values of Ω_a and Ω_b amounts to subscribing to the two parameter theorem of corresponding states. However, as pointed by Pitzer (97), a three parameter theorem must be used in order to be applicable to a large class of substances.

Therefore, Chueh and Prausnitz (81) proposed to fit the R-K equation of state to the P-V-T data of the pure saturated liquid and evaluate the best Ω_a and Ω_b for each pure component. These constants for saturated liquids and saturated vapors, for nineteen common liquids are tabulated in (98). It has been found, after careful analysis, that at different values of saturation temperature, different values of Ω_a and Ω_b are obtained and Chueh and Prausnitz failed to give any criteria for the selection of the best values. However, in this work, an arithmetic mean of all the values obtained at different saturation temperatures is used. These constants for normal octane and oxygen, both in saturated liquid and saturated vapor phases, are given in table 3.1.

Utilizing the 'V', the saturated liquid molar volume of the mixture calculated previously (Fig.3.1) and the constants as defined above, the partial molar volume of each component in a mixture can be determined from equation 3.11. The partial molar volumes of n-octane and oxygen are plotted against the mole fraction of oxygen as shown in figure 3.4.

3.3 ISOMETRIC MIXING PRESSURE

The isometric mixing pressure is the pressure at which the gaseous solute and the liquid solvent mix isothermally and isopiestically without change of volume. The partial molar volume is a function of pressure. The isometric mixing pressure is of the order of several hundred atmospheres and since the partial molar volume at the isometric mixing pressure is to be used in equation 3.7, the effect of pressure on the partial molar volume cannot be neglected. The variation of the partial molar volume with the pressure (81) can be approximated by the relation :

$$\overline{V} = \overline{V}_0 (1 - \beta P) \qquad (3.12)$$

where $\overline{V}_0$ is the partial molar volume obtained from equation 3.12 and β is the compressibility of the gaseous component.

To compute the isometric mixing pressure, an estimate of the partial molar volume and the compressibility

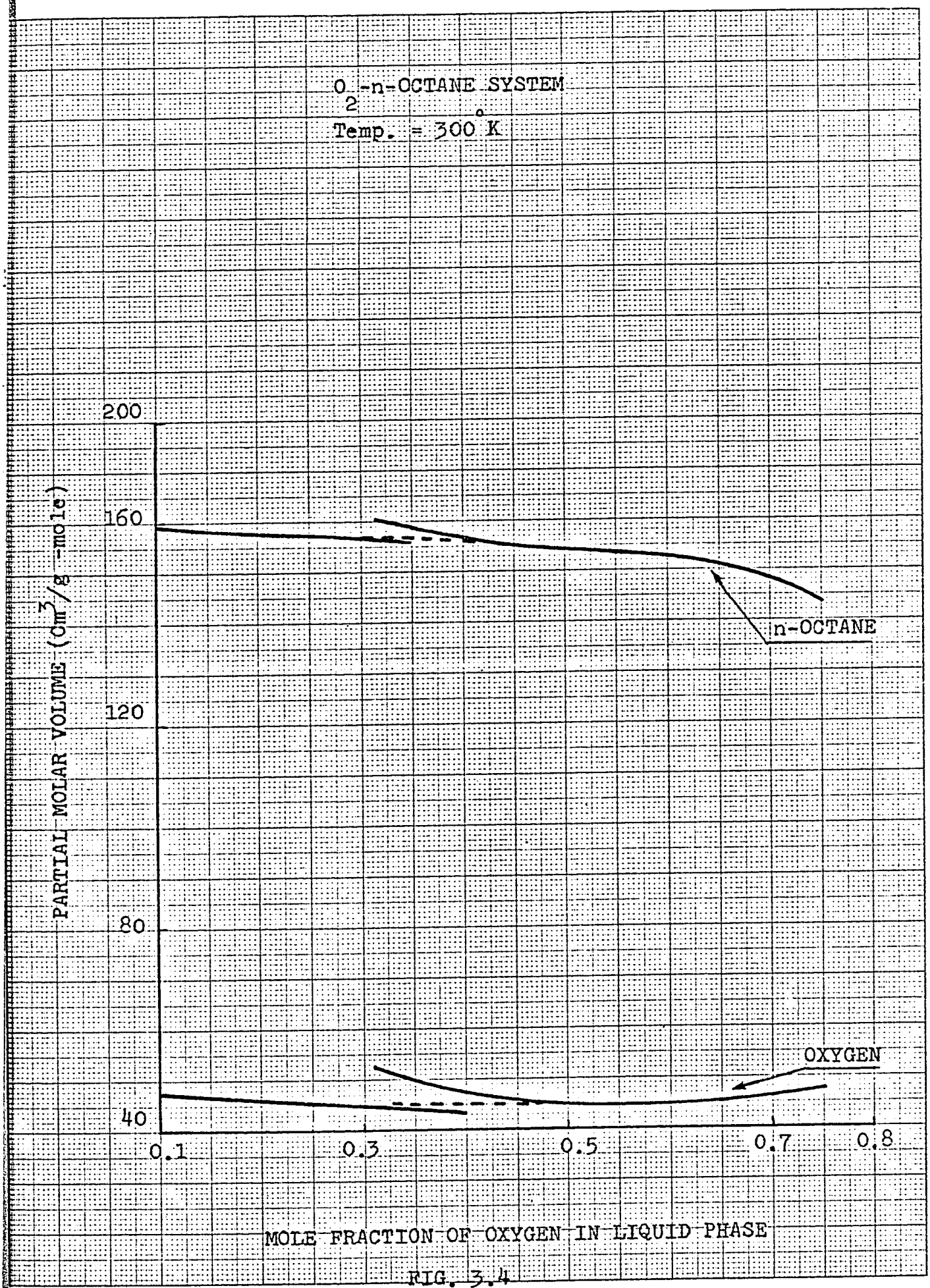
O_2-n-OCTANE SYSTEM
Temp. = 300° K
PARTIAL MOLAR VOLUME (Cm³/g-mole)
200
160
120
80
40
n-OCTANE
OXYGEN
0.1
0.3
0.5
0.7
0.8
MOLE FRACTION OF OXYGEN IN LIQUID PHASE

FIG. 3.4

β is required. There are very few experimental results available for the compressibility of the dissolved gases (102, 103). Prausnitz [81] suggested a good estimate of compressibility β as 10^{-4} atm^{-1} and the same value will also be used in this analysis. Prausnitz computed the isometric mixing pressure by finding the intersection of equation (3.12) with the isothermal pressure-volume curve for the pure gas. This approach will not be followed in the present analysis for two reasons.

(1) The P-V-T data for the gas may not be available at temperature and pressure of concern.

(2) It is not suitable for the quantitative work.

In the present analysis, the isometric mixing pressure is determined by equation (3.12) and the R-K equation of state as follows. An initial value of volume V_1 is chosen and substituted into the R-K equation of state.

$$P = \frac{RT}{(V_1 - B)} - \frac{A}{V_1(V_1 + B)T^{0.5}}$$

The constants A and B are calculated from the critical constants of the pure gas. The value of pressure as determined above is substituted into equation (3.12)and the new value of volume $\bar{V}$ is compared with V_1. If the two are not equal, then a new value of V_1 is chosen and the process repeated till they become equal (o.0001 tolerance). The pressure at this particular value of volume and at the temperature considered is the isometric mixing pressure.

3.4 FUGACITY

Equation (3.7) needs a knowledge of the fugacity of the gaseous component at the total and isometric mixing pressures. The fugacity of the pure gas at the total pressure and temperature can be taken from the tables in reference (100) or from the charts of reference (104). It is not always possible to find the fugacity at the isometric mixing pressure from these references since the isometric mixing pressure is of the order of several hundred atmospheres and the charts may not be available for such a high range of the reduced pressure. Even if the charts are available, they cannot be used for the quantitative work involved here, because of the nature of the iterative process.

In this analysis, the fugacity at total pressure and the isometric mixing pressure is determined from the fugacity coefficient relation for the pure components derived from the R-K equation of state (55)

$$\ln \phi = (Z-1) - \ln(Z-BP) - \frac{A^2}{B} \ln\left(1+\frac{BP}{Z}\right) \qquad (3.13)$$

where ϕ = Fugacity Coefficient of Pure Component = f/P.

$$Z = \frac{1}{(1-h)} - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \qquad (3.14)$$

$$A^2 = \frac{\Omega_a T_c^{2.5}}{P_c T^{2.5}}$$

$$B = \frac{\Omega_b T_c}{P_c T}$$

$$h = \frac{BP}{Z}$$

Equation (3.14) must be solved first to obtain the fugacity coefficient. It is a cubic in Z and has three roots. The root of interest in the present calculations is the largest value of Z. It is incorrect to use any other value of Z than the one given by equation (3.14) in solving equation (3.15) for the fugacity coefficient. After finding Z, the solution of equation (3.13) for the fugacity coefficient and hence fugacity is straightforward.

3.5 SOLUBILITY PARAMETERS

The solubility parameter of the gaseous solute is computed from the thermodynamic properties of the pure gas at the temperature of the solution and the isometric mixing pressure. As defined before : $\delta_i = \left(\frac{\Delta E}{\bar{V}_i}\right)^{1/2}$ where $\bar{V}_i$ is the partial molar volume of the gaseous solute and

$$\Delta E = \Delta H - RT + \pi \bar{V}_i$$

$$\text{and} \quad \Delta H = H(\text{at } P=0) - H(\text{at } P=\pi)$$

The isometric mixing pressure changes with every assumed value of mole fraction required in the iterative process. Thus, the values of enthalpy at all those unknown pressures cannot be taken from the tables giving the

enthalpy at various pressures, because of the nature of the iterative process. Therefore, it is not possible to calculate the solubility parameter at the isometric pressure and temperature of the solution. This is a drawback in this analysis. However, the solubility parameters available in the literature (100) will be used in this analysis.

3.6 ESTIMATION OF SOLUBILITY OF GAS

Denoting the sub-script 1 for the gaseous solute and 2 for the gaseous solvent, the equation (3.7) for the solubility of the gaseous solute can be re-written as :

$$RT \ln\left(\frac{f_1(P)}{x_1 f_1(\pi)}\right) = \overline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 - \int_P^{\pi} \overline{V}_1 \, dP \qquad (3.7)$$

where $\overline{V}_1$ is the partial molar volume at pressure .

Substituting equation (3.12) into the above integral :

$$RT \ln\left(\frac{f_1(P)}{x_1 f_1(\pi)}\right) = \overline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 - \int_P^{\pi} \overline{V}_{01} (1 - \beta P) dP$$

where $\overline{V}_{01}$ is the partial molar volume computed from equation (3.11), or

$$RT \ln\left(\frac{f_1(P)}{x_1 f_1(\pi)}\right) = \overline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 - \overline{V}_{01}\left[\left(\pi - \frac{\beta \pi^2}{2}\right) - \left(P - \frac{\beta P^2}{2}\right)\right]$$

Since the units of solubility parameter are $(Cal/Cm^3)^{1/2}$ and those of the partial molar volume are $Cm^3/g\text{-mole}$ and if R is taken as $82.06 (cm)^3 (atm)/(^\circ K)(g\text{-mole})$, then the first expression on the right hand side of above equation, i.e. $\overline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2$ must be multiplied by a factor (82.06/1.987 = 41.2984) in order to make both sides of the equation dimensionally

equal. Thus the equation takes the form :

$$RT \ln\left(\frac{f_1(P)}{x_1 f_1(\pi)}\right) = 41.2984 \overline{V}_1 \phi_2^2 (\delta_1 - \delta_2)^2 - \overline{V}_{01}\left[(\pi - P\frac{\pi}{2}^2) - (P - P\frac{P}{2}^2)\right] \quad (3.15)$$

Knowing the partial molar volume, isometric mixing pressure, the fugacity and the solubility parameters of the solute and the solvent, the mole fraction x_1 of the solute in the solvent can be calculated from equation (3.15). As it has been seen before, the calculation of partial molar volume requires knowledge of the mole fraction x_1. Hence, an iterative process involving the assumption of mole fraction is adopted. Since the lower and upper limits of x_1 (0.0 and 1.0 resp.) are known, the iterative process begins by assuming the mole fraction x_1 equal to the arithmetic mean. of the two extreme values. The partial molar volumes of the solute and solvent at this particular x_1 are determined and the partial molar volume of the solvent is used to evaluate the isometric mixing pressure π. The calculations for the isometric mixing pressure are performed in a separate sub-routine. Knowing the isometric mixing pressure, the fugacities at the total pressure and the isometric mixing pressure can be calculated. Now, the solubility parameters δ_1 and δ_2 are read as data and the left hand and the right hand sides of equation (3.15) are evaluated. The two sides of equation (3.15) are compared and if the left side is smaller than the right side, the upper limit of x_1 is set equal to

the previously assumed value of x_1. On the other hand, if the left side is greater than the right side of equation (3.15), then the previously assumed value of x_1 becomes its lower limit. With one of the limits changed, a new value of x_1 equal to the arithmetic mean of the new limits is assumed and the process is repeated till the difference in both sides of equation (3.15) is within the permissible limits (0.0001). This particular value of x_1, at which both sides of equation (3.15) are almost equal, is the mole fraction of the gaseous solute in the solvent at the equilibrium conditions at the given pressure P and the temperature T.

The variation of the mole fraction of oxygen with the pressure at constant temperature is shown in figure 3.5. The figure gives the plot for T=300°K and T = 350°K.

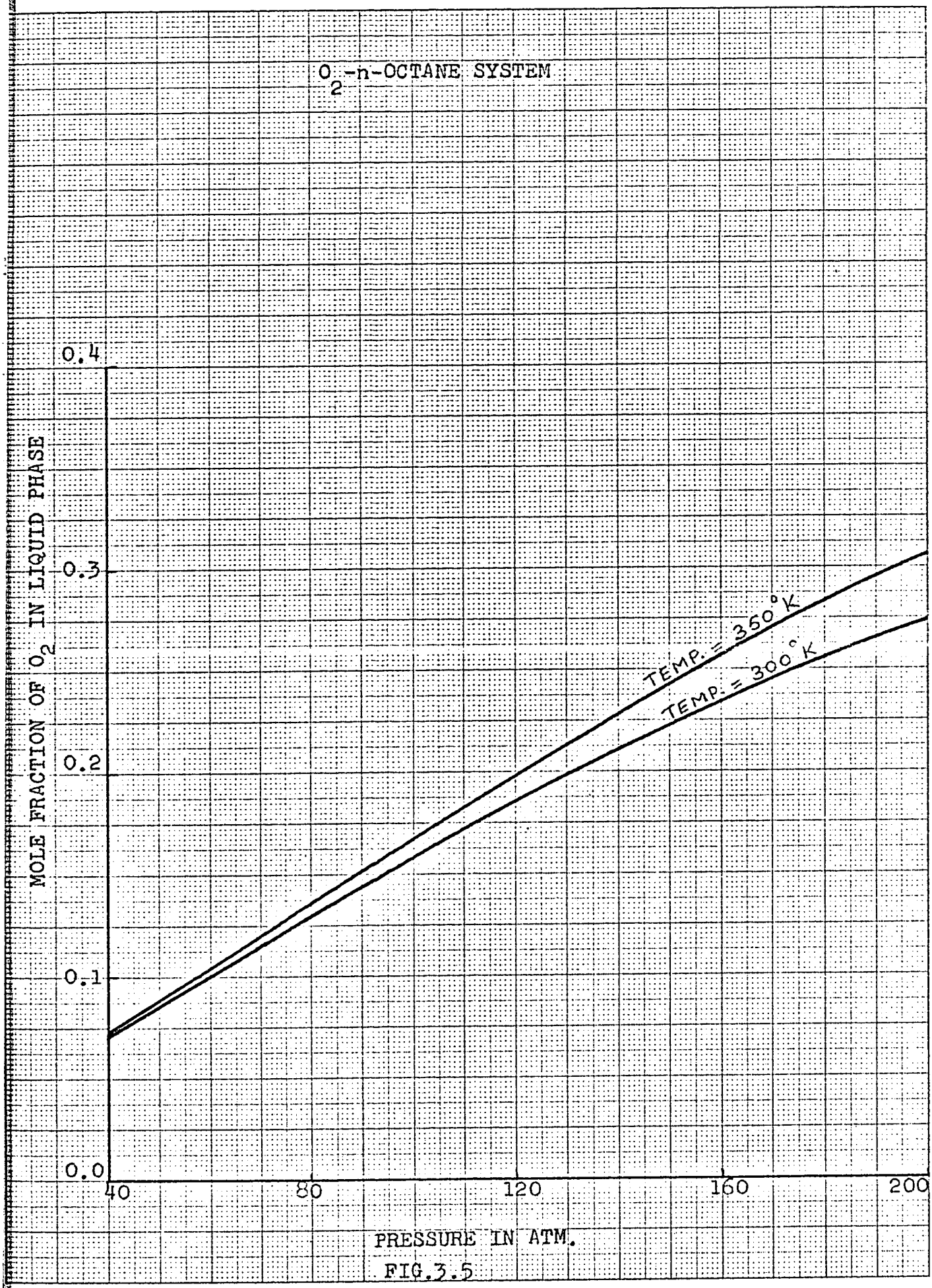
O_2-n-OCTANE SYSTEM
MOLE FRACTION OF O_2 IN LIQUID PHASE
0.4
0.3
0.2
0.1
0.0
TEMP. = 350°K
TEMP. = 300°K
40
80
120
160
200
PRESSURE IN ATM.

FIG.3.5

3.7 RESULTS AND DISCUSSION

Fig. 3.1 gives the variation of saturated liquid volume with the mole fraction of oxygen in the liquid phase and Fig. 3.4 gives that of the partial molar volumes of normal octane and oxygen with the mole fraction of oxygen in the liquid phase. The sudden jump in the curves of both the figures can be explained by the fact that different relations for calculating the saturated molar volume have been used. Equation (3.8) has been used for the reduced temperatures between 0.56 and 0.995, whereas equation (3.10) is used for reduced temperatures below 0.56. The use of these two different relations results in the discontinuity in the curves. In Fig. 3.1, the experimental value of saturated molar volume of pure liquid has also been plotted. It can be seen that the extrapolated value of mixture at the zero mole fraction of oxygen in the liquid phase is very close to the experimental value. Fig. 3.5 gives a plot of pressure vs. the mole fraction of oxygen in the liquid phase at different temperatures. It is evident that the mole fraction varies almost linearly with pressure and that the temperature has a very slight effect on it.

The mole fraction of the gas in the fuel, calculated above, may not be very accurate because of many

reasons. Firstly, the interaction constant K_{ij} has been assumed as zero, whereas this has quite a significant value for the oxygen-n-octane system, as will be seen in section 4. This assumption for the value of the K_{ij} for the system gives low values of saturated molar volumes and consequently, the partial molar volumes. The partial molar volume , in turn, effects the solubility calculations. However, the assumption of K_{ij} equal to zero, may not be bad for systems of like molecules for which the interaction constant is usually very small.

The value of compressibility β used has a great significance on the estimated value of isometric mixing pressure. Therefore, an experimental value of compressibility of the gas should be used for better results. Since the solubility parameters used have not been calculated at the isometric mixing pressure and the temperature of the mixture, therefore the calculated solubility is of questionable accuracy. Moreover, it has been assumed in this analysis that the vapor phase consists of the oxidiser only, whereas, in reality, it does have some fuel vapors also. However, this assumption is quite reasonable for the systems at low pressures or for the systems in which the fuel does not have the high vapor pressure at the temperature of the mixture.

In section 4, the interaction coefficient K_{ij} will be calculated for the system and the quantity of fuel present in the vapor phase will also be taken into account. Thus the results obtained in section 4 will be more satisfactory.

4. VAPOR LIQUID EQUILIBRIUM

In section three it is assumed that the vapor phase consists of the oxidising component only and the composition of liquid phase is predicted. In this section it is, however, assumed that some of the fuel vaporizes, which represents the actual situation in a combustion chamber. This section deals with the estimation of the equilibrium composition of both liquid and vapor phases.

In the previous section, it has been pointed out that Ω_a and Ω_b , the so called constants of Redlich and Kwong equation, are not constants but are functions of temperature. Wilson (77) considered Ω_a as a constant, equal to the original constant proposed by Redlich and Kwong, and Ω_b as temperature dependent for both liquid and vapor phases. Joffe and Zudkevitch (88) treated these parameters as functions of temperature for both phases but also showed that the use of one set of constants for both phases gives very good approximations. The constants for the liquid phase were recommended for both phases. The use of one set of constants, apart from simplifying the prediction of phase behavior of a mixture, has the advantage that the analysis can be extended to the critical region where the two separate sets of constants may not result in the compliance of the stability requirements (i.e $\hat{f}_i^L = \hat{f}_i^V$).

Joffe and Zudkevitch determined the equilibrium constants for single component systems. They extended their scheme of finding equilibrium constants to the binary and multicomponent systems by the introduction of an interaction constant C_{ij} is different from that of Chueh's constant K_{ij} [81]. While K_{ij} reflects the deviation of T_{cij} from the geometric mean of critical temperatures, C_{ij} gives the deviation of a_{ij}, the R-K constant for the mixtures, from the classical geometric mean assumption.*

Working along the same lines, Chang and Lu [90] evaluated one set of R-K equation constants for components below the critical temperatures. Chang and Lu did not make use of the generalized fugacity coefficient relation of Lyckman et. al. [89] and instead set up an iterative procedure similar to that of Chueh and Prausnitz. [82] Their method requires at least one experimental x-y data point and the value of the liquid phase compressibility factor. The method of Chang and Lu has the advantage of being applicable at all temperatures, except near the critical region, while that of Joffe and Zudkevitch [88] is limited for reduced temperatures between 0.56 and 0.93. They used these temperature dependent constants for the prediction of partial molal volumes of normal fluids. It was

---

* $a_{ij} = (a_{ii}\ a_{jj})^{\frac{1}{2}}\ (1 - c_{ij})$

noted [104] that Chang's technique has been extended for calculating the parameters Λ_a and Λ_b for the case in which the temperature is above the critical temperature of one of the components.

Hsi and Lu [91] assumed that Λ_a and Λ_b values are unique for a component. In other words, if the values are known for a component in one binary system, then these values can be used for the same component in any other binary system. Thus, to evaluate these parameters, for a component above its critical temperature, at least one experimental x-y point must be known for the component in any binary system. It is preferred and recommended that the known data point be for a binary system similar to the system under study. The iterative scheme is described in detail in reference [91]. Hsi and Lu used these parameters for predicting the gas solubilities and phase equilibria of normal fluid mixtures with one supercritical component. They studied methane with other hydrocarbons and used methane-propane system for calculating Λ_a and Λ_b. The predicted results are in good agreement with the experimental results.

4-1 EQUILIBRIUM EQUATIONS

Hsi and Lu made use of the basic relationship for defining phase equilibria that at equilibrium the fugacity of a component 'i' in the liquid phase is equal to

the fugacity in the vapor-phase.

$$\text{i.e.} \quad \hat{f}_i^L = \hat{f}_i^V \tag{4.1}$$

The fugacity in liquid and vapor phase, respectively, is given by :

$$\hat{f}_i^L = \hat{\Phi}_i^L \, x_i \, P \tag{4.2}$$

$$\hat{f}_i^V = \hat{\Phi}_i^V \, y_i \, P \tag{4.3}$$

Chang and Lu have expressed, for simplicity in calculations, the fugacity coefficient as follows : (90)

For the liquid phase :

$$\ln \hat{\Phi}_i^L = (Z_L - 1)\frac{B_i}{B} - \ln(Z_L)(1-h_L) - \frac{A^2}{B}\left(\frac{2\sum_j x_j A_{ij}^2}{A^2} - \frac{B_i}{B}\right)\ln(1+h_L) \tag{4.4}$$

And for the vapor phase:

$$\ln \hat{\Phi}_i^V = (Z_V - 1)\frac{B_i}{B} - \ln(Z_V)(1-h_V) - \frac{A^2}{B}\left(\frac{2\sum_j y_j A_{ij}^2}{A^2} - \frac{B_i}{B}\right)\ln(1+h_V) \tag{4.5}$$

The derivation of equation (4.4) and (4.5) is given in the appendix 2. In using equations (4.4) and (4.5) it is assumed that the R-K equation can be applied to both liquid and vapor phases and also that for i = j (i.e. single component system) both the equations yield the same fugacity, (or fugacity coefficient) at the vapor

pressure of the pure component.

The mixing rules used for equations (4.4) and (4.5) are given below:

$$\omega_{ij} = 0.5(\omega_i + \omega_j) \tag{4.6}$$

$$Z_{cij} = 0.291 - 0.08\,\omega_{ij} \tag{4.7}$$

$$V_{cij} = \frac{1}{8}\left(V_{ci}^{1/3} + V_{cj}^{1/3}\right)^3 \tag{4.8}$$

$$P_{cij} = Z_{cij} R T_{cij} / V_{cij} \tag{4.9}$$

$$\Omega a_{ij} = 0.5(\Omega a_{ii} + \Omega a_{jj}) \tag{4.10}$$

$$T_{cij} = (T_{cii}\,T_{cjj})^{0.5}(1 - K_{ij}) \tag{4.11}$$

$$b_i = \Omega b_i R T_{cii} / P_{cii} \tag{4.12}$$

$$a_{ij} = \Omega a_{ij} R^2 T_{cij}^{2.5} / P_{cij} \tag{4.13}$$

$$A_i^2 = a_{ii} / R^2 T^{2.5} \tag{4.14}$$

$$B_i = b_i / RT \tag{4.15}$$

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{4.16}$$

$$b = \sum_i z_i b_i \tag{4.17}$$

$$A^2 = a / R^2 T^{2.5} \tag{4.18}$$

$$B = b / RT \tag{4.19}$$

z_i represents the mole fraction of component 'i' either in the vapor or in the liquid phase. The values of z_L, z_V and

h_L, h_V to be used in equations (4.4) and (4.5) are obtained by solving the simultaneous equations :

$$Z = \frac{1}{(1-h)} - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \qquad (4.20)$$

$$h = \frac{BP}{Z} \qquad (4.21)$$

Equations (4.20) and (4.21) result in a cubic equation in z which is solved by using equations (4.6) to (4.19). The largest root of this cubic gives the value of z_V and the smallest root that of z_L. Thus, knowing the critical properties, accentric factors and the mole fractions in both the phases, the fugacity coefficients for both liquid and vapor phases may be evaluated. Since the whole problem is, in fact, to find the compositions, an iterative procedure is set up which results in the evaluation of the mole fractions.

Combining equations (4.2) and (4.3), the mole fraction in the vapor phase is given by :

$$y_i = \left(\hat{\Phi}_i^L / \hat{\Phi}_i^V\right) x_i \qquad (4.22)$$

Also the pressure is calculated by :

$$P = \sum_i \left(\hat{f}_i^L / \hat{\Phi}_i^V\right) \qquad (4.23)$$

Using equations (4.22) and (4.23) and the condition $\sum_i y_i = 1$, the mole fractions in both phases can be predicted.

Hsi and Lu[91] are, in fact, not the first to use this approach in phase equilibria calculations. Manrique

and Borman [105,106] in their study of the rates of vaporization of spherical droplets in a stagnant inert atmosphere, utilized the same approach graphically, for the carbon-dioxide-nitrogen binary system. They claim to have calculated the fugacities of both the components at different mole fractions by the use of R-K equation. A plot of fugacity versus mole fraction is drawn for both components on the same graph and the two points are located on the curves which simultaneously give equal fugacities in the liquid and the vapor phases for both the components. The corresponding abcissas give the mole fractions in the liquid and the vapor phases at the equilibrium conditions. It is observed that the selection of the two points is somewhat arbitrary and the mole fractions predicted may not be very accurate. Moreover, this approach is not suitable for quantitative work.

Manrique, while using the R-K equation, adopted Chueh's mixing rules. However, he did not take into consideration the interaction term K_{ij} when defining the pseudo-critical temperature, T_{cij} for the mixture. Furthermore, the parameters Ω_a and Ω_b of the R-K equation were treated as constants for all the components and the values as originally proposed by Redlich and Kwong [55] were used.

Hsi and Lu [91], while following the same basic approach, gave a computational method which is very useful for quantitative work. The interaction coefficient K_{ij} is taken into account by making use of the experimental solubility or phase equilibria data for the binary systems. As pointed out earlier, Hsi and Lu considered the parameters Λ_a and Λ_b as a function of temperature in their analysis and also gave an iterative technique for the evaluation of these parameters.

The iterative scheme of Hsi and Lu requires the liquid phase mole fractions and temperature as input and gives the vapor phase mole fractions and the total pressure as the output. In essence, their iterative scheme is the one for the bubble point calculations and is described in detail in reference [91].

4.2 ITERATIVE TECHNIQUE

As pointed out in the previous section, the aim of the present study is to calculate the vapor-liquid equilibria of hydrocarbon fuels and oxidisers. As an example, n-octane and oxygen system is chosen. It has been mentioned before that no data regarding the solubility or phase equilibrium is available in the literature for this system. The temperature dependent parameters Λ_a and Λ_b

for n-octane can be calculated from any binary system such as n-octane and nitrogen system. But these parameters for oxygen cannot be evaluated since no data is available in the literature for any hydrocarbon and oxygen system. Data is available for systems like oxygen and carbon dioxide. But, since this system is quite different from oxygen and n-octane system, this data is not used. For uniformity, these parameters should be either treated as temperature dependent or independent of temperature for both the components. In the present study, these parameters are considered as independent of temperature. In fact, these parameters are treated as temperature independent for all the systems studied here. However, for the sake of comparison, these parameters are also treated as temperature dependent for n-octane and the values as originally proposed by Redlich and Kwong for these parameters are used for oxygen, The values of these parameters are calculated for both liquid and vapor phases by the method suggested by Chueh and Prausnitz[81].

In the present study, the primary interest is to predict the phase equilibria of systems for which no experimental data other than the total pressure and temperature is available. An iterative technique using equations (4.1) through (4.23), which is different from that of Hsi and Lu,

is, therefore, adopted. The technique used is as outlined below :

1. Assume a value of X_i and calculate $\hat{f}_i^L$ and $\hat{f}_j^L$ using equations (4.4) and (4.2).
2. Set $\hat{\Phi}_i^V$ and $\hat{\Phi}_j^V$ both equal to one.
3. Calculate y_i and y_j from equation (4.22) and using normalized y'S* calculate, $\hat{\Phi}_i^V$ and $\hat{\Phi}_j^V$ from equation (4.5).
4. Compare $\hat{\Phi}_i^V$ with its previous value and if they are not equal within a reasonable tolerance (o.0002 used in this study) repeat step 3 with this new value.
5. Compare $\hat{\Phi}_j^V$ calculated in step 3 with its previous value and if the two values differ by more than a reasonable tolerance (0.0002 used in this investigation) repeat steps 3 through 5. When both $\hat{\Phi}_i^V$ and $\hat{\Phi}_j^V$ are constant, $\sum_i y_i = 1$ is invariably satisfied.
6. Calculate total pressure from equation (4.23) and compare it with the given value of total pressure. If different, assume a new value of X_i and repeat steps 1 to 6. When the given pressure and the calculated total pressure are equal, the assumed value of X_i in step 1 and the calculated value of y_i in step 3 give the liquid and vapor phase mole fractions at the given pressure and temperature.

---

* $Y_1 = Y_1/(Y_1+Y_2)$

$Y_2 = Y_2/(Y_1+Y_2)$

The value of z used in equations (4.4) and (4.5) is found by solving the cubic equation in z (formed by combining equations (4.20) and (4.21) by Newton's method which is quadratically convergent. For rapid convergence of the iteration, a method similar to that used in section 3 (see page 53) is used for assuming the x_i values.

4-3 RESULTS AND DISCUSSION

In order to test the validity of the proposed method, the mole fractions in vapor and liquid phases of nitrogen with n-heptane, n-octane and butane are predicted and compared with the experimental values. The composition of nitrogen and n-heptane system is predicted at 305.38°K, 352.60°K, 399.83°K and 455.38°K and compared with the experimental data of Akers and Kehn [107]. Since the interaction coefficient K_{ij} is not available in the literature for this system, it is evaluated by using the data of Akers and Kehn [107] and bubble-point calculation technique of Hsi and Lu. The critical constants used, through out this section, are from the compilation of Kobe and Lynn [108]. K_{ij} values for nitrogen and hydrocarbon systems, as reported by Chueh [98] are plotted against the number of carbon atoms. The extrapolated value of K_{ij} for nitrogen and n-heptane systems obtained from this plot is used as the first guess in the iteration. The method of the evaluation of the constant

K_{ij} can be clearly followed from Fig. 4.1 which gives a plot of K_{ij} against the average of square of the deviation in the calculated and observed total pressure $(\Delta P)^2$. It is evident from Fig. 4.1 that $K_{ij} = 0.23$ gives the minimum deviation in observed and calculated pressure and, thus, this value of K_{ij} is used in this analysis. It may be mentioned that since K_{ij} values for higher hydrocarbons and nitrogen or oxygen are quite high, calculations are made only to two decimal figures accuracy.

As mentioned earlier, the parameters Ω_a and Ω_b are treated as independent of temperature and their values are taken from references [81] [82]. The results are reported in table 4.1. It can be seen that the results are quite satisfactory for lower temperatures, but at higher temperatures (260°F and above), there is a considerable difference in the vapor phase mole fractions. This is because of the fact that this technique does not give good results near the critical region. Figures 4.2 to 4.4 give the variation of mole fraction of nitrogen, in liquid and vapor phase, at different temperatures.

Results for nitrogen and normal octane system for 323.16°K, 348.16°K and 373.16°K are given in table 4.2. The experimental data used is that of Graham and Weale [109]. The interaction coefficient is calculated, as described

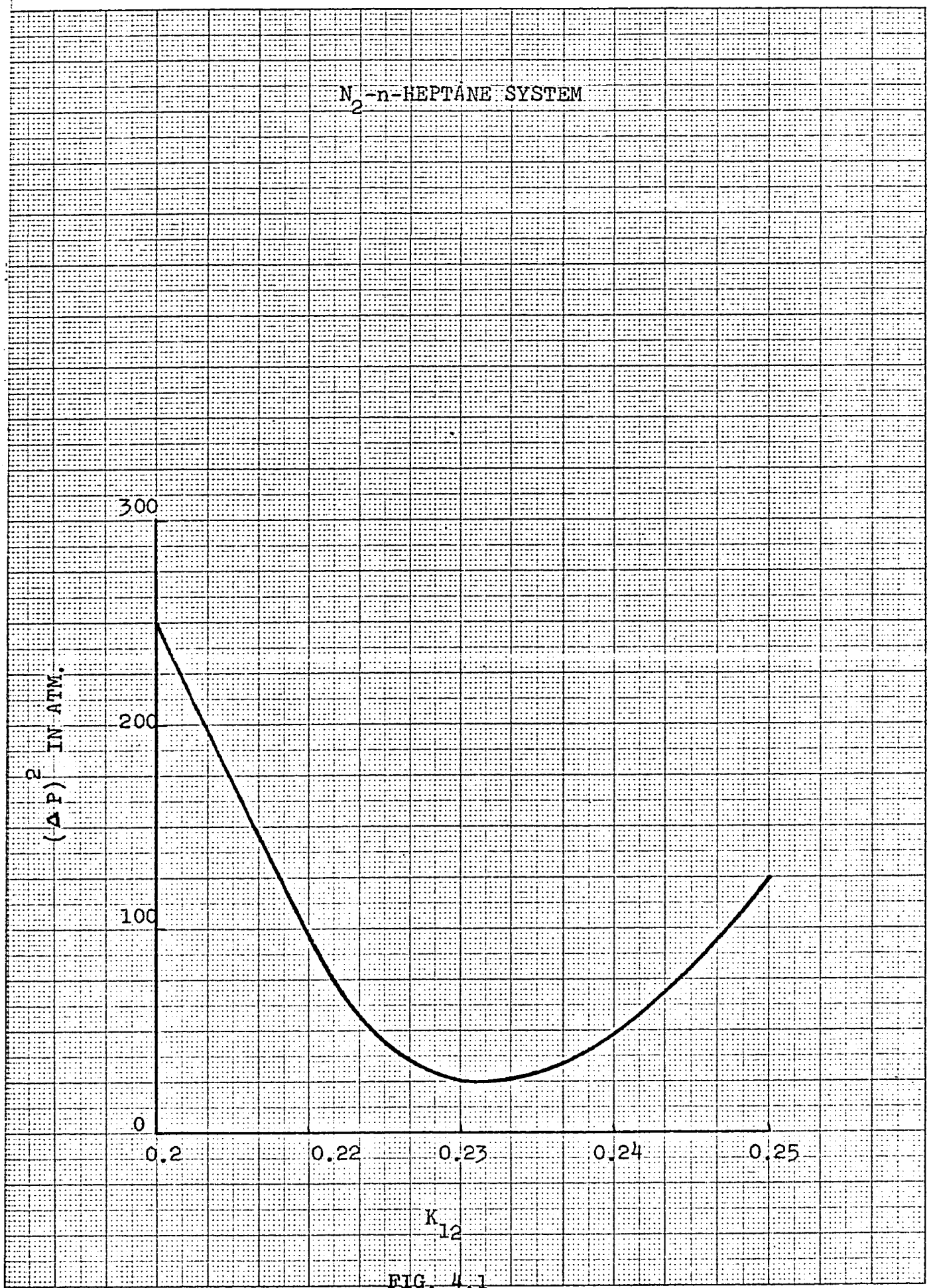
N_2-n-HEPTANE SYSTEM
300
200
100
0
$(\Delta P)^2$ IN ATM.
0.2
0.22
0.23
0.24
0.25
K_{12}

FIG. 4.1

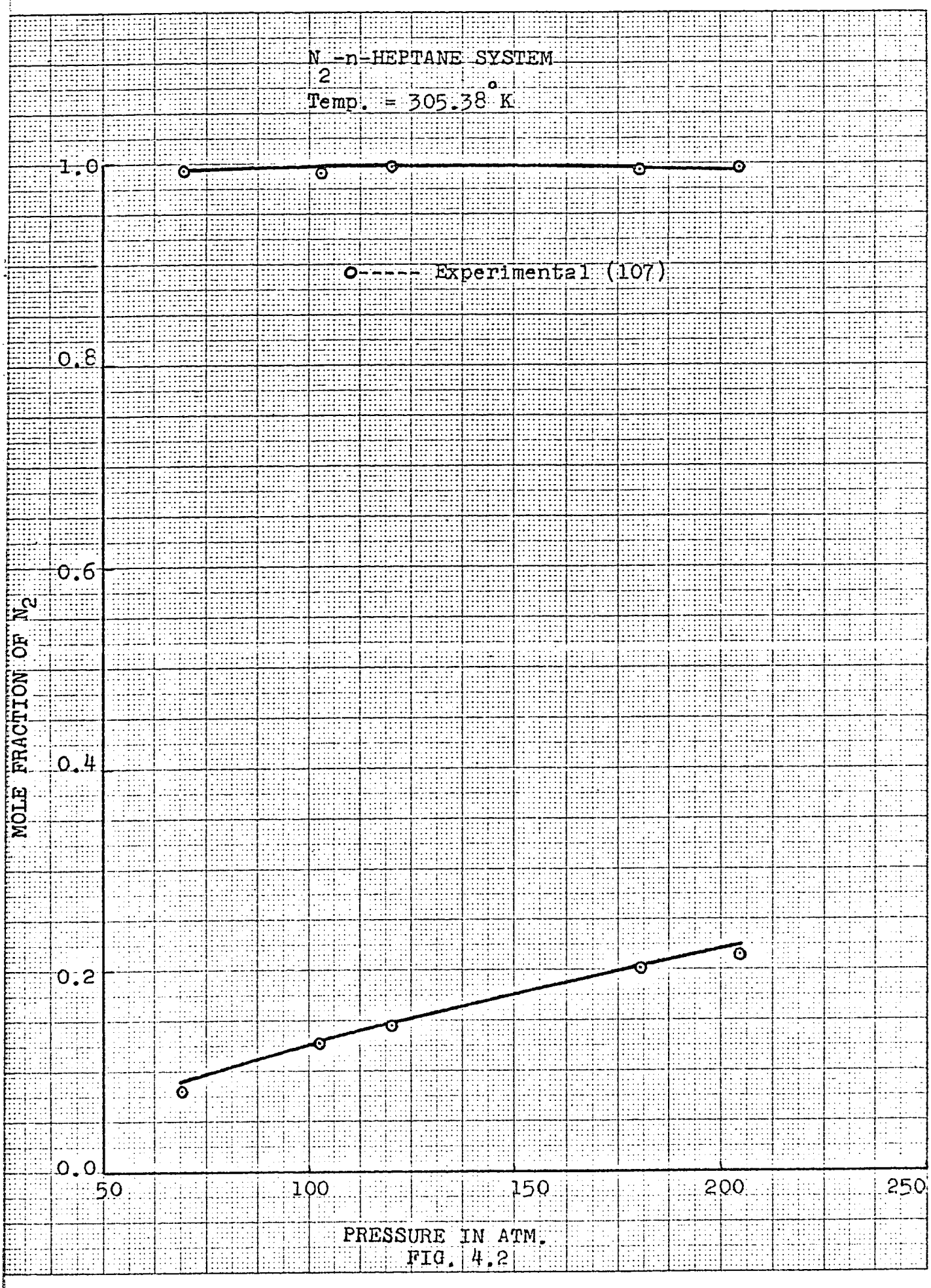
N2 -n-HEPTANE SYSTEM
Temp. = 305.38° K
o----- Experimental (107)
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N2
50
100
150
200
250
PRESSURE IN ATM.

FIG. 4.2

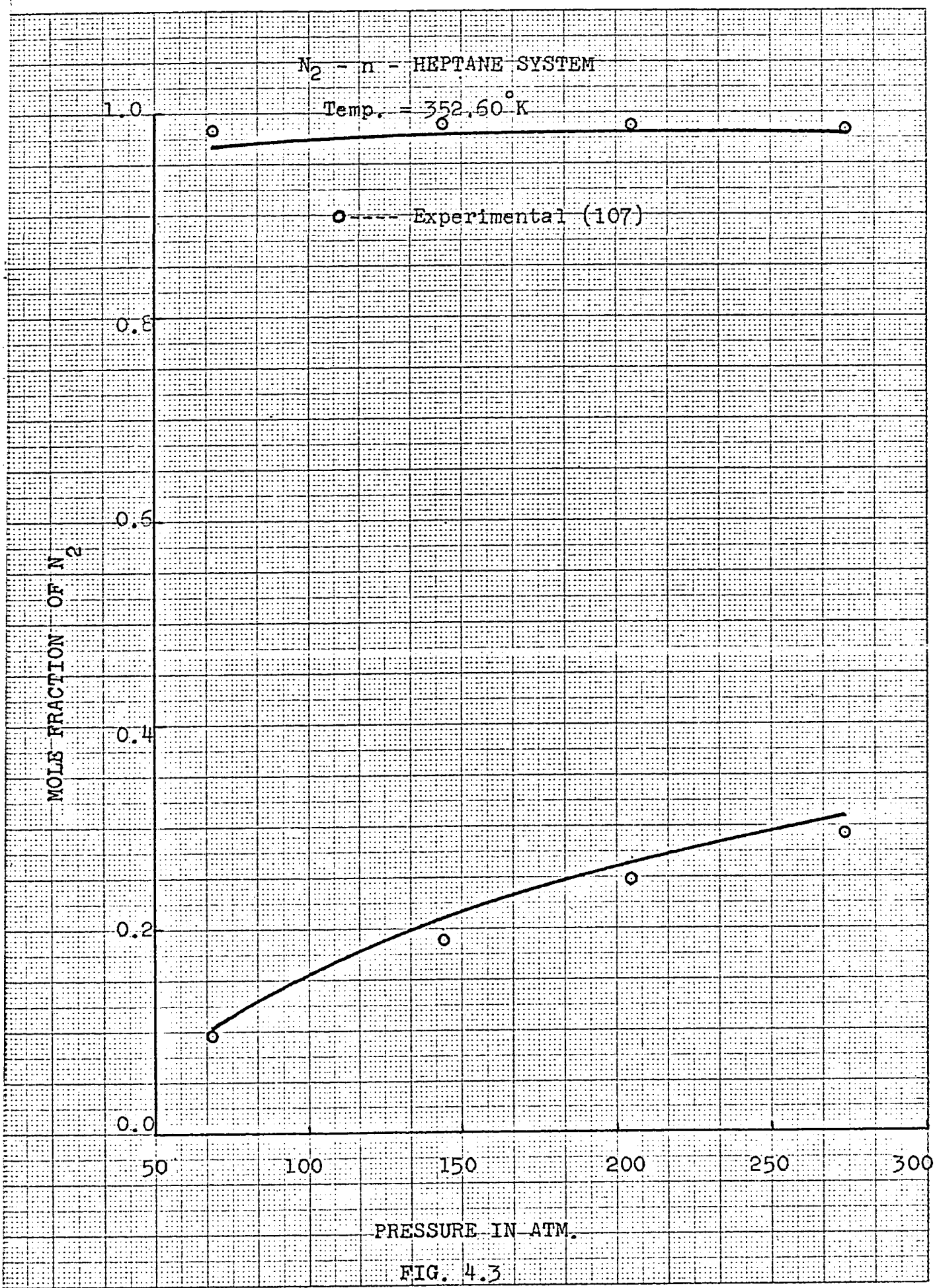
N_2 - n - HEPTANE SYSTEM
Temp. = 352.60°K
Experimental (107)
MOLE FRACTION OF N_2
1.0
0.8
0.6
0.4
0.2
0.0
50
100
150
200
250
300
PRESSURE IN ATM.

FIG. 4.3

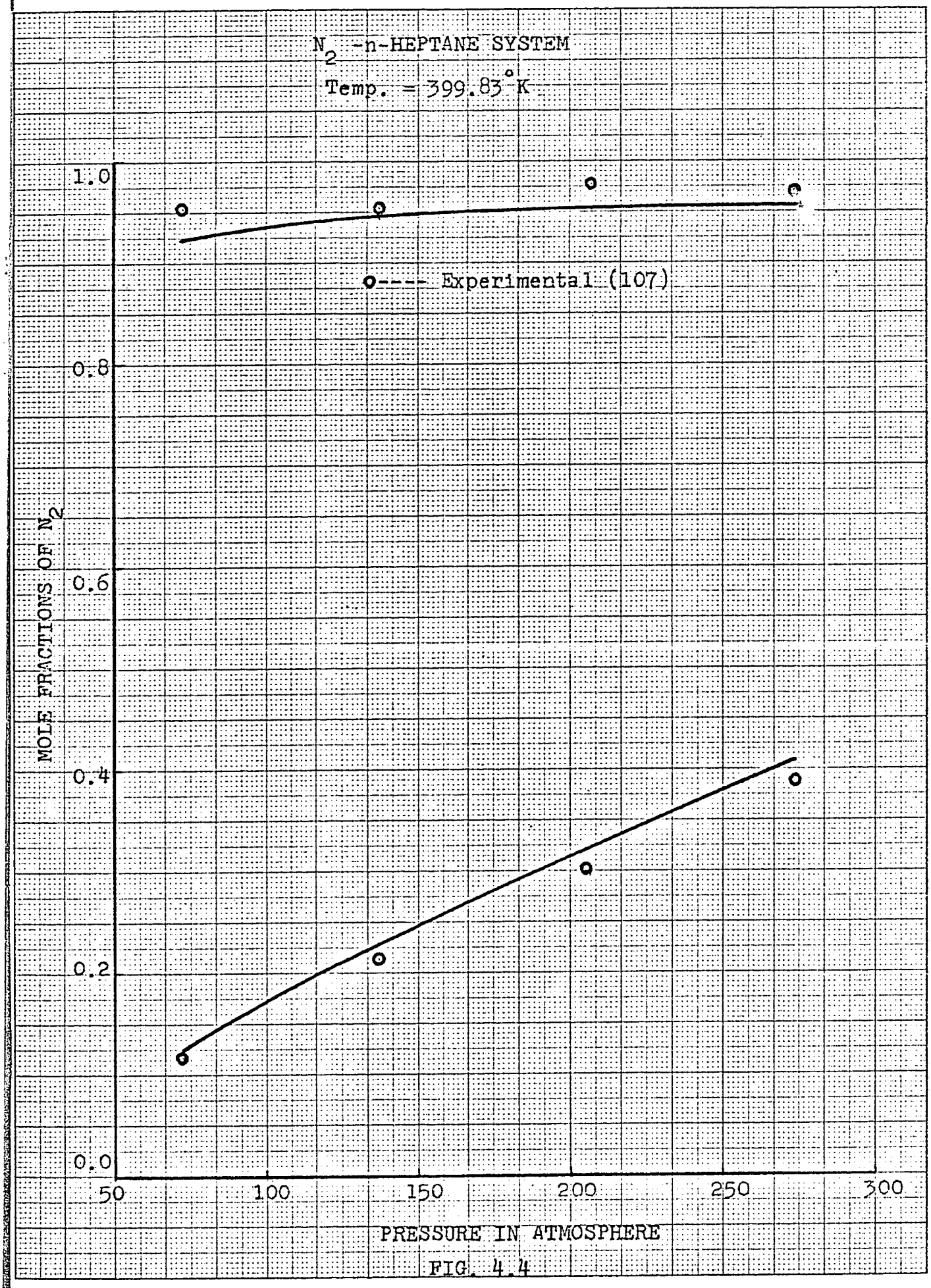
N_2 -n-HEPTANE SYSTEM
Temp. = 399.83°K
o---- Experimental (107)
MOLE FRACTIONS OF N_2
1.0
0.8
0.6
0.4
0.2
0.0
50
100
150
200
250
300
PRESSURE IN ATMOSPHERE

FIG. 4.4

above, using previously calculated (table 3.1) Ω_a and Ω_b values for n-octane. The K_{ij} versus $(\Delta P)^2$ has been plotted in figure 4.5. The maximum deviations in the vapor phase mole fractions of nitrogen are 0.49 % and 1.05 % at 348.16°K, and 373.16°K, respectively. Figures 4.6 to 4.8 give plots of pressure versus mole fractions in liquid and vapor phase, at different temperatures.

Table 4.3 shows the comparison for nitrogen-butane system between the predicted and the experimental results of Roberts and McKetta [110], at 310.94°K, 344.27°K, 377.60°K, and 410.94°K. The values of K_{ij}, Ω_a and Ω_b are those of Chueh and Prausnitz [81, 82]. It can be seen that there is closer agreement between the predicted and the experimental results at higher temperatures (377.60°K and 410.94°K). This tends to discount what has been said previously that at higher temperatures (near critical) this method does not give accurate results. But it will be seen a little later that the difference in results at the lower temperatures is due to the somewhat arbitrary choice of the interaction constant. Figures 4.9 to 4.12 give the graphical representation of these results.

Finally, the solubility data for the oxygen and iso-octane (2,2,4 Trimethylpentane) system is tested. The solubility of oxygen is given at four different temperatures (over a narrow range) and one atmosphere pressure.

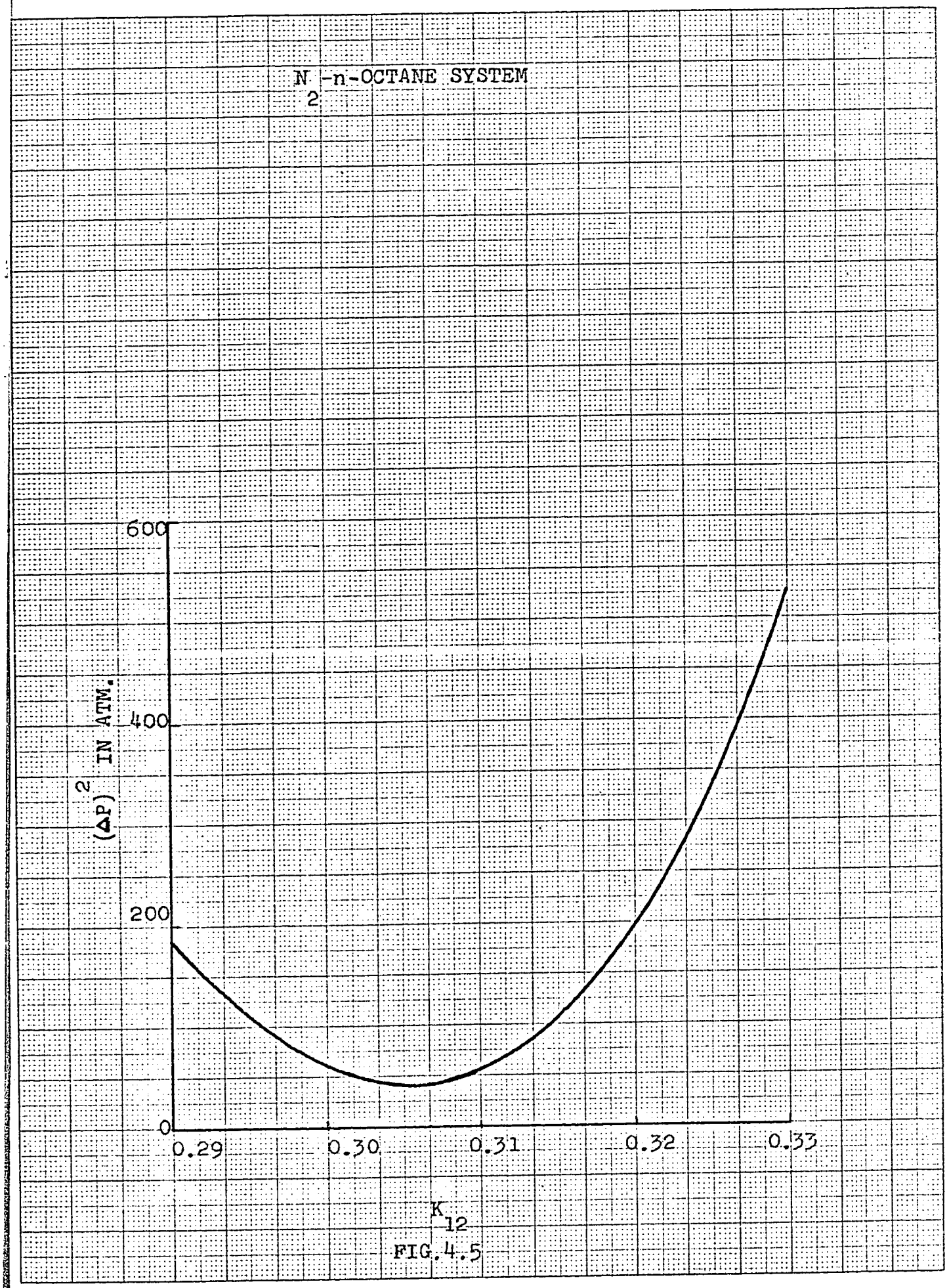
N -n-OCTANE SYSTEM
2
600
400
200
0
$(\Delta P)^2$ IN ATM.
0.29
0.30
0.31
0.32
0.33
K_{12}

FIG. 4.5

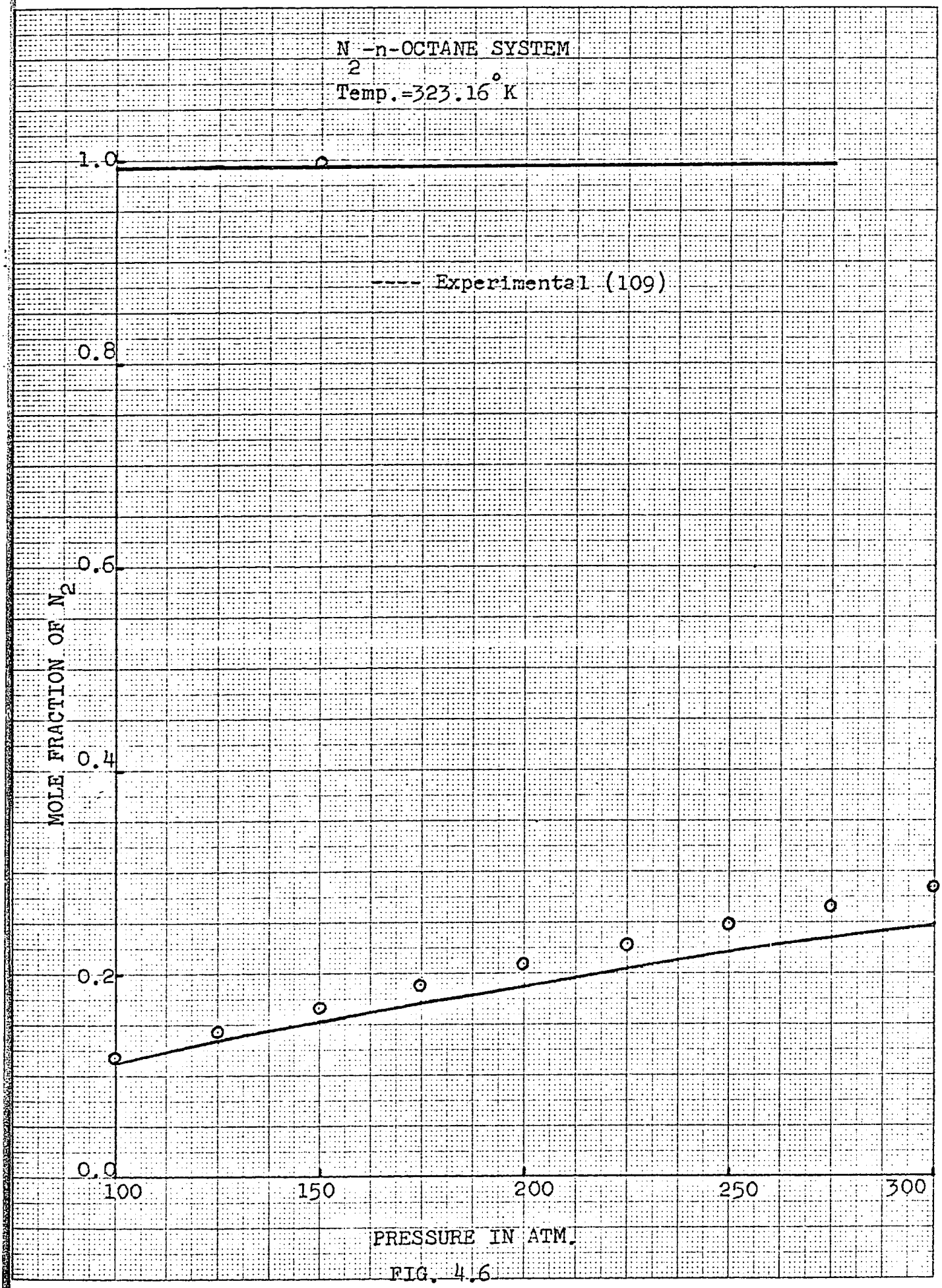
N2-n-OCTANE SYSTEM
Temp.=323.16° K
---- Experimental (109)
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N2
100
150
200
250
300
PRESSURE IN ATM.

FIG. 4.6

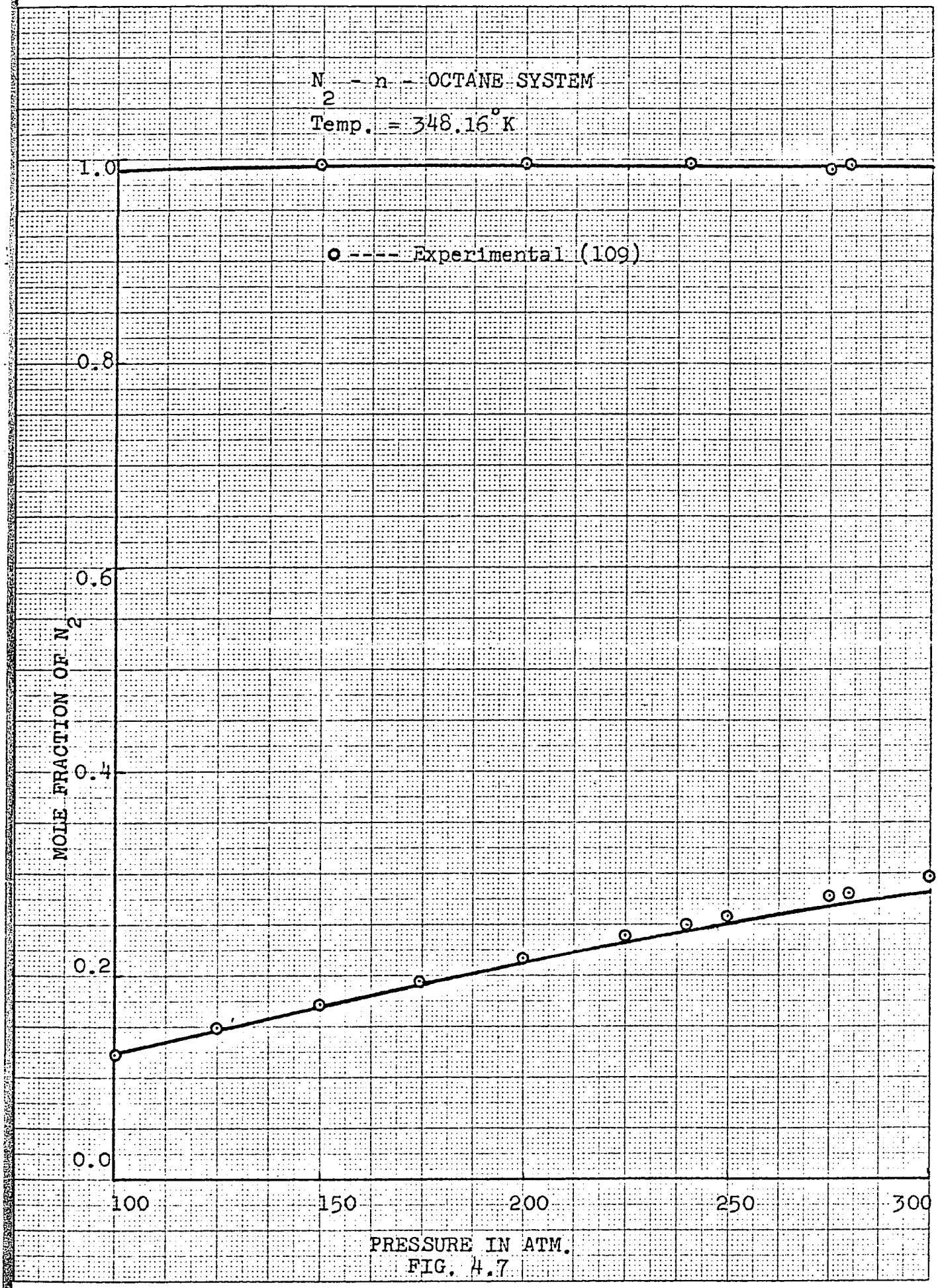
N_2 - n - OCTANE SYSTEM
Temp. = 348.16°K
o ---- Experimental (109)
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N_2
100
150
200
250
300
PRESSURE IN ATM.

FIG. 4.7

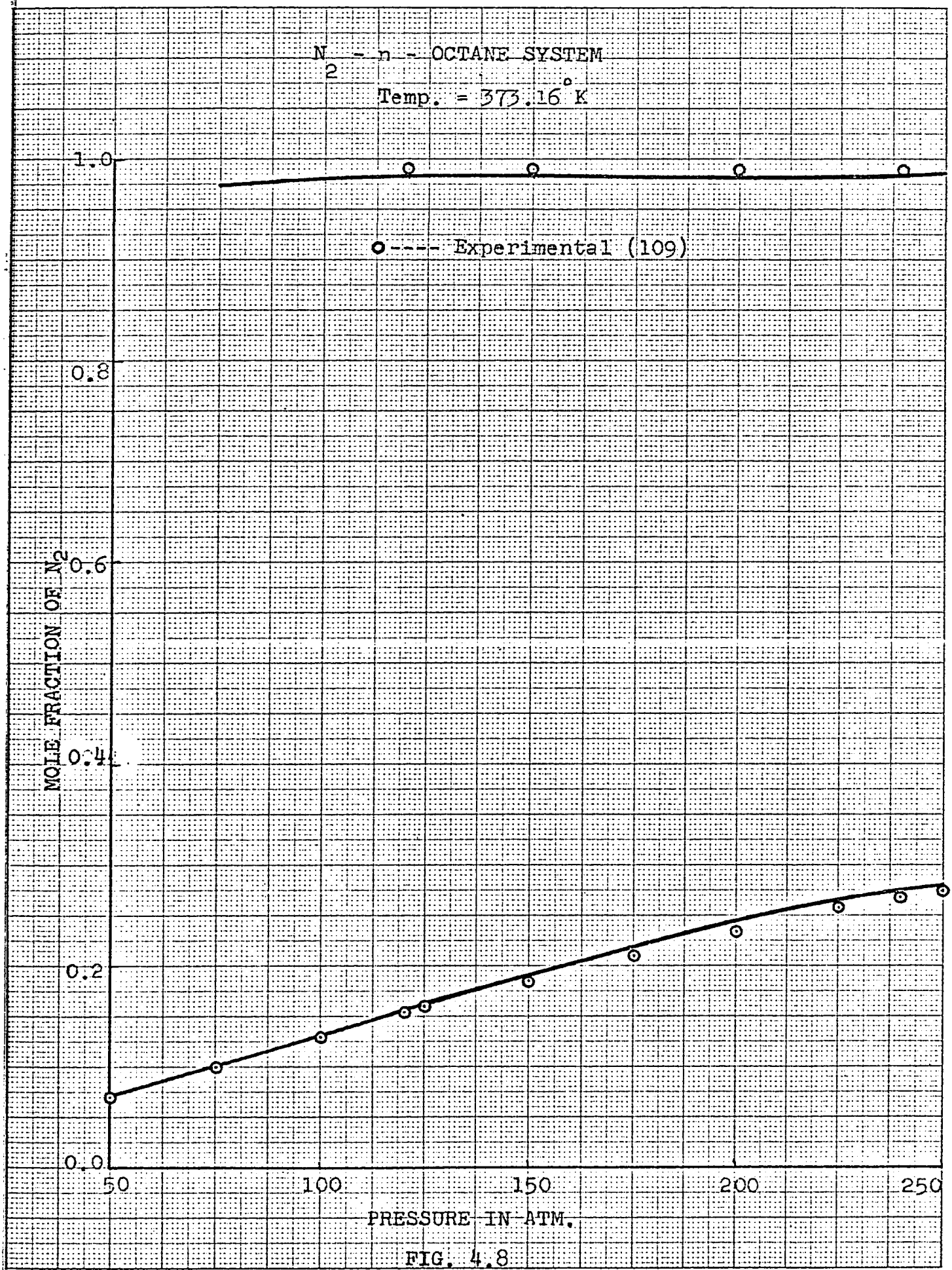
N_2 - n - OCTANE SYSTEM
Temp. = 373.16° K
o---- Experimental (109)
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N_2
50
100
150
200
250
PRESSURE IN ATM.

FIG. 4.8

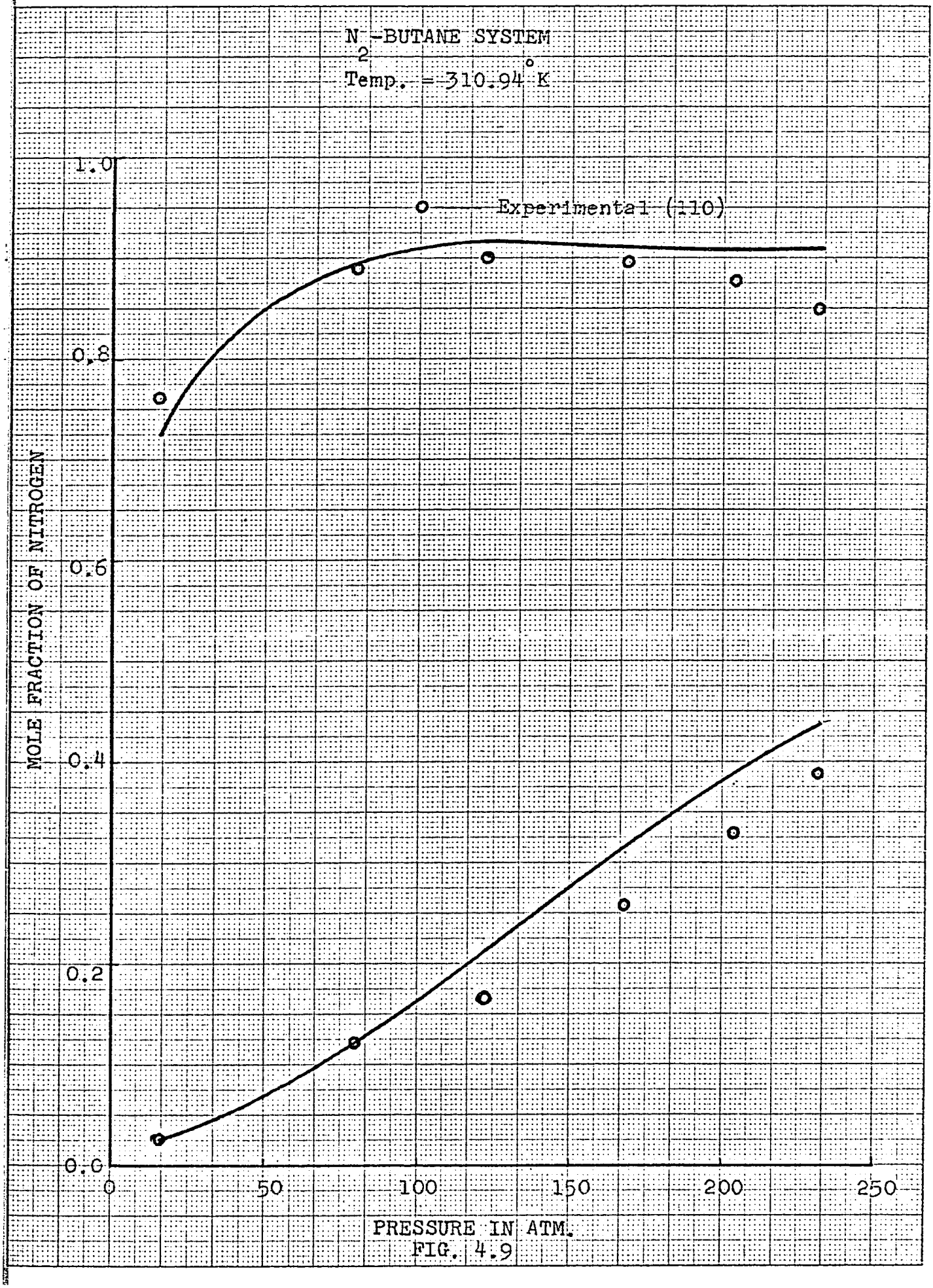
N -BUTANE SYSTEM
2
Temp. = 310.94° K
Experimental (110)
MOLE FRACTION OF NITROGEN
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
PRESSURE IN ATM.

FIG. 4.9

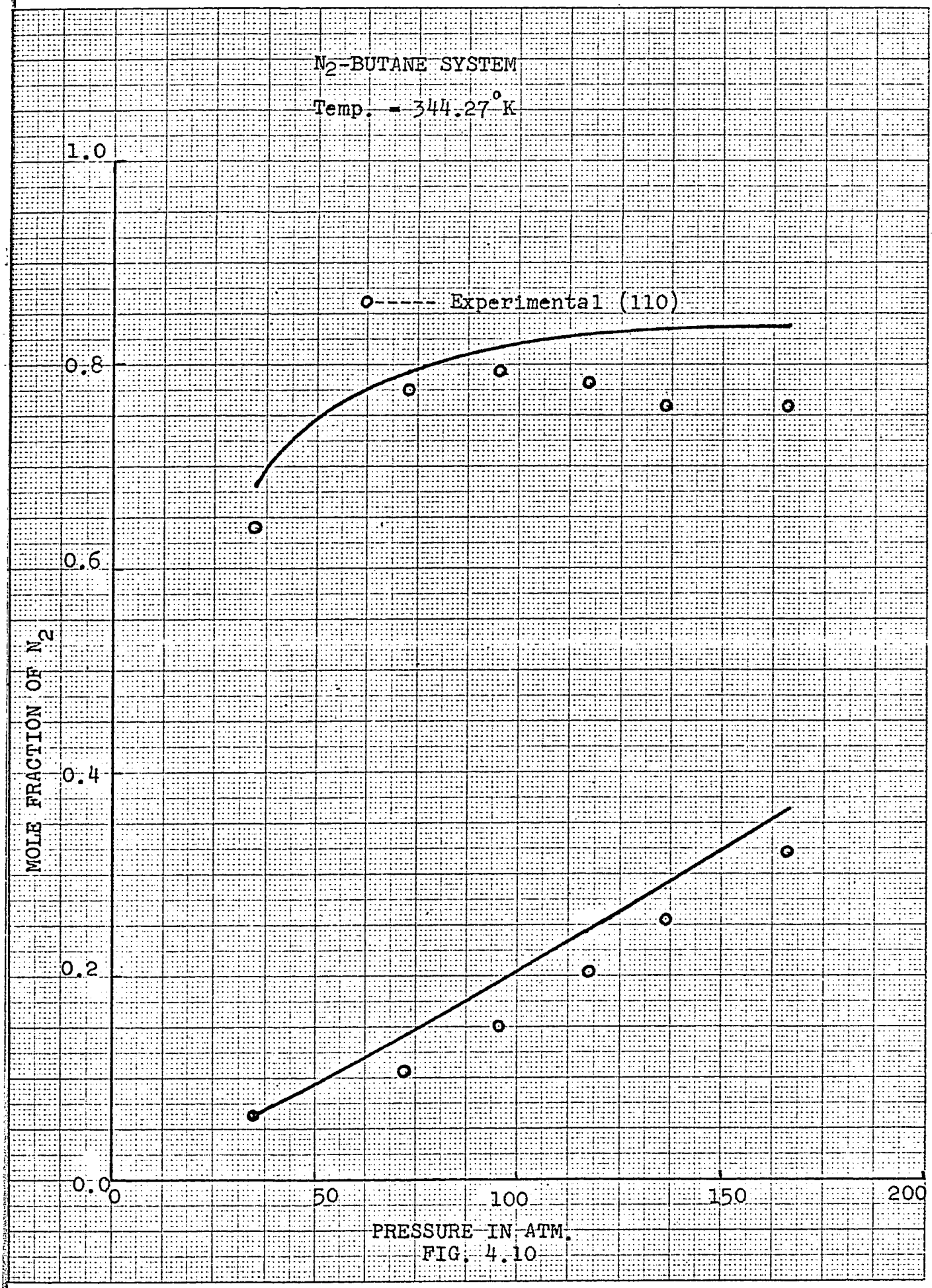
N_2-BUTANE SYSTEM
Temp. = 344.27°K
o----- Experimental (110)
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N_2
0
50
100
150
200
PRESSURE IN ATM.

FIG. 4.10

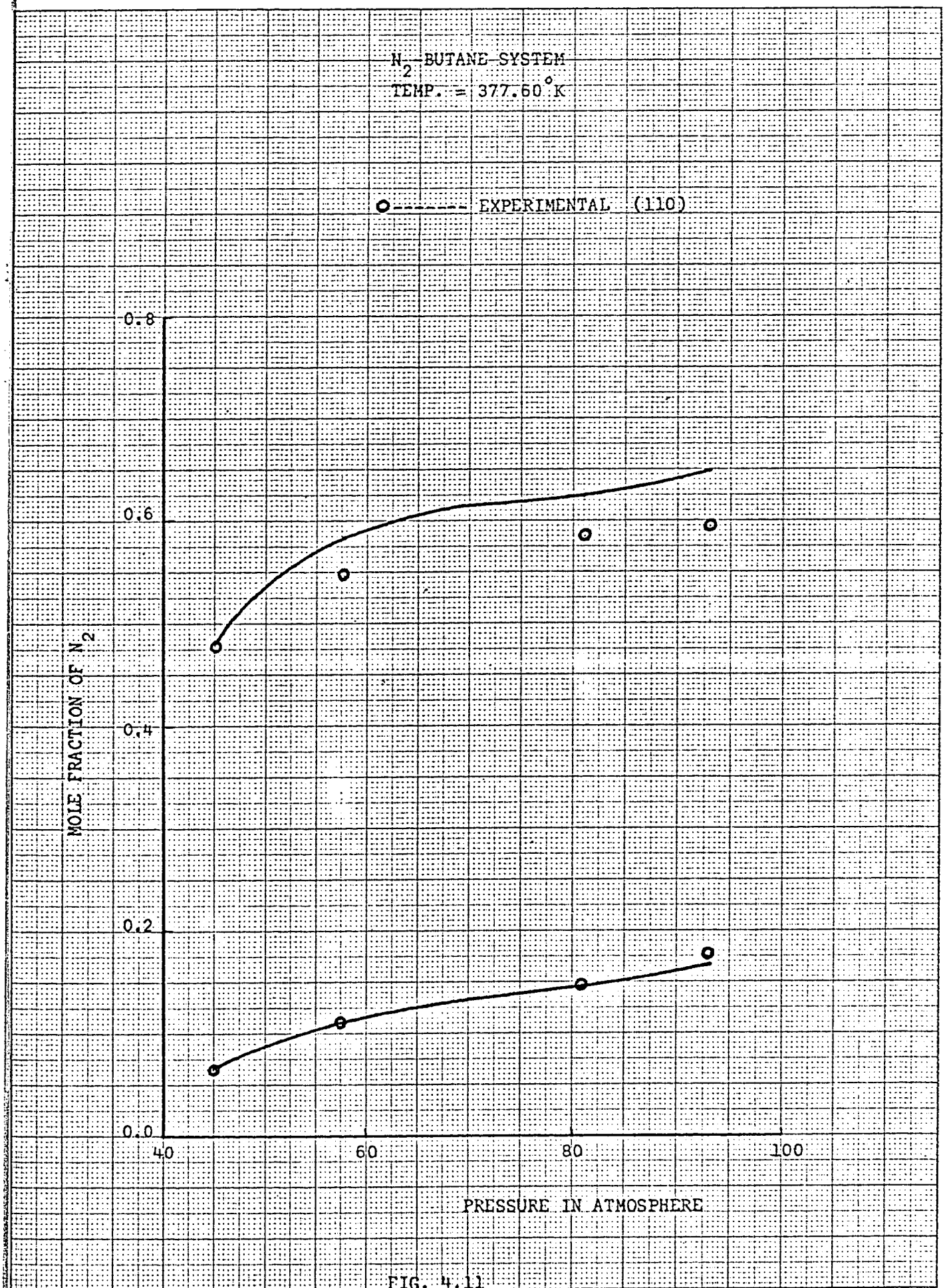
N_2-BUTANE SYSTEM
TEMP. = 377.60°K
EXPERIMENTAL (110)
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF N_2
40
60
80
100
PRESSURE IN ATMOSPHERE

FIG. 4.11

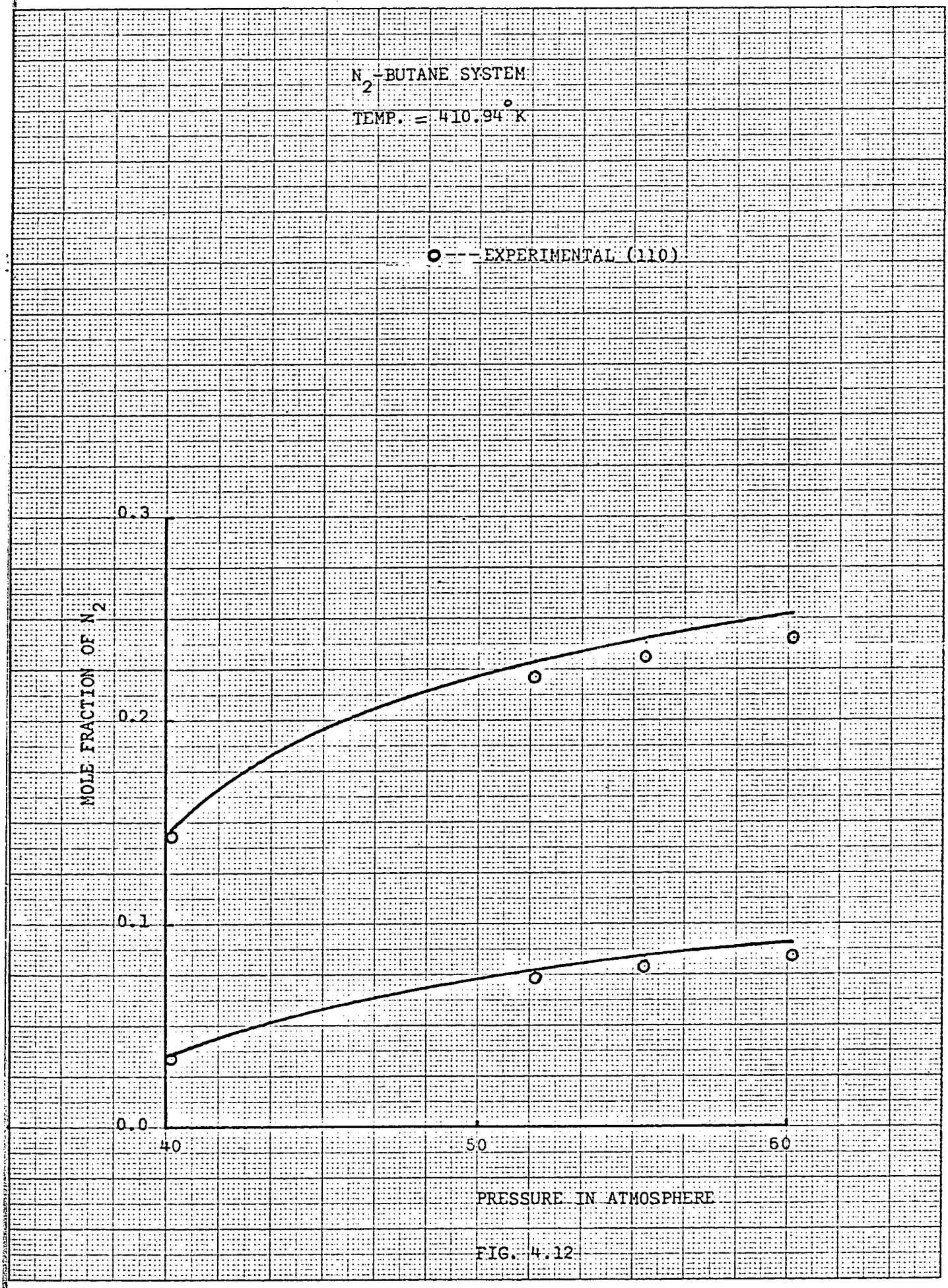
N_2-BUTANE SYSTEM
TEMP. = 410.94° K
O---EXPERIMENTAL (110)
MOLE FRACTION OF N_2
0.3
0.2
0.1
0.0
40
50
60
PRESSURE IN ATMOSPHERE

FIG. 4.12

The interaction coefficient K_{ij} for this system is found by the usual technique and is equal to 0.22. This value of K_{ij} fits the data quite well as shown in table 4.4. For lack of values of Ω_a and Ω_b for iso-octane in the literature, the original values as proposed by the Redlich and Kwong have been used for these parameters.

At this point an assumption is made that the molecular interaction between oxygen and normal octane is similar to that between oxygen and iso-octane. In other words, the interaction constant K_{ij} has the same value for both the systems. This assumption is very reasonable in the light of the fact that predicted results for nitrogen-iso-octane (2,2,4 Trimethylpentane) system are quite comparable with the experimental results of Graham and Weale[109]. Results given in table 4.5 for nitrogen-iso-octane system are obtained by using the same K_{ij} value as for the nitrogen-normal octane system. It can be seen that the accuracy of results for this system is in the same range as for any other system reported in this work.

Using the parameters Ω_a and Ω_b as calculated and tabulated in table 3.1 of the previous section (section 3) and the interaction constant for nitrogen-iso-octane system (K_{ij} = 0.22) mole fractions are predicted for oxygen and n-octane system at various pressures and temperatures.

The results are tabulated in table 4.6 and plotted in figures 4.13 and 4.14. The results are given for pressures as high as 300 atm and for temperatures 300°K and 350°K. At pressures of 300 atmospheres, the mole fraction of oxygen in the liquid phase is quite high (about 60 %- table 4.6) and above this pressure, the iterations do not converge and it is not possible to predict the mole fractions. This may be attributed to the fact that the 'near critical region' is entered, and as stated before, this technique may not give results in that region.

A value of the solubility of oxygen in n-octane at 25°C and 1 atm was found in the literature [111], after the compositions for this system had been predicted. For the sake of comparison, the solubility of oxygen in normal octane was then predicted at 25°C and one atmosphere pressure. The predicted solubility is 18.94×10^{-4} whereas the experimental value is 20.90×10^{-4}. Thus it is confirmed that the assumption made in the choice of K_{ij} for this system is very good. Further, it can be said that the predicted results for systems, for which no experimental equilibrium compositions are available, can be regarded as quite reliable.

Chang [112] generalized the temperature dependent parameters Ω_a and Ω_b for normal liquids. He tabulated these parameters for reduced temperatures ranging from 0.56 to

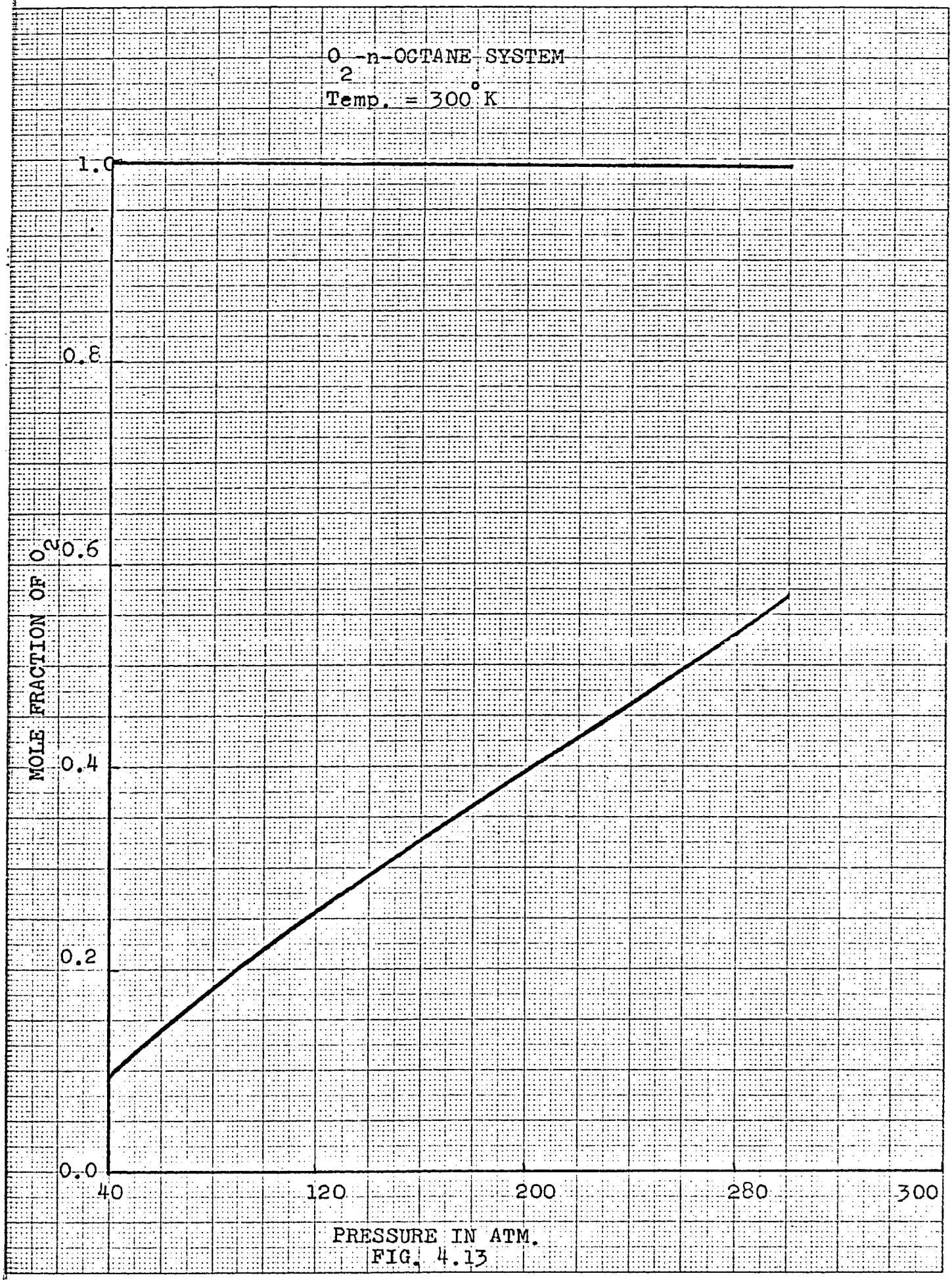
O_2 -n-OCTANE SYSTEM
Temp. = 300° K
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF O_2
40
120
200
280
300
PRESSURE IN ATM.

FIG. 4.13

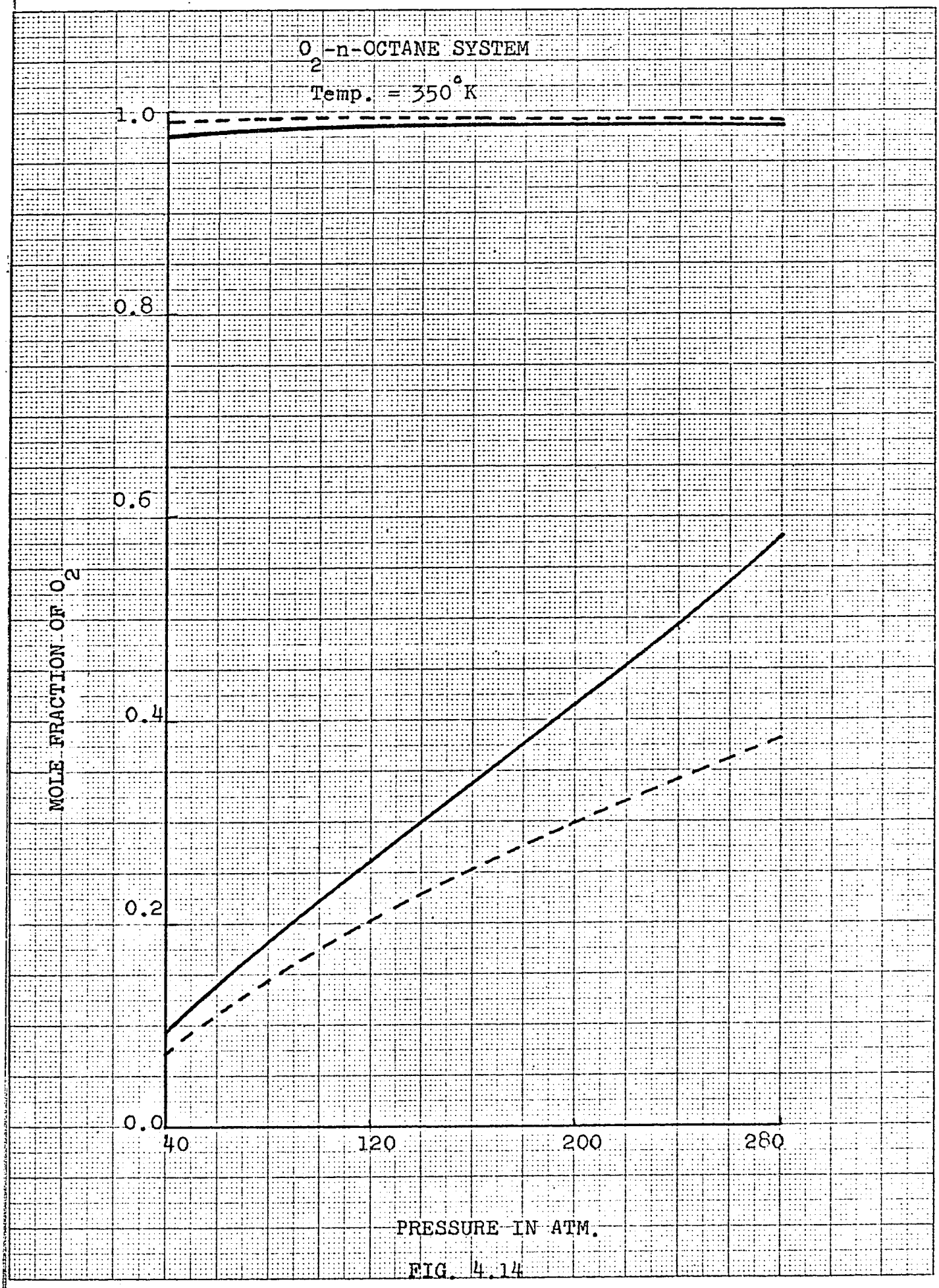
O_2-n-OCTANE SYSTEM
Temp. = 350°K
1.0
0.8
0.6
0.4
0.2
0.0
MOLE FRACTION OF O_2
40
120
200
280
PRESSURE IN ATM.

FIG. 4.14

0.99 at different values of accentric factors. Table 4.7 gives the results for oxygen-n-octane system at 350°K, using Chang's generalized parameters (Ω_a = 0.45488 Ω_b=0.075943 at 350°K) for normal octane and the original coefficients (Ω_a = 0.4278 and Ω_b = 0.0867) for oxygen. It may be mentioned that the same values of these parameters are used for both liquid and vapor phases. A comparison between the results of tables 4.6 and 4.7 shows the effect of temperature on the parameters Ω_a and Ω_b. The dotted line in figure 4.14 is the curve obtained by using the results of table 4.7.

As a general rule, the solubility of a gas rises with increasing temperature whenever x_1 is small and it falls with increasing temperature whenever x_1 is large. However, this is only a general rule and there are differences in behavior between different gases and different solvents. It is a fact that the solubility of gases like oxygen and nitrogen etc. at temperatures above the room temperature, increases with temperature. This is confirmed by the results obtained (table 4.6) for the oxygen and normal octane system.

To demonstrate the influence of the interaction coefficient K_{ij} on the equilibrium composition calculations, curves are plotted (Fig. 4.15) for different values of K_{ij} at 300°K for oxygen and n-octane system. It can be

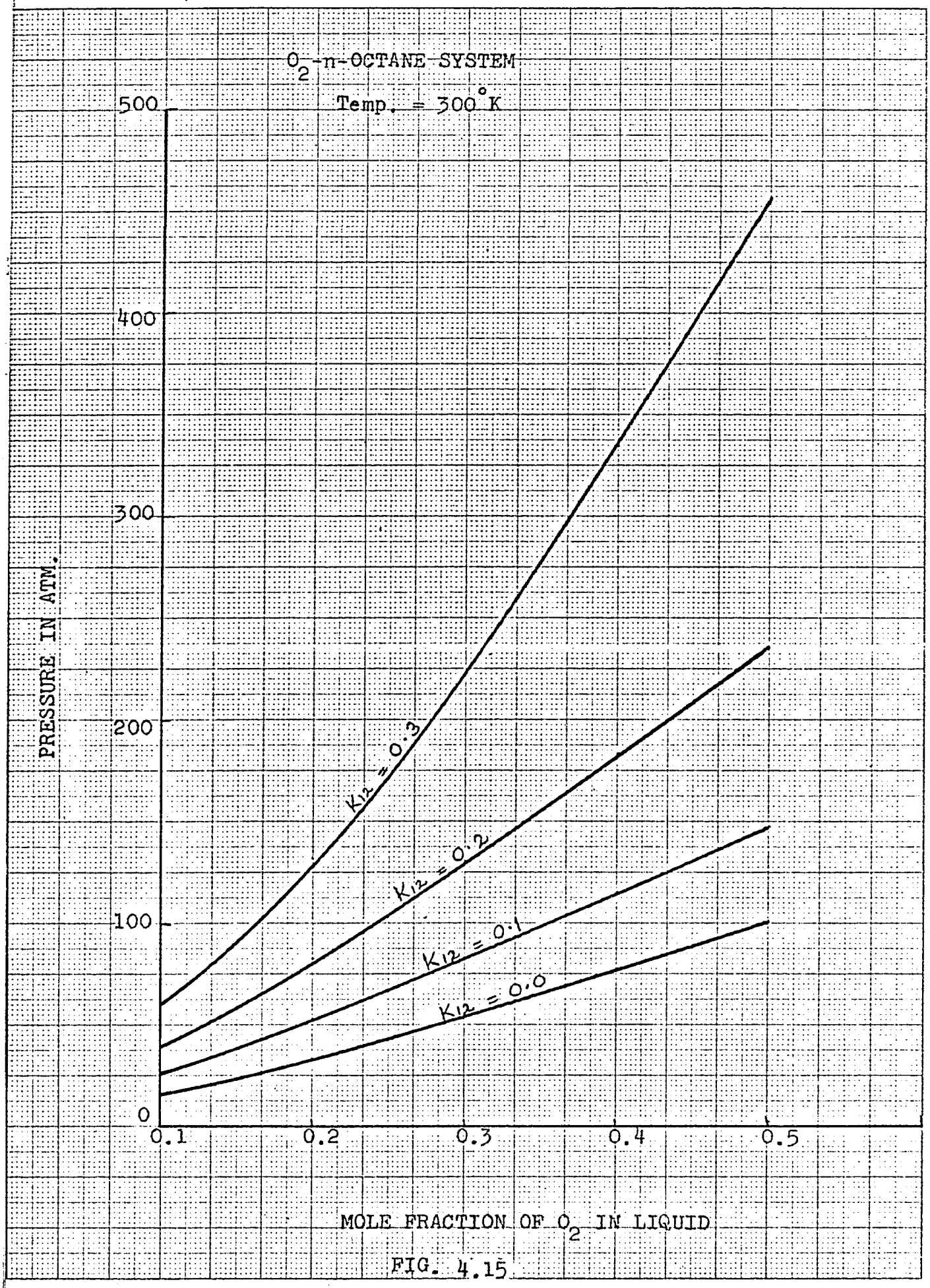
O_2-n-OCTANE SYSTEM
Temp. = 300°K
PRESSURE IN ATM.
500
400
300
200
100
0
0.1
0.2
0.3
0.4
0.5
K_{12} = 0.3
K_{12} = 0.2
K_{12} = 0.1
K_{12} = 0.0
MOLE FRACTION OF O_2 IN LIQUID

FIG. 4.15

seen that the mole fraction of oxygen in liquid phase at a pressure of 100 atmospheres varies from 0.16 at $K_{ij} = 0.3$ to 0.5 at $K_{ij} = 0.0$. Thus the importance of the use of proper K_{ij} can be clearly understood.

As stated earlier, the interaction constant can be evaluated if at least one experimental solubility or x-y data point is known. The experimental data used must be of high accuracy since the mole fractions are quite sensitive to the interaction coefficient. The importance of the accurate experimental data can be realised from the fact that many of the interaction constants evaluated by Chueh and Prausnitz [98], when fitted to the data of other workers do not give comparable results at all. For example, $K_{12} = 0.12$, as suggested by Chueh and Prausnitz has been used for the calculations of nitrogen-butane system, the results of which are shown in table 4.3. It is seen that the use of this value does not give very good results for this system.* It is recommended, therefore, that Chueh's constants should not be used with blind faith and, where ever required, new coefficients be evaluated by using the data of a reputed worker.

Using the technique previously described, K_{ij} has been evaluated for nitrogen-butane system and was found to be equal to 0.16 . Using this value the calculated equilibrium compositions for this system are

---

* Errors as high as 37 % can be seen in the table 4.3.

indicated in table 4.8. The use of this new K_{12} is seen to result in substantially greater accuracy.

Experience shows that the values of interaction coefficients obtained by using only one data point, do not predict comparable results for most of the systems. Joffe and Zudkevitch[88] recommended that at least four sets of x-y points be used to account for possible scatter in the experimental data.However, it has been observed that even if the interaction coefficient is obtained by using a number of points at a particular temperature, the predicted results for the same system, at other temperatures may not be reasonably close to the experimental observations. In fact, for some systems, the deviations between the predicted and observed results are quite high for temperatures other than those at which K_{ij} has been evaluated. As an example, there are significant deviations in results at 399.83°K and 455.38°K for nitrogen-normal heptane system for which the interaction coefficients are calculated at 305.38°K (see table 4.1). Thus it can be stated with reasonable confidence that the interaction coefficient is somewhat temperature dependent. In fact Lu is currently working on the correlation of the interaction coefficient with temperature. It is recommended, for best results, that the interaction coefficient be determined under temperature conditions which approximate those under which it is used to predict the results.

There is not significant evidence available, as yet, that the interaction coefficient is a function of pressure or mole fraction. However, Joffe and Zudkevitch (88) observed that in hydrocarbon systems the interaction coefficients are somewhat smaller at relatively high pressures than those obtained at low pressures (below 100 psia data). Thus, if large changes in temperature and pressure, from those at which K_{ij} is evaluated, are envisaged, then the interaction coefficient may have to be treated as a function of temperature and pressure.

Another assumption made in this work, like others (77, 88, 91) is that the interaction coefficient has the same value in both the phases. The interaction between the molecules in the vapor and liquid phases may or may not be similar. No work has been reported in the literature about this aspect of the interaction coefficient. A lot of work has been done in the vapor-liquid equilibria field but much work is required to predict the fugacity, solubility or phase equilibrium accurately.

5. CONSEQUENCES OF LIQUID-VAPOR EQUILIBRIUM STUDIES ON LIQUID DROPLET EVAPORATION AND COMBUSTION.

Several theories have been suggested to study the vaporization of fuel droplets. Some of the basic assumptions made in all these theories are :

(1) Steady state heat and mass transfer correlations are applicable to non-steady conditions.

(2) Average film properties based on the mean temperature and composition in the film can be used, assuming ideal gas and ideal mixture behavior in obtaining suitable corrections for high pressure cases.

(3) The mole fraction of droplet vapor at the droplet surface can be calculated from knowledge of the vapor pressure of the pure liquid.

(4) No ambient gas is absorbed in the liquid phase.

In light of the present analysis it can be stated that all these assumptions are very simple approximations leading to the results of low accuracy.

Recently, Savery and Borman (113) attempted to overcome some of the simplifications but have overlooked the importance of others. Their application of the equations of heat and mass transfer to a spherical liquid droplet lead to :

$$\frac{\pi D^3}{6} \rho_L C_{P_L} \frac{dT_L}{d\theta} = \pi D^2 \dot{h} (T_\infty - T_L) + \lambda \frac{dm}{d\theta} \qquad (5.1)$$

$$\frac{dm}{d\theta} = \frac{-\pi D^2 M_A K_x (y_{A_0} - y_{A_\infty})}{1 - y_{A_0}(1 + N_R)}$$

where D is the diameter of the fuel droplet, C_{PL} is the specific heat of the liquid and λ the heat of vaporization of the fuel. y_{A_0} and y_{A_∞} are the mole fractions of the vapor at the surface of the droplet and in the free stream. The complete nomenclature for equations (5.1) and (5.2) is presented in reference 113.

The importance of the knowledge of the composition of the gaseous phase at the droplet surface can be clearly understood from the fig. 5.1. Fig. 5.1 gives plots of the mole fraction y_2 vs. pressure P for three cases.

(1) $y_i = \frac{P_{v_i}}{P}$ *

where P_{v_i} = equilibrium vapor pressure of pure fuel at the temperature of the droplet.

(2) $y_i = \frac{P^*_{v_i}}{P}$ **

$P^*_{v_i}$ = corrected vapor pressure of fuel at the temperature T and pressure P of the droplet.

$= P_{v_i} e^{\bar{V}_l (P - P_{v_i})/RT}$

$\bar{V}_l$ = average saturated liquid molar volume.

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* $Y_i = \frac{P_{v_i}}{P}$ is a customary approximation for low pressure evaporation and combustion studies.

** is an improved approximation valid for high pressures assuming no gas adsorption at the liquid surface.

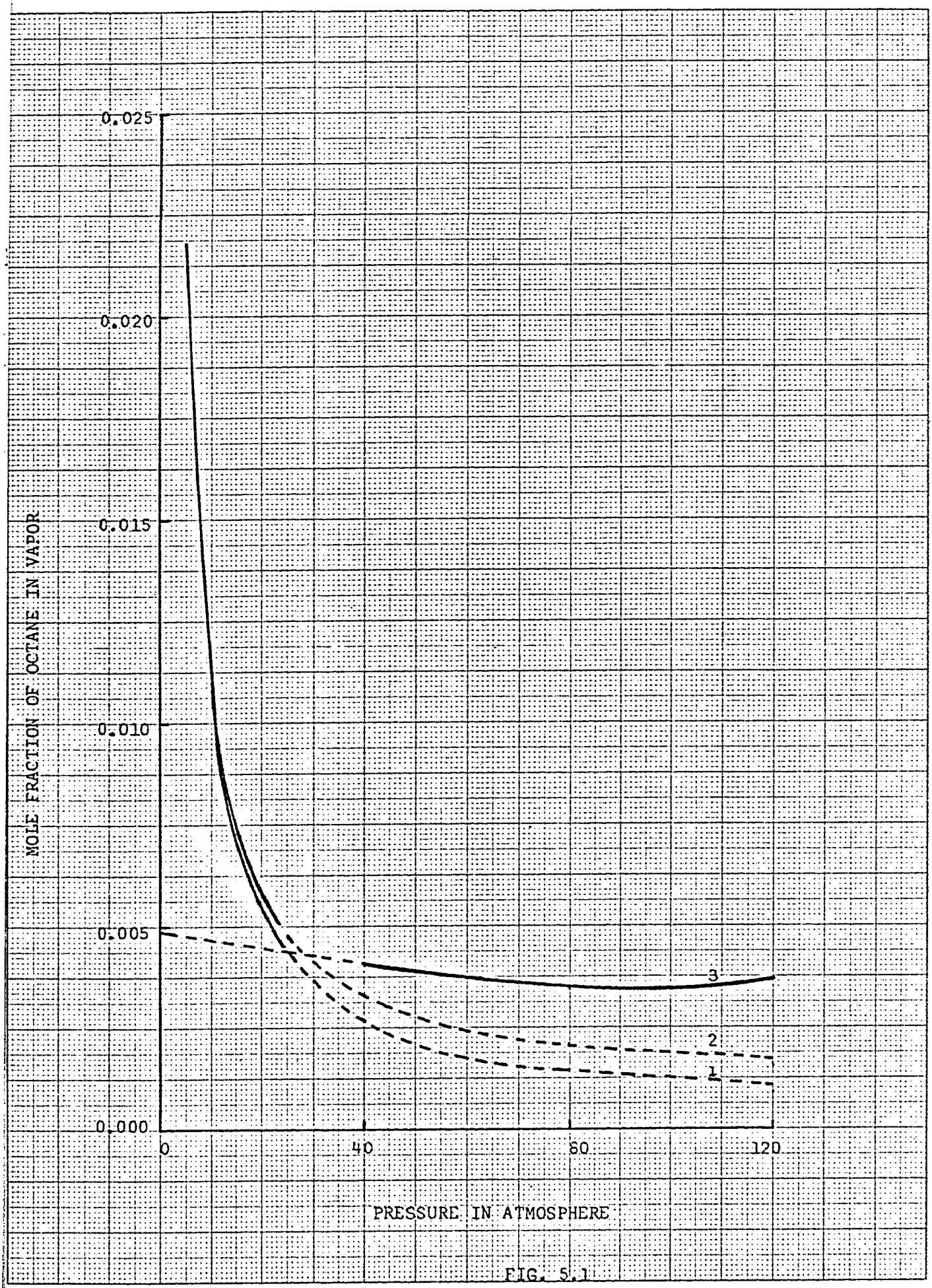
0.025
0.020
0.015
0.010
0.005
0.000
MOLE FRACTION OF OCTANE IN VAPOR
0
40
80
120
PRESSURE IN ATMOSPHERE
1
2
3

FIG. 5.1

(3) Mole fractions of the fuel as calculated in Section 4.*

Evaporation rate is a function of droplet size which is further a function of surface tension. The larger the droplet size, the higher the evaporation rate. It has been seen in the present work that the liquid fuel adsorbs a significant amount of the gas and therefore the size of the droplet tends to increase. Surface tension can increase since significant amounts of gas are adsorbed by the liquid.

Further, the increase in the size of the droplet changes the Reynold and Prandtl numbers. Change in Reynold and Prandtl numbers results in a change in the Nusselt number and hence the heat transfer rate to the droplet.

Because of the absorption of the gas at the droplet surface, the specific heat of the droplet shall be different from that of the pure liquid resulting in a droplet heat-up time much different than that normally expected.

At high pressures the change in enthalpy in going from the liquid to the vapor state can no longer be approximated by the latent heat of vaporization of the pure liquid. The correct enthalpy of vaporization can however be calculated from deviation equations (105) using the modified R-K equation. This can be accomplished using the liquid and vapor composition calculations described herein.

---

* An even better estimation of y_i is that when gas adsorption is considered.

The value of D to be used in equations (5.1) and (5.2) needs to be averaged by some approximation since it keeps on changing throughout the droplet life. The effects of the specific heat, enthalpy of vaporization coefficient of heat transfer etc. on equation (5.1) and (5.2) cannot be explicitly stated here without a detailed mathematical analysis. Unquestionably, such an analysis would lead to other areas of research.

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APPENDIX 1

(1) The R-K equation of state is :

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b)T^{0.5}}$$

The compressibility factor form is :

$$Z = \frac{1}{(1-h)} - \frac{A^2}{B}\left(\frac{h}{1+h}\right)$$

$$h = \frac{BP}{Z}$$

The various constants for pure components and mixtures have been defined in sections 3 and 4.

(2) The compressibility factor form of B-W-R equation of state is :

$$Z = 1+(B_o - A_o/RT - C_o/RT^3)(1/V) + (b - a/RT)(1/V^2)$$

$$+ (a\alpha/RT)(1/V^5) + (c/RT^3)\left[(1+\gamma V^{-2})/V^{-2}\right] e^{-\gamma V^{-2}}$$

(3) The H-B-M-S equation of state in various regions is :

REGION I: GAS

$$\left[P + a(T)/V^2 + a'(T)/V^3\right] \times \left[V - b + b'/V\right] = RT$$

REGION II: HIGH DENSITY GAS.

$$P_{II}/t = -w_1(t)\rho^2 - w_2(t)\rho^3 + 1 + \beta\rho^2 + \delta(\rho-1)^5/\rho + D(\rho,t)$$

REGION III: LIQUID

$$P_{III}(\rho,t) = P_{II}(\rho,t) - P_{II}\left[\rho_\ell(t), t\right] + P_v(t)$$

APPENDIX 2

DERIVATION OF FUGACITY COEFFICIENT EQUATION

A step by step derivation of the equation for the fugacity coefficient of a component 'i' in a mixture is given below.

The compressibility form of R-K equation is :

$$Z = \frac{1}{(1-h)} - \frac{A^2}{B}\,\frac{h}{(1+h)} \qquad (1)$$

$$h = \frac{BP}{Z} \qquad (2)$$

The various constants are defined by the following mixing rules.

$$A^2 = \frac{a}{R^2 T^{2.5}}$$

$$B = \frac{b}{RT} \qquad (3)$$

$$a = \sum_i \sum_j y_i y_j a_{ij}$$

$$b = \sum_i y_i b_i$$

y_i represents the mole fraction of the component 'i', either in the vapor or in the liquid phase.

The quantities a_{ij} and b_i are as defined before in section 4.

The fugacity coefficient of a pure component is given by :

$$\ln \frac{f}{P} = (Z-1) - \ln(Z-BP) - \frac{A^2}{B} \ln\left(1+\frac{BP}{Z}\right) \qquad (4)$$

The fugacity coefficient of a component 'i' in the mixture is defined as :

$$\ln \hat{\Phi}_i = \ln \frac{\hat{f}_i}{P y_i} = \frac{1}{RT} \int_0^P \left(\bar{v}_i - \frac{RT}{P}\right) dP \qquad (5)$$

$$\text{or} \quad \ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1)\,\frac{dP}{P} \qquad (6)$$

A parameter G is defined as :

$$G = \ln \frac{f}{P} = \sum y_i \ln \hat{\Phi}_i \qquad (7)$$

From equations (4) and (7), the derivative of G (or $\ln \frac{f}{P}$) is found as :

$$\left(\frac{\partial G}{\partial Z}\right)_{P,T,y_i} = \left(\frac{\partial \ln \frac{f}{P}}{\partial Z}\right)_{P,T,y_i} = 1 - \frac{1}{(Z-BP)} + \frac{A^2 P}{Z(Z+BP)} \qquad (8)$$

Combining equations (1) and (2) and rearranging

$$1 - \frac{1}{(Z-BP)} + \frac{A^2 P}{Z(Z+BP)} = 0 \qquad (9)$$

Therefore

$$\left(\frac{\partial G}{\partial Z}\right)_{P,T,y_i} = 0 \qquad (10)$$

Defining G as a function of z and y_i at constant T and P :

$$dG = \left(\frac{\partial G}{\partial y_i}\right)_{P,T,Z} dy_i + \left(\frac{\partial G}{\partial Z}\right)_{P,T,y_i} dZ$$

or

$$\frac{dG}{dy_i} = \left(\frac{\partial G}{\partial y_i}\right)_{P,T,Z} + \left(\frac{\partial G}{\partial Z}\right)_{P,T,y_i} \frac{dZ}{dy} \qquad (11)$$

From equations (10) and (11)

$$\frac{dG}{dy_i} = \left(\frac{\partial G}{\partial y_i}\right) \qquad (12)$$

Differentiating equation (4) partially w,r.t. y_i and combining with equation (12)

$$\frac{dG}{dy_i} = \left(\frac{\partial G}{\partial y_i}\right)_{P,T,Z} = \frac{\partial}{\partial y_i}\left(\ln \frac{f}{P}\right) = \frac{-1}{(Z-BP)} \frac{\partial}{\partial y_i}(-BP) - \frac{A^2}{B} \frac{\partial}{\partial y_i} \ln\left(1+\frac{BP}{Z}\right) - \ln\left(1+\frac{BP}{Z}\right) \frac{\partial}{\partial y_i}\left(\frac{A^2}{B}\right)$$

or

$$\frac{dG}{dy_i} = \left(\frac{\partial G}{\partial y_i}\right)_{P,T,Z} = \frac{B_i P}{(Z-BP)} - \frac{A^2}{B} \frac{B_i P}{(Z+BP)} - \ln\left(1+\frac{BP}{Z}\right) \times \left(\frac{B \times 2(y_i A_{ii}^2 + y_j A_{ij}^2) - A^2 B_i}{B^2}\right)$$

or

$$\frac{dG}{dy_i} = \left(\frac{\partial G}{\partial y_i}\right)_{P,T,Z} = \frac{B_i P}{(Z-BP)} - \frac{A^2 P}{(Z+BP)} \frac{B_i}{B} - \ln\left(1+\frac{BP}{Z}\right) \times \left(\frac{2 \sum_j y_j A_{ij}^2}{B} - \frac{A^2 B_i}{B^2}\right) \qquad (13)$$

From equation (7)

$$\frac{\partial G}{\partial y_i} = \ln \hat{\Phi}_i + \sum_{j=1}^{n} y_j \left(\frac{\partial \ln \hat{\Phi}_i}{\partial y_i}\right) \qquad (14)$$

Using Gibbs-Duhem relation

$$\sum_{j=1}^{n} y_j \left(\frac{\partial \ln \hat{\Phi}_j}{\partial y_i}\right) = 0 \qquad (15)$$

Therefore,

$$\frac{\partial G}{\partial y_i} = \ln \hat{\Phi}_i \qquad (16)$$

From equation (7) and (16)

$$G = \sum_{j=1}^{n} y_j \left(\frac{\partial G}{\partial y_j}\right) \qquad (17)$$

From equation (16) and (17)

$$\ln \hat{\Phi}_i = G + \frac{\partial G}{\partial y_i} - \sum_{j=1}^{n} y_j \left(\frac{\partial G}{\partial y_j}\right) \qquad (18)$$

Combining equation (4), (13) and (18)

$$\ln \hat{\Phi}_i = (Z-1) - \ln(Z-BP) - \frac{A^2}{B}\ln\left(1+\frac{BP}{Z}\right) + \frac{B_i P}{(Z-BP)} - \frac{A^2 P}{(Z+BP)}\frac{B_i}{B} - \ln\left(1+\frac{BP}{Z}\right)\times$$
$$\left(\frac{2\sum_j y_j A_{ij}^2}{B} - \frac{A^2 B_i}{B^2}\right) - \frac{P}{(Z-BP)}\sum y_i B_i + \frac{A^2 P}{B(Z+BP)}\sum y_i B_i + \ln\left(1+\frac{BP}{Z}\right)\left(\frac{2A^2}{B} - \frac{A^2 B}{B^2}\right) \qquad (19)$$

Equation (19) can be simplified and rearranged as follows :

$$\ln \hat{\Phi}_i = (Z-1) - \ln(Z-BP) - \frac{A^2}{B}\ln\left(1+\frac{BP}{Z}\right) + \frac{B_i P}{(Z-BP)} - \frac{A^2 P}{(Z+BP)}\frac{B_i}{B} - \ln\left(1+\frac{BP}{Z}\right)\times$$
$$\left(\frac{2\sum_j y_j A_{ij}^2}{B} - \frac{A^2 B_i}{B}\right) \qquad (20)$$

Combining equations (1) and (2) and rearranging it can be shown that :

$$(Z-1) = \frac{BP}{(Z-BP)} - \frac{A^2 P}{(Z+BP)} \qquad (21)$$

or

$$\frac{B_i}{B}(Z-1) = \frac{B_i P}{(Z-BP)} - \frac{A^2 P}{(Z+BP)}\frac{B_i}{B} \qquad (22)$$

Substituting equations (21) and (22) in equation (20) and rearranging

$$\ln \hat{\Phi}_i = (Z-1)\frac{B_i}{B} - \ln(Z-BP) - \frac{A^2}{B}\left(\frac{2\sum_j y_j A_{ij}^2}{A^2} - \frac{B_i}{B}\right)\ln\left(1+\frac{BP}{Z}\right) \quad (23)$$

Using equation (2), the equation for the fugacity coefficient takes the form

$$\ln \hat{\Phi}_i = (Z-1)\frac{B_i}{B} - \ln(z)(1-h) - \frac{A^2}{B}\left(\frac{2\sum_j y_j A_{ij}^2}{A^2} - \frac{B_i}{B}\right)\ln(1+h) \quad (24)$$

The same equation can be used for calculating the fugacity coefficient in liquid and vapor phase by using the appropriate values of z and h.

TABLE 3.1

	LIQUID		VAPOR	
	Ω_a	Ω_b	Ω_a	Ω_b
OXYGEN	0.47975	0.08967	0.41151	0.094968
N-OCTANE	0.37212	0.07191	0.4760	0.09680

$N_2^{(1)}$ - n- HEPTANE$^{(2)}$ SYSTEM

$K_{12} = 0.23$

P ATM	T °K	OBSERVED (107) X_1	OBSERVED (107) Y_1	CALCULATED X_1	CALCULATED Y_1	DEVIATION ΔX_1	DEVIATION %	DEVIATION ΔY_1	DEVIATION %
70.05	305.38	0.080000	0.99276	0.09048	0.99340	0.01048	12.91	0.00064	0.07
03.74	305.38	0.12800	0.99000	0.12579	0.99384	-0.00040	0.31	0.00384	0.41
120.70	305.38	0.14500	0.99610	0.14489	0.99387	-0.00011	0.08	-0.00233	0.22
181.70	305.38	0.20100	0.99400	0.20038	0.99358	-0.00062	0.32	-0.00042	0.04
205.58	305.38	0.21500	0.99500	0.2196	0.99344	0.00460	2.12	-0.00156	0.16
69.40	352.60	0.09600	0.98220	0.10400	0.97342	0.00833	8.92	-0.00877	0.89
143.63	352.60	0.18700	0.98820	0.19929	0.97924	0.01229	6.72	-0.00895	0.87
205.62	352.60	0.24700	0.98690	0.26694	0.98020	0.01994	8.15	-0.00670	0.83
274.00	352.60	0.29100	0.98460	0.30840	0.98123	0.01740	5.69	-0.00337	0.35
72.12	399.83	0.11600	0.95420	0.12424	0.92386	0.00824	7.08	-0.03034	3.12
137.58	399.83	0.21300	0.95450	0.22680	0.94430	0.01380	6.17	-0.01019	1.07
205.62	399.83	0.30100	0.97720	0.32136	0.95133	0.02036	6.87	-0.02587	2.53
274.00	399.83	0.38700	0.97040	0.40860	0.95589	0.02160	5.16	-0.01450	3.69
76.95	455.38	0.128	0.93530	0.15402	0.79249	0.02602	20.80	-0.14280	14.82
171.46	455.38	0.321	0.94860	0.34713	0.86763	0.02613	8.81	-0.08096	8.23
239.84	455.38	0.442	0.95060	0.46062	0.89051	0.01806	4.08	-0.06009	6.06

N_2 (1) - n - OCTANE (2) SYSTEM

$K_{12} = 0.31$

P ATM	T °K	OBSERVED (109)		CALCULATED		DEVIATION		DEVIATION	
		X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
100.0	323.16	0.11700	-	0.11014	0.99442	-0.00686	5.86	-	-
125	323.16	0.14300	-	0.13251	0.99474	-0.01049	7.33	-	-
150	323.16	0.16600	0.9975	0.15314	0.99493	-0.01286	7.74	-0.00257	2.43
175	323.16	0.18800	-	0.17219	0.99506	-0.01580	8.41	-	-
200	323.16	0.20900	-	0.18982	0.99517	-0.01918	9.18	-	-
225	323.16	0.22900	-	0.20614	0.99527	-0.02285	9.98	-	-
250	323.16	0.24900	-	0.22129	0.99538	-0.02770	11.12	-	-
275	323.16	0.26700	-	0.23538	0.99551	-0.03161	11.84	-	-
300	323.16	0.28500	-	0.24850	0.99564	-0.03649	12.80	-	-
50	373.16	0.07000	-	0.07141	0.96745	0.00141	2.01	-	-
75	373.16	0.10200	-	0.10428	0.097494	0.00278	2.23	-	-
100	373.16	0.13200	-	0.13492	0.97856	0.00292	2.21	-	-
120	373.16	0.15400	0.99080	0.15794	0.98034	0.00394	2.56	-0.01045	1.05
125	373.16	0.16000	-	0.16350	0.98070	0.00350	2.18	-	-
150	373.16	0.18600	0.99030	0.19018	0.98212	0.00418	2.25	-0.00818	0.83

P ATM	T °K	OBSERVED (109)		CALCULATED		DEVIATION		DEVIATION	
		X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
175	373.16	0.21000	-	0.21512	0.98317	0.00512	2.44	-	-
200	373.16	0.23400	0.98900	0.23846	0.98402	0.00446	1.91	-0.00498	0.50
225	373.16	0.25700	-	0.26032	0.98474	0.00332	1.29	-	-
240	373.16	0.26900	0.988500	0.27278	0.98515	0.00378	1.40	-0.00335	0.34
250	373.16	0.27800	-	0.28083	0.98541	0.00283	1.02	-	-
100	348.16	0.12200	-	0.12228	0.98855	0.00028	0.23	-	-
125	348.16	0.14800	-	0.14768	0.98948	-0.00032	0.21	-	-
150	348.16	0.17200	0.99500	0.17127	0.99008	-0.00073	0.43	-0.00491	0.49
175	348.16	0.19400	-	0.19319	0.99052	-0.00085	0.41	-	-
200	348.16	0.21600	0.9948	0.21360	0.99088	-0.00239	1.11	-0.00392	0.39
225	348.16	0.23700	-	0.23262	0.99119	-0.00437	1.84	-	-
240	348.16	0.24900	0.9945	0.24342	0.99137	-0.00558	2.24	-0.00312	0.31
250	348.16	0.25700	-	0.25038	0.99149	-0.00662	2.57	-	-
275	348.16	0.277	-	0.26697	0.99178	-0.01003	3.62	-	-
280	348.16	0.281	0.9938	0.27015	0.99184	-0.01084	3.86	0.00195	0.19
300	348.16	0.296	-	0.28249	0.99208	-0.01350	4.56	-	-

N_2 (1) - BUTANE (2) SYSTEM

$K_{12} = 0.12$

P ATM	T °K	OBSERVED (110)		CALCULATED		DEVIATION		DEVIATION	
		X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
16.06	310.94	0.02500	0.75900	0.02467	0.72582	-0.00033	1.32	-0.03318	4.37
63.35	310.94	0.12100	0.89000	0.11615	0.89471	-0.00485	4.00	0.00471	0.53
122.47	310.94	0.16400	0.90000	0.22520	0.91282	0.06120	37.32	0.01282	1.42
168.81	310.94	0.25800	0.89700	0.31006	0.91253	0.05206	20.18	0.01553	1.73
204.67	310.94	0.33200	0.87900	0.37998	0.91055	0.04798	14.45	0.03155	3.59
231.48	310.94	0.38800	0.84900	0.44148	0.90935	0.05348	13.78	0.06035	7.11
35.18	344.27	0.05800	0.63900	0.05979	0.68000	0.00179	3.10	0.04133	6.47
72.46	344.27	0.10500	0.77600	0.14190	0.79488	0.03690	35.14	0.01888	2.43
95.73	344.27	0.14900	0.79100	0.19314	0.81755	0.04414	29.62	0.02655	3.35
117.30	344.27	0.20200	0.77900	0.24141	0.82841	0.03941	19.51	0.04941	6.34
136.22	344.27	0.25600	0.75800	0.28527	0.83392	0.02927	11.43	0.07592	10.01
166.67	344.27	0.32100	0.75700	0.36347	0.83934	0.04247	13.23	0.08234	10.87

P ATM	T °K	OBSERVED (110)		CALCULATED		DEVIATION		DEVIATION	
		X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
44.975	377.60	0.06600	0.47900	0.06529	0.48047	-0.00071	1.08	0.00147	0.30
57.631	377.60	0.11200	0.54800	0.11082	0.58151	-0.00118	1.01	0.03351	6.01
81.921	377.60	0.14800	0.58500	0.14520	0.62566	- 0.00280	1.96	0.04066	7.16
93.352	377.60	0.17700	0.59400	0.16782	00.64985	-0.00918	5.08	0.05585	9.24
40.552	410.94	0.03400	0.14400	00.03512	0.14572	0.00112	3.32	0.00172	1.20
53.956	410.94	0.07300	0.22200	0.07608	0.22978	0.00308	4.08	0.00778	3.78
56.950	410.94	0.07800	0.23100	0.08112	0.23802	0.00312	4.00	0.00702	3.06
60.352	410.94	0.08500	0.24000	0.09017	0.25229	0.00517	6.00	0.01229	5.12

OXYGEN (1) - ISO-OCTANE (2, 2, 4 , TRIMETHYL PENTANE) (2) SYSTEM

$K_{12} = 0.22$

P	T	OBSERVED		CALCULATED		DEVIATION	
ATM	°K	$X_1 \times 10^2$	Y_1	$X_1 \times 10^2$	Y_1	ΔX_1	%
1.0	282.88	0.29120	-	0.30684	0.90109	+0.00015	5.37
1.0	292.01	0.28530	-	0.28724	0.85178	0.00002	0.68
1.0	298.16	0.28140	-	0.27151	0.80870	-0.00010	3.51
1.0	303.37	0.27330	-	0.25625	0.76498	-0.00011	3.95

$N_2^{(2)}$ - ISOCTANE$^{(2)}$ SYSTEM

$K_{12} = 0.31$

P	T	OBSERVED[109]		CALCULATED		DEVIATIONS		DEVIATIONS	
ATM	°K	X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
50	348.16	0.08300	-	0.09450	0.96909	0.01150	13.85	-	-
100	348.16	0.15500	-	0.17605	0.97765	0.02105	13.58	-	-
150	348.16	0.22100	0.989500	0.24502	0.97938	0.02402	10.87	-0.01012	1.02
175	348.16	0.25200	-	0.27547	0.97952	0.02347	9.31	-	-
200	348.16	0.28000	0.98750	0.30354	0.97946	0.02354	8.41	-0.00803	0.81
225	348.16	0.30700	-	0.32945	0.97927	0.02245	7.31	-	-
250	348.16	0.33100	0.98550	0.35340	0.97901	0.02240	6.76	-0.00649	0.66
300	348.16	0.36900	-	0.39609	0.97839	0.02709	7.34	-	-

O_2 (1) - n - OCTANE (2) SYSTEM

$K_{12} = 0.22$

P	T	CALCULATED	
ATM	°K	X_1	Y_1
40	300	0.09468	0.99591
80	300	0.17953	0.99655
120	300	0.25633	0.99635
160	300	0.32709	0.99595
200	300	0.39403	0.99553
240	300	0.46007	0.99521
280	300	0.53014	0.99503
300	300	0.57105	0.99489
40	350	0.09441	0.97808
80	350	0.18191	0.98447
120	350	0.26281	0.98590
160	350	0.33903	0.98620
200	350	0.41304	0.98625
240	350	0.48905	0.98638
280	350	0.58121	0.98647

CO_2 (1) - n - OCTANE (2) SYSTEM

$K_{12} = 0.22$

P	T	CALCULATED	
ATM	°K	X_1	Y_1
40	350	0.07385	0.99222
80	350	0.14004	0.99404
120	350	0.19913	0.99407
160	350	0.25197	0.99354
200	350	0.29932	0.99272
240	350	0.34184	0.99168
280	350	0.38013	0.99050

TABLE 4.8

$N_2^{(1)}$ - BUTANE $^{(2)}$ SYSTEM

$K_{12} = 0.16$

P ATM	T °K	OBSERVED[110]		CALCULATED		DEVIATION		DEVIATION	
		X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
16.06	310.94	0.02500	0.75900	0.02472	0.72566	-0.00028	1.12	-0.03334	4.46
63.35	310.94	0.12100	0.89000	0.11729	0.89523	-0.00371	3.17	0.00523	0.58
122.47	310.94	0.16400	0.90000	0.20116	0.91369	0.03716	18.51	0.01369	1.52
168.81	310.94	0.25800	0.89700	0.28123	0.91344	0.03323	8.62	0.01644	1.80
204.67	310.94	0.33200	0.87900	0.35626	0.91276	0.02426	6.97	0.03372	3.71
231. 48	310.94	0.38800	0.84900	0.42169	0.91085	0.3369	8.02	0.06185	7.31
35.18	344.27	0.05800	0.63900	0.05936	0.67326	0.00136	2.31	0.03426	5.37
72.46	344.27	0.10500	0.77600	0.12600	0.79667	0.02120	17.39	0.02067	2.51
95.73	344.27	0.14900	0.71900	0.17069	0.81629	0.02169	12.82	0.02529	3.28
117.30	344.27	0.20200	0.77900	0.22136	0.42655	0.01936	8.93	0.04755	6.09
136.22	344.27	0.25600	0.75800	0.26638	0.82867	0.01038	3.96	0.07067	9.21
166.67	344.27	0.32100	0.75700	0.34699	0.83094	0.02599	7.52	0.07395	9.82

TABLE 4.8 (CONTD.)

P	T	OBSERVED[110]		CALCULATED		DEVIATION		DEVIATION	
ATM	°K	X_1	Y_1	X_1	Y_1	ΔX_1	%	ΔY_1	%
44.975	377.60	0.06600	0.47900	0.06502	0.48082	-0.00098	1.49	0.00182	0.37
57.631	377.60	0.11200	0.54800	0.11018	0.56927	-0.00182	1.63	0.02127	3.93
81.921	377.60	0.14800	0.58500	0.14612	0.61321	-0.00188	1.30	0.02821	4.72
93.352	377.60	0.17700	0.59400	0.16902	0.62382	-0.00798	4.78	0.02982	4.91
40.552	410.94	0.03400	0.14400	0.03572	0.14603	0.00172	5.06	0.00203	1.43
53.956	410.94	0.07300	0.22200	0.07582	0.22812	0.00282	3.91	0.00612	2.86
56.950	410.94	0.07800	0.23100	0.08192	0.23873	0.00392	5.00	0.00773	3.38
60.352	410.94	0.08500	0.24000	0.09077	0.25372	0.00577	6.80	0.01372	5.41

```
      C     PROGRAM TO FIND OUT SATURATED MOLAR VOLUME OF MIXTURE,PARTIAL
      C     MOLAR VOLUME OF OXYGEN AND N-OCTANE,THE MOL-FRACTION OF OXYGENIN
      C     THE LIQUID PHASE.
      C
      C     PRESSURE VARYING,TEMP CONSTANT.
      C
0001        IMPLICIT REAL*8(A-H,O-Z)
0002        DIMENSION AAA(3),BBB(3),C(3),D(3),E(3),F(3),VR(3)
      C
      C     THE VARIOUS THERMODYNAMICAL CONSTANTS ARE READ AS DATA
      C
0003        READ(1,21)P,T,PC1,PC2,TC1,TC2,VC1,VC2
0004  21    FORMAT(8F10.5)
0005        READ(1,31)W1,W2,WWA1,WWA2,WWB1,WWB2,DEL1,DEL2
0006  31    FORMAT(8F10.5)
0007        READ(1,701)WWAA1,WWAA2,WWBB1,WWBB2
0008  701   FORMAT(4F15.6)
0009        READ(1,41)(AAA(J),BBB(J),C(J),D(J),E(J),F(J),J=1,3)
0010  41    FORMAT(6F12.9)
0011        WRITE(3,51)P,T,PC1,PC2,TC1,TC2,VC1,VC2
0012        WRITE(3,61)W1,W2,WWA1,WWA2,WWB1,WWB2,DEL1,DEL2
0013        WRITE(3,71)WWAA1,WWAA2,WWBB1,WWBB2
0014  51    FORMAT(8F10.5)
0015  61    FORMAT(8F10.5)
0016  71    FORMAT(4F15.6)
0017        BE=0.0001
0018        R=82.06
0019        PII=3.1415926536
0020        AK12=0.0
0021        TC12=(DSQRT(TC1*TC2))*(1.0-AK12)
      C
      C     THE ITERATION STARTS FOR THE MOL-FRACTION X1
      C
      C     LET THE LOWER AND UPPER LIMIT OF X1 BE S AND U RESP.
      C
0022        S=0.0
0023        U=1.0
0024  11    X1=(S+U)/2.0
0025  91    PH1=X1*VC1/(X1*VC1+(1.0-X1)*VC2)
0026        PH2=(1.0-X1)*VC2/(X1*VC1+(1.0-X1)*VC2)
0027        WM=PH1*W1+PH2*W2
0028        TCM=2.0*PH1*PH2*TC12+(PH1**2)*TC1+(PH2**2)*TC2
0029        TR=T/TCM
```

```
0030                VCM=X1*VC1+(1.0-X1)*VC2
                C
                C       CALCULATIONS FOR THE SATURATED MOLAR VOLUME OF THE MIXTURE.
                C
0031                IF(TR.LT.0.56)GOTO121
0032                DO 3J=1,3
0033                VR(J)=AAA(J)+BBB(J)*TR+C(J)*(TR**2)+D(J)*(TR**3)+E(J)/TR+F(J)*
                   1DLOG(1.0-TR)
0034            3    CONTINUE
0035                VRR=VR(1)+WM*VR(2)+(WM**2)*VR(3)
0036                GOTO131
0037            121 VRR0=0.34037+0.C09531*TR+0.1131*(TR**2)
0038                VRR1=-0.16262+0.20403*TR-0.64159*(TR**2)+0.77987*(TR**3)
0039                VRR=VRR0+WM*VRR1
0040            131 V=VRR*VCM
                C
                C       SATURATED MOLAR VOLUME OF THE MIXTURE IS KNOWN.
                C
                C       CONSTANTS FOR PARTIAL MOLAR VOLUME AS PROPSED BY PRAUSNITZ ARE.
                C
0041                A11=WWA1*(R**2)*(TC1**2.5)/PC1
0042                B1=WWB1*R*TC1/PC1
0043                WRITE(3,311)VRR,V,A11,B1
0044            311 FORMAT(4D25.18)
0045                A12=(WWA1+WWA2)*R*(TC12**1.5)*(VC1+VC2)/(4.0*(0.291-0.04*(W1+W2)))
0046                A22=WWA2*(R**2)*(TC2**2.5)/PC2
0047                B2=WWB2*R*TC2/PC2
0048                A=(X1**2)*A11+((1.-X1)**2)*A22+2.0*X1*(1.-X1)*A12
0049                B=X1*B1+(1.-X1)*B2
0050                AA11=WWAA1*(R**2)*(TC1**2.5)/PC1
0051                BB1=WWBB1*R*TC1/PC1
0052                WRITE(3,321)A12,A22,B2,A,B,AA11,BB1
0053            321 FORMAT(7D16.9)
0054                V01=(R*T*(1.+B1/(V-B))/(V-B)-(2.0*(X1*A11+(1.-X1)*A12)-(A*B1/(V+B)
                   1))/(V*(V+B)*DSQRT(T)))/(R*T/((V-B)**2)-(A*(2.0*V+B)/(DSQRT(T)*(V**
                   22)*((V+B)**2))))
0055                V02=(R*T*(1.+B2/(V-B))/(V-B)-(2.0*(X1*A12+(1.-X1)*A22)-(A*B2/(V+B)
                   1))/(V*(V+B)*DSQRT(T)))/(R*T/((V-B)**2)-(A*(2.0*V+B)/(DSQRT(T)*(V**
                   22)*((V+B)**2))))
0056                WRITE(3,101)X1,V01,V02,TR
0057            101 FORMAT(4D25.10)
                C
                C       THE PARTIAL MOLAR VOLUME OF BOTH COMPONENTS IS KNOWN
```

```
      C
      C     CALCULATIONS FOR ISOMETRIC PRESSURE.
      C
0058        CALL PIM(AA11,BB1,BE,R,T,V01,PI1,V1)
0059        WRITE(3,901)X1,PI1,V1
006C  901   FORMAT(/,' X1=',D15.8,10X,'PI1=',D15.8,10X,'V1=',D15.8)
      C
      C     THE ISOMETRIC PRESSUE IS KNOWN.
      C
0061        V2=V02*(1.0-BE*PI1)
0062        PHH2=(1.0-X1)*V2/(X1*V1+(1.0-X1)*V2)
      C
      C     CALCULATIONS FOR FUGACITY OF OXYGEN AT VARIOUS PRESSURES.
      C
0063        AG=DSQRT(WWAA1*(TC1**2.5)/(PC1*(T**2.5)))
0064        BG=WWBB1*TC1/(PC1*T)
0065        WRITE(3,331)AG,BG
0066  331   FORMAT(2D25.18)
0067        PP1=-1.0
0068        QQ1=(AG**2)*P-BG*P-(BG*P)**2
0069        RR1=-(AG**2)*BG*(P**2)
0070        CALL CUBE(PP1,QQ1,RR1,Z1,Z2,Z3)
0071        WRITE(3,902)Z1,Z2,Z3
0072  902   FORMAT(/,' Z1=',F15.10,10X,'Z2=',F15.10,10X,'Z3=',F15.10)
0073        IF(Z1.GE.Z2.AND.Z1.GE.Z3)Z=Z1
0074        IF(Z2.GE.Z1.AND.Z2.GE.Z3)Z=Z2
0075        IF(Z3.GE.Z1.AND.Z3.GE.Z2)Z=Z3
0076  151   ALNPH   =(Z-1.0)-DLOG(Z-BG*P)-((AG**2)*DLOG(1.0+BG*P/Z))/BG
0077        FP=P*DEXP(ALNPH)
      C
      C     FUGACITY AT TOTAL PRESSUE P IS KNOWN.
      C
0078        PP2=-1.0
0079        QQ2=(AG**2)*PI1-BG*PI1-(BG*PI1)**2
0080        RR2=-(AG**2)*BG*(PI1**2)
0081        CALL CUBE(PP2,QQ2,RR2,ZZ1,ZZ2,ZZ3)
0082        WRITE(3,903)ZZ1,ZZ2,ZZ3
0083  903   FORMAT(/,' ZZ1=',F15.10,10X,'ZZ2=',F15.10,10X,'ZZ3=',F15.10)
0084        IF(ZZ1.GE.ZZ2.AND.ZZ1.GE.ZZ3)ZZ=ZZ1
0085        IF(ZZ2.GE.ZZ1.AND.ZZ2.GE.ZZ3)ZZ=ZZ2
0086        IF(ZZ3.GE.ZZ1.AND.ZZ3.GE.ZZ2)ZZ=ZZ3
0087  171   ALNPHH   =(ZZ-1.0)-DLOG(ZZ-BG*PI1)-((AG**2)*DLOG(1.0+BG*PI1/ZZ))/
           1BG
```

```
0088                FPI=PI1*DEXP(ALNPHH)
                C
                C       FUGACITY AT ISOMETRIC PRESSURE IS KNOWN.
                C
0089                WRITE(3,341)ALNPH,ALNPHH,FP,FPI
0090            341 FORMAT(4D25.18)
                C
                C       VALUES ARE SUBSTITUTED IN BOTH SIDES OF THE EQUATION.
                C
0091                HLS=R*T*DLOG(FP/(X1*FPI))
0092                HRS=41.2984*V1*(PHH2**2)*((DEL1-DEL2)**2)-V01*((PI1-BE*(PI1**2)/
                   12.0)-(P-BE*(P**2)/2.0))
0093                WRITE(3,301)HLS,HRS
0094            301 FORMAT(2X,2D25.18)
0095                IF((HLS-HRS).LE.0.1D-2.AND.(DABS(HLS)-HRS).LE.0.1D-2)GOTO601
0096                IF((HLS-HRS).LE.0.1D-2.AND.(-HLS-DABS(HRS)).LE.0.1D-2)GOTO601
                C
                C       THE EQUALITY OF LEFT-HAND SIDE AND RT-HAND SIDE OF THE EQUATION IS
                C       CHECKED AND A NEW VALUE OF MOL-FRACTION IS ASSUMED UNTILL BOTH
                C       SIDES OF THE EQUATION ARE EQUAL.
                C
0097                DIFF=HLS-HRS
0098                IF(DIFF)17,601,18
0099            17  U=X1
0100                GOTO11
0101            18  S=X1
0102                GO TO11
0103            601 WRITE(3,401)X1,V,V01,V02,PI1,FP,FPI,P,T
0104            401 FORMAT(1H1,' MOL-FRACTION OF OXYGEN=',E15.8,/,' SATURATED MOLARVOL
                   1OF MIXTURE=',E15.8,/,' PARTIAL MOLAR VOLUME  OF OXYGEN=',E15.8,/,
                   2' PARTIAL MOLAR VOLUME OF N-OCTANE=',E15.8,/,' ISOMETRIC MIXING
                   3PRESSURE=',E15.8,/,' FUGACITY AT PRESSURE P=',E15.8,/,' FUGACITY
                   4 AT ISOMETRIC MIXING PRESSURE=',E15.8,/,'TOTAL PRESSURE=',E15.8,/,
                   5'TEMPERATURE=',E15 8)
                C
                C       THE MOL-FRACTION OF OXYGEN IN LIQUID PHASE IS KNOWN.
0105            111 RETURN
0106                END
```

```
0001            SUBROUTINE CUBE(PP,QQ,RR,Z1,Z2,Z3)
0002            IMPLICIT REAL*8(A-H,O-Z)
0003            AA=(3.0*QQ-(PP**2))/3.0
0004            BB=(2.0*(PP**3)-9.0*PP*QQ+27.0*RR)/27.0
0005            CC=(BB**2)/4.0+(AA**3)/27.0
0006            IF(CC)40,20,30
0007      20    GAM=DSQRT(-AA/3.0)
0008            IF(BB)22,22,21
0009      21    Z1=-2.0*GAM-PP/3.0
0010            Z2=GAM-PP/3.0
0011            Z3=Z2
0012            GO TO 50
0013      22    Z1=2.0*GAM-PP/3.0
0014            Z2=-GAM-PP/3.0
0015            Z3=Z2
0016            GO TO 50
0017      30    EPS=DSQRT(CC)
0018            TAU=-BB/2.0
0019            RCU=TAU+EPS
0020            SCU=TAU-EPS
0021            SIR=1.0
0022            SIS=1.0
0023            IF(RCU)31,32,32
0024      31    SIR=-1.0
0025      32    IF(SCU)33,34,34
0026      33    SIS=-1.0
0027      34    R=SIR*((SIR*RCU)**(1.0/3.0))
0028            S=SIS*((SIS*SCU)**(1.0/3.0))
0029            Z1=R+S-PP/3.0
0030            Z2=-(R+S)/2.0-PP/3.0
0031            Z3=0.86602540*(R-S)
0032            GO TO 50
0033      40    QUOT=((BB/2.0)**2)/((AA/3.0)**3   )
0034            ROOT=DSQRT(-QUOT)
0035            IF(BB)42,41,41
0036      41    PEI=(1.5707963+DATAN(ROOT/DSQRT(1.0-ROOT**2)))/3.0
0037            GO TO 43
0038      42    PEI=DATAN(DSQRT(1.0-ROOT**2)/ROOT)/3.0
0039      43    FACT=2.0*DSQRT(-AA/3.0)
0040            Z1=FACT*DCOS(PEI)-PP/3.0
0041            Z2=FACT*DCOS(PEI+2.0943951)-PP/3.0
0042            Z3=FACT*DCOS(PEI+4.1887902)-PP/3.0
0043      50    RETURN
0044            END
```

```
0001                SUBROUTINE PIM(A,B,B1,R,T,V0,P,V2)
0002                IMPLICIT REAL*8(A-H,O-Z)
0003                S=25.0
0004                U=75.0
0005          15    V1=(S+U)/2.0
0006                P=R*T/(V1-B)-A/(V1*(V1+B)*(T**0.5))
0007                V2=V0*(1.-B1*P)
0008                IF(DABS(V2-V1).LE.0.1D-5)GOTO11
0009                IF(V2-V1)10,11,12
0010          10    U=V1
0011                GO TO 15
0012          12    S=V1
0013                GO TO 15
0014          11    RETURN
0015                END
```

```
C PROGRAM FOR LIQUID-VAPOR EQUILIBRIUM CALCULATIONS.
0001          IMPLICIT REAL*8(A-H,O-Z)
              C     *** SUBHASH KAPOOR ***
              C     GIVEN P & T , PREDICT X & Y.
              C     1---OXYGEN
              C     2-----N-OCTANE
0002          READ(1,11)    PC1,PC2,TC1,TC2,VC1,VC2
0003          READ(1,21)WA1,WA2,WB1,WB2,WWA1,WWA2,WWB1,WWB2
0004     11   FORMAT(6F10.6)
0005     21   FORMAT(8F10.6)
0006          READ(1,31)W1,W2
0007     31   FORMAT(2F10.6)
0008          WRITE(3,11)    PC1,PC2,TC1,TC2,VC1,VC2
0009          WRITE(3,21)WA1,WA2,WB1,WB2,WWA1,WWA2,WWB1,WWB2
0010          WRITE(3,31)W1,W2
0011          DO 5 K=1,6
0012          READ(1,651)P,T,XO,YO
0013     651  FORMAT(4F10.5)
0014          WRITE(3,651)P,T,XO,YO
0015          AK12=0.22
0016     511  R=82.06
0017          W12=0.5*(W1+W2)
0018          ZC12=0.291-0.08*W12
0019          VC12=(0.5*((VC1**(1.0/3.0))+(VC2**(1.0/3.0))))**3
0020          TC12=DSQRT(TC1*TC2)*(1.0-AK12)
0021          PC12=ZC12*R*TC12/VC12
0022          WA12=0.5*(WA1+WA2)
0023          WRITE(3,131)W12,ZC12,VC12,TC12,PC12,WA12
0024     131  FORMAT(6D15.6)
0025          A1=WA1*(R**2)*(TC1**2.5)/PC1
0026          A2=WA2*(R**2)*(TC2**2.5)/PC2
0027          B1=WB1*R*TC1/PC1
0028          B2=WB2*R*TC2/PC2
0029          A12=WA12*(R**2)*(TC12**2.5)/PC12
0030          WRITE(3,121)A1,A2,B1,B2,A12
0031     121  FORMAT(5D15.6)
0032          AA1=DSQRT(A1/((R**2)*(T**2.5)))
0033          AA2=DSQRT(A2/((R**2)*(T**2.5)))
0034          BB1=B1/(R*T)
0035          BB2=B2/(R*T)
0036          WRITE(3,151)AA1,AA2,BB1,BB2
0037     151  FORMAT(4D15.6)
0038          WAV12=0.5*(WWA1+WWA2)
0039          AV1=WWA1*(R**2)*(TC1**2.5)/PC1
```

```
0040                AV2=WWA2*(R**2)*(TC2**2.5)/PC2
0041                BV1=WWB1*R*TC1/PC1
0042                BV2=WWB2*R*TC2/PC2
0043                AV12=WAV12*(R**2)*(TC12**2.5)/PC12
0044                WRITE(3,121)AV1,AV2,BV1,BV2,AV12
0045                AAV1=DSQRT(AV1/((R**2)*(T**2.5)))
0046                AAV2=DSQRT(AV2/((R**2)*(T**2.5)))
0047                BBV1=BV1/(R*T)
0048                BBV2=BV2/(R*T)
0049                WRITE(3,151)AAV1,AAV2,BBV1,BBV2
0050                PL=P-0.0001
0051                PH=P+0.0001
0052                SS=0.0
0053                U=0.5
0054          761   X1=(SS+U)/2.0
0055                WRITE(3,811)X1
0056          811    FORMAT( ' X1=',D15.6)
0057                X2=1.0-X1
0058                AS=A1*(X1**2)+A2*(X2**2)+2.0*X1*X2*A12
0059                BS=X1*B1+X2*B2
0060                A=DSQRT(AS/((R**2)*(T**2.5)))
0061                B=BS/(R*T)
0062                WRITE(3,141)AS,BS,A,B
0063          141   FORMAT(4D15.6)
0064          311   PP=-1.0
0065                QQ=P*(A**2)-((B*P)**2)-(B*P)
0066                RR=-B*((A*P)**2)
0067                CALL CUBE(PP,QQ,RR,Z1,Z2,Z3)
0068                IF(Z1.LT.0.0)Z1=1000.0
0069                IF(Z2.LT.0.0)Z2=1000.0
0070                IF(Z3.LT.0.0)Z3=1000.0
0071                IF(Z1.LE.Z2.AND.Z1.LE.Z3)ZL=Z1
0072                IF(Z2.LE.Z1.AND.Z2.LE.Z3)ZL=Z2
0073                IF(Z3.LE.Z1.AND.Z3.LE.Z2)ZL=Z3
0074                HL=B*P/ZL
0075                L=0
0076                CALL EQNRK(A,B,P,HL,ZL,L)
0077          603   WRITE(3,421)ZL,HL
0078          421   FORMAT(' ZL=',D15.6,5X,' HL=',D15.6)
0079                EE=DLOG(ZL*(1.-HL))
0080                FC1L=(ZL-1.0)*BB1/B-EE                -(DLOG(1.0+HL)*(A**2)*(2.0*(X1
                   1*A1+X2*A12)/AS-BB1/B))/B
0081                FC2L=(ZL-1.0)*BB2/B-EE                -(DLOG(1.0+HL)*(A**2)*(2.0*(
```

```
     1X1*A12+X2*A2)/AS-BB2/B))/B
0082          F1L=DEXP(FC1L)
0083          F2L=DEXP(FC2L)
0084          FL1=F1L*P*X1
0085          FL2=F2L*P*X2
0086          WRITE(3,111)FC1L,FC2L,F1L,F2L,FL1,FL2
0087      111 FORMAT(' FC1L=',D15.6,5X,'FC2L=',D15.6,5X,' F1L=',D15.6,5X,'F2L=',
     1D15.6,5X,' FL1=',D15.6,/,' FL2=',D15.6)
0088          F1V=1.0
0089          F2V=1.0
0090          DFL=F1V-0.0001
0091          DFH=F1V+0.0001
0092      701 Y1=FL1/(F1V*P)
0093          Y2=FL2/(F2V*P)
0094          S=Y1+Y2
0095          Y1=Y1/S
0096          Y2=Y2/S
0097          WRITE(3,791)Y1,Y2,S
0098      791 FORMAT( ' Y1=',D15.6,5X,'Y2=',D15.6,5X,'S=',D15.6)
0099      211 ASV=AV1*(Y1**2)+AV2*(Y2**2)+2.0*Y1*Y2*AV12
0100          BSV=Y1*BV1+Y2*BV2
0101          AV=DSQRT(ASV/((R**2)*(T**2.5)))
0102          BV=BSV/(R*T)
0103          PS=-1.0
0104          QS=P*(AV**2)-((BV*P)**2)-(BV*P)
0105          RS=-BV*((AV*P)**2)
0106          CALL CUBE (PS,QS,RS,Z1,Z2,Z3)
0107          IF(Z1.GE.Z2.AND.Z1.GE.Z3)ZV=Z1
0108          IF(Z2.GE.Z1.AND.Z2.GE.Z3)ZV=Z2
0109          IF(Z3.GE.Z1.AND.Z3.GE.Z2)ZV=Z3
0110          HV=BV*P/ZV
0111          L=1
0112          CALL  EQNRK (AV,BV,P,HV,ZV,L)
0113          WRITE(3,431)ZV,HV
0114      431 FORMAT(' ZV=',D15.6,5X,'HV=',D15.6)
0115          FC1V=(ZV-1.0)*BBV1/BV-DLOG(ZV*(1.0-HV))-(DLOG(1.0+HV)*(AV**2)*(2.0
     1*(Y1*AV1+Y2*AV12)/ASV-BBV1/BV))/BV
0116          FC2V=(ZV-1.0)*BBV2/BV-DLOG(ZV*(1.0-HV))-(DLOG(1.0+HV)*(AV**2)*(2.0
     1*(Y1*AV12+Y2*AV2)/ASV-BBV2/BV))/BV
0117          F1V=DEXP(FC1V)
0118          F2V=DEXP(FC2V)
0119          WRITE(3,271)FC1V,FC2V,F1V,F2V
0120      271 FORMAT(' FC1V=',D15.6,5X,'F2CV=',D15.6,5X,'FF1V=',D15.6,5X,'F2V=',
```

```
                1D15.6)
0121                IF(F1V.GE.OFL.AND.F1V.LE.OFH) GO TO 711
0122                OFH=F1V+0.0001
0123                OFL=F1V-0.0001
0124                OF2H=F2V+0.0001
0125                OF2L=F2V-0.0001
0126                GO TO 701
0127          711   IF(F2V.GE.OF2L.AND.F2V.LE.OF2H)GO TO 781
0128                OF2L=F2V-0.0001
0129                OF2H=F2V+0.0001
0130                OFL=F1V-0.0001
0131                OFH=F1V+0.0001
0132                GO TO 701
0133          781   PO=FL1/F1V+FL2/F2V
0134                WRITE(3,721)X1,Y1,F1V,F2V,PO
0135          721   FORMAT(/,' X1=',D15.6,2X,'Y1=',D15.6,2X,'F1V=',D15.6,2X,'F2V=',
                   1D15.6,2X,'PO=',D15.6)
0136                IF(PO.GE.PL.AND.PO.LE.PH) GO TO 731
0137                IF(PO-P)741,751,751
0138          741   SS=X1
0139                GO TO 761
0140          751   U=X1
0141                GO TO 761
0142          731   DX=X1-XO
0143                DY=Y1-YO
0144                WRITE(3,361)X1,X2,Y1,Y2,F1L,F2L,F1V,F2V,P,AK12,T,XO,YO,DX,DY
0145          361   FORMAT(1H1,' X1=',D15.6,/,' X2=',D15.6,/,' Y1=',D15.6,/,' Y2=',
                   1D15.6,/,' F1L=',D15.6,/,'F2L=',D15.6,/,' F1V=',D15.6,/,' F2V=',
                   2D15.6,/,' P=',D15.6,/,' AK12=',D15.6,/,' T=',D15.6,/,' XO=',D15.6
                   3,/,' YO=',D15.6,/,' DX=',D15.6,/,' DY=',D15.6)
0146          5     CONTINUE
0147          501   RETURN
0148                END
```

```
0001                SUBROUTINE EQNSK(A,B,P,H,Z,L)
0002                IMPLICIT REAL*8(A-H,O-Z)
0003                TOL=1.0E-6
0004                I=0
0005                J=0
0006          11    IF(L.EQ.1) GO TO 41
0007                IF(H.LT.1.0)GO TO 21
0008                H=H-0.02
0009                I=I+1
0010                IF(I.LT.20)GO TO 11
0011                H=0.98
0012                GO TO 21
0013          41    IF(H.GT.0.0) GO TO 21
0014                H=H+0.01
0015                I=I+1
0016                IF(I.LT.20) GO TO 41
0017                H=0.02
0018          21    J=J+1
0019                DH=-B*P/H+1.0/(1.0-H)-(A**2/B)*H/(1.0+H)
0020                DDH=B*P/H**2+1.0/(1.0-H)**2-(A**2/B)/(1.0+H)**2
0021                TEST=DH/DDH
0022                H=H-TEST
0023                IF(J.GT.40)GO TO 31
0024                IF(DABS(TEST/H).GT.TOL)GO TO 11
0025          31    Z=B*P/H
0026                RETURN
0027                END
```