I APPLICATION OF DIGITAL COMPUTER TECHNIQUES TO THE CALCULATION OF THERMODYNAMIC PROPERTIES OF HYDROCARBON SYSTEMS

II ISOBARIC HEAT CAPACITIES OF N-HEXANE, METHYLCYCLOPENTANE, AND N-OCTANE AT THE BUBBLE POINT

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Abstract

I

The thermodynamic properties of mixtures of real substances may be calculated rigorously from certain calorimetric or spectroscopic measurements on the components together with volumetric measurements on the mixtures. The practical impossibility of making sufficient volumetric measurements precludes application of such an analysis to all mixtures of interest. One possible solution of this problem is the use of an equation of state which satisfactorily represents the volumetric behavior of mixtures. Benedict, Webb, and Rubin (9,10) met with considerable success in developing such an equation for mixtures of light hydrocarbons. These authors have proposed an equation of state and derived thermodynamic equations which give accurate predictions of properties of both homogeneous and heterogeneous hydrocarbon systems.

These equations are quite complex and their solution a very time-consuming operation when performed by conventional computational techniques. It was proposed that this difficulty could be overcome by use of recently developed high-speed digital computers. Accordingly, an investigation has been made into the feasibility of solving the equations of Benedict et al on a punched card digital computer known as the Electronic Calculating Punch, Type 604, manufactured by the International Business Machines Corporation. The results of the investigation are reported in the first part of this thesis. The development and application of digital techniques for the calculation of thermodynamic properties of coexisting phases in light hydrocarbon systems are discussed. A routine procedure for such a calculation which may be completed in about one and one half hours is presented. Results of calculations on the methane-ethylene-ethane system and the methane-propane system are presented in graphical and tabular form. Where possible, comparison is made with experimental measurements.

II

The isobaric heat capacity at bubble point has been determined at temperatures from 80° to 200° F. for n-hexane, methylcyclopentane, and n-octane. This quantity was calculated from directly measured values of the isochoric heat capacity in the two-phase region by the use of supplementary volumetric data. The latter were obtained from experimental measurements, when available, or estimated from the law of corresponding states. The results are presented in graphical and tabular form.

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I

APPLICATION OF DIGITAL COMPUTER TECHNIQUES TO THE CALCULATION OF THERMODYNAMIC PROPERTIES OF HYDROCARBON SYSTEMS

I

Introduction

A. Statement of Problem

A significant portion of physical chemical research is devoted to the experimental determination of thermodynamic properties of multicomponent systems in both the homogeneous and heterogeneous regions. Even when restricted to hydrocarbon mixtures in the single phase and vapor-liquid regions this work is very extensive. From this laboratory alone over a period of almost 20 years, more than 100 articles have appeared dealing exclusively with thermodynamic properties and phase equilibria in hydrocarbon systems. When it is realized that this amount of laboratory work has given experimental information on only a small fraction of the hydrocarbon systems of possible interest the need of mathematical procedures for extending experimental information is apparent. This fact was recognized at an early date, and procedures for the prediction of properties of hydrocarbon systems have appeared in the literature at frequent intervals.

The mathematical treatments advanced for these calculations have been of two general types. One of these has been the so-called generalized correlation and the other, the empirical equation of state. The former is based on the law of corresponding states or a modification thereof. These correlations were presented for the prediction of volumetric or PVT behavior of hydrocarbons as a function of their reduced state (1,2). They were applied to the prediction of phase behavior (3) by the use of generalized fugacity plots and the assumptions of ideal solutions (4). Kay (5) extended the use of the generalized correlation to mixtures by introduction of the concept of the pseudocritical constants.

The generalized correlation has proved a useful engineering tool. It has widespread applicability, is easy to use and, in predicting volumetric behavior, gives results which are sufficiently accurate for many purposes. The "equilibrium constant", a conventional expression for the ratio of the concentration of a component in the vapor to that in the liquid (3), was not predicted with as high a degree of accuracy, particularly in regions above the critical temperature of one of the components. Recently, corrections to the original equilibrium constant correlations have been proposed (6,7,8) which improve the accuracy considerably.

The second mathematical approach to a thermodynamic analysis of hydrocarbon systems is the use of the empirical equation of state together with appropriate thermodynamic relations. The derivation of these thermodynamic relations and a discussion of equations of state will be presented in Sections I-B and I-C. This method is limited only by the ability of the equation of state employed to describe accurately the volumetric behavior of the substance. With the development of a highly accurate equation of state for light hydrocarbons and their mixtures by Benedict, Webb, and Rubin (9,10) and the recent tabulations of heat capacities for a large number of hydrocarbons (11,12), the accurate prediction of thermodynamic properties and phase equilibria in hydrocarbon systems has become possible.

Difficulty arises in the practical aspects of this treatment, however, because the relationships involved are complex and the calculations time consuming. This objection presents a serious obstacle to the more widespread use of this treatment. As a means of obviating this difficulty it was suggested that the application of high speed digital computers to the calculations be studied. Should this approach prove practicable, it would be a useful contribution in the field of prediction of thermodynamic behavior, and it would facilitate research on equations of state particularly for mixtures by reducing the time involved in exploratory calculations with proposed functions.

The use of computing aids offers two possible approaches to the prediction problem. One involves the calculation and tabulation of the thermodynamic properties of a large number of hydrocarbon mixtures. This procedure is open to the criticism that any significant change in the experimental data or in equations of state as a result of new work would require a relatively extended revision of the tabular information. Also, because such tabulations would probably require a prohibitively large number of values of the desired quantities, this approach was not considered advisable. The other possibility would be to compute as required the desired properties of hydrocarbon mixtures. A calculation procedure of sufficient rapidity to make this latter method practical would have obvious advantages and it was this approach that was investigated in the present work.

This thesis reports research on the application of digital computing techniques to the calculation of the composition and thermodynamic properties of coexisting phases in hydrocarbon systems. More specifically, it concerns the development of procedures for solution of the equations of Benedict, Webb, and Rubin (10), using the Electronic Calculator, Type 604, manufactured by the International Business Machines Corp. Results of calculations on the methane-ethylene-ethane system and methane-propane system made in the course of the development are tabulated and compared with experimental data reported in the literature.

B. Equations for thermodynamic properties of mixtures of real gases

J. A. Beattie (13) gives a comprehensive review of various treatments of thermodynamic properties of real gas mixtures. These he classifies as: 1) the ideal gas formulation, 2) the method of van der Waals, 3) the Gibbs-Dalton law, 4) the Lewis and Randall rule and 5) the general limit method. The last, with which the present work is concerned consists in the derivation of expressions for thermodynamic properties of mixtures by establishing the relationships as the volume is increased without limit or the pressure decreased to zero. Under these conditions the rules of ideal solutions may be considered to apply rigorously. Therefore, a thermodynamic property such as the molal enthalpy of a mixture may be written

$$H^* = \sum_k n_k H_k^* \qquad (1)$$

The expression for the enthalpy at the desired state is completed by addition of the definite integral of the type

$$H = H^* + \int_0^P \left(\frac{\partial H}{\partial P}\right)_{T,n} dP \qquad (2)$$

or

$$H = H^{*} - \int_{V}^{\infty} \left(\frac{\partial H}{\partial V}\right)_{T,n} dV \tag{3}$$

The partial derivatives are obtained from experimental data by graphical treatment or from an equation of state. This procedure is quite rigorous, and the accuracy of the quantities calculated depends only on the accuracy of the data or the equation used in their stead. Since the present work involves calculation of values of entropy, enthalpy, and fugacity, the expressions for these properties have been derived (Appendix I). They are written

$$S = \sum_{k} n_k \left[S_{ok}^{*} + R \ln \frac{V}{n_k RT} + \int_{T_o}^{T} \frac{C_{pk}^{*}}{T} dT \right] + \int_{V}^{\infty} \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV \tag{4}$$

$$H = \sum_{k} n_k \left[H_{ok}^{*} + \int_{T_o}^{T} C_{pk}^{*} dT \right] + PV - RT + \int_{V}^{\infty} \left[P - T \left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV \tag{5}$$

$$RT \ln f_k = RT \ln \frac{m_k RT}{\underline{V}} + \int_{V}^{\infty} \left[\left(\frac{\partial P}{\partial m_k}\right)_{\underline{V},T,m_i} - \frac{RT}{\underline{V}} \right] d\underline{V} \tag{6}$$

These expressions have been derived with temperature and molal volume as independent variables because the equation of state used in the calculations is in this form. When the definite integrals of Equations 4, 5, and 6 are evaluated from an equation of state, calculation of any of the thermodynamic properties involves only the substitution of values of the independent variables. In the calculation of the thermodynamic properties of coexisting phases of a multicomponent system, the composition of each phase is obtained by solving simultaneously a set of equations equal in number to the number of components:

$$f_{kb}(T, V_b, x_1, \cdots, x_N) = f_{kd}(T, V_d, y_1, \cdots, y_N) \tag{7}$$

C. Equations of state

The application of the relations derived in the previous section depends on the determination of the integral terms of those expressions. These terms may be evaluated from experimental compressibility data. For this purpose the equation of state is perhaps the most convenient method of summarizing the data. Much work has been done on the development of equations of state and to discuss even the most important would require a lengthy treatise. However, since these equations are so important to the determination of thermodynamic properties by the method discussed in this thesis, a review of the major developments up to the present time seems desirable. Equations of state may be conveniently divided into two catagories: 1) empirical equations which are primarily attempts to obtain good representation of experimental PVT data and 2) theoretical equations which are derived from statistical mechanical and quantum mechanical treatments. They will be discussed in that order.

The simplest equation of state for gases is the so-called perfect gas law

$$PV = RT \tag{8}$$

This may be obtained by combining Boyle's and Charles' laws. It may also be derived from kinetic considerations or from statistical mechanics (14) considering the gas as a body of non-interacting particles. This equation was inadequate to describe the volumetric behavior of gases over wide ranges of temperature and pressure. One of the first and most widely known attempts to improve this equation was made by van der Waals (15) who proposed the equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \tag{9}$$

where a and b are specific constants for a given gas. This equation gives a considerably more accurate description of volumetric behavior than the perfect gas relation. Moreover it gives a semi-quantitative description of volumetric behavior of both liquid and vapor phases at temperatures below the critical, having as one real root the dew-point volume and as another the bubble-point volume with an inflection between these points. An interesting feature of any equation of state with three constants is the fact that the constants for a substance may be determined from the critical properties of the substance although these constants may not agree with those calculated to give the best fit of PVT data.

Two of the better known attempts to improve on the van der Waals equation are the Dieterici equation

$$P = \frac{RT}{V-b} \exp\left(-\frac{a}{RTV}\right) \tag{10}$$

and the Berthelot equation

$$P = \frac{RT}{V-b} - \frac{a}{TV^2} \tag{11}$$

The relative accuracy of Equations 9, 10, and 11 varies with the particular compounds and the range of temperature and pressure involved. Over a reasonably wide range of conditions their accuracy is less than that of the generalized correlations based on the law of corresponding states. Another equation of this form quite recently proposed by Redlich and Kwong (16) is

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2} V(V+b)} \tag{12}$$

Using only experimentally determined critical temperature and pressure of pure compounds for the calculation of the constants the authors obtained a remarkably accurate fit of PVT data for several gases.

A somewhat more complicated modification of the van der Waals relation proposed by Keyes (17) is

$$P = \frac{RT}{V - b\exp(c/V)} - \frac{a}{(V-d)^2} \tag{13}$$

This equation was used with considerable success to correlate and compute the thermodynamic properties of several gases.

Perhaps one of the better known equations of state is that presented by Beattie and Bridgeman in 1928 (18) and generally known as the Beattie-Bridgeman equation. It may be written

$$P = \frac{RT}{V} + \left[B_0 RT - A_0 - \frac{Rc}{T^2}\right]\frac{1}{V^2} + \left[A_0 a - \frac{RB_0 c}{T^2} - RB_0 bT\right]\frac{1}{V^3} + \left[\frac{RB_0 bc}{T^2}\right]\frac{1}{V^4} \tag{14}$$

At the expense of considerable complexity this equation achieves a high degree of accuracy in describing volumetric behavior of gases up to pressures as high as 1000 atmospheres. More recently Benedict, Webb, and Rubin (9) have modified the Beattie-Bridgeman equation to obtain an equation which gives an excellent representation of PVT data over a wide range of conditions including the region below the critical temperature:

$$P = \frac{RT}{V} + \left[B_0 RT - A_0 - \frac{C_0}{T^2}\right]\frac{1}{V^2} + \left[bRT - a\right]\frac{1}{V^3} + \left[\frac{c}{T^2}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right]\frac{1}{V^3} + \frac{a\alpha}{V^6} \tag{15}$$

This equation was developed to do what the van der Waals equation does in a semi-quantitative way, namely, describe in a single equation the behavior of both the vapor and the saturated liquid of a substance. In their original article the authors obtained the eight constants in the equation for methane, ethane, propane and n-butane by analysis of PVT data. The high degree of accuracy obtainable with this equation and the fact that it applies in the two phase region made it particularly suitable for the purposes of this research. For this reason it will be discussed in more detail in Section I-D.

It will be noted that in all the relations mentioned the pressure has been expressed explicitly. This is unfortunate since pressure and temperature are usually the independent variables in practical problems. However, such theory as has been applied to equations of state has indicated that an expression explicit in pressure should result, and experience seems to have borne out the fact that such expressions give a more accurate description of volumetric behavior than expressions explicit in volume, for a given complexity. Moreover, when a single equation is used to represent the properties of two-phase mixtures, it becomes necessary to make the molal volume an independent variable. Otherwise, if the pressure is used as an independent variable, a two-valued function would be required to represent properties of liquids and gases since at the same temperature and pressure each phase has widely differing molal volumes, enthalpies, etc. However, several equations of state have been proposed which are explicit in volume and which give a description of the volumetric behavior of gases sufficiently accurate for many purposes. One of these is that of Beattie (19)

$$V = \frac{RT}{P}(1 - B_0 b) + B_0 + \frac{c(B_0 b - 1)}{T^2} - \frac{A_0}{RT} \qquad (16)$$

This equation applies to states above the critical temperature and above the critical specific volume. A more recent expression proposed by Maron and Turnbull (20) is the power series expression

$$V = \frac{RT}{P} + \alpha_1 + \alpha_2 P + \alpha_3 P^2 + \alpha_4 P^3 \qquad (17)$$

This gives excellent results at temperatures above 1.5 times critical.

The equation of state for a pure substance provides a useful means of correlating and summarizing experimental compressibility data. Being essentially empirical, it does not give reliable prediction outside of the range of the data on which it is based. However, it has been observed that accurate prediction of properties of mixtures of similar substances can be obtained from an equation identical in form to that for the pure components using relatively simple functions of the composition to obtain the parameters. It is this fact which permits the computation of the properties of mixtures from thermal and compressibility data on the pure constituents alone. For example, the partial derivative $\left(\frac{\partial P}{\partial m_k}\right)_{T,\underline{V},m_i}$ in Equation 6 for fugacity may be evaluated from an equation of state in which the parameters are some known function of composition and the parameters of the pure components. Only a few combination functions have found widespread use. These are generally based on an equation of the type

$$\begin{aligned} A &= \sum_{jk} n_j n_k A_{jk} \\ &= n_1^2 A_{11} + n_1 n_2 A_{12} + \cdots + n_1 n_N A_{1N} + n_2 n_1 A_{12} + \cdots + n_N^2 A_{NN} \end{aligned} \tag{18}$$

where A is any parameter in the equation for the mixture. A_{jk}, $j = k$, are the parameters for the pure components and A_{jk}, $j \neq k$, are the so-called interaction constants. Empirical studies on the nature of the interaction constant have been limited to evaluation of relatively simple functions. The three most important of these together with the resulting expression for A are:

Linear combination

$$A_{jk} = \frac{1}{2}\left(A_j + A_k\right) \tag{19}$$

$$A = \sum_k n_k A_k = n_1 A_1 + n_2 A_2 + \cdots + n_N A_N \tag{20}$$

Square-root combination

$$A_{jk} = \left(A_j A_k\right)^{1/2} \tag{21}$$

$$A = \left[\sum_k n_k A^{1/2}\right]^2 = \left[n_1 A_1^{1/2} + n_2 A_2^{1/2} + \cdots + n_N A_N^{1/2}\right] \tag{22}$$

Lorentz combination

$$A_{jk} = \frac{1}{8}\left(A_j^{1/3} + A_k^{1/3}\right)^3 \tag{23}$$

$$A = \frac{1}{8} \sum_{jk} \left[n_j n_k \left(A_j^{1/3} + A_k^{1/3}\right)^3\right] = n_1^2 A_1 + \frac{1}{8}\left(A_1^{1/3} + A_2^{1/3}\right)^3 + \cdots + n_N^2 A_N \tag{24}$$

The parameters of the pure components are written with a single subscript. A study (21) of various methods of combining the constants A_o, B_o, and c of the Beattie-Bridgeman equation for the methane-n-butane system indicated that the best representation of PVT data was obtained by using a square-root combination for A_{ojk} and C_{jk} and the Lorentz combination for B_{ojk}. The average deviation of calculated from observed pressures was 0.74% or about twice the error of the equation in representing the behavior of the pure gases.

This discussion has included only a brief outline of the work which has been done on the development of equations of state for real gases and their mixtures. In addition to this work, during the past twenty years considerable progress has been made in the derivation of a quantitative equation of state from statistical mechanical and quantum mechanical considerations. Although the a priori derivation of an equation which gives results comparable with existing empirical equations seems unlikely in the near future, these treatments have demonstrated the existence of a theoretical basis for several functions which have been developed in the empirical approach. Among these is the virial form of the equation of state

$$PV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots\right) \qquad (25)$$

and the form of the combination functions for parameters in the equations for mixtures. The possibility of the derivation of a complete equation of state is enhanced by the fact that current mathematical treatments are able to predict condensation by indicating that the pressure will remain essentially constant when the molal volume is decreased below a certain value. Comprehensive reviews of the theoretical treatments of equations of state are given by Fowler and Guggenheim (22), and by Mayer and Mayer (23).

D. The Benedict equation of state

Any of the equations of state discussed in Section I-C could be used to evaluate the partial derivatives in the expressions of Section I-B. However, as may be seen from Equations 6 and 7, the calculation of phase equilibria requires a continuous function which describes volumetric behavior of the gas phase and of saturated liquid in the region between the limits of integration in the thermodynamic expressions. By far the most successful attempt to realize such a function is that of Benedict, Webb, and Rubin (9). For this reason their equation of state

$$P = \frac{RT}{V} + \left[B_0 RT - A_0 - \frac{C_0}{T^2}\right]\frac{1}{V^2} + \left[bRT - a\right]\frac{1}{V^3} + \left[\frac{c}{T^2}\left(1+\frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right]\frac{1}{V^3} + \frac{a\alpha}{V^6} \qquad (15)$$

was used to evaluate requisite partial derivatives in Equations 4, 5, and 6. The general form of isotherms calculated from Equation 15 is shown in Figure 1. Plots of P vs 1/V or the moles per cubic foot, at various temperatures are presented for a hydrocarbon mixture of invariant composition. Equation 15, which for convenience will be referred to as the Benedict equation, was developed to describe volumetric and phase behavior of low molecular weight hydrocarbons. The eight parameters have been determined from PVT data for methane, ethylene, ethane, propane, n-butane and isobutane (9,24). Vapor pressures may be calculated from the Benedict equation by simultaneous solution of the expressions

$$P_b(T, V_b) = P_d(T, V_d) \qquad (26)$$

$$f_b(T, V_b) = f_d(T, V_d) \qquad (27)$$

For the pure hydrocarbons methane, ethane, propane and n-butane, the equation was found to predict the vapor pressure to within 1.1% of the experimental values (9). Pressures calculated from molal volumes for a wide range of conditions agreed with experimental values to within 0.4% for gases.

In a later paper (10) these authors showed that by using simple combination functions for the eight parameters in the equation, a highly accurate description of both volumetric and phase behavior of multicomponent systems was obtained. This was further demonstrated by Benedict et al (24) and by Hough and Sage (25). Pressures were calculated with an average deviation of 0.4% and equilibrium constant values with an average deviation of less than 2.0% from experiment.

As was discussed in Section I-C, the values of parameters in an equation of state for a mixture may be calculated by equations of the form

$$\begin{aligned} A &= \sum_{jk} n_j n_k A_{jk} \\ &= n_1^2 A_{11} + n_1 n_2 A_{12} + \cdots + n_1 n_N A_{1N} + n_2 n_1 A_{12} + \cdots + n_N^2 A_{NN} \end{aligned} \tag{18}$$

where A_{jk} for $j = k$ are the parameters for the pure components and A_{jk} for $j \neq k$ are the interaction constants. The statistical mechanical treatment of imperfect gas mixtures by Mayer (26) indicates that an equation of the form of Equation 18 should be used for the parameters in the $1/V$ term of the virial equation of state (Equation 25) and that an equation of the form

$$
\begin{aligned}
A &= \sum_{ijk} n_i n_j n_k A_{ijk} \\
&= n_1^3 A_{111} + n_1^2 n_2 A_{112} + \cdots + n_1^2 n_N A_{11N} + n_1^2 n_2 A_{112} + n_1 n_2^2 A_{122} + \cdots + n_N^3 A_{NNN} \qquad (28)
\end{aligned}
$$

should be used in the $1/V^2$ term. In accordance with this theory Benedict et al (10) assumed the parameters B_o, A_o, and C_o in Equation 15 to be represented by a function of the form of Equation 18 and b, a, and c by Equation 28. The parameters γ and α do not have a corresponding term in the virial equation of state. Equation 18 was assumed for the evaluation of γ and Equation 28 for α. The equations are summarized as follows:

$$B_o = \sum_{jk} n_j n_k B_{ojk} \qquad (29)$$

$$A_o = \sum_{jk} n_j n_k A_{ojk} \qquad (30)$$

$$C_o = \sum_{jk} n_j n_k C_{ojk} \qquad (31)$$

$$b = \sum_{ijk} n_i n_j n_k b_{ijk} \qquad (32)$$

$$a = \sum_{ijk} n_i n_j n_k a_{ijk} \qquad (33)$$

$$c = \sum_{ijk} n_i n_j n_k c_{ijk} \qquad (34)$$

$$\gamma = \sum_{jk} n_j n_k \gamma_{jk} \qquad (35)$$

$$\alpha = \sum_{ijk} n_i n_j n_k \alpha_{ijk} \tag{36}$$

The assignment of values to the various interaction constants arising in these equations was made by arbitrarily assuming them to be simple functions of the pure component parameters as follows:

$$B_{ojk} = \tfrac{1}{2}(B_{oj} + B_{ok}) \tag{37A}$$

$$B_{ojk} = \tfrac{1}{8}(B_{oj}^{1/3} + B_{ok}^{1/3})^3 \tag{37B}$$

$$A_{ojk} = (A_{oj} A_{ok})^{1/2} \tag{38}$$

$$C_{ojk} = (C_{oj} C_{ok})^{1/2} \tag{39}$$

$$b_{ijk} = (b_i b_j b_k)^{1/3} \tag{40}$$

$$a_{ijk} = (a_i a_j a_k)^{1/3} \tag{41}$$

$$c_{ijk} = (c_i c_j c_k)^{1/3} \tag{42}$$

$$\gamma_{jk} = (\gamma_j \gamma_k)^{1/2} \tag{43}$$

$$\alpha_{ijk} = (\alpha_i \alpha_j \alpha_k)^{1/3} \tag{44}$$

The single subscript denotes the parameter of a pure component. The expressions used for the evaluation of each parameter are obtained by substituting the relation for the interaction constant into the corresponding combination function in the group of equations 29 to 36. The resulting equations are as follows:

$$B_o = \sum_k n_k B_{ok} = n_1 B_{o1} + n_2 B_{o2} + \cdots + n_N B_{oN} \tag{45A}$$

$$B_o = \frac{1}{8} \sum_{jk} n_j n_k \left(B_{oj}^{1/3} + B_{ok}^{1/3}\right)^3$$

$$= n_1^2 B_{o1} + \frac{n_1 n_2}{8} \left(B_{o1}^{1/3} + B_{o2}^{1/3}\right)^3 + \cdots + n_N^2 B_{oN} \tag{45B}$$

$$A_o = \left[\sum_k n_k A_{ok}^{1/2}\right]^2 = \left[n_1 A_{o1}^{1/2} + n_2 A_{o2}^{1/2} + \cdots + n_N A_{oN}^{1/2}\right]^2 \tag{46}$$

$$C_o = \left[\sum_k n_k C_{ok}^{1/2}\right]^2 \tag{47}$$

$$b = \left[\sum_k n_k b_k^{1/3}\right]^3 = \left[n_1 b_1^{1/3} + n_2 b_2^{1/3} + \cdots + n_N b_N^{1/3}\right]^3 \tag{48}$$

$$a = \left[\sum_k n_k a_k^{1/3}\right]^3 \tag{49}$$

$$c = \left[\sum_k n_k c_k^{1/3}\right]^3 \tag{50}$$

$$\gamma = \left[\sum_k n_k \gamma_k^{1/2}\right]^2 \tag{51}$$

$$\alpha = \left[\sum_k n_k \alpha_k^{1/3}\right]^3 \tag{52}$$

Calculations were made (10) in which the linear and Lorents combination for B_o were compared. For the methane-n-butane system calculations of pressure by Equation 15 in which the Lorents combination for B_o was used gave values with an average deviation of

0.4% from observed (21), while use of the linear combination gave values with an average deviation of 1.4%. In the methane-n-butane and ethane-n-butane systems calculations of the equilibrium constant using the Lorentz combination gave values with an average deviation of about 3.0% from observed (27,28), while calculations using the linear combination gave values with an average deviation of about 1.1%. Since composition of coexisting phases was of primary interest in the present work, the linear combination was used throughout.

By combining the thermodynamic equations 4, 5, and 6 with the equation of state 15 and the parameter equations 45 to 52, one may derive algebraic expressions for such thermodynamic properties as the entropy and enthalpy of mixtures and the fugacities of the components. These functions are given by Benedict et al (10) as follows:

$$S = \sum_k n_k \left[S^*_{ok} + R \ln \frac{V}{n_k RT} + \int_{T_0}^{T} \frac{C^*_{pk}}{T} \, dT \right] - \left[B_o R + \frac{2C_o}{T^3} \right] \frac{1}{V} - \frac{bR}{2V^2} + \frac{2c}{T^3 V^2} \left[\frac{1 - \exp(-\gamma/V^2)}{\gamma/V^2} - \frac{\exp(-\gamma/V^2)}{2} \right] \tag{53}$$

$$H = \sum_k n_k \left[H^*_{ok} + \int_{T_0}^{T} C^*_{pk} \, dT \right] + \left[B_o RT - 2A_o - \frac{4C_o}{T^2} \right] \frac{1}{V} + \frac{6a\alpha}{5V^5} + \left[2bRT - 3a \right] \frac{1}{2V^2} + \frac{c}{T^2 V^2} \left[3 \frac{1 - \exp(-\gamma/V^2)}{\gamma/V^2} - \frac{\exp(-\gamma/V^2)}{2} + \frac{\gamma}{V^2} \exp(-\gamma/V^2) \right] \tag{54}$$

$$RT\ln f_k = RT\ln\frac{n_k RT}{V} + \left[(B_o + B_{ok})RT - 2(A_oA_{ok})^{1/2} - \frac{2(C_oC_{ok})^{1/2}}{T^2}\right]\frac{1}{V}$$

$$+\frac{3}{2}\left[RT(b^2b_k)^{1/3} - (a^2a_k)^{1/3}\right]\frac{1}{V^2} + \frac{3}{5}\left[a(\alpha^2\alpha_k)^{1/3} + \alpha(a^2a_k)^{1/3}\right]\frac{1}{V^5}$$

$$+\frac{3(c^2c_k)^{1/3}}{T^2V^2}\left[\frac{1-\exp(-\gamma/V^2)}{\gamma/V^2} - \frac{\exp(-\gamma/V^2)}{2}\right]$$

$$-\frac{2c}{T^2V^2}\left(\frac{\gamma_k}{\gamma}\right)^{1/2}\left[\frac{1-\exp(-\gamma/V^2)}{\gamma/V^2} - \exp(-\gamma/V^2) - \frac{\gamma}{2V^2}\exp(-\gamma/V^2)\right] \qquad (55)$$

The derivation of these expressions is given in Appendix II.

II

Digital Computing Equipment

A. Introductory remarks

Before a discussion of the solution of Equations 53, 54, and 55, it seems appropriate to describe the digital computing equipment which was available to this project and which was the determining factor in the mathematical approach. All of the work to be discussed was done with punched card equipment manufactured and leased by the International Business Machines Corp. These machines, which were developed primarily for expediting accounting procedures, have in recent years been applied to scientific computations. A punched card machine may be defined as one whose operations are controlled by a 3.25" x 7.375" manila card passing through it. The nature of the operation depends on the type of machine, the way in which the machine is operated, and the number and position of perforations in the card. The card, a diagram of which is shown in Figure 2, contains spaces for 80 columns and 12 rows of perforations. Ten of the rows serve for the digits 0 to 9, and the remaining two, generally called the "X" and "12" punches, serve as control punches, several uses for which will be mentioned. The 80 columns are used for numerical or alphabetical information at the discretion of the operator. Thus, an eight-digit number could be represented by punches in eight columns, the punch in each column representing the value of the corresponding digit. A negative number is represented by an "X" punch generally in the extreme right column of the group containing the number. Perforations may be punched manually in cards by use of the Key Punch which is operated in a manner similar to a typewriter.

In the remaining machines to be discussed, cards are fed to the machine automatically. Perforations are detected as the cards pass between a brass roll and a brush, certain designated circuits being closed at the occurrence of a perforation. This operation is termed "reading". With the exception of the Sorter, which has a single adjustable brush, the machines discussed have 80 reading brushes corresponding to the eighty columns on the card at a reading station. The operation of the machines is controlled by use of a detachable control panel on which the fixed internal wiring of the machine is connected by means of external jumper wires to perform the desired operations.

B. Electronic Calculating Punch, Type 604

The principal item of equipment with which the present work is concerned is the IBM Electronic Calculating Punch, Type 604. The Type 604 consists of two machines, one of which performs the calculating operations, while the second serves to read and punch the cards. Cards are handled at a constant rate of one hundred per minute. Each card in passing through the Type 604, encounters a "first read" station, a punch station and a "second read" station. The arrangement is such that when a card is at the punch station the preceding card is at the second read station and the following card is at the first read station. In describing the operation of the Type 604 it is convenient to speak of "card cycles" time as the time during which the card is at one of these stations being read or punched as the case may be, and of the calculate time as the intervening period during which arithmetic operations are being performed and the cards progressing between stations.

During card cycles time, information may be read from a card at either of the two read stations into the electronic storage of the calculator. The latter consists of 4 electron tubes per digit which are either charged or discharged in a unique sequence for each number from 0 to 9. A number introduced to a storage unit remains there until another number is read in. There is a total of 37 digits of storage into which numbers may be read although for technical reasons it would usually not be practical to use all of these for receiving information. In the present work the control panel was wired so that all values were treated as eight-digit numbers and further discussion will be limited to this case. During card cycles time, punching of the card at the punch station occurs while cards at the read stations are being read. The information to be punched may come either directly from the card at the second read station ("gang punching") or it may come from any of 29 electronic storage spaces of the machine. In the latter case 16 of these digits may also receive information from cards. However, since reading and punching occur simultaneously the same space may not serve both functions. The remaining 13 digit spaces from which information may be punched constitute the counter. The counter is the space in which sums and products occur on addition and multiplications respectively, and as such it is directly analogous to the counter of a desk calculator.

During calculate time arithmetic operations are performed on the numbers which are read into storage during card cycles time and the desired results put in the digit spaces designated for punching. During this period a series of "program" impulses is activated. These impulses will cause various individual functions of which the calculator is capable such as addition, multiplication, etc., to occur in any desired sequence as controlled by control panel wiring. There may be from 20 to 60 sets of these impulses per calculate cycle depending on how the machine is equipped. A discussion of the various factors which limit the complexity of mathematical operations that may be performed during a single calculate cycle would be quite involved. It will suffice for the present purpose to state that the operation $P = \frac{A \times B}{C} + C$ would be a representative calculation for eight-digit numbers in a 40 program calculate cycle.

An important feature of the Type 604 and one which was a major factor in the calculation technique to be described is the program suppression. By wiring this device a program or a sequence of programs may be omitted from a particular cycle. Control is achieved through devices known as "calculate selectors" which are two-way relays always closed in one of two possible positions, normal or transferred. Transfer of these relays from normal position is accomplished by use of an "X" or "12" punch and appropriate wiring. In this manner considerable flexibility of operation is possible. To consider a simple example, it would be possible to perform the operation $P = \frac{A \times B}{C} + C$ on some cards of a group and $P = \frac{A \times B}{C}$ on the others of the same group by punching an "X" punch in a designated column of those cards on which the first calculation is desired and omitting it in the others. This feature is also employed during card cycle time if it is desired to control transfer of information from cards to the machine or from the machine to the cards. For example, when the numbers in a group of cards are to be multiplied by a common factor, this factor may be read into the machine from a "master" card designated by a specified "X" or "12" punch and will remain there until the next master card reaches the read station.

C. Auxiliary equipment

The machines used along with the Type 604 in the procedure to be described were those conventionally employed in an accounting or computing installation, and little discussion will be devoted to them. They included:

(1) The Reproducing Punch, on which any or all information on a set of cards may be transferred to any desired position on another set.

(2) The Sorter, on which cards may be separated according to the space punched in a single column.

(3) The Collator, on which cards may be separated or merged according to numbers punched in a designated column or group of columns.

(4) The Tabulator, use of which was limited to printing of information read from punched cards containing the results of calculations.

III

Digital Computer Techniques Developed for Calculation of Thermodynamic Properties of Hydrocarbon Systems

A. Introductory remarks

The aim of the present work was to develop a digital procedure for the solution of algebraic expressions exemplified by Equations 53, 54, and 55. For reasons stated in Section I-A it is desirable to solve these equations for a small number or even a single hydrocarbon system at a time. This requirement precluded conventional punched card calculation procedures which rely for their efficiency on performing a large number of identical calculations. The first phase of the present work, therefore, was devoted entirely to development of a practical procedure for the solution of a relatively small number of complex algebraic equations. The principal novel operational techniques developed in the course of the work and used on the Electronic Calculating Punch, Type 604, are described in the following sections. It should be emphasised that this presentation is not a resumé of information to be found in operating manuals but an attempt to describe as simply as possible what is believed to be a definite contribution to the computing art.

B. General purpose control panel for the Electronic Calculating Punch, Type 604; calculate section

In cases where problems involve a mathematical operation of greater complexity than can be completed in a single card cycle on the Type 604, it is customary to divide the problem into a minimum number of parts and solve each part in a separate pass through the calculator with the appropriate control panel. Because of the time consumed in changing wiring, this becomes practical only when there is a large number of similar problems to solve. Since the problem at hand did not meet this requirement a different procedure was sought which led to the development of what will be called the general purpose control panels, one for each machine composing the Type 604 as discussed in Section II-B.

The calculate panel will be discussed first. Briefly, this is a panel which is wired to perform all the basic arithmetic operations required in the entire solution. In addition each sequence of programs performing an operation is wired to "suppress hubs" through selector relays as discussed in Section II-B. The operations performed during a particular calculate cycle depend on the combination of calculate selectors which are transferred which in turn is controlled by the code ("X" or "12") punches in the card at the read station.

The details of programming of the calculate control panel are shown in Table I and the wiring in Figure 3. Much of its development was the result of experience and numerous practical considerations and no attempt will be made to explain all the reasons for the particular layout finally used. The principal features of the panel are tabulated in Table II. The solution of a problem can best be illustrated by taking a simple example. Consider the problem

$$y = A + Bx + Cx^2 + Dx^3 \qquad (56)$$

Rearrange this to

$$y = \left[(Dx + C)x + B\right] x + A \qquad (57)$$

This problem can be solved by introducing to the calculator a sequence of cards containing the values of the various terms of the equation and the code ("X" or "12") punches causing the proper series of arithmetic operations. The planning of a sequence or deck of cards will be referred to as coding. In the present case the first card could contain the value of x along with instructions for it to be read into storage space 3-4 during the card cycles time and to be read into the counter during calculate time. Referring to Table II we find this operation would require code punches in columns 4 and 12. In this case the code punch in column 4 causes the counter to be cleared of its previous number (program 24) and causes the number in storage space 3-4 to be put in the counter (program 25). All other programs occurring during this particular card cycle are either suppressed or result in no change to the number in the counter.

In the solution of Equation 57, the second card might contain the value of D and instructions for D to be placed in storage space 1-2 (it being desirable to retain x in storage space 3-4) and to form the product Dx. Again referring to Table II we see this would require code punches in columns 3 and 15. In all arithmetic operations the number in the counter is one of two factors involved. Furthermore, a number in the counter at the end of a given calculate cycle is there at the beginning of the next. At the end of this card cycle the product Dx will be in the counter. The third card may contain C which can be read into storage space 1-2 replacing D and can be added to Dx to give Dx + C at the end of this calculate cycle. This operation requires code punches in columns 6 and 15. The fourth card may contain the value of B and the value of the term (Dx + C)x + B may be completed by putting code punches in columns 3, 6, 8, and 15. The code punch in 8 controls the selection of factors for the different arithmetic operations. Omission of the code punch in 8 would have given (Dx + C)B + x. It has been assumed in this example that the decimal point was always correctly placed for addition. If such is not the case, the number in the counter may be shifted one place to the right or left at the beginning of the calculate cycle by use of a code punch in column 2 or 1 respectively. The value of A may be entered on the fifth card and the solution for y completed by using code punches 3, 6, 8, 13, and 15. A code punch in column 13 is used to cause the value of y to be punched into the second following card (number 7 in this deck) which completes the problem.

To recapitulate, the coding of a deck of cards to obtain the solution of Equation 57 for y using the general purpose calculation panel in the Type 604 calculator is:

Card Number	Value on card	Code punches in columns	Term in counter at end of calculate cycle
1	x	4,12	x
2	D	3,15	Dx
3	C	6,15	Dx + C
4	B	3,6,8,15	(Dx + C)x + B
5	A	3,6,8,13,15	$y = \left[(Dx + C)x + B\right] x + A$
6	-	-	
7	-	-	

If a solution to an equation of this nature is desired at frequent intervals it becomes practical to keep on file a set of cards (in this case the seven described above) which contain the values of constants in the equation and the necessary coding for its solution. Obtaining a value of y involves key punching of the argument x on the first card of the prepared deck and passing the deck through the Type 604 using the general purpose panel. In the initial preparation of such a deck the term values and coding are key punched on the cards. Additional decks are prepared using the Reproducing Punch (Section II-C).

This example has presented only a few of the many operations that may be performed by using various combinations of coding. However, it is believed that it does illustrate the general approach. A more detailed discussion of coding problems is given in Appendix III. If the reader desires further details on this matter it is suggested that he consult Appendix III and follow the coding sheets of actual problems given in Tables III to VI, referring either to the program charts in Table I or to Table II for the function of individual code punches.

C. General purpose control panel for the Electronic Calculating Punch, Type 604; punching section

The control panel for the punching section of the Type 604 controls the reading and punching of the cards at card cycles time. Its functions include control of the columns read, the storage space into which the number goes, the storage place from which numbers are taken, and columns into which they are punched. The principal novel feature introduced in this work is an arrangement by which the cards serve as storage space supplementary to the electronic storage of the machine. This feature may be illustrated by a simple example. In the previous section the equation

$$y = A + Bx + Cx^2 + Dx^3 \tag{56}$$

was solved for y by a sequential calculation in the Type 604. Suppose now that it is desired to obtain a value of x for a given value of y. One way to accomplish this would be to select two trial values of x, obtain y from these values and then obtain a third trial value of x by a linear interpolation of the form

$$x_3 = x_2 + \left(\frac{x_2 - x_1}{y_2 - y_1}\right)(y - y_2) \tag{58}$$

The value of y_3 can be calculated and a new interpolation made. This process may be continued until the value of y is obtained to the desired accuracy. In carrying out this calculation by means of the general purpose calculation panel in the Type 604 as described in the previous section the problem of assembling the values of y and x required in Equation 58 arises. As has been pointed out, the storage space in the machine is limited and not adequate for this purpose. One possible solution to this difficulty would be to remove cards containing the calculated values from the machine and reproduce the values on another deck of cards properly coded for the next calculation. This procedure would be very time-consuming and a more satisfactory solution was sought. The procedure finally evolved will be described.

A calculated value, say y_1, is punched in a designated eight columns of a card. The punching control panel is wired in such a way that when this card reaches the second read station the value of y_1 is punched in the following card. As mentioned in Section II-B this operation is known as gang punching. By this means the value of y can be punched on every card following the one on which it is originally punched. This feature will be referred to as card storage. Meanwhile, the sequential calculation is continuing as described in the previous section. When the point is reached where y_1 is needed, say in the solution of Equation 58, it may be read from the card at the second read into the storage space of the calculator. It is still kept in card storage by gang punching as usual. A number is removed from card storage by punching a new value from the machine into its space. A total of 64 columns on the cards or space for eight eight-digit numbers is devoted to card storage as shown on the card diagram in Figure 2. The coding ("12" punches) on a given card determines whether a number in card storage is read into the machine and whether a new number is punched into card storage.

This description has only outlined the principles and use of card storage. The actual details are considerably more complicated (Appendix III) due principally to the fact that the Type 604 used did not have sufficient selector relays to permit each eight-digit group in card storage to be handled independently.

D. Card layout and further remarks on sequential calculations

Some of the procedures described in the previous two sections may be made more concrete by referring to the card layout diagram in Figure 2. The code punches already referred to in these sections and in Table II, are placed in columns 1 through 15. As shown in Figure 2 the digit zone of the first eight columns is divided into spaces for a number to identify the problem being worked (columns 1-2), a number to identify the card in a deck (columns 3-6), and a sort number (columns 7-8). Columns 17 to 80 are used for card storage space as described in the previous section. Columns 9 to 16 are used for values required for the solution of a problem which are not to be stored, i.e., not to be gang punched from card to card. Such values, referred to as card factors, are entered in the appropriate cards of a deck prior to passing the deck through the calculator. Examples of such values are the terms A, B, C, and

D of Equation 56 in the illustrative example of Section III-B.

In a long problem it is probable that the number of intermediate values desired in subsequent calculations will exceed the eight which may be stored in card storage. In such a case the procedure is to punch these values as they are obtained on the Type 604. No attempt is made to store them until required, i.e., additional values are punched into the card storage space as calculated. When the calculation has proceeded as far as possible, or until one of the intermediate values being discussed is required, the deck is removed from the Type 604. This deck is run through the Sorter (Section II-C) and cards containing desired values are selected according to the number in columns 7 and 8 (see Figure 2). These cards are passed through the Reproducing Punch and the values transferred to columns 9 to 16 of a deck of cards already coded for the next calculation. The calculation on the Type 604 is now resumed.

IV

The Application of Computing Techniques to the Calculation of Thermodynamic Properties of Hydrocarbon Systems

A. Nature of problems selected for solution

There is of course a great variety of calculations that might be made with the relationships obtainable from the thermodynamic equations of Section I-B and the Benedict equation of state. For the initial work in developing digital calculation techniques the analysis of a three-component system in the two-phase region was chosen as representative of a reasonable degree of computational complexity. Specifically, it was decided to solve for composition, molal volume, enthalpy and entropy of the coexisting phases in a ternary system, given the temperature, pressure and the composition of one component in one phase. This calculation involves the simultaneous solutions of the equations

$$\begin{aligned} P_b(T, V_b, x_1, x_2, x_3) &= P_d(T, V_d, y_1, y_2, y_3) \\ f_{1b}(T, V_b, x_1, x_2, x_3) &= f_{1d}(T, V_d, y_1, y_2, y_3) \\ f_{2b}(T, V_b, x_1, x_2, x_3) &= f_{2d}(T, V_d, y_1, y_2, y_3) \\ f_{3b}(T, V_b, x_1, x_2, x_3) &= f_{3d}(T, V_d, y_1, y_2, y_3) \end{aligned} \qquad (59)$$

for the composition and molal volumes of the phases followed by calculation of enthalpy and entropy. The pressure and fugacity functions are given by Equations 15 and 55 where the parameters are functions of composition as given by Equations 45 to 52. Actual calculations were limited to this type problem and to solution of binary two-phase systems. However, it is thought that the techniques developed are directly applicable to solution of other problems differing in number of components or in the nature of the restraints imposed.

B. Outline of procedure for calculation of composition of coexisting phases

Before discussing some of the details involved in the separate steps of the procedure it seems advisable to outline the entire algebraic solution of the composition of coexisting phases. The steps involved are as follows:

1. Trial values of composition of each phase are obtained. The parameters in the expressions for the pressure and fugacities, Equations 15 and 55, are calculated for each phase from Equations 45 to 52.
2. The value of molal volume is calculated for each phase by a trial and error solution of Equation 15 using the parameters calculated in step (1) above and the values of temperature and pressure given for the problem.
3. Using the values of the parameters from step (1) and the molal volumes from step (2), the fugacity of each component in each phase is calculated from Equation 55.

4. On the basis of results obtained in step (3) new values of the composition of each phase are obtained and steps (1) to (3) repeated.
5. The trial and calculated values of compositions from two successive iterative calculations of compositions are correlated and the composition extrapolated to the convergence of trial and calculated values. If the extrapolated values are not too far removed from the last values calculated in step (4), they are accepted as final. Otherwise, steps (1) to (4) are repeated.
6. Using the values of composition obtained in step (5), steps (1) and (2) are repeated to obtain the final values of the dew-point and bubble-point molal volumes and then the entropy and enthalpy calculated from Equations 53 and 54 respectively.

C. Calculation of parameter values

The values of the parameters in Equations 15, 53, 54, and 55 for mixtures are given by the equations (Section I-D):

$$B_o = \sum_k n_k B_{ok} \tag{45A}$$

$$A_o = \left[\sum_k n_k A_{ok}^{1/2}\right]^2 \tag{46}$$

$$C_o = \left[\sum_k n_k C_{ok}^{1/2}\right]^2 \tag{47}$$

$$b = \left[\sum_k n_k b_k^{1/3} \right]^3 \qquad (48)$$

$$a = \left[\sum_k n_k a_k^{1/3} \right]^3 \qquad (49)$$

$$c = \left[\sum_k n_k c_k^{1/3} \right]^3 \qquad (50)$$

$$\gamma = \left[\sum_k n_k \gamma_k^{1/2} \right]^2 \qquad (51)$$

$$\alpha = \left[\sum_k n_k \alpha_k^{1/3} \right]^3 \qquad (52)$$

In addition, the various coefficient terms of Equation 55 for the fugacity of each component must be evaluated. Values of the parameters for the pure components were taken from Benedict et al (10). These values were converted to English units and the roots required in the calculations of Equations 45 to 52 are tabulated in Table VII. Since the composition of the coexisting phases is calculated by trial and error, first approximations of these values are required. For this purpose it was decided to use two nomograms given by Hadden (6) for the "ideal equilibrium vaporization constant", because they were convenient to use and covered a wide range of temperatures and pressures. When calculating several ternary mixtures at the same pressure and temperature it is generally better to use K values resulting from one of these calculations. The value of the composition of one component, defined as component 1, in the liquid phase is given as a condition of the problem as mentioned in Section IV-A. The remaining compositions are calculated using the above-mentioned values of K_k in the equations

$$x_2 = \frac{1 - K_3 + x_1(K_3 - K_1)}{K_2 - K_3} \tag{59}$$

$$x_3 = 1 - x_1 - x_2 \tag{60}$$

$$y_1 = K_1 x_1 \tag{61}$$

$$y_2 = K_2 x_2 \tag{62}$$

$$y_3 = K_3 x_3 \tag{63}$$

The values of the parameters listed above can now be calculated from Equations 45 to 52. This is done in a sequential calculation of the type described in Section III-B.

For details of the calculations the reader is referred to Table III. This table contains a description of each card used in the sequential calculation together with an expression of the status of the calculation at the end of the corresponding calculate cycle in the IBM Calculating Punch, Type 604. The information listed consists in the card number, a sort number and such numerical terms as are common to all problems. The positioning of these various numbers on a card are shown in the card diagram of Figure 2. Values which change with the problem such as compositions in the present case are entered in card storage space (Section III-C).

The deck for the calculation of all the parameters in the pressure and fugacity equations for a ternary mixture consists of 112 cards for each phase. The calculation is started by key punching the trial values of y_3, y_2, y_1 in columns 17 to 40 of a card and placing it at the beginning of the deck for vapor phase parameters (cards 2001 to 2140 in Table III), and doing likewise for the liquid phase (cards 3001 to 3140). The cards are then passed through the Type 604 using the general purpose control panels. Each ternary mixture requires a different deck which may be prepared by a procedure described in Appendix IV. As the decks proceed through the Type 604 the values of all the desired parameters are calculated and punched in cards designated by preassigned sort numbers. The cards containing these values are separated from the others and arranged in a desired order by the Sorter, which selects the cards according to the sort number in columns 7 and 8. The parameters are now available for the calculation of the molal volume of each phase and of the fugacities of each component in each phase.

D. Solution of Benedict equation of state for the molal volume

In calculations with the Benedict equations it is more convenient to use the molal density* in place of volume, When this

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* Actually, this quantity is not a density in the English units used in this paper. It is a weight rather than a mass per unit volume. However, it is convenient to use the term "density" and it is believed that such usage will not lead to any ambiguity in the present instance.

substitution is made, Equation (15) becomes

$$P = RTd + \left[B_0RT - A_0 - \frac{C_0}{T^2}\right]d^2 + \left[bRT - a\right]d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1+\gamma d^2)\exp(-\gamma d^2) \tag{64}$$

which is the form in which the equation is written by Benedict et al (9). The calculation of molal density, given pressure, temperature, and composition from this equation involves a trial and error solution. When a trial value of the density is selected, the calculation of pressure may be done by the sequential calculation procedure described in Section III-B. For this purpose Equation 64 is written

$$P = \Big\{\Big(\Big(\Big[\frac{c}{T^2}(1+\gamma d^2)\exp(-\gamma d^2) + a\alpha d^3 - a + bRT\Big]d + B_0RT - A_0 - \frac{C_0}{T^2}\Big)d + RT\Big\}d \tag{65}$$

A trial and error procedure for the calculation of the density was evolved from a consideration of the form of the d vs P isotherms as calculated from this equation. A series of such isotherms for a methane-propane mixture of invariant composition are presented in Figure 1. For calculation of dew-point density two trial values of the density are calculated by letting Z = 0.7 and Z = 0.7/1.8 = 0.389 in the equation

$$d = \frac{P}{ZRT} \tag{66}$$

Experience showed these values of Z to be about optimum over a wide range of conditions. The pressure is calculated for each of these densities by Equation 65 and a new trial value of density calculated from the interpolation formula

$$d_n = d_{n-1} + \left(\frac{d_{n-1} - d_{n-2}}{P_{n-1} - P_{n-2}}\right)(P - P_n) \tag{67}$$

The pressure is again calculated using the new value of density and the interpolation repeated. It was found from experience that a total of four calculations of pressure was sufficient to obtain an accurate value of the density. The entire procedure is done in a single pass of the Type 604 calculator by making use of card storage (Section III-C) to hold values of temperature and density and the various terms required for the interpolation.

The calculation of bubble-point density differs slightly from that of the dew-point density. Briefly, the procedure consists in making one trial guess of the bubble-point density and a guess of the value $s = \left(\frac{\Delta d}{\Delta P}\right)_{T,m}$. The pressure is calculated from Equation 65 and a new trial value of the density calculated by the interpolation formula

$$d_2 = d_1 + s(P - P_1) \tag{68}$$

This process is repeated to obtain a third trial value of density. Then two additional iterations are made using an interpolation of the form of Equation 67. As with the dew-point density a total of four iterations was found to give a sufficiently accurate value of the bubble-point density in all calculations made. The first trial value of the density may be obtained by taking the weighted average of the bubble-point densities of the pure components at the given temperature. For components whose critical temperature is below the temperature of the mixture, values of bubble-point density extrapolated from below the critical gave satisfactory results. The first value of s used was estimated from experience. When this procedure is repeated for new values of the composition (Section IV-B) the values of density and s calculated from the final iteration of the previous calculation are used as the first trial values. This fact makes the accuracy of the original selections less critical.

The evaluation of the exponential term exp(γd^2) required in the course of each calculation of pressure has not yet been explained. The calculation of this term is done by a sequential process on the Type 604 using about twenty cards which are part of the deck for the solution of the entire equation. The mechanics of the calculation involve progressive multiplications of values $e^{-5.0}$, $e^{-2.5}$, $e^{-1.25}$, ..., $e^{-0.00007629}$, suppressing those which are not required to sum to the given value of γd^2. The first value $e^{-5.0}$, is used because it was decided from physical considerations that the value of γd^2 would always be less than 10. The actual calculator operations to effect this calculation occur in programs 6 to 11 and 14 to 22 (Table I) of the calculate cycle. The calculation is described in more detail in Appendix III. The exponential operation is performed by the calculator when code punches in columns 3, 6, and 7 occur on a card (Table II).

A deck of cards required for the sequential calculation of pressure for a given density and temperature would consist of cards numbered 0002 to 0062 of Table IV. The entire iterative calculation to obtain the density of both phases is done on cards 0002 to 0564. This table lists the cards required to carry the calculation as far as the new trial values of compositions (steps 2 to 4 in Section IV-B). It will be noted that there are two decks listed in Table IV. The larger of these two decks (B deck) is made up of cards which remain the same for all problems. The other (A deck) is made of cards which are to contain values of the parameters which, of course, change with each problem. The values of the parameters are calculated and arranged as described in the previous section. The sort numbers on which they were arranged were so chosen to put the values in the proper order for the density and fugacity calculations. The next step in the calculation is to transfer these values of the parameters to columns 9 to 16 in the cards of A deck for the density and fugacity calculations. The Reproducing Punch is used for this operation. The cards of A and B decks are then merged or arranged in a single deck by the Collator according to the card number in columns 3 to 6. The deck thus obtained is ready for sequential calculation in the Type 604. Values of the pressure and temperature and a trial value of the bubble-point density are key punched in the card storage space of a lead card.

E. Calculation of fugacities and values of composition

The calculation of the fugacities of each component is made on the Type 604 calculator using cards numbered 0565 to 1045 of the deck described in the previous section and listed in Table IV. For the purpose of this calculation Equation 55 is written

$$\frac{f_k}{n_k} = RTd \exp \frac{1}{RT} \left\{ \left(\frac{3(c^2 c_k)^{1/3}}{T^2} \left[\frac{1-\exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} \right] \right.\right.$$

$$- \frac{2c}{T^2} \left(\frac{\gamma_k}{\gamma} \right)^{1/2} \left[\frac{1-\exp(-\gamma d^2)}{\gamma d^2} - \exp(-\gamma d^2) - \frac{\gamma d^2 \exp(-\gamma d^2)}{2} \right] \tag{69}$$

$$\left.+ \frac{3}{5} \left[a(\alpha^2 \alpha_k)^{1/3} + \alpha (a^2 a_k)^{1/3} \right] d^3 + \frac{3}{2} \left[RT(b^2 b_k)^{1/3} - (a^2 a_k)^{1/3} \right] \right) d$$

$$\left. + (B_o + B_{ok})RT - 2(A_o A_{ok})^{1/2} - 2 \frac{(C_o C_{ok})^{1/2}}{T^2} \right\} d$$

The values of the bubble-point and dew-point densities are calculated as described in the previous section and are held in card storage for the sequential calculation of fugacities.

Since it is a necessary condition of equilibrium that the fugacity of each component in all phases be equal the equilibrium constant should be obtained by the equation

$$K_k = \frac{f_{kb}}{x_k} \bigg/ \frac{f_{kd}}{y_k} \tag{70}$$

If the values of the composition used to calculate the parameters had been correct solutions of the problem, this would be so. Since this is not generally the case, the values of K calculated from Equation 70 may only be considered corrected values of the original approximations. New trial values of composition are calculated from these K values using Equation 59 to 63. This calculation is made by means of cards 1046 to 1064 (Table IV) of the same deck used for the density and fugacity calculations. Cards numbered 1061 and 1064 have new values of the liquid and vapor phase compositions punched so that these cards may be placed at the front of the parameter calculation decks (Section IV-C) and the entire calculation repeated as described.

In general, satisfactory convergence of the composition values or K values is obtained in two or three iterations. The number of iterations is found to vary depending on the agreement of the original trial K values with the correct solution and the proximity of the temperature, pressure, and composition conditions to the critical state of the system. Regarding the latter point, the composition values for mixtures near the critical point were found to converge relatively slowly to the correct solution. However, in all cases calculated there has been definite convergence. The rate of this convergence may be seen from a tabulation of the values of K and of composition calculated in each iteration of a typical problem given in Table VIII. In order to hasten convergence it was found practical to correlate linearly two sets of K values used as approximations with the corresponding K values calculated and extrapolate to the point where these are equal. Taking the trial and the calculated K values from two successive iterations of the type described in Sections IV-C to IV-E and remembering that the set of K values calculated in the first iteration is used as the trial set in the second, we obtain as the extrapolation equation

$$K_{n+3} = \frac{K_{n+2} - K_{n+1}\left(\frac{K_{n+2} - K_{n+1}}{K_{n+1} - K_n}\right)}{1 - \left(\frac{K_{n+2} - K_{n+1}}{K_{n+1} - K_n}\right)} \qquad (71)$$

K_n and K_{n+1} represent trial and calculated values respectively in the first iteration and K_{n+1} and K_{n+2}, the corresponding values in the second iteration. This calculation is made for each of the three components of the mixture on the Type 604 by a sequential calculation using the deck of 67 cards listed in Table V. The cards containing the appropriate K values for solution of Equation 71 are selected from the decks of the completed fugacity calculations and the K values reproduced on the cards of the A deck of Table V. The composition corresponding to the extrapolated K values are calculated from Equations 59 to 63 as part of the sequential calculation of this deck.

These values may either be accepted as final or used as trial values in further iterations of the type described in Section IV-C to IV-E. This decision is made at the discretion of the operator on the basis of the agreement between the K values obtained by the above extrapolation and those obtained from the last fugacity calculation. In most problems this agreement is sufficiently close after two fugacity calculations to permit acceptance of the extrapolated K values and corresponding composition values as final. In cases of mixtures near the critical state, two additional trial and error calculations are required to give satisfactory convergence.

F. Calculations of entropy and enthalpy

When the final values of composition are obtained as described in the previous section, completion of the problem (Section IV-A) requires calculation of the entropy and enthalpy of both phases.

The first requirement is to calculate the parameters in the equation for entropy and enthalpy using the final values of the composition. These parameters are the same as those in the pressure equation and are calculated using the deck listed in Table III and the procedure described in Section IV-C. Since Equations 53 and 54 for entropy and enthalpy respectively are in terms of the density, the density of each phase is calculated using these parameters in the procedure described in IV-D. This is a questionable refinement over taking the density values calculated in the final iteration of the composition calculation. The density, and the entropy and enthalpy functions for both phases are calculated using a single deck of cards listed in Table VI. For the purpose of the sequential calculation Equation 53 for entropy is rewritten

$$S - \sum_k n_k \left[S_k^* - R \ln(dRTn_k) \right] = \left\{ \left(\frac{2c}{T^3} \left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} \right] - \frac{bR}{2} \right) d - B_0 R - 2\frac{C_0}{T^3} \right\} d \tag{72}$$

and Equation 54 for enthalpy rewritten

$$H - \sum_k n_k H_k^* = \left\{ \left(\frac{c}{T^2} \left[3\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} + \gamma d^2 \exp(-\gamma d^2) \right] + \frac{6}{5} a\alpha d^3 + bRT - \frac{3}{2} a \right) d + B_0 RT - 2A_0 - 4\frac{C_0}{T^2} \right\} d \tag{73}$$

The right hand sides of these equations are evaluated by a sequential calculation in the Type 604. The remaining terms are calculated on a desk calculator using the given value of temperature and calculated values of the composition and densities. Values of H_k^* and S_k^* for each component were obtained by integration of C^*_{Pk} and C^*_{Pk}/T values obtained from tabulations of Souders et al (12). The datum values for entropy were obtained from Selected Values of Properties of Hydrocarbons (11).

G. Outline of machine operations

The principal work involved in preparations to solve a particular equation by a sequential calculation on the Electronic Calculating Punch, Type 604, is that of preparing decks of cards of the type shown in Tables III to VI, and discussed in the previous sections. The coding of the cards is described in Section III-B and Appendix III. Testing of a deck is done by comparing solutions obtained on a desk calculator with the solutions obtained by the Type 604. Once these decks are prepared and tested the machine operations are quite routine. The sequence of machine operations required for the complete solution of an individual problem of the type discussed is diagrammed in Figure 4.

As Figure 4 indicates, the initial step in the procedure is to pass the parameter calculation deck for each phase through the Type 604 using the general purpose control panels. Except for two lead cards containing the key-punched trial values of composition the cards are obtained from files. The calculated decks are then run through the Sorter and arranged in order of the value punched in columns 7 and 8. The parameter values on these cards are transferred to the A deck listed in Table IV by passing them both through the Reproducing Punch using an appropriately wired control panel. The A and B decks listed in Table IV are placed in the Collator and merged in a single deck arranged in order of the card number punched in columns 3 to 6. A card containing values of the temperature and pressure and a trial value of the density is placed at the head of this deck and the deck introduced to the Type 604. During this pass of the 604, the density of each phase, fugacity of each component in each phase, K values, and new approximations of composition are calculated. If another iteration is to be performed, cards 1064 and 1061 of the calculated deck are put at the head of the parameter decks and the calculation repeated exactly as above. Card numbered 0281 from the calculated deck of the previous iteration is used as the lead card for the density-fugacity calculation deck for the second and subsequent iterations. Values of the composition obtained in each iteration may be sight read and recorded so that the operator may observe the proximity of composition values to convergence. The calculation of final composition values by the extrapolation described in Section IV-E is performed in a similar way using the deck listed in Table V. The same applies to calculation of entropy and enthalpy functions.

The various decks which are passed through the Type 604 are simultaneously being reproduced (first 16 columns) on the Reproducing Punch. This is necessary since every calculation results in the card storage space being punched with values unique to that calculation. A completed deck is therefore thrown away after the few cards containing certain required values are selected.

In actual practice about one half hour was required to complete an iteration, i.e., calculation of new approximations of composition values from trial values. An average problem required about one and one-half hours to complete.

H. Recording of results

When the final calculations on a particular hydrocarbon system have been completed it is, of course, desirable to record the results in printed form. This is accomplished by a routine punched card procedure. The values of the required properties are punched in designated cards dispersed throughout a completed sequential calculation deck. The particular cards desired are selected from the final calculation decks (cards numbered 5001 to 5083 of Table V and 6002 to 6777 of Table VI), and simultaneously inserted in the proper position in a "listing" deck. The latter consists of cards containing alphabetic descriptions of results interspersed with cards containing numerical values. The operation of selecting the proper cards and inserting them in the listing deck is performed on the Collator. The listing deck is now run through the Tabulator and the values of the equilibrium constants, composition, molal densities, and the pressure correction terms for the entropy and enthalpy of each phase are properly titled and recorded. The form in which this information is obtained is shown in Table VIII.

V

Results of Calculations

A. Methane-ethylene-ethane system

The methane-ethylene-ethane system was selected for the purpose of making the calculations incident to development of the computing techniques discussed in the previous sections. This system is one that met the requirements that the parameters in the Benedict equation for each of the components were available (9,24) and that experimental data had been published (29). Calculations of the composition, molal volume, entropy and enthalpy of each phase were made for this system at several states by the procedures described in Section IV-C to IV-F. For the sake of comparison, some of these calculations were made at the same state, i.e., same pressure, temperature, and liquid phase concentration of ethane, as some of the experimental measurements of Guter et al (29). A tabulation of the calculated and experimental values of the equilibrium constant is presented in Table IX. The composition and the molal volume, entropy and enthalpy of each phase are tabulated in Table X. Also included are the results of calculations for the methane-ethylene-ethane system at 70° F and 734.8 lb. per sq. inch absolute (50 atm.), for which no experimental information is available. Ternary phase diagrams for this system at the four states calculated are given in Figures 5 to 8.

The large discrepancy between calculated and experimental results is not surprising since PVT data which adequately covered this range of conditions were not available for the determination of the numerical values of the parameters used. That the results improve markedly with increase in temperature is further demonstration of this.

B. Methane-propane system

In addition to the calculations on the methane-ethylene-ethane system discussed above, a few states were calculated for the methane-propane system. The states were chosen so as to obtain a comparison of results with data of this laboratory (30). In these calculations a binary mixture was treated as a ternary with the composition of the third component set equal to zero. In this way the identical sets of cards used in ternary mixture calculations could be used for the binary. Actually this is wasteful of cards and machine time and if the demand warrants it, a special set of cards should be prepared for the calculation of binary mixtures. A tabulation of calculated and experimental values of the equilibrium constants is given in Table XI. Calculated values of the composition, molal volume, entropy, and enthalpy of coexisting phases at 40°F. and 190°F. are tabulated in Table XII. A comparison of calculated and experimental values of composition is shown graphically in Figure 9. In general the agreement is within the experimental error.

It is to be expected that the use of the Lorentz combination for the calculation of the parameter B_o (Equation 45B) when making the final calculation of the molal volumes would give more accurate predictions of these properties. This was found to be the case in the calculations of Benedict et al (10). The present card deck used in calculations of the parameters (Table III) could be easily modified to include calculation of B_o by the Lorentz combination.

VI

Conclusions

The results of the present work may be summarized as follows:

1. Techniques have been developed which facilitate the solution of complex polynomials in a single operation of the IBM Electronic Calculating Punch, Type 604.
2. These techniques have been applied to the solution of the relationships of Benedict et al (9,10) for the composition and thermodynamic properties of coexisting phases in light hydrocarbon systems.
3. A punched card machine procedure for the solution of the composition, molal volume, entropy, and enthalpy of coexisting phases in ternary mixtures has been evolved. A calculation time of one and one half hours was found from experience to be reasonable for an average problem. It is estimated that the same calculation performed on a desk calculator would require about 40 hours of work.
4. The procedures developed were applied to the calculation of several states in the methane-ethylene-ethane and methane-propane systems. Where possible, these calculations have been compared with experimental data. The agreement is good except in those regions not covered in the original development of the equations of state for the pure components.

Nomenclature

C_p	Isobaric heat capacity at constant composition for a system, B.t.u. per lb.-molecular wt. per °R
C_V	Isochoric heat capacity at constant composition for a system, B.t.u. per lb.-molecular wt. per °R
d	Refers to weight per unit volume, termed density in this paper, lb.-molecular wt. per cu. ft.
E	Internal energy, molal internal energy, B.t.u. per lb.-molecular wt.
f	Fugacity, lb. per sq. in.
F	Free energy, molal free energy, B.t.u. per lb.-molecular wt.
H	Enthalpy, molal enthalpy, B.t.u. per lb.-molecular wt.
K	Equilibrium constant; $K = y/x$
m	Weight of system, lb.-molecular wt.
n	Mole fraction
N	Number of components in a mixture
P	Pressure, lbs. per sq. in. absolute
R	Molal gas constant
s	Slope of d vs P isotherm $= \left(\frac{\Delta d}{\Delta P}\right)_{T,n}$
S	Entropy, molal entropy, B.t.u. per lb.-molecular wt. per °R
T	Temperature, °R
V	Volume, molal volume, cu. ft. per lb.-molecular wt.
$\underline{V}$	Total volume, cu. ft.
x	Mole fraction referring to liquid phase
y	Mole fraction referring to vapor phase
Z	Compressibility factor; $Z = PV/RT$
μ	Chemical potential, B.t.u. per lb.-molecular wt.

A_o B_o C_o a b c	Parameters in Benedict equation

Subscripts

b	Refers to bubble-point conditions
d	Refers to dew-point conditions
i	Refers to the ith component of a mixture
j	Refers to the jth component of a mixture
k	Refers to the kth component of a mixture
m_i	Indicates that the moles of all components except component k are held constant
n	Indicates that the composition of the system is held constant
N	Refers to the Nth component of a mixture
o	Indicates state at datum temperature

Superscripts

*	Refers to condition at infinite attenuation

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List of Tables

TABLE I

IBM ELECTRONIC CALCULATING PUNCH, TYPE 604

PLANNING CHART FOR GENERAL PURPOSE CONTROL PANEL

	OPERATION NOTES		PROGRAM SUPPRESS	PROGRAM NUMBER	FACTOR STORAGE ASSIGNMENT 6-4 8-6 1	FACTOR STORAGE ASSIGNMENT 2	FACTOR STORAGE ASSIGNMENT 8-6 3	FACTOR STORAGE ASSIGNMENT 4	MULT. QUOT.	COUNTER	GENERAL STORAGE ASSIGNMENT 6-4 8-6 1	GENERAL STORAGE ASSIGNMENT 2	GENERAL STORAGE ASSIGNMENT 8-6 3	GENERAL STORAGE ASSIGNMENT 4
R	READ PROGRAM SEQUENCE FUNCTIONS *	SINGLE PROG. FUNCTIONS	*	R										
1	FACTOR TRANSFER			1	RI	RI							RO	RO
2				2						RO 5 or 6			RI	RI
3	DECIMAL SHIFT			3						RI(-) 5 or 6			RO	RO
4				4					RI	R&R 1 or 2				
5		Balance Test		5										
6				6						RI	RO	RO		
7				7						RI	RO	RO		
8	EXPONENTIAL FEATURE			8			RO	RO		RI(-) 2				
9		Balance Test		9										
10				10			RO	RO		RI 2				
11				11						R&R	RI	RI		
12	DECIMAL SHIFT (Concluded)			12					RO	RI 1 or 2				
13				13						RI 5 or 6			RO	RO
14				14					RI	RO 4				
15				15						R&R 6			RI	RI
16				16						RI			RO	RO
17				17						R&R 4			RI	RI
18	MULTIPLICATION	Multiply +		18		RO	or	RO						
19				19					RI				RO	RO
20				20						R&R 6			RI	RI
P	* For explanation see Appendix III			P										

TABLE I (Continued)

IBM ELECTRONIC CALCULATING PUNCH, TYPE 604

PLANNING CHART FOR GENERAL PURPOSE CONTROL PANEL

OPERATION NOTES			PROGRAM SUPPRESS	PROGRAM NUMBER	FACTOR STORAGE ASSIGNMENT				MULT. QUOT.	COUNTER	GENERAL STORAGE ASSIGNMENT			
					6-4 8-6 1	2	8-6 3	4			6-4 8-6 1	2	8-6 3	4
R	READ PROGRAM SEQUENCE FUNCTIONS *	SINGLE PROG. FUNTIONS	*	R						▨				
21				21						RI			RO	RO
22		Multiply +		22		RO or	RO							
23				23						RI 6	RO	RO		
24	DIVISION INVERSION			24	RO	or	RO		or	R & R 6	RI	or	RI	
25				25	RO	or	RO			RI 6				
26		Divide		26									RO	RO
27				27						R & R	RI	RI		
28				28						RI 6	RO	RO		
29				29					RO		RI	RI		
30	DIVISION	Divide		30									RO	RO
31				31						R & R				
32				32						RI 4	RO	RO		
33				33						R & R	RI	RI		
34				34						RI 6	RO	RO		
35				35					RO	RI 4				
36	ADDITION or SUBTRACTION			36	RO	or	RO			RI (+) or (-) 6				
37		Balance Test		37										
38	ROUNDING	½ Adjust 5		38										
39				39						RO 6			RI	RI
40		Digit Emit 5		40						RI (-) 5				
41		Digit Emit 5		41						RI (+) 5				
P	PUNCH *For explanation see Appendix III			P	▨	▨	▨	▨	▨				RO	RO

TABLE II

Summary of Code Punch Functions for General Purpose Control Panels

Calculate Section

Code Punch in Column	Function	Programs[a]
1[b]	C[c] x 10	2 - 4, 12 - 13
2	C x 10^{-1}	" "
3	Multiplication (C x A[c])	14 - 22
4	Clear counter, insert B[c]	24 - 25
5	Division (C ÷ B)	26 - 35
6	Addition (C + A)	36
7	Subtraction (C - A)	36
8	Factor selection[d]	-
3 + 5[e]	(C x A) ÷ B	

---

[a] See Table I

[b] In columns 12 and 15, code punch is an X; in all others a 12.

[c] A represents number in Factor Storage 1-2
B represents number in Factor Storage 3-4
C represents number in Counter at start of calculate cycle

[d] e.g., in each function indicated, B will be substituted for A or vice versa when a code punch in column eight is added.

[e] For explanation of combinations see Appendix III.

TABLE II. (continued)

Calculate Section

Code Punch in Column	Function	Programs
3 + 6[f]	(C x A) + B	
4 + 5	B ÷ C	
5 + 6	(C ÷ B) + A	
6 + 7	Transfer from General Storage 3 - 4 to Factor Storage 1 - 2	1
1 + 2 + 3	Accumulative multiplication[e]	14 - 23
3 + 4 + 5	B ÷ (C x A)	
3 + 4 + 6	2 x B	
3 + 5 + 6	[(C x A) ÷ B] + B	
3 + 5 + 8	(C x B) ÷ A	
3 + 6 + 7	Exponential operation[e]	8 - 13
3 + 6 + 8	(C x B) + A	
4 + 5 + 6	(B ÷ C) + A	
5 + 6 + 8	(C ÷ A) + B	
3 + 4 + 6 + 8	2 x A	
3 + 5 + 6 + 8	[(C x B) ÷ A] + A	

---

[f] Any addition is changed to subtraction by substitution of a code punch in column 7 for one in 6.

TABLE II. (continued)

Punch Section

Code Punch in Column	Function
12	Factor Storage 3-4 read in from columns 9 to 16
9 + 12	" " " " " " " 25 to 32
9 + 10 + 12	" " " " " " " 41 to 48
9 + 11 + 12	" " " " " " " 57 to 64
9 + 10 + 11 + 12	" " " " " " " 73 to 80
13	Punch number from General Storage 3-4 (i.e., rounded Counter number) only on columns 17-24
15	Factor Storage 1-2 read in from columns 9 to 16

Table III.

Details of Punched Cards Used for Sequential Calculation of Parameters in the Benedict Equation

LEAD CARD: 17 - 24 y_3
25 - 32 y_2
33 - 40 y_1

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2001	4 89 10 12 15		$c_1^{1/3}$*	18592840	$c_1^{1/3}$	
2002	34 8 15		$c_3^{1/3}$	16060900	$c_3^{1/3}$	
2003	1234 89 10 12 15		$c_2^{1/3}$	07932338	$c_2^{1/3}$	
2004	123 89 11 12				$c^{1/3}$	
2005	67				$c^{1/3}$	
2006	3				$c^{2/3}$	
2007	3 5 12 13			10000000	c	8
2010	3 8 12			30000000	$3c$	
2011	3 5 8 12 13	12	$c_1^{1/3}$	18592840	$3(c^2c_1)^{1/3}$	6
2012	3 5 13 15		$c_2^{1/3}$	07932338	$3(c^2c_2)^{1/3}$	5
2013	3 5 8 12 13	32	$c_3^{1/3}$	16060900	$3(c^2c_3)^{1/3}$	4
2014	4 9 11 12	41			y_2	
2015	34 9 10 11 12 15	50	$\gamma_2^{1/2}$	12416480	y_1	
2016	123 15		$\gamma_1^{1/2}$	17413740	$y_1\gamma_1^{1/2} + y_2\gamma_2^{1/2}$	
2017	4 9 10 11 12 15		$\gamma_3^{1/2}$	15401200	y_3	
2020	12345 12			10000000	$1/\gamma^{1/2}$	

* Values listed are for: 1) ethane, 2) methane, 3)ethylene

TABLE III PARAMETERS VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2021	67				$1/\gamma^{1/2}$	
2022	345 12 13			01000000	γ	5
2023	4 8 12				$1/\gamma^{1/2}$	
2024	3 89 10 12	11			$c/\gamma^{1/2}$	
2025	12			50000000		
2026	3 5 15		$\gamma_1^{1/2}$	17413740	$2c(\gamma_1/\gamma)^{1/2}$	
2027	13				"	8
2030	3 5 8 12 13		$\gamma_2^{1/2}$	12416480	$2c(\gamma_2/\gamma)^{1/2}$	7
2031	3 5 13 15	31	$\gamma_3^{1/2}$	15401200	$2c(\gamma_3/\gamma)^{1/2}$	6
2032	4 9 10 12	40			y_2	
2033	34 9 11 12 15	49	$(Rb_2)^{1/3}$	21044931	y_1	
2034	123 15	30	$(Rb_1)^{1/3}$	31302822	$y_1(Rb_1)^{1/3} + y_2(Rb_2)^{1/3}$	
2035	4 9 11 12 15		$(Rb_3)^{1/3}$	28731789	y_3	
2036	123				$(Rb)^{1/3}$	
2037	67				$(Rb)^{1/3}$	
2040	3				$(Rb)^{2/3}$	

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2041	3 13				Rb	6
2042	3 8 12			15000000	1.5Rb	
2043	1 3 5 8 12 13	15	$(Rb_1)^{1/3}$	31302822	$1.5R(b^2b_1)^{1/3}$	4
2044	3 5 15		$(Rb_2)^{1/3}$	21044931	$1.5R(b^2b_2)^{1/3}$	
2045		36			"	
2046					"	
2047	13				$1.5R(b^2b_2)^{1/3}$	8
2050	3 5 8 12 13		$(Rb_3)^{1/3}$	28731789	$1.5R(b^2b_3)^{1/3}$	7
2051	4 89 10 12 15	45	$a_1^{1/3}$	27543890	$a_1^{1/3}$	
2052	34 8 15	54	$a_3^{1/3}$	25029700	$a_3^{1/3}$	
2053	1234 89 10 12 15		$a_2^{1/3}$	14406750	$a_2^{1/3}$	
2054	123 89 11 12				$a^{1/3}$	
2055	67				$a^{1/3}$	
2056	3				$a^{2/3}$	
2057	3 13				a	8
2060	3 8 12			15000000	1.5a	

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2061	1 3 5 8 12 13	14	$a_1^{1/3}$	27543890	$1.5(a^2a_1)^{1/3}$	6
2062	3 5 13 15		$a_2^{1/3}$	14406750	$1.5(a^2a_2)^{1/3}$	5
2063	3 5 8 12 13	35	$a_3^{1/3}$	25029700	$1.5(a^2a_3)^{1/3}$	4
2064	4 9 11 12	44			y_2	
2065	34 9 10 11 12 15	53	$\alpha_2^{1/3}$	08001080	y_1	
2066	123 15		$\alpha_1^{1/3}$	10008870	$y_1\alpha_1^{1/3} + y_2\alpha_2^{1/3}$	
2067	4 9 10 11 12 15		$\alpha_3^{1/3}$	09017690	y_3	
2070	123				$\alpha^{1/3}$	
2071	67				$\alpha^{1/3}$	
2072	3				$\alpha^{2/3}$	
2073	1 3 5 12			10000000	α	
2074	3 89 10 11 12				$1.5\alpha(a^2a_3)^{1/3}$	
2075	5 12			25000000	$0.6\alpha(a^2a_3)^{1/3}$	
2076					"	
2077					"	
2080	13				$0.6\alpha(a^2a_3)^{1/3}$	7

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2081	3 89 11 12				$0.9\alpha(a^2a_3)^{1/3}(a^2a_2)^{1/3}$	
2082	5 9 11 12 13	52			$0.6\alpha(a^2a_2)^{1/3}$	5
2083	2 5 9 10 11 12				0.4α	
2084	3 89 12	43			$0.6\alpha(a^2a_1)^{1/3}$	
2085	1				"	
2086					"	
2087					"	
2090	13				$0.6\alpha(a^2a_1)^{1/3}$	7
2091	2 5				0.4α	
2092	5 12 13	34		40000000	α	5
2093	3 5 8 12			06000000	$0.6\alpha^{2/3}$	
2094	3 89 10 12	13			$0.6a\alpha^{2/3}$	
2095	1				"	
2096	12			10000000	"	
2097	3 5 13 15		$\alpha_1^{1/3}$	10008870	$0.6a(\alpha^2\alpha_1)^{1/3}$	8
2100	3 5 8 12 13		$\alpha_2^{1/3}$	08001080	$0.6a(\alpha^2\alpha_2)^{1/3}$	7

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS								SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2101	3	5					13	15	33	$\alpha_3^{1/3}$	09017690	$0.6a(\alpha^2\alpha_3)^{1/3}$	6
2102	4		9	10		12			42			y_2	
2103	34		9		11	12		15	51	RB_{o2}	00732836	y_1	
2104	123							15		RB_{o1}	01079928	$y_1RB_{o1} + y_2RB_{o2}$	
2105	4		9		11	12		15		RB_{o3}	00957978	y_3	
2106	123											RB_o	
2107		67					13					RB_o	8
2110		6	8			12	13			RB_{o1}	01079928	$RB_o + RB_{o1}$	7
2111	4	6				12	13		16	RB_{o2}	00732836	$RB_o + RB_{o2}$	6
2112	4	6				12	13		37	RB_{o3}	00957978	$RB_o + RB_{o3}$	5
2113	4		89		11	12		15	46	$C_{o1}^{1/2}$	04687776	$C_{o1}^{1/2}$	
2114	34		8					15	55	$C_{o3}^{1/2}$	04005870	$C_{o3}^{1/2}$	
2115	1234		89		11	12		15		$C_{o2}^{1/2}$	01661732	$C_{o2}^{1/2}$	
2116	123		89	10	11	12						$C_o^{1/2}$	
2117		67										$C_o^{1/2}$	
2120	3	5				12	13				10000000	C_o	7

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
2121	3 5 8 12		$C_{o1}^{1/2}$	04687776	$(C_oC_{o1})^{1/2}$	
2122	5 8 13 15	18		50000000	$2(C_oC_{o1})^{1/2}$	5
2123	3 5 13 15		$C_{o2}^{1/2}$	01661732	$2(C_oC_{o2})^{1/2}$	4
2124	3 5 8 12 13	39	$C_{o3}^{1/2}$	04005870	$2(C_oC_{o3})^{1/2}$	3
2125	4 89 10 11 12 15	48	$A_{o1}^{1/2}$	12527530	$A_{o1}^{1/2}$	
2126	34 8 15	57	$A_{o3}^{1/2}$	11230500	$A_{o3}^{1/2}$	
2127	1234 89 10 11 12 15		$A_{o2}^{1/2}$	08369404	$A_{o2}^{1/2}$	
2130	123 89 12				$A_o^{1/2}$	
2131	67				$A_o^{1/2}$	
2132	3 13				A_o	5
2133	3 5 8 12		$A_{o1}^{1/2}$	12527530	$(A_oA_{o1})^{1/2}$	
2134	5 8 13 15	17		50000000	$2(A_oA_{o1})^{1/2}$	3
2135	3 5 13 15		$A_{o2}^{1/2}$	08369404	$2(A_oA_{o2})^{1/2}$	2
2136	3 5 8 12 13	38	$A_{o3}^{1/2}$	11230500	$2(A_oA_{o3})^{1/2}$	1
2137		47				
2140		56				

LEAD CARD: 17 - 24 x_3
25 - 32 x_2
33 - 40 x_1

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3001	4 89 10 12 15			18592840	CARDS 3001 TO 3140	
3002	34 8 15			16060900	ARE FOR LIQUID PHASE	
3003	1234 89 10 12 15			07932338	OTHERWISE IDENTICAL	
3004	123 89 11 12				TO CARDS 2001 TO 2140	
3005	67					
3006	3					
3007	3 5 12 13			10000000		
3010	3 8 12			30000000		
3011	3 5 8 12 13	2		18592840		
3012	3 5 13 15			07932338		
3013	3 5 8 12 13	60		16060900		
3014	4 9 11 12	69				
3015	34 9 10 11 12 15	78		12416480		
3016	123 15			17413740		
3017	4 9 10 11 12 15			15401200		
3020	12345 12			10000000		

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3021	67					
3022	345 12 13			01000000		
3023	4 8 12					
3024	3 89 10 12	1				
3025	12			50000000		
3026	3 5 15			17413740		
3027	13					
3030	3 5 8 12 13			12416480		
3031	3 5 13 15	59		15401200		
3032	4 9 10 12	68				
3033	34 9 11 12 15	77		21044931		
3034	123 15	58		31302822		
3035	4 9 11 12 15			28731789		
3036	123					
3037	67					
3040	3					

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3041	3 13					
3042	3 8 12			15000000		
3043	1 3 5 8 12 13	5		31302822		
3044	3 5 15			21044931		
3045		64				
3046						
3047	13					
3050	3 5 8 12 13			28731789		
3051	4 89 10 12 15	73		27543890		
3052	34 8 15	82		25029700		
3053	1234 89 10 12 15			14406750		
3054	123 89 11 12					
3055	67					
3056	3					
3057	3 13					
3060	3 8 12			15000000		

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3061	1 3 5 8 12 13	4		27543890		
3062	3 5 13 15			14406750		
3063	3 5 8 12 13	63		25029700		
3064	4 9 11 12	72				
3065	34 9 10 11 12 15	81		08001080		
3066	123 15			10008870		
3067	4 9 10 11 12 15			09017690		
3070	123					
3071	67					
3072	3					
3073	1 3 5 12			10000000		
3074	3 89 10 11 12					
3075	5 12			25000000		
3076						
3077						
3080	13					

```
                 TABLE III      PARAMETER VALUES
CARD        CODE PUNCHES       SORT  CARD FACTOR  COUNTER PUNCH
 NO           IN COLUMNS        NO  TERM   VALUE    TERM  INDEX
3081   3    89    11 12
3082     5   9    11 12  13     80
3083  2  5   9 10 11 12
3084   3    89       12         71
3085 1
3086
3087
3090                     13
3091  2  5
3092     5           12  13     62      40000000
3093   3 5  8        12                 06000000
3094   3    89 10    12          3
3095 1
3096                 12                 10000000
3097   3 5               13 15          10008870
3100   3 5  8        12  13             08001080
```

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3101	3 5 13 15	61		09017690		
3102	4 9 10 12	70				
3103	34 9 11 12 15	79		00732836		
3104	123 15			01079928		
3105	4 9 11 12 15			00957978		
3106	123					
3107	67 13					
3110	6 8 12 13			01079928		
3111	4 6 12 13	6		00732836		
3112	4 6 12 13	65		00957978		
3113	4 89 11 12 15	74		04687776		
3114	34 8 15	83		04005870		
3115	1234 89 11 12 15			01661732		
3116	123 89 10 11 12	86				
3117	67					
3120	3 5 12 13			10000000		

TABLE III PARAMETER VALUES

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
3121	3 5 8 12			04687776		
3122	5 8 13 15	8		50000000		
3123	3 5 13 15			01661732		
3124	3 5 8 12 13	67		04005870		
3125	4 89 10 11 12 15	76		12527530		
3126	34 8 15	85		11230500		
3127	1234 89 10 11 12 15			08369404		
3130	123 89 12					
3131	67					
3132	3 13					
3133	3 5 8 12			12527530		
3134	5 8 13 15	7		50000000		
3135	3 5 13 15			08369404		
3136	3 5 8 12 13	66		11230500		
3137		75				
3140		84				

Table IV.

Details of Punched Cards Used for Sequential Calculation of Molal Density, Fugacities of Components and Composition of Coexisting Phases in Ternary Mixtures

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS		SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0005	1 3 5 8 12		1	γ	(LIQUID PHASE)	γd^2 *	
0036	3 5 9 10 12	15	2	$c \times 10^{-6}$		? $[c/T(1 + \gamma d^2)e^{-\gamma d^2}]$	
0043	1 3 78 12		3	α		$\alpha d^3 - 1$	
0044	1 3	15	4	a		$(a\alpha d^3 - a)$	
0047	123	15	5	bR		$\{bRT + [\ ?\ ] + (\ ?\ )\}$	
0051	1 4 8	15	6	B_oR		B_oR	
0052	123 789 10 11 12	15	7	A_o		$B_oRT + \{\ \} d - A_o$	
0053	4 67 12		8	$C_o \times 10^{-6}$		C_o	
0071	1 3 5	15	1	γ		SAME AS FIRST	
0102	3 5 9 10 11 12	15	2	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0107	1 3 78 12		3	α			
0110	1 3	15	4	a			
0113	123	15	5	bR			
0115	1 4 8	15	6	B_oR			
0116	123 789 10 12	15	7	A_o			
0117	4 67 12		8	$C_o \times 10^{-6}$			

*For continuity in sequential calculation refer also to cards in Table IV B

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0141	1 3 5 15	1	γ		SAME AS FIRST	
0172	3 5 9 10 11 12 15	2	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0177	1 3 78 12	3	α			
0180	1 3 15	4	a			
0183	123 15	5	bR			
0185	1 4 8 15	6	B_oR			
0186	123 789 10 12 15	7	A_o			
0187	4 67 12	8	$C_o \times 10^{-6}$			
0211	1 3 5 15	1	γ		SAME AS FIRST	
0242	3 5 9 10 11 12 15	2	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0247	1 3 78 12	3	α			
0250	1 3 15	4	a			
0253	123 15	5	bR			
0255	1 4 8 15	6	B_oR			
0256	123 789 10 12 15	7	A_o			
0257	4 67 12	8	$C_o \times 10^{-6}$			

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0285	1 3 5 15	11	γ (VAPOR PHASE)		SAME AS FIRST	
0316	3 5 9 10 12 15	12	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0323	1 3 78 12	13	α			
0324	1 3 15	14	a			
0327	123 15	15	bR			
0331	1 4 8 15	16	B_oR			
0332	123 789 10 11 12 15	17	A_o			
0333	4 67 12	18	$C_o \times 10^{-6}$			
0351	1 3 5 15	11	γ		SAME AS FIRST	
0382	3 5 9 10 11 12 15	12	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0387	1 3 78 12	13	α			
0390	1 3 15	14	a			
0393	123 15	15	bR			
0395	1 4 8 15	16	B_oR			
0396	123 789 10 12 15	17	A_o			
0397	4 67 12	18	$C_o \times 10^{-6}$			

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0425	1 3 5 15	11	γ		SAME AS FIRST	
0456	3 5 9 10 12 15	12	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0463	1 3 78 12	13	α			
0464	1 3 15	14	a			
0467	123 15	15	bR			
0471	1 4 8 15	16	B_oR			
0472	123 789 10 11 12 15	17	A_o			
0473	4 67 12	18	$C_o \times 10^{-6}$			
0497	1 3 5 15	11	γ		SAME AS FIRST	
0530	3 5 9 11 12 15	12	$c \times 10^{-6}$		SEQUENCE OF EIGHT	
0535	1 3 78 12	13	α			
0536	1 3 15	14	a			
0541	123 15	15	bR			
0543	1 4 8 15	16	B_oR			
0544	123 789 12 15	17	A_o			
0545	4 67 12	18	$C_o \times 10^{-6}$			

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0567	1 3 5 13 15	30	γ (VAPOR PHASE)		γd^2	8
0614	3 5 8 12	31	$2c(\gamma_1/\gamma)^{1/2} \times 10^{-6}$		$-2c(\gamma_1/\gamma)^{1/2}\Gamma/T^2$*	
0615	4 67 12	32	$3(c^2c_1)^{1/3} \times 10^{-6}$		$3(c^2c_1)^{1/3}$	
0617	1 4 8 12	33	$0.6a(\alpha^2\alpha_1)^{1/3}$		$-2c(\alpha_1/\gamma)^{1/2}\Gamma/T^2$	
0620	12 4 6 15	34	$0.6\,(a^2a_1)^{1/3}$		$0.6[a(\alpha^2\alpha_1)^{1/3}+\alpha(a^2a_1)^{1/3}]$	
0624	1 7 15	35	$1.5(a^2a_1)^{1/3}$		$a\alpha d^3 - 1.5(a^2a_1)^{1/3}$	
0625	12 4 8 15	36	$1.5R(b^2b_1)^{1/3}$		$1.5R(b^2b_1)^{1/3}$ γ,	
0630	1 4 9 11 12 15	37	$RB_o + RB_{o1}$		T	
0631	123 7 12	38	$2(A_oA_{o1})^{1/2}$		$(RB_o + RB_{o1})T - 2(A_oA_{o1})^{1/2}$ $+[\quad]d$	
0632	4 67 12	39	$2(C_oC_{o1})^{1/2} \times 10^{-6}$		$2(C_oC_{o1})^{1/2}$	
0671	4 8 15	40	TO 0690 SAME AS 0614 TO 0632			
0673	4 67 12	41	FOR COMPONENT 2			
0675	1 4 8 12	42				
0676	12 4 6 15	43				
0682	1 7 15	44				
0683	12 4 8 15	45				

$$*\ \Gamma = \frac{2 - 2e^{-\gamma d^2} - \gamma d^2 e^{-\gamma d^2}}{2\gamma d^2} - \frac{(1+\gamma d^2)e^{-\gamma d^2}}{2}$$

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0686	1 4 9 10 12 15	46				
0687	123 7 12	47				
0690	4 67 12	48				
0733	4 8 15	49		TO 0752 SAME AS 0614 TO 0632		
0735	4 67 12	50		FOR COMPONENT 3		
0737	1 4 8 12	51				
0740	12 4 6 15	52				
0744	1 7 15	53				
0745	12 4 8 15	54				
0750	1 4 9 11 12 15	55				
0751	123 7 12	56				
0752	4 67 12	57				
0796	1 3 5 8 12	58	γ	(LIQUID PHASE)	γd^2	8
0846	3 5 8 12	59		TO 0864 SAME AS 0614 TO 0632		
0847	4 67 12	60		FOR COMPONENT 1 (LIQUID PHASE)		
0851	1 4 8 12	61				

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0852	12 4 6 15	62				
0856	1 7 15	63				
0857	12 4 8 15	64				
0862	1 4 9 11 12 15	65				
0863	123 7 12	66				
0864	4 67 12	67				
0905	4 8 15	68		TO 0924 SAME AS 0614 TO 0632		
0907	4 67 12	69		FOR COMPONENT 2		
0911	1 4 8 12	70				
0912	12 4 6 15	71				
0916	1 7 15	72				
0917	12 4 8 15	73				
0922	1 4 9 11 12 15	74				
0923	123 7 12	75				
0924	4 67 12	76				
0973	4 8 15	77		TO 0992 SAME AS 0614 TO 0632		
				FOR COMPONENT 3		

TABLE IV A

DENSITY - FUGACITY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS						SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0975		4	67	12			78				
0977	1	4	8	12			79				
0980	12	4	6			15	80				
0984	1		7			15	81				
0985	12	4	8			15	82				
0990	1	4	9 10	12		15	83				
0991	123		7	12			84				
0992		4	67	12			85				
1037		4	89	12	13	15	86	x_1		x_1	8

NOTE:- CARD 0001 KEYPUNCHED - DENSITY (1)
PRESSURE (5)
TEMPERATURE (6)
S (3)

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0002						
0003	4 9 10 12 13				d_1 Liquid	4
0004	3 8	15		01000000	d_2^2	
0006	4 678 12		*	10000000	γd^2	
0007	6 8				$1+\gamma d^2$	
0010	3 67	15	$e^{-5.0}$	00673795	↓	
0011	3 67	15	$e^{-2.5}$	08208500		
0012	3 67	15	$e^{-1.25}$	28650480	To 0030 Calculation	
0013	3 67	15	$e^{-0.625}$	53526143	of $(1+\gamma d^2)e^{-\gamma d^2}$	
0014	3 67	15	$e^{-0.3125}$	73161563		
0015	3 67	15	etc.	85534533		
0016	3 67	15	to 0030	92484881		
0017	3 67	15		96169060		
0020	3 67	15		98065825		
0021	3 67	15		99028190		
0022	3 67	15		99512909		

* For continuity in sequential calculation refer to cards in Table IV A in proper card No. order

DENSITY (1)
PRESSURE (5)
TEMPERATURE (6)
S (3)

Note : – CARD 0001 KEY PUNCHED

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0023	3 67	15		99756157		
0024	3 67	15		99878004		
0025	3 67	15		99938983		
0026	3 67	15		99969487		
0027	3 67	15		99984742		
0030	3 67	15	$e^{-.000076}$	99992371	$(1+\gamma d^2)e^{-\underline{\gamma d}^2}$	
0031	67				"	
0032	123 8 12					
0033	2 5 12		2^{17}	13107200	$\gamma d^2_{Residual} \times 2^{17}$	
0034	3				$(1+\gamma d^2)e^{-\underline{\gamma d}^2}(\gamma d^2)_{Resid.}$	
0035	3 6 8 12			00010000-~~00000~~	$(1+\gamma d^2)e^{-\gamma d^2}$	
0037	5		*		$\frac{c}{T^2}(1+\gamma d^2)e^{-\gamma d^2}$	
0040	4 9 10 12				d_1	
0041	3 8				d_1^2	
0042	1 3 8	15		01000000	d_1^3	
0045	1		*		$a\alpha d_1^3 - a$	

* For continuity in sequential calculation refer to cards in Table IV A in proper card number order

TABLE IV-B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0046	12 4 9 10 12				T	
0050	3 89 10 12				$\{[\ ]+(\ )+bRT\}d$	
0054	5 9 12				$d_1\left\{bRT+\frac{c}{T^2}(1+\gamma d^2)e^{-\gamma d^2}+a\alpha d^3-a\right\}$	
0055	2 5 7				$\left[-B_0RT+\frac{C_0}{T^2}+A_0-\{\ \}\right]$	
0056	3 5 89 12	15		10000000-	~~B_0RT~~ $[\ ]d_1$	
0057	4 8	15	R	01073185	R	
0060	123 89 11 12				$RT+[\ ]d_1$	
0061					$RT+[\ ]d_1$	
0062	3 5 89 11 12	15		10000000-	$-P_1$	
0063	6 89 10 11 12				$P-P_1$	
0064					$P-P_1$	
0065	5 9 10 11 12				$s(P-P_1)$	
0066	6 89 12				d_2	
0067	67 13				d_2	8
0070	3 12			01000000	d_2^2	
0072	4 678 12			10000000	$1+\gamma d^2$	

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0073	6 8				↓	
0074	3 67	15		00673795	TO CARD NO.	
0075	3 67	15		08208500	0126 -- SAME	
0076	3 67	15		28650480	AS 0007 TO 0062	
0077	3 67	15		53526143		
0080	3 67	15		73161563		
0081	3 67	15		85534533		
0082	3 67	15		92484881		
0083	3 67	15		96169060		
0084	3 67	15		98065825		
0085	3 67	15		99028190		
0086	3 67	15		99512909		
0087	3 67	15		99756157		
0090	3 67	15		99878004		
0091	3 67	15		99938983		
0092	3 67	15		99969487		

```
                  TABLE IVB
CARD           CODE PUNCHES            SORT   CARD  FACTOR   COUNTER  PUNCH
 NO              IN COLUMNS             NO    TERM   VALUE     TERM   INDEX

0093   3  67                            15          99984742
0094   3  67                            15          99992371
0095      67
0096 123     8        12
0097  2  5            12                            13107200
0100   3
0101   3  6 8         12                            00010000-
0103     5
0104    4     9 10    12
0105   3     8
0106 1 3     8                          15          01000000
0111 1
0112 12 4     9 10 11 12
0114   3     89 10    12
0120     5    9    11 12
0121  2  5 7
```

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0122	3 5 89 12 15			10000000-		
0123	4 8 15			01073185		
0124	123 89 12					
0125						
0126	3 5 89 11 12 13 15			10000000-	$-P_2$	1
0127	6 89 10 12				$P-P_2$	
0130					$P-P_2$	
0131	5 9 10 12				$s(P-P_2)$	
0132	4 67 9 12				d_2	
0133	13				d_2	4
0134	6				d_3	
0135					d_3	
0136					d_3	
0137	67 13				d_3	8
0140	3 12			01000000	↓ TO CARD 0196 SAME AS 0004	
0142	4 678 12			10000000	TO 0062	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0143	6 8					
0144	3 67	15		00673795		
0145	3 67	15		08208500		
0146	3 67	15		28650480		
0147	3 67	15		53526143		
0150	3 67	15		73161563		
0151	3 67	15		85534533		
0152	3 67	15		92484881		
0153	3 67	15		96169060		
0154	3 67	15		98065825		
0155	3 67	15		99028190		
0156	3 67	15		99512909		
0157	3 67	15		99756157		
0160	3 67	15		99878004		
0161	3 67	15		99938983		
0162	3 67	15		99969487		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0163	3 67	15		99984742		
0164	3 67	15		99992371		
0165	67					
0166	123 8 12					
0167	2 5 12			13107200		
0170	3					
0171	3 6 8 12			00010000-		
0173	5					
0174	4 9 10 12					
0175	3 8					
0176	1 3 8	15		01000000		
0181	1					
0182	12 4 9 10 11 12					
0184	3 89 10 12					
0190	5 9 11 12					
0191	2 5 7					

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0192	3 5 89 12 15			10000000-		
0193	4 8 15			01073185		
0194	123 89 12					
0195						
0196	3 5 89 11 12 13 15			10000000	$+P_3$	1
0197	6 89 10 11 12				P_3-P_2	
0200	4 67 9 10 11 12 13				d_3	7
0201					d_3	
0202	789 11 12				d_3-d_2	
0203	45 89 10 11 12				P_3-P_2/d_3-d_2	
0204	4 67				P	
0205	789 11 12				$P-P_3$	
0206	56 89 11 12				d_4	
0207	67 13				d_4	8
0210	3 12			01000000	↓	
0212	4 678 12			10000000	TO 0266 SAME AS 0004 TO 0062	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0213	6 8					
0214	3 67	15		00673795		
0215	3 67	15		08208500		
0216	3 67	15		28650480		
0217	3 67	15		53526143		
0220	3 67	15		73161563		
0221	3 67	15		85534533		
0222	3 67	15		92484881		
0223	3 67	15		96169060		
0224	3 67	15		98065825		
0225	3 67	15		99028190		
0226	3 67	15		99512909		
0227	3 67	15		99756157		
0230	3 67	15		99878004		
0231	3 67	15		99938983		
0232	3 67	15		99969487		

```
                 TABLEIVB
CARD        CODE PUNCHES       SORT  CARD FACTOR  COUNTER PUNCH
 NO           IN COLUMNS        NO  TERM   VALUE    TERM  INDEX
0233   3  67                15          99984742
0234   3  67                15          99992371
0235      67
0236 123    8        12
0237  2  5           12                 13107200
0240   3
0241   3  6 8        12                 00010000-
0243     5
0244    4    9 10    12
0245   3    8                   50
0246 1 3    8               15          01000000
0251 1
0252 12 4    9 10 11 12
0254   3    89 10    12
0260     5   9    11 12
0261  2  5 7
```

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0262	3 5 89 12 15			10000000-		
0263	4 8 15			01073185		
0264	123 89 12					
0265						
0266	3 5 89 11 12 13 15			10000000-	$-P_4$	
0267	1 3 7 9 10 11 12				P_4-P_3	
0270	4 67 9 10 11 12				d_4	
0271	789 10 11 12				d_4-d_3	
0272	45 8				P_4-P_3/d_4-d_3	
0273	4 67 9 10 11 12				P	
0274	4 8 13				$S = P_4-P_3/d_4-d_3$	3
0275	12 4 7 9 11 12				$-P_4-\left(\frac{P_4-P_3}{d_4-d_3}\right)$	
0276	12 56 89 11 12 13				d_5 (final value)	1
0277	4 12		0.7 R	07512295	0.7 R	
0280	3 89 11 12				0.7 RT	
0281	45 9 11 12				$d_1^{Gas} = \frac{P}{.7RT}$	

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0282	67				d_1^{Gas}	
0283	13				d_1^{Gas}	4
0284	3 12			01000000	↓	
0286	4 678 12			10000000	TO 0342	
0287	6 8				SAME AS	
0290	3 67	15		00673795	0004TO 0062	
0291	3 67	15		08208500		
0292	3 67	15		28650480		
0293	3 67	15		53526143		
0294	3 67	15		73161563		
0295	3 67	15		85534533		
0296	3 67	15		92484881		
0297	3 67	15		96169060		
0300	3 67	15		98065825		
0301	3 67	15		99028190		
0302	3 67	15		99512909		

```
                       TABLE IVB
CARD            CODE PUNCHES           SORT  CARD  FACTOR    COUNTER  PUNCH
 NO               IN COLUMNS            NO  TERM    VALUE     TERM    INDEX

0303   3  67                      15           99756157
0304   3  67                      15           99878004
0305   3  67                      15           99938983
0306   3  67                      15           99969487
0307   3  67                      15           99984742
0310   3  67                      15           99992371
0311      67
0312 123   8         12
0313  2  5           12                        13107200
0314   3
0315   3  6 8        12                        00010000-
0317     5
0320    4    9 10    12
0321   3   8
0322 1 3   8                      15           01000000
0325 1
```

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0326	12 4 9 10 12					
0330	3 89 10 12					
0334	5 9 12					
0335	2 5 7					
0336	3 5 89 12 15			10000000-		
0337	4 8 15			01073185		
0340	123 89 11 12					
0341						
0342	3 5 89 11 12 15			10000000-	$-P_1$	
0343					$-P_1$	
0344	13				$-P_1$	3
0345	4 15			18000000	d_1	
0346	3 5 12			10000000	$1.8d_1 = d_2$	
0347	67 13				d_2	8
0350	3 12			01000000	↓	
0352	4 678 12			10000000	TO 0406 SAME AS 0004 TO 0062	

```
                        TABLE IVB
CARD            CODE  PUNCHES          SORT   CARD  FACTOR   COUNTER  PUNCH
 NO               IN  COLUMNS           NO   TERM    VALUE     TERM   INDEX

0353        6  8
0354    3   67                    15            00673795
0355    3   67                    15            08208500
0356    3   67                    15            28650480
0357    3   67                    15            53526143
0360    3   67                    15            73161563
0361    3   67                    15            85534533
0362    3   67                    15            92484881
0363    3   67                    15            96169060
0364    3   67                    15            98065825
0365    3   67                    15            99028190
0366    3   67                    15            99512909
0367    3   67                    15            99756157
0370    3   67                    15            99878004
0371    3   67                    15            99938983
0372    3   67                    15            99969487
```

```
                 TABLE IVB

CARD        CODE PUNCHES       SORT  CARD FACTOR  COUNTER PUNCH
 NO           IN COLUMNS        NO  TERM   VALUE    TERM  INDEX

0373   3  67                15          99984742
0374   3  67                15          99992371
0375      67
0376 123    8        12
0377  2  5           12                  13107200
0380   3
0381   3  6 8        12                  00010000-
0383     5
0384    4    9 10    12
0385   3    8
0386 1 3    8               15          01000000
0391 1
0392 12 4    9 10 11 12
0394   3    89 10    12
0400     5   9    11 12
0401  2  5 7
```

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0402	3 5 89 12	15		10000000-		
0403	4 8	15		01073185		
0404	123 89 12					
0405						
0406	3 5 89 11 12	15		10000000	P_2	
0407					P_2	
0410	13				P_2	7
0411	6 89 10 12				$P_2 - P_1$	
0412	4 67 9 12				d_2	
0413					d_2	
0414	789 10 11 12				$d_2 - d_1$	
0415	45 89 12				$P_2 - P_1 / d_2 - d_1$	
0416	4 67				P	
0417	789 11 12				$P - P_2$	
0420	56 89 10 11 12				d_3	
0421	67				d_3	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0422					d_3	
0423	13				d_3	4
0424	3 12			01000000	↓	
0426	4 678 12			10000000	TO 0482	
0427	6 8				SAME AS	
0430	3 67	15		00673795	0004 TO 0062	
0431	3 67	15		08208500		
0432	3 67	15		28650480		
0433	3 67	15		53526143		
0434	3 67	15		73161563		
0435	3 67	15		85534533		
0436	3 67	15		92484881		
0437	3 67	15		96169060		
0440	3 67	15		98065825		
0441	3 67	15		99028190		
0442	3 67	15		99512909		

```
                              TABLE IV B
CARD                    CODE  PUNCHES                      SORT    CARD  FACTOR   COUNTER  PUNCH
 NO                        IN COLUMNS                       NO    TERM    VALUE     TERM   INDEX

0443     3   67                                  15               99756157
0444     3   67                                  15               99878004
0445     3   67                                  15               99938983
0446     3   67                                  15               99969487
0447     3   67                                  15               99984742
0450     3   67                                  15               99992371
0451         67
0452   123     8            12
0453    2  5                12                                    13107200
0454     3
0455     3   6 8            12                                    00010000-
0457       5
0460      4     9 10        12
0461     3     8
0462   1 3     8                                 15               01000000
0465   1
```

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0466	12 4 9 10 12					
0470	3 89 10 12					
0474	5 9 12					
0475	2 5 7					
0476	3 5 89 12	15		10000000-		
0477	4 8	15		01073185		
0480	123 89 11 12					
0481						
0482	3 5 89 11 12	15		10000000	P_3	
0483					P_3	
0484	13				P_3	3
0485	789 10 12				$P_3 - P_2$	
0486	4 67 9 12				d_3	
0487					d_3	
0490	789 10 11 12				$d_3 - d_2$	
0491	45 89 11 12				$P_3 - P_2 / d_3 - d_2$	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0492	4 67				P	
0493	789 11 12				$P-P_3$	
0494	56 89 10 11 12				d_4	
0495	67 13				d_4	2
0496	3 12			01000000	↓	
0500	4 678 12			10000000	TO 0554	
0501	6 8				SAME AS	
0502	3 67	15		00673795	0004 TO 0062	
0503	3 67	15		08208500		
0504	3 67	15		28650480		
0505	3 67	15		53526143		
0506	3 67	15		73161563		
0507	3 67	15		85534533		
0510	3 67	15		92484881		
0511	3 67	15		96169060		
0512	3 67	15		98065825		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0513	3 67	15		99028190		
0514	3 67	15		99512909		
0515	3 67	15		99756157		
0516	3 67	15		99878004		
0517	3 67	15		99938983		
0520	3 67	15		99969487		
0521	3 67	15		99984742		
0522	3 67	15		99992371		
0523	67					
0524	123 8 12					
0525	2 5 12			13107200		
0526	3					
0527	3 6 8 12			00010000-		
0531	5					
0532	4 9 10 12					
0533	3 8					

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TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0534	1 3 8	15		01000000		
0537	1					
0540	12 4 9 11 12					
0542	3 89 10 12					
0546	5 9 10 12					
0547	2 5 7					
0550	3 5 89 12	15		10000000-		
0551	4 8	15		01073185		
0552	123 89 10 11 12					
0553						
0554	3 5 89 11 12 13	15		10000000	P_4	3
0555	789 10 11 12				P_4-P_3	
0556	4 67 9 10 11 12				d_4	
0557					d_4	
0560	789 10 12				d_4-d_3	
0561	45 89 11 12				P_4-P_3/d_4-d_3	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0562	4 67				P	
0563	789 11 12				$P-P_4$	
0564	56 89 11 12 13				d_5^{Gas} (Final Value) 3	
0565	67				START FUGACITY CALC.	
0566	3 12			01000000	Gas d^2	
0570	4 12			10000000	γd^2	
0571	3 67	15		00673795	↓	
0572	3 67	15		08208500	TO 0595	
0573	3 67	15		28650480	SAME AS	
0574	3 67	15		53526143	0010 TO 0034	
0575	3 67	15		73161563		
0576	3 67	15		85534533		
0577	3 67	15		92484881		
0580	3 67	15		96169060		
0581	3 67	15		98065825		
0582	3 67	15		99028190		

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0583	3 67	15		99512909		
0584	3 67	15		99756157		
0585	3 67	15		99878004		
0586	3 67	15		99938983		
0587	3 67	15		99969487		
0590	3 67	15		99984742		
0591	3 67	15		99992371		
0592	67					
0593	123 8 12					
0594	2 5 12			13107200		
0595	3					
0596	3 78 12			00010000	$-e^{-\gamma d^2}$	
0597	567 12			50000000	$-2e^{-\gamma d^2}$	
0600	4 89 10 11 12 13				$-e^{-\gamma d^2}$	7
0601	1 3 8				$-\gamma d^2 e^{-\gamma d^2}$	
0602	12 6	15		20000000	$2-2e^{-\gamma d^2}-\gamma d^2 e^{-\gamma d^2}$	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0603	3 5 13 15			50000000	$\left\{\frac{2-2e^{-\gamma d^2}-\gamma d^2 e^{-\gamma d^2}}{2\gamma d^2}\right\}$	4
0604	2 5 9 12				$\{\}/T$	
0605	5 13				$\{\}/T^2$	2
0606	4 6 9 11 12 15			10000000	$1+\gamma d^2$	
0607	3 5 89 11 12 15			02000000	$-\frac{(1+\gamma d^2)e^{-\gamma d^2}}{2}$	
0610	6 89 10 12				$\left[\{\}\cancel{\tfrac{6}{10}}-\frac{(1+\gamma d^2)e^{-\gamma d^2}}{2}\right]$	
0611					"	
0612	5 9 10 11 12				$[\,]/T$	
0613	2 5 13 15			10000000-	$[\,]/T^2$	4
0616	3 89 10 11 12				$3(c^2c_1)^{1/3}\{\}/T^2$	
0621	3 89 10 12				$a\alpha d$	
0622	1 3 8				$a\alpha d^2$	
0623	1 3 8				$a\alpha d^3$	
0626	123 89 10 12				$\left[1.5P(b_0^2b_1)^{1/3}T+a\alpha d^3-1.5(c_0^2c_1)^{1/3}\right]$	
0627	3 89 12				$[\,]d$	
0633	3 8 12			10000000-	$-2(C_0C_{01})^{1/2}\times10^{-6}$	

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0634	5 9 12				$-2(C_0C_{01})^{1/2}/T$	
0635	56					
0636	5					
0637	3 5 89 12	15		01073185-		
0640	4 9 11 12				T	
0641	3 89 10 12	15		10731850	Td	
0642	1 3 12			10000000	RTd	
0643	3 67	15		00673795	|	
0644	3 67	15		08208500	TO 0667	
0645	3 67	15		28650480	SAME AS 0011 TO 0034	
0646	3 67	15		53526143		
0647	3 67	15		73161563		
0650	3 67	15		85534533		
0651	3 67	15		92484881		
0652	3 67	15		96169060		
0653	3 67	15		98065825		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0654	3 67 15			99028190		
0655	3 67 15			99512909		
0656	3 67 15			99756157		
0657	3 67 15			99878004		
0660	3 67 15			99938983		
0661	3 67 15			99969487		
0662	3 67 15			99984742		
0663	3 67 15			99992371		
0664	67					
0665	123 8 12					
0666	2 5 12			13107200		
0667	3					
0670	3 6 8 12 13			00010000-	$RTd\ e^{[\ ]} = f/y_1$ 7	
0672	3 5 89 11 12 15			10000000-	$-2c\left(\frac{\gamma_2}{\gamma}\right)^{1/2}$	
0674	3 89 11 12				↓	
0677	3 89 12				TO 0732	

SAME CALCN. AS 0565
TO 0670

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0680	1 3 8					
0681	1 3 8					
0684	123 89 12					
0685	3 89 10 11 12					
0691	3 8 12			10000000-		
0692	5 9 10 11 12				↑	
0693	56				CALCULATION OF f_2/y_2	
0694	5				↓	
0695	3 5 89 10 11 12	15		01073185-		
0696	4 9 10 12					
0697	3 89 12	15		10731850		
0700	1 3 12			10000000		
0701	3 67	15		00673795		
0702	3 67	15		08208500		
0703	3 67	15		28650480		
0704	3 67	15		53526143		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0705	3 67	15		73161563		
0706	3 67	15		85534533		
0707	3 67	15		92484881		
0710	3 67	15		96169060		
0711	3 67	15		98065825		
0712	3 67	15		99028190	↑	
0713	3 67	15		99512909	CALCULATION	
0714	3 67	15		99756157	OF f_2/y_2	
0715	3 67	15		99878004	↓	
0716	3 67	15		99938983		
0717	3 67	15		99969487		
0720	3 67	15		99984742		
0721	3 67	15		99992371		
0722	67					
0723	123 8 12					
0724	2 5 12			13107200		

TABLE IVB

```
CARD          CODE PUNCHES          SORT  CARD  FACTOR     COUNTER   PUNCH
 NO             IN COLUMNS           NO   TERM   VALUE      TERM     INDEX

0725   3
0726
0727
0730
0731
0732   3  6 8        12  13                   00010000-   f2/y2       5
0734   3 5  89 10 11 12     15                10000000-     ↕
0736   3    89 10 11 12                                  TO 0791
0741   3    89 10    12                                  CALCULATION
0742 1 3    8                                            OF f3/y3
0743 1 3    8                                               ↓
0746 123    89 10    12
0747   3    89       12
0753   3    8        12                       10000000-
0754     5   9       12
0755     56
```

                  TABLE IVB

```
CARD        CODE PUNCHES          SORT  CARD  FACTOR    COUNTER  PUNCH
 NO           IN COLUMNS           NO   TERM   VALUE      TERM   INDEX

0756     5
0757   3 5   89      12           15          01073185-
0760    4     9   11 12
0761   3     89 10   12           15          10731850
0762 1 3             12                       10000000
0763   3  67                      15          00673795        ↑
0764   3  67                      15          08208500    CALCULATION
0765   3  67                      15          28650480     OF  f3/y3
0766   3  67                      15          53526143        ↓
0767   3  67                      15          73161563
0770   3  67                      15          85534533
0771   3  67                      15          92484881
0772   3  67                      15          96169060
0773   3  67                      15          98065825
0774   3  67                      15          99028190
0775   3  67                      15          99512909
```

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0776	3 67 15			99756157		
0777	3 67 15			99878004		
0780	3 67 15			99938983		
0781	3 67 15			99969487		
0782	3 67 15			99984742		
0783	3 67 15			99992371		
0784	67					
0785	123 8 12					
0786	2 5 12			13107200		
0787	3					
0790	3 6 8 12			00010000-		
0791	13				f_3/y_3	6
0792	4 9 10 11 12				T	
0793	9 10 12 13				T	
0794	4				d^{Liquid}	
0795	3 8 15			01000000	d^2	

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS				SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0797			12	13			10000000	γd^2	8
0800	4		12				10000000		
0801	3	67			15		00673795	↓ TO 0820	
0802	3	67			15		08208500	SAME AS	
0803	3	67			15		28650480	0570 TO 0590	
0804	3	67			15		53526143		
0805	3	67			15		73161563		
0806	3	67			15		85534533		
0807	3	67			15		92484881		
0810	3	67			15		96169060		
0811	3	67			15		98065825		
0812	3	67			15		99028190		
0813	3	67			15		99512909		
0814	3	67			15		99756157		
0815	3	67			15		99878004		
0816	3	67			15		99938983		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0817	3 67	15		99969487		
0820	3 67	15		99984742		
0821	1 3 67	15		99992371	$e^{-\gamma d^2}$	
0822	67					
0823	123 8 12					
0824	2 5 12			13107200		
0825	3					
0826	3 78 12			00010000	$e^{-\gamma d^2}$	
0827	2 567 12			50000000	$2e^{-\gamma d^2}$	
0830	4 9 10 11 12				γd^2	
0831	123 6 12			20000000	$2-2e^{-\gamma d^2}-\gamma d^2 e^{-\gamma d^2}$	
0832	2 5 9 12				$\left[\frac{2-2e^{-\gamma d^2}-\gamma d^2 e^{-\gamma d^2}}{\gamma d^2}\right]$	
0833	5 12			20000000	$[\ ]\div 2=\theta$	
0834					"	
0835		13			θ	2
0836	2 5 9 12				θ/T	

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0837	5 13				θ/T^2	8
0840	4 9 10 11 12				γd^2	
0841	6 8 12			10000000	$1+\gamma d^2$	
0842	3 9 10 12				$-(1+\gamma d^2)e^{-\gamma d^2}$	
0843	56 8 15			20000000	$\theta-\frac{(1+\gamma d^2)}{2}e^{-\gamma d^2}=\Gamma$	
0844	5 9 10 11 12				Γ/T	
0845	2 5 13 15			10000000-	~~00000~~ Γ/T^2	2
0850	3 89 10 11 12				↓	
0853	3 89 10 12				TO 0902	
0854	1 3 8				CALCULATION OF	
0855	1 3 8				f_1/x_1 same	
0860	123 89 10 12				as 0614 TO 677	
0861	3 89 12					
0865	3 8 12			10000000-	~~00000~~	
0866	5 9 12					
0867	56					

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TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0870	5					
0871	3 5 89 12	15		01073185-		
0872	4 9 11 12					
0873	3 89 10 12	15		10731850	↑	
0874	1 3 12			10000000	CALCULATION	
0875	3 67	15		00673795	OF f_1/x_1	
0876	3 67	15		08208500	↓	
0877	3 67	15		28650480		
0880	3 67	15		53526143		
0881	3 67	15		73161563		
0882	3 67	15		85534533		
0883	3 67	15		92484881		
0884	3 67	15		96169060		
0885	3 67	15		98065825		
0886	3 67	15		99028190		
0887	3 67	15		99512909		

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0890	3 67	15		99756157		
0891	3 67	15		99878004		
0892	3 67	15		99938983		
0893	3 67	15		99969487		
0894	3 67	15		99984742		
0895	3 67	15		99992371		
0896	67					
0897	123 8 12					
0900	2 5 12			13107200		
0901	3					
0902	3 6 8 12			00010000-	~~00000~~	f_1/x_1
0903	3 5 9 12	15		00100000	$K_1 = \frac{f_1}{x_1} / \frac{f_1}{y_1} = \frac{y_1}{x_1}$	
0904	13				K_1	3
0906	3 5 89 10 11 12	15		10000000-	~~00000~~ $-2c\left(\frac{\gamma_2}{\gamma}\right)^{\frac{1}{2}}(\Gamma/\Gamma_2)$	
0910	3 89 10 11 12				↓	
0913	3 89 10 12					

To 0962 CALCULATION OF f_2/x_2 SAME AS 0615 to 0667

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0914	1 3 8					
0915	1 3 8					
0920	123 89 10 12					
0921	3 89 12					
0925	3 8 12			10000000-	~~00000~~	
0926	5 9 12					↑
0927	56					CALCULATION
0930	5					OF f_2/X_2
0931	3 5 89 12	15		01073185-	~~00000~~	↓
0932	4 9 11 12					
0933	3 89 10 12	15		10731850		
0934	1 3 12			10000000		
0935	3 67	15		00673795		
0936	3 67	15		08208500		
0937	3 67	15		28650480		
0940	3 67	15		53526143		

TABLE IVB

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0941	3 67	15		73161563		
0942	3 67	15		85534533		
0943	3 67	15		92484881		
0944	3 67	15		96169060		
0945	3 67	15		98065825		
0946	3 67	15		99028190		
0947	3 67	15		99512909		
0950	3 67	15		99756157		
0951	3 67	15		99878004		
0952	3 67	15		99938983		
0953	3 67	15		99969487		
0954	3 67	15		99984742		
0955	3 67	15		99992371		
0956	67					
0957	123 8 12					
0960	2 5 12			13107200		

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
0961	3					
0962	3 6 8 12			00010000-~~00000~~	f^2/x_2	
0963	3 5 9 10 11 12	15		00100000	K_2	
0964					"	
0965					"	
0966					"	
0967					"	
0970					"	
0971	13				K_1	6
0972	4 9 10 11 12 13				f_3/y_3	5
0974	3 5 89 11 12	15		10000000-~~00000~~	↓	
0976	3 89 11 12				To 1027 SAME as	
0981	3 89 12				0671 to 0725	
0982	1 3 8				CALCULATION OF f_3/x_3	
0983	1 3 8					
0986	123 89 12					

```
                 TABLE IVB
CARD        CODE PUNCHES               SORT  CARD FACTOR     COUNTER  PUNCH
 NO            IN COLUMNS               NO   TERM  VALUE       TERM   INDEX
0987   3    89 10 11 12
0993   3    8        12                  10000000-
0994     5    9 10 11 12
0995     56
0996     5
0997   3 5  89 10 11 12      15          01073185-
1000    4    9 10    12
1001   3    89       12      15          10731850
1002 1 3             12                  10000000
1003   3  67                 15          00673795
1004   3  67                 15          08208500
1005   3  67                 15          28650480
1006   3  67                 15          53526143
1007   3  67                 15          73161563
1010   3  67                 15          85534533
1011   3  67                 15          92484881
```

↑

CACCULATION

OF f_3/X_3

↓

```
                   TABLE IV B
CARD         CODE PUNCHES         SORT  CARD  FACTOR   COUNTER  PUNCH
 NO             IN COLUMNS         NO   TERM   VALUE     TERM   INDEX
1012    3  67                  15           96169060
1013    3  67                  15           98065825
1014    3  67                  15           99028190
1015    3  67                  15           99512909
1016    3  67                  15           99756157
1017    3  67                  15           99878004
1020    3  67                  15           99938983
1021    3  67                  15           99969487
1022    3  67                  15           99984742
1023    3  67                  15           99992371
1024       67
1025 123     8         12
1026   2  5            12                   13107200
1027    3
1030
1031
```

CALCULATION
OF f_3/x_3

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
1032						
1033						
1034	3 6 8 12			00010000-	f_3/x_3	
1035	3 5 9 12 13 15			00100000	K_3	2
1036	789 10 12 13				K_3-K_2	1
1040	3 5 8 13 15			00100000	$K_1x_1=y_1$	7
1041	3 7 12			00100000	K_1x_1-1	
1042	6 89 10 12				$K_3+K_1x_1-1$	
1043	4 67	91			K_3	
1044	3 789 10 12				$K_3x_1+1-K_1x_1-K_3$	
1045	3 5 9 11 12 15			10000000-	x_2	
1046	1 13	92			x_2	1
1047		93			x_2	
1050	3 89 11 12				$K_2x_2=y_2$	
1051	5 12 13 15	94		00100000	y_2	6
1052	3 5 9 10 11 12 15			00010000	x_2	

TABLE IV B

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
1053	7 15			10000000	$x_2 - 1$	
1054	4 67 9 10 12				X_1	
1055	13				x_1	2
1056	2 6 9 10 11 12				$X_1 + X_2 - 1$	
1057	5 8 13 15			10000000-	$1 - X_1 - X_2 = X_3$	8
1060	3 5 8 15			00100000	$K_3 X_3 = Y_3$	
1061					"	
1062	13				Y_3	5
1063						
1064						

Table V.

Details of Punched Cards Used for Sequential Calculation of Extrapolated K Values and Phase Composition

TABLE V A K VALUES EXTRAPOLATION

CARD NO	CODE	PUNCHES IN COLUMNS			SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
5001	4	12	13		91	$K_2^{(1)}$ *		$K_2^{(1)}$	6
5002	4	12	13		92	$K_1^{(1)}$		$K_1^{(1)}$	5
5003	4	12	13		93	$K_3^{(1)}$		$K_3^{(1)}$	4
5004	4	12	13		91	$K_2^{(2)}$		$K_2^{(2)}$	3
5005	4	12	13		92	$K_1^{(2)}$		$K_1^{(2)}$	2
5006	4	12	13		93	$K_3^{(2)}$		$K_3^{(2)}$	1
5007	4	12	13		91	$K_2^{(3)}$		$K_2^{(3)}$	8
5010	4	12	13		92	$K_1^{(3)}$		$K_1^{(3)}$	7
5011	4	12	13		93	$K_3^{(3)}$		$K_3^{(3)}$	6
5057	123			15	94	x_1		$1 - K_3 + x_1(K_3 - K_1)$ **	

* Superscripts refer to iteration in which K values are calculated

~~* For continuity in sequential calculation refer also to cards in Table V B in proper order~~

TABLE V B K VALUES EXTRAPOLATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
5012	4 9 10 11 12				$K_2^{(1)} - K_2^{(2)}$	
5013	789 11 12				$K_2^{(3)}$	
5014	4 67 9 10 12				$K_2^{(3)} - K_2^{(2)}$	
5015	789 10 11 12				$1 - (\frac{K_2^{(3)} - K_2^{(2)}}{K_2^{(2)} - K_2^{(1)}})$	
5016	2 56 8 12			10000000	"	
5017	67				"	
5020	78				$-\left(\frac{K_2^{(3)} - K_2^{(2)}}{K_2^{(2)} - K_2^{(1)}}\right)$	
5021	3 89 10 12				$-K_2^{(2)}(\quad)$	
5022	1 6 89 12				$K_2^{(3)} - K_2^{(2)}(\quad)$	
5023	2 5 8				K_2 (FINAL VALUE)	
5024	13				K_2	3
5025	4 9 12				CARDS 5025 TO 5037	
5026	789 10 11 12				SAME AS 5011 TO 5023	
5027	4 67 9 11 12				FOR K_1	
5030	789 12					
5031	2 56 8 12			10000000		

TABLE VB K VALUES EXTRAPOLATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
5032	67					
5033	78					
5034	3 89 11 12					
5035	1 6 89 10 12					
5036	2 5 8				K_1 (FIN VALUE)	
5037	13				K_1(FIN VALUE)	8
5040	4 9 10 12				CARDS 5040 TO 5051	
5041	789 12				SAME AS 5025 TO 5036	
5042	4 67 9 10 11 12				FOR K_3	
5043	789 10 12					
5044	2 56 8 12			10000000		
5045	67					
5046	78					
5047	3 89 10 11 12					
5050	1 6 89 11 12					
5051	2 5 89 10 12 13				K_3(FIN VALUE)	6

TABLE V B K VALUES EXTRAPOLATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
5052	78				$K_3 - K_2$ *	
5053	2 5 12 13			10000000-	$K_2 - K_3$	4
5054	4 789 12 15			00100000	$1 - K_3$	
5055	4				K_3	
5056	789 11 12				$K_3 - K_1$	
5060	5 9 10 12 13				$x_2 = \frac{1 - K_3 + x_1(K_3-K_1)}{K_2 - K_3}$	7
5061	2 4 8				x_1	
5062	13				x_1	5
5063	2 6 15			10000000-	$x_1 - 1$	
5064	12 5 8 13				$x_3 = 1 - x_1 - x_{\overset{2}{3}}$	3
5065	4 9 10 11 12				K_2	
5066					K_2	
5067	3 5 89 11 12 13 15			00100000	$y_2 = K_2x_2$	8
5070	4 9 10 11 12				K_1	
5071	3 5 89 11 12 13				$y_1 = K_1x_1$	6
5072	4 9 10 11 12				K_3	

* K values used in this calculation are all final values

TABLE V B K VALUES EXTRAPOLATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
5073	4 67 9 12 13				x_2	4
5074	4 8				K_3	
5075	3 5 89 10 11 12 13 15			00100000	$y_3 = K_3x_3$	2
5076	4 67 9 10 12				y_1	
5077	13				y_1	8
5080	4 9 10 11 12 13				y_2	7
5081	4 8 13				y_3	6
5082						
5083						

Table VI.

Details of Punched Cards Used for Sequential Calculation of Molal Density, Entropy, and Enthalpy at the Bubble Point and Dew Point

TABLE VI A DENSITY – ENTROPY – ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6005	1 3 5 8 12	1			CARDS 6005 TO 6257	
6036	3 5 9 10 12 15	2			SAME AS 0005 TO 0257	
6043	1 3 78 12	3			(TABLE IV A)	
6044	1 3 15	4				
6047	123 15	5				
6051	1 4 8 15	6				
6052	123 789 10 11 12 15	7				
6053	4 67 12	8				
6071	1 3 5 15	1				
6102	3 5 9 10 11 12 15	2				
6107	1 3 78 12	3				
6110	1 3 15	4				
6113	123 15	5				
6115	1 4 8 15	6				
6116	123 789 10 12 15	7				
6117	4 67 12	8				

TABLE VI A DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS		SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6141	1 3 5	15	1				
6172	3 5 9 10 11 12	15	2				
6177	1 3 78 12		3				
6180	1 3	15	4				
6183	123	15	5				
6185	1 4 8	15	6				
6186	123 789 10 12	15	7				
6187	4 67 12		8				
6211	1 3 5	15	1				
6242	3 5 9 10 11 12	15	2				
6247	1 3 78 12		3				
6250	1 3	15	4				
6253	123	15	5				
6255	1 4 8	15	6				
6256	123 789 10 12	15	7				
6257	4 67 12		8				

TABLE VI A DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6287	1 3 5 13 15	1	γ	(LIQUID PHASE)	γ, d^2	8
6333	3 5 8 12	2	c		$2c\{\ \}$ *	
6334	5 9 12	3	α		$2c\{\ \}/T$	
6335		4	a		"	
6336	4 12	5	bR		bR	
6340	3 8 15	6	B_oR		$(2c\{\ \}/T - bR/2)d$	
6341	1 7	7	A_o		$(\ )d - B_oR$	
6342	4 67 12	8	C_o		C_o	
6355	3 5 89 10 12	1	γ		$(1 + \gamma d^2)e^{-\gamma d^2}$	
6362	3 15	2	c		$c(3\{\ \} + [\ ])$	
6366	1 3 78 12	3	α		$\alpha d^3 - 1.25$	
6367	1 3 15	4	a		$a\alpha d^3 - 1.25a$	
6373	123 9 11 12 15	5	bR		$[c(\ ) + 1.2a\alpha d^3 - 1.5a + bRT]$	
6375	4 12	6	B_oR		B_oR	
6376	123 789 10 12 15	7	A_o		$[\ ]d + B_oRT - A_o$	
6380	4 67 12	8	C_o		C_o	

* For continuity in sequential calculation refer to cards in Table VI B in proper Card No. order

TABLE VI A DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS		SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6395	1 3 5	15	11			CARDS 6395 TO 6677	
6426	3 5 9 10 12	15	12			SAME AS 0285 TO 0567	
6433	1 3 78 12		13			(TABLE IV A)	
6434	1 3	15	14				
6437	123	15	15				
6441	1 4 8	15	16				
6442	123 789 10 11 12	15	17				
6443	4 67 12		18				
6461	1 3 5	15	11				
6492	3 5 9 10 11 12	15	12				
6497	1 3 78 12		13				
6500	1 3	15	14				
6503	123	15	15				
6505	1 4 8	15	16				
6506	123 789 10 12	15	17				
6507	4 67 12		18				

TABLE VI A DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS		SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6535	1 3 5	15	11				
6566	3 5 9 10 12	15	12				
6573	1 3 78 12		13				
6574	1 3	15	14				
6577	123	15	15				
6581	1 4 8	15	16				
6582	123 789 10 11 12	15	17				
6583	4 67 12		18				
6607	1 3 5	15	11				
6640	3 5 9 11 12	15	12				
6645	1 3 78 12		13				
6646	1 3	15	14				
6651	123	15	15				
6653	1 4 8	15	16				
6654	123 789 12	15	17				
6655	4 67 12		18				

TABLE VI A DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6677	1 3 5 13 15	11				
6723	3 5 8 12	12			CARDS 6723 TO 6770	
6724	5 9 12	13			SAME AS 6333 TO 6380	
6725		14				
6726	4 12	15				
6730	3 8 15	16				
6731	1 7	17				
6732	4 67 12	18				
6745	3 5 89 10 12	11				
6752	3 15	12				
6756	1 3 78 12	13				
6757	1 3 15	14				
6763	123 9 11 12 15	15				
6765	4 12	16				
6766	123 789 10 12 15	17				
6770	4 67 12	18				

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

LEAD CARD:
25 - 32 density
41 - 48 s
57 - 64 pressure
65 - 72 temperature

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6002					LIQUID PHASE	
6003	4 9 10 12 13				CARDS 6002 TO 6276	
6004	3 8	15		01000000	ARE IDENTICAL TO CARDS	
6006	4 678 12			10000000	0002 TO 0276 (TABLE IV)	
6007	6 8					
6010	3 67	15		00673795		
6011	3 67	15		08208500		
6012	3 67	15		28650480		
6013	3 67	15		53526143		
6014	3 67	15		73161563		
6015	3 67	15		85534533		
6016	3 67	15		92484881		
6017	3 67	15		96169060		
6020	3 67	15		98065825		
6021	3 67	15		99028190		
6022	3 67	15		99512909		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6023	3 67	15		99756157		
6024	3 67	15		99878004		
6025	3 67	15		99938983		
6026	3 67	15		99969487		
6027	3 67	15		99984742		
6030	3 67	15		99992371		
6031	67					
6032	123 8 12					
6033	2 5 12			13107200		
6034	3					
6035	3 6 8 12			00010000-		
6037	5					
6040	4 9 10 12					
6041	3 8					
6042	1 3 8	15		01000000		
6045	1					

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

```
CARD         CODE PUNCHES       SORT  CARD FACTOR  COUNTER  PUNCH
 NO            IN COLUMNS        NO  TERM   VALUE    TERM   INDEX
6046 12 4    9 10    12
6050   3    89 10    12
6054     5   9       12
6055  2  5 7
6056   3 5  89       12      15          10000000-
6057    4   8                15          01073185
6060 123    89    11 12
6061
6062   3 5  89    11 12      15          10000000-
6063      6 89 10 11 12
6064
6065     5   9 10 11 12
6066      6 89       12
6067      67              13
6070   3             12                  01000000
6072    4 678        12                  10000000
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE	PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6073		6 8					
6074	3	67	15		00673795		
6075	3	67	15		08208500		
6076	3	67	15		28650480		
6077	3	67	15		53526143		
6080	3	67	15		73161563		
6081	3	67	15		85534533		
6082	3	67	15		92484881		
6083	3	67	15		96169060		
6084	3	67	15		98065825		
6085	3	67	15		99028190		
6086	3	67	15		99512909		
6087	3	67	15		99756157		
6090	3	67	15		99878004		
6091	3	67	15		99938983		
6092	3	67	15		99969487		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6093	3 67	15		99984742		
6094	3 67	15		99992371		
6095	67					
6096	123 8 12					
6097	2 5 12			13107200		
6100	3					
6101	3 6 8 12			00010000-		
6103	5					
6104	4 9 10 12					
6105	3 8					
6106	1 3 8	15		01000000		
6111	1					
6112	12 4 9 10 11 12					
6114	3 89 10 12					
6120	5 9 11 12					
6121	2 5 7					

```
                   TABLE  VI B  DENSITY - ENTROPY - ENTHALPY CALCULATION
  CARD        CODE PUNCHES       SORT  CARD FACTOR COUNTER  PUNCH
   NO           IN COLUMNS        NO  TERM   VALUE   TERM   INDEX
  6122   3 5  89       12     15           10000000-
  6123    4   8               15           01073185
  6124 123    89       12
  6125
  6126   3 5  89    11 12  13 15           10000000-
  6127      6 89 10    12
  6130
  6131     5   9 10    12
  6132    4 67 9       12
  6133                       13
  6134      6
  6135
  6136
  6137      67               13
  6140   3             12                  01000000
  6142    4 678        12                  10000000
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO		CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6143		6 8					
6144	3	67	15		00673795		
6145	3	67	15		08208500		
6146	3	67	15		28650480		
6147	3	67	15		53526143		
6150	3	67	15		73161563		
6151	3	67	15		85534533		
6152	3	67	15		92484881		
6153	3	67	15		96169060		
6154	3	67	15		98065825		
6155	3	67	15		99028190		
6156	3	67	15		99512909		
6157	3	67	15		99756157		
6160	3	67	15		99878004		
6161	3	67	15		99938983		
6162	3	67	15		99969487		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6163	3 67	15		99984742		
6164	3 67	15		99992371		
6165	67					
6166	123 8 12					
6167	2 5 12			13107200		
6170	3					
6171	3 6 8 12			00010000-		
6173	5					
6174	4 9 10 12					
6175	3 8					
6176	1 3 8	15		01000000		
6181	1					
6182	12 4 9 10 11 12					
6184	3 89 10 12					
6190	5 9 11 12					
6191	2 5 7					

```
                 TABLE VI B  DENSITY - ENTROPY - ENTHALPY CALCULATION
CARD        CODE PUNCHES       SORT  CARD FACTOR COUNTER  PUNCH
 NO           IN COLUMNS        NO  TERM   VALUE   TERM   INDEX
6192   3 5  89       12      15         10000000-
6193    4   8                15         01073185
6194 123    89       12
6195
6196   3 5  89    11 12   13 15         10000000
6197      6 89 10 11 12
6200    4 67 9 10 11 12   13
6201
6202       789    11 12
6203    45  89 10 11 12
6204    4 67
6205       789    11 12
6206     56 89    11 12
6207      67              13
6210   3             12                 01000000
6212    4 678        12                 10000000
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6213	6 8					
6214	3 67	15		00673795		
6215	3 67	15		08208500		
6216	3 67	15		28650480		
6217	3 67	15		53526143		
6220	3 67	15		73161563		
6221	3 67	15		85534533		
6222	3 67	15		92484881		
6223	3 67	15		96169060		
6224	3 67	15		98065825		
6225	3 67	15		99028190		
6226	3 67	15		99512909		
6227	3 67	15		99756157		
6230	3 67	15		99878004		
6231	3 67	15		99938983		
6232	3 67	15		99969487		

```
                                  TABLE VI B   DENSITY - ENTROPY - ENTHALPY CALCULATION
CARD                    CODE      PUNCHES                     SORT        CARD      FACTOR        COUNTER           PUNCH
  NO                         IN   COLUMNS                       NO       TERM         VALUE          TERM           INDEX
6233          3     67                                    15                      99984742
6234          3     67                                    15                      99992371
6235                67
6236      123         8                 12
6237        2     5                     12                                        13107200
6240          3
6241          3     6   8                 12                                      00010000-
6243              5
6244            4         9   10          12
6245          3         8                                       50
6246      1   3         8                               15                      01000000
6251      1
6252      12    4         9   10    11    12
6254          3         89    10          12
6260              5       9         11    12
6261        2     5    7
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6262	3 5 89 12 15			10000000-		
6263	4 8 15			01073185		
6264	123 89 12					
6265						
6266	3 5 89 11 12 13 15			10000000-		
6267	1 3 7 9 10 11 12					
6270	4 67 9 10 11 12					
6271	789 10 11 12					
6272	45 8					
6273	4 67 9 10 11 12					
6274	4 8 13					
6275	12 4 7 9 11 12					
6276	12 56 89 11 12 13				d LIQUID FINAL VALUE	
6277					"	
6280					"	
6281					"	

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS				SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6282								d	
6283								d	
6284				13				d	3
6285		67						d	
6286	3		12				01000000	d^2	
6290	4		12				10000000	CARDS 6290 TO 6325	
6291	3	67			15		00673795	SAME AS 0567 TO	
6292	3	67			15		08208500	0605 (TABLE IV B)	
6293	3	67			15		28650480		
6294	3	67			15		53526143		
6295	3	67			15		73161563		
6296	3	67			15		85534533		
6297	3	67			15		92484881		
6300	3	67			15		96169060		
6301	3	67			15		98065825		
6302	3	67			15		99028190		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6303	3 67	15		99512909		
6304	3 67	15		99756157		
6305	3 67	15		99878004		
6306	3 67	15		99938983		
6307	3 67	15		99969487		
6310	3 67	15		99984742		
6311	3 67	15		99992371		
6312	67					
6313	123 8 12					
6314	2 5 12			13107200		
6315	3					
6316	3 78 12			00010000		
6317	567 12			50000000		
6320	4 89 10 11 12 13					
6321	1 3 8					
6322	12 6	15		20000000		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6323	3 5 13 15			50000000		
6324	2 5 9 12					
6325	5 13				$\frac{2 - 2e^{-\gamma d^2} - \gamma d^2 e^{-\gamma d^2}}{2\gamma d^2 T^2}$	2
6326					"	
6327					"	
6330					"	
6331					"	
6332	4 9 10 12 15			50000000	"	
6337	123 9 12 15			50000000 –	$\left(2c\{\ \}/T - bR/2\right)$ *	
6343					C_o	
6344	2 5 9 12				C_o/T	
6345	5				C_o/T^2	
6346	5				C_o/T^3	
6347	56 12			50000000 –	$\left[(\ )d - B_oR - 2C_o/T^3\right]$	
6350					"	
6351	3 5 89 10 12 15		CONV. FACTOR	54038889	$S - S^*$ LIQUID BTU PER M °R	

* For continuity in sequential calculation refer also to cards in Table VI A in proper Card No. order

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6352					$S - S^*$	
6353	13				$S - S^*$	4
6354	4 7 9 10 12	15		10000000-	$1 + \gamma d^2$	
6356	5 9 10 12				$(1 + \gamma d^2) e^{-\gamma d^2} / T$	
6357	2 5				" $/T^2$	
6360	4 6 7 9 12				$\left\{ \frac{2 - 2e^{-\gamma d^2} - \gamma d^2 e^{-\gamma d^2}}{2 \gamma d^2 T^2} \right\}$	
6361	3 6 8 12			30000000	$\left(3 \{ \ \} + [\ ] \right)$	
6363	1 4 9 11 12				d	
6364	3 8				d^2	
6365	1 3 8	15		01250000	d^3	
6370	1 3	15		12000000	$1.2a \alpha d^3 - 1.5a$	
6371	1				"	
6372	12 4 9 10 11 12				T	
6374	3 5 8	15		10000000	$\left[c(\ ) + 1.2a \ \ d^3 - 1.5a + bRT \right] d$	
6377	7				$[\ ] d + B_o RT - 2A_o$	
6381	3 8 12			40000000-	$-4C_o$	

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6382	5 9 10 11 12				$-4C_o/T$	
6383	56				$[\ ]d + B_oRT - 2A_o - 4C_o/T^2$	
6384					"	
6385	3 5 89 10 11 12 13 15		CONV. FACTOR	54038889	$H - H^*$ LIQUID BTU PER M	2
6386					CARDS 6387 to 6715	
6387	4 12			07512295	SAME AS 0277 TO 0605	
6390	3 89 11 12				(TABLE IV B)	
6391	45 9 11 12					
6392	67					
6393	13					
6394	3 12			01000000		
6396	4 678 12			10000000		
6397	6 8					
6400	3 67 15			00673795		
6401	3 67 15			08208500		
6402	3 67 15			28650480		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

```
CARD        CODE PUNCHES        SORT  CARD FACTOR COUNTER  PUNCH
 NO           IN COLUMNS         NO  TERM   VALUE   TERM   INDEX
6423  2  5           12                  13107200
6424   3
6425   3  6 8        12                  00010000-
6427     5
6430    4    9 10    12
6431   3    8
6432 1 3    8               15           01000000
6435 1
6436 12 4    9 10    12
6440   3    89 10    12
6444     5   9       12
6445  2  5 7
6446   3 5  89       12     15           10000000-
6447    4   8               15           01073185
6450 123    89    11 12
6451
```

```
                  TABLE  TABLE VI B  DENSITY - ENTROPY - ENTHALPY CALCULATION
CARD         CODE PUNCHES        SORT   CARD FACTOR COUNTER   PUNCH
 NO            IN COLUMNS         NO   TERM   VALUE    TERM   INDEX
6452    3 5  89    11 12      15            10000000-
6453
6454                       13
6455     4                    15            18000000
6456    3 5           12                    10000000
6457       67              13
6460    3             12                    01000000
6462     4 678        12                    10000000
6463       6 8
6464    3  67                 15            00673795
6465    3  67                 15            08208500
6466    3  67                 15            28650480
6467    3  67                 15            53526143
6470    3  67                 15            73161563
6471    3  67                 15            85534533
6472    3  67                 15            92484881
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6473	3 67	15		96169060		
6474	3 67	15		98065825		
6475	3 67	15		99028190		
6476	3 67	15		99512909		
6477	3 67	15		99756157		
6480	3 67	15		99878004		
6481	3 67	15		99938983		
6482	3 67	15		99969487		
6483	3 67	15		99984742		
6484	3 67	15		99992371		
6485	67					
6486	123 8 12					
6487	2 5 12			13107200		
6490	3					
6491	3 6 8 12			00010000-		
6493	5					

```
            TABLE VI B   DENSITY - ENTROPY - ENTHALPY CALCULATION
CARD        CODE PUNCHES    SORT  CARD FACTOR COUNTER  PUNCH
 NO           IN COLUMNS     NO  TERM   VALUE   TERM    INDEX
6494    4    9 10    12
6495   3    8
6496 1 3    8               15         01000000
6501 1
6502 12 4    9 10 11 12
6504   3    89 10    12
6510     5   9    11 12
6511  2  5 7
6512   3 5  89       12     15         10000000-
6513    4   8               15         01073185
6514 123    89       12
6515
6516   3 5  89    11 12     15         10000000
6517
6520                     13
6521      6 89 10    12
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6522	4 67 9 12					
6523						
6524	789 10 11 12					
6525	45 89 12					
6526	4 67					
6527	789 11 12					
6530	56 89 10 11 12					
6531	67					
6532						
6533	13					
6534	3 12			01000000		
6536	4 678 12			10000000		
6537	6 8					
6540	3 67	15		00673795		
6541	3 67	15		08208500		
6542	3 67	15		28650480		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6543	3 67	15		53526143		
6544	3 67	15		73161563		
6545	3 67	15		85534533		
6546	3 67	15		92484881		
6547	3 67	15		96169060		
6550	3 67	15		98065825		
6551	3 67	15		99028190		
6552	3 67	15		99512909		
6553	3 67	15		99756157		
6554	3 67	15		99878004		
6555	3 67	15		99938983		
6556	3 67	15		99969487		
6557	3 67	15		99984742		
6560	3 67	15		99992371		
6561	67					
6562	123 8 12					

```
                  TABLE VI B   DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD       CODE PUNCHES      SORT  CARD FACTOR COUNTER PUNCH
 NO          IN COLUMNS       NO  TERM   VALUE  TERM   INDEX
6563  2  5           12               13107200
6564   3
6565   3  6 8        12               00010000-
6567     5
6570    4    9 10    12
6571   3    8
6572 1 3    8              15         01000000
6575 1
6576 12 4    9 10    12
6580   3    89 10    12
6584     5   9        12
6585  2  5 7
6586   3 5  89       12    15         10000000-
6587    4   8              15         01073185
6590 123    89    11 12
6591
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6592	3 5 89 11 12 15			10000000		
6593						
6594	13					
6595	789 10 12					
6596	4 67 9 12					
6597						
6600	789 10 11 12					
6601	45 89 11 12					
6602	4 67					
6603	789 11 12					
6604	56 89 10 11 12					
6605	67 13					
6606	3 12			01000000		
6610	4 678 12			10000000		
6611	6 8					
6612	3 67 15			00673795		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE	PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6613	3	67	15		08208500		
6614	3	67	15		28650480		
6615	3	67	15		53526143		
6616	3	67	15		73161563		
6617	3	67	15		85534533		
6620	3	67	15		92484881		
6621	3	67	15		96169060		
6622	3	67	15		98065825		
6623	3	67	15		99028190		
6624	3	67	15		99512909		
6625	3	67	15		99756157		
6626	3	67	15		99878004		
6627	3	67	15		99938983		
6630	3	67	15		99969487		
6631	3	67	15		99984742		
6632	3	67	15		99992371		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6633	67					
6634	123 8 12					
6635	2 5 12			13107200		
6636	3					
6637	3 6 8 12			00010000-		
6641	5					
6642	4 9 10 12					
6643	3 8					
6644	1 3 8	15		01000000		
6647	1					
6650	12 4 9 11 12					
6652	3 89 10 12					
6656	5 9 10 12					
6657	2 5 7					
6660	3 5 89 12	15		10000000-		
6661	4 8	15		01073185		

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TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6662	123 89 10 11 12					
6663						
6664	3 5 89 11 12 13 15			10000000		
6665	789 10 11 12					
6666	4 67 9 10 11 12					
6667						
6670	789 10 12					
6671	45 89 11 12					
6672	4 67					
6673	789 11 12					
6674	56 89 11 12 13					
6675	67					
6676	3 12			01000000		
6680	4 12			10000000		
6681	3 67 15			00673795		
6682	3 67 15			08208500		

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6683	3 67	15		28650480		
6684	3 67	15		53526143		
6685	3 67	15		73161563		
6686	3 67	15		85534533		
6687	3 67	15		92484881		
6690	3 67	15		96169060		
6691	3 67	15		98065825		
6692	3 67	15		99028190		
6693	3 67	15		99512909		
6694	3 67	15		99756157		
6695	3 67	15		99878004		
6696	3 67	15		99938983		
6697	3 67	15		99969487		
6700	3 67	15		99984742		
6701	3 67	15		99992371		
6702	67					

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6703	123 8 12					
6704	2 5 12			13107200		
6705	3					
6706	3 78 12			00010000		
6707	567 12			50000000		
6710	4 89 10 11 12 13					
6711	1 3 8					
6712	12 6 15			20000000		
6713	3 5 13 15			50000000		
6714	2 5 9 12					
6715	5 13				$\frac{2 - 2e^{-d^2} - d^2e^{-d^2}}{2\ d^2T^2}$	
6716					"	
6717					"	
6720					"	
6721					CARDS 6721 TO 6775	
6722	4 9 10 12 15			50000000	SAME AS 6332 TO 6385	

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

```
CARD        CODE PUNCHES       SORT  CARD FACTOR COUNTER  PUNCH
 NO           IN COLUMNS        NO  TERM   VALUE   TERM   INDEX
6727 123     9       12     15          50000000-
6733
6734  2  5   9       12
6735     5
6736     5
6737     56          12                 50000000-
6740
6741   3 5  89 10    12     15          54038889   S - S* (VAPOR)
6742
6743                     13
6744    4  7 9 10    12     15          10000000-
6746     5   9 10    12
6747  2  5
6750    4 67 9       12
6751   3  6 8        12                 30000000
6753 1  4    9    11 12
```

TABLE VI B DENSITY - ENTROPY - ENTHALPY CALCULATION

CARD NO	CODE PUNCHES IN COLUMNS	SORT NO	CARD TERM	FACTOR VALUE	COUNTER TERM	PUNCH INDEX
6754	3 8					
6755	1 3 8 15			01250000		
6760	1 3 15			12000000		
6761	1					
6762	12 4 9 10 11 12					
6764	3 5 8 15			10000000		
6767	7					
6771	3 8 12			40000000-		
6772	5 9 10 11 12					
6773	56					
6774						
6775	3 5 89 10 11 12 13 15			54038889	$H - H^*$ (VAPOR)	
6776						
6777						

TABLE VII.

Fractional Powers of Parameters in Benedict Equation[a]

Parameter	Units	Methane	Ethylene	Ethane	Propane	n-Butane
RB_o[b]	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)\left(\frac{\text{ft.}^3}{\text{mole}}\right)^2\left(\frac{1}{°\text{R}}\right)$	7.32836	9.57978	10.79928	16.74161	21.48603
$A_o^{1/2}$	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)^{1/2}\left(\frac{\text{ft.}^3}{\text{mole}}\right)$	83.6940	112.3050	125.2553	161.1019	195.1565
$C_o^{1/2}\ x10^{-3}$	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)^{1/2}\left(\frac{\text{ft.}^3}{\text{mole}}\right)(°\text{R})$	16.61732	40.05870	46.87776	78.86151	110.2203
$(Rb)^{1/3}$	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)^{1/3}\left(\frac{\text{ft.}^3}{\text{mole}}\right)\left(\frac{1}{°\text{R}}\right)^{1/3}$	2.104493	2.873179	3.30282	3.959013	4.795935
$a^{1/3}$	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)^{1/3}\left(\frac{\text{ft.}^3}{\text{mole}}\right)$	14.40675	25.02970	27.54389	38.56938	48.48226
$c^{1/3}x10^{-2}$	$\left(\frac{\text{lb.}}{\text{in.}^2}\right)^{1/3}\left(\frac{\text{ft.}^3}{\text{mole}}\right)(°\text{R})^{2/3}$	7.93234	16.06090	18.59284	29.35827	39.59250
$\gamma^{1/2}$	$\left(\frac{\text{ft.}^3}{\text{mole}}\right)$	1.241648	1.540120	1.741374	2.37732	2.955910
$\alpha^{1/3}$	$\left(\frac{\text{ft.}^3}{\text{mole}}\right)$	0.800108	0.901769	1.000887	1.357447	1.655476

[a] Converted to English units from values of Benedict et al (9,24)

[b] $R = 10.73185$

Table VIII.

Example of Calculation Results as Listed by the Tabulator

```
1ST  ITRN                                 PROB  CARD
                                           NO    NO

METHANE K          2 13108                 7 5003
ETHANE  K            71920                 7 5004
ETHENE  K            91576                 7 5005

2ND  ITRN

METHANE K          1 90865                 7 5016
ETHANE  K            75183                 7 5017
ETHENE  K            92778                 7 5020

3RD  ITRN

METHANE K          1 84883                 7 5031
ETHANE  K            76067                 7 5032
ETHENE  K            92984                 7 5033

FIN  VALUES

METHANE K          1 82682                 7 5046
ETHANE  K            76395                 7 5051
ETHENE  K            93027                 7 5053

METHANE X            1947963               7 5062
ETHANE  X            6308000               7 5064
ETHENE  X            1744037               7 5066

METHANE Y            3558578               7 5071
ETHANE  Y            4818996               7 5073
ETHENE  Y            1622425               7 5077
```

```
                                       PROB CARD
                                        NO   NO
TEMP    R          491 69000            7  6003
PRESS PSIA         734 80               7  6014

LIQ PHASE
PRESS CALC         734 85               7  6270
DENS MPCF              7619401          7  6280
S BTUPMR     -       3 39575            7  6355
H BTUPM      -3857 87                   7  6387

VAP PHASE
PRESS CALC         734 21               7  6666
DENS MPCF              2564352          7  6676
S BTUPMR     -       1 24178            7  6745
H BTUPM      -1569 53                   7  6777
```

TABLE IX.

Calculated and Experimental Values of Equilibrium Constants
in the Methane-Ethylene-Ethane System

Mole Fraction Ethane at Bubble Point	Equilibrium Constants								
	Methane			Ethylene			Ethane		
	Calc.	Expt.[a]	Dev.[b]	Calc.	Expt.	Dev.	Calc.	Expt.	Dev.
			At -155.2°F., 147 Lb. per Sq. Inch Absolute						
0.1049	2.177	2.607	-16.5	0.120	0.172	-30.2	0.047	0.152	-67.7
0.2525	2.218	2.649	-16.5	0.118	0.196	-39.8	0.046	0.116	-60.3
0.5000	2.296	2.734	-16.8	0.117	0.212	-44.8	0.044	0.098	-55.1
			At -108.4°F., 514.4 Lb. per Sq. Inch Absolute						
0.0440	1.254	1.254	0.0	0.295	0.211	+39.8	0.186	0.318	-41.5
0.1111	1.261	1.220	+3.4	0.289	0.191	+51.3	0.180	0.261	-31.0
0.2200	1.274	1.283	-0.9	0.281	0.229	+22.7	0.173	0.227	-23.8

[a] From Reference (29)

[b] $\text{Dev.} = \frac{\text{Calc.} - \text{Expt.}}{\text{Expt.}} \times 100$

TABLE IX (continued)

Mole Fraction Ethane at Bubble Point	Equilibrium Constants								
	Methane			Ethylene			Ethane		
	Calc.	Expt.	Dev.	Calc.	Expt.	Dev.	Calc.	Expt.	Dev.
At 32°F., 734.8 Lb. per Sq. Inch Absolute									
0.1900	1.612	1.900	-15.2	0.944	0.948	-0.4	0.811	0.769	+5.5
0.4418	1.742	1.923	- 9.4	0.935	0.902	+3.5	0.781	0.793	-1.5
0.6308	1.827	2.075	-12.0	0.930	0.775	+16.7	0.764	0.800	-4.5
At 70°F., 734.8 Lb. per Sq. Inch Absolute									
0.4905	1.269	-	-	1.028	-	-	0.970	-	-
0.5429	1.346	-	-	1.036	-	-	0.961	-	-
0.6646	1.486	-	-	1.048	-	-	0.949	-	-
0.7533	1.571	-	-	1.055	-	-	0.942	-	-
0.8503[c]	1.637	-	-	-	-	-	0.936	-	-

[c] Methane-Ethane binary

TABLE X.

Calculated Values of Properties of the Coexisting Phases in the Methane-Ethylene-Ethane System

Mole Fraction						Molal Volume Cu.Ft./Mole		Molal Enthalpy[a] B.t.u./Mole		Molal Entropy[b] B.t.u./Mole/°R	
Methane		Ethylene		Ethane							
Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point
At −155.2°F., 147 Lb. per Sq. Inch Absolute											
0.9395	0.4316	0.0556	0.4635	0.0049	0.1049	19.34	0.858				
0.9507	0.4286	0.0378	0.3189	0.0115	0.2525	19.38	0.786				
0.9689	0.4220	0.0091	0.0780	0.0220	0.5000	19.46	0.795				
At −108.4°F., 514.4 Lb. per Sq. Inch Absolute											
0.9281	0.7402	0.0637	0.2158	0.0082	0.0440	4.679	0.912	1977.6	−508.2	33.36	29.08
0.9380	0.7436	0.0420	0.1453	0.0200	0.1111	4.718	0.906	1993.4	−562.2	33.31	29.14
0.9531	0.7482	0.0089	0.0318	0.0380	0.2200	4.776	0.899	2017.1	−651.4	33.16	28.91

[a] Enthalpies at infinite attenuation obtained from Souders et al (12); $H^* = 0$ at 0°R.

[b] Datum was taken as the value given (11) for the entropy (exclusive of nuclear spin) of the pure hydrocarbons in the standard gaseous state at 540°R.

TABLE X. (continued)

Mole Fraction						Molal Volume Cu.Ft./Mole		Molal Enthalpy B.t.u./Mole		Molal Entropy B.t.u./Mole/°R	
Methane		Ethylene		Ethane							
Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point
At 32°F., 734.8 Lb. per Sq. Inch Absolute											
0.1957	0.1214	0.6503	0.6886	0.1540	0.1900	3.390	1.404	2306.3	618.2	41.41	38.62
0.2866	0.1645	0.3682	0.3937	0.3452	0.4418	3.703	1.344	2545.4	554.6	41.85	38.94
0.3559	0.1948	0.1622	0.1744	0.4819	0.6308	3.900	1.312	2706.6	518.4	41.64	38.71
At 70°F., 734.8 Lb. per Sq. Inch Absolute											
0.0063	0.0050	0.5032	0.4894	0.4905	0.5056	2.584	1.777	2634.8	1374.5	42.95	41.49
0.0269	0.0200	0.4302	0.4153	0.5429	0.5647	2.863	1.777	2333.4	1408.3	43.40	41.70
0.0713	0.0479	0.2642	0.2521	0.6646	0.7000	3.046	1.629	2531.8	1284.9	43.64	41.41
0.1088	0.0692	0.1379	0.1308	0.7533	0.8000	3.309	1.616	2708.9	1275.2	43.62	41.16
0.1497	0.0915	0.0000	0.0000	0.8503	0.9085	3.460	1.577	2844.1	1251.8	43.08	40.46

TABLE XI

Calculated and Experimental Values of Compositions of the Coexisting Phases and Equilibrium Constants in the Methane-Propane System

Pressure, Lb./Sq. Inch Absolute	Mole Fraction Methane				Equilibrium Constants					
	Dew Point		Bubble Point		Methane			Propane		
	Calc.	Expt.[a]	Calc.	Expt.	Calc	Expt.	Dev.[b]	Calc.	Expt.	Dev.
				At 40°F.						
100	0.1969	0.2034	0.0109	0.0099	18.08	20.55	-12.0	0.8119	0.8046	+0.9
500	0.7809	0.7819	0.2015	0.1923	3.875	4.07	-4.8	0.2744	0.2700	+1.6
1000	0.8284	0.8208	0.4227	0.4226	1.960	1.942	+0.9	0.2972	0.3104	-4.3
1450	0.7475	0.7924	0.6859	0.6891	1.090	1.150	-5.2	0.8038	0.6677	+20.4
				At 190°F.						
600	0.0665	0.0798	0.0288	0.0333	2.311	2.396	-3.5	0.9611	0.9519	+1.0
750	0.1302	0.1601	0.1198	0.1120	1.087	1.429	-23.9	0.9881	0.9458	+4.5

[a] From Reference (30)

[b] $\text{Dev.} = \frac{\text{Calc.} - \text{Expt.}}{\text{Expt}} \times 100$

TABLE XII.

Calculated Values of Properties of the Coexisting Phases in the Methane-Propane System

Pressure, Lb./Sq. Inch Absolute	Mole Fraction Methane		Molal Volume Cu. Ft./Mole		Molal Enthalpy[a] B.t.u./Mole		Molal Entropy[b] B.t.u./Mole/°R.	
	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point	Dew Point	Bubble Point
				At 40°F.				
100	0.1969	0.0109	47.14	1.379	4952.0	-1761.1	56.07	46.32
500	0.7809	0.2015	8.887	1.317	3779.3	- 938.5	41.33	43.21
1000	0.8284	0.4227	3.749	1.282	3166.5	70.1	38.08	40.46
1450	0.7475	0.6859	1.801	1.537	2063.7	1589.5	37.18	37.58
				At 190°F.				
600	0.0665	0.0288	5.46	2.091	5736.1	4754.3	56.67	53.57
750	0.1302	0.1198	3.481	3.158	4814.0	4586.7	54.15	53.96

[a] Enthalpies at infinite attenuation obtained from Souders et al (12); $H^* = 0$ at 0°R.

[b] Datum was taken as the value given (11) for the entropy (exclusive of nuclear spin) of the pure hydrocarbons in the standard gaseous state at 540°R.

List of Figures

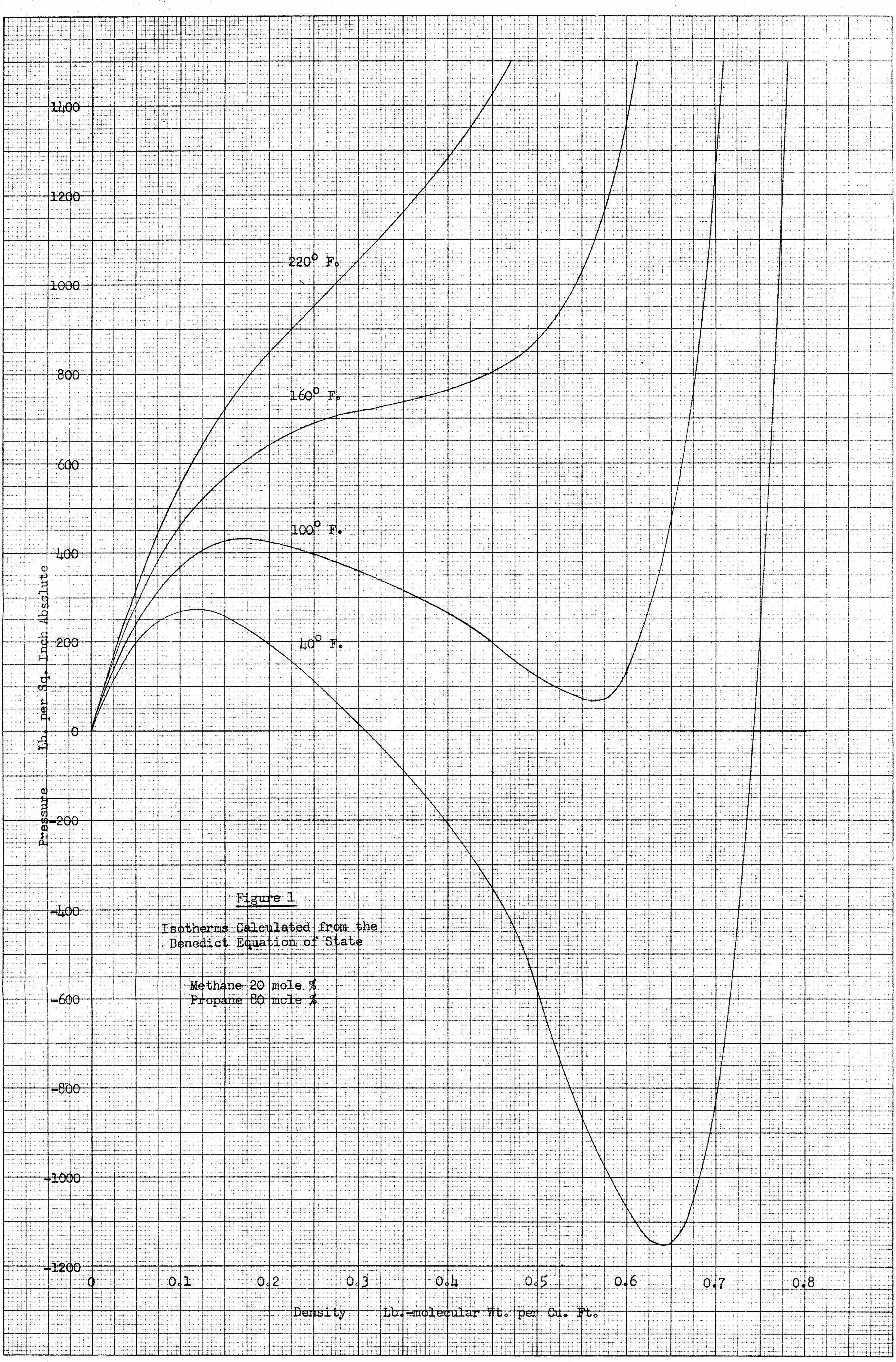


Figure 1

Isotherms Calculated from the
Benedict Equation of State

Methane 20 mole %
Propane 80 mole %

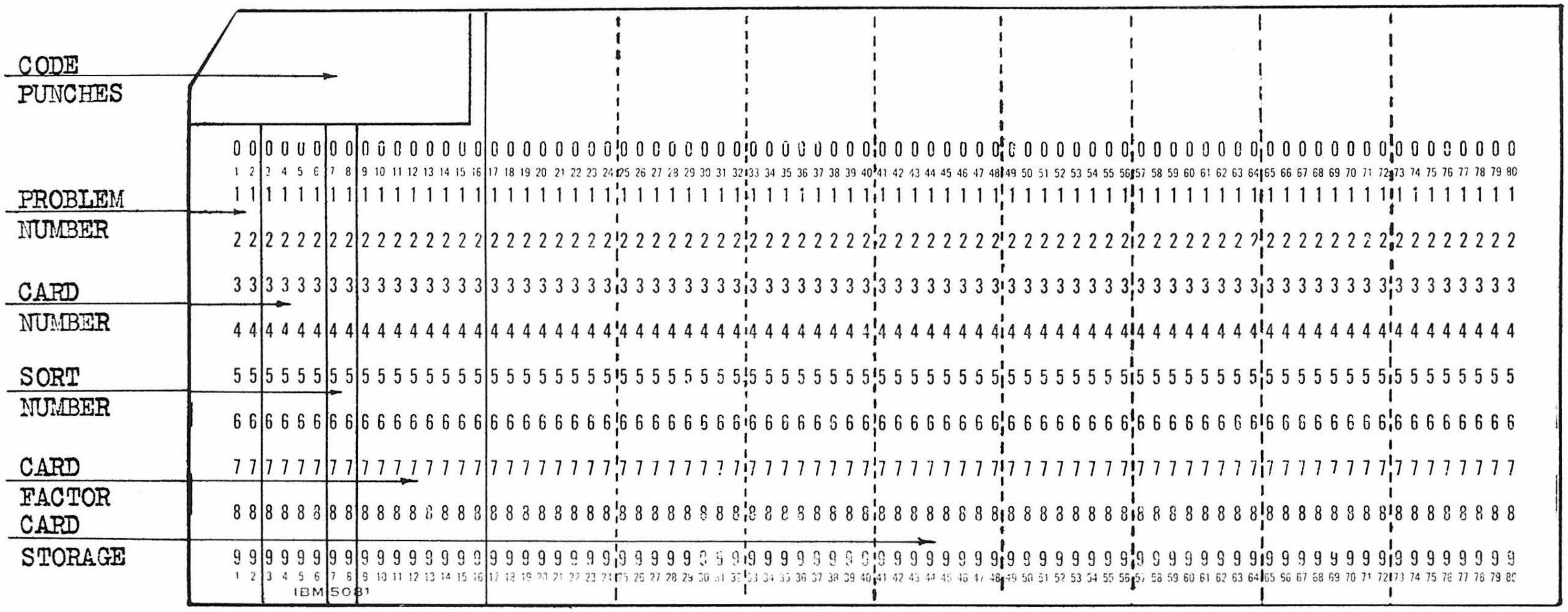


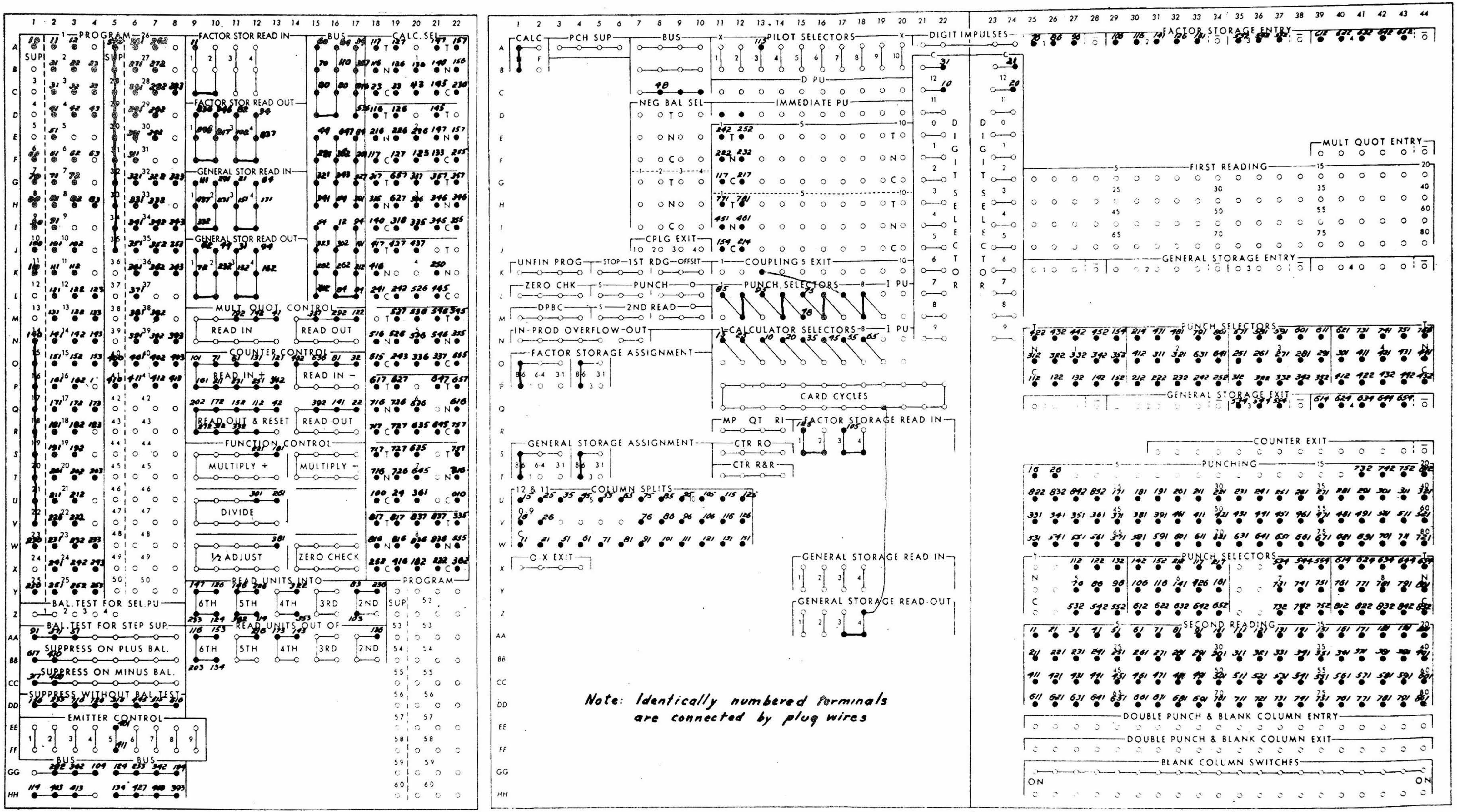
Figure 2

PUNCHED CARD LAYOUT FOR SEQUENTIAL CALCULATION

Figure 3

IBM ELECTRONIC CALCULATING PUNCH, TYPE 604

WIRING DIAGRAM FOR GENERAL PURPOSE CONTROL PANELS



CALCULATE SECTION

PUNCH SECTION

Note: Identically numbered terminals are connected by plug wires

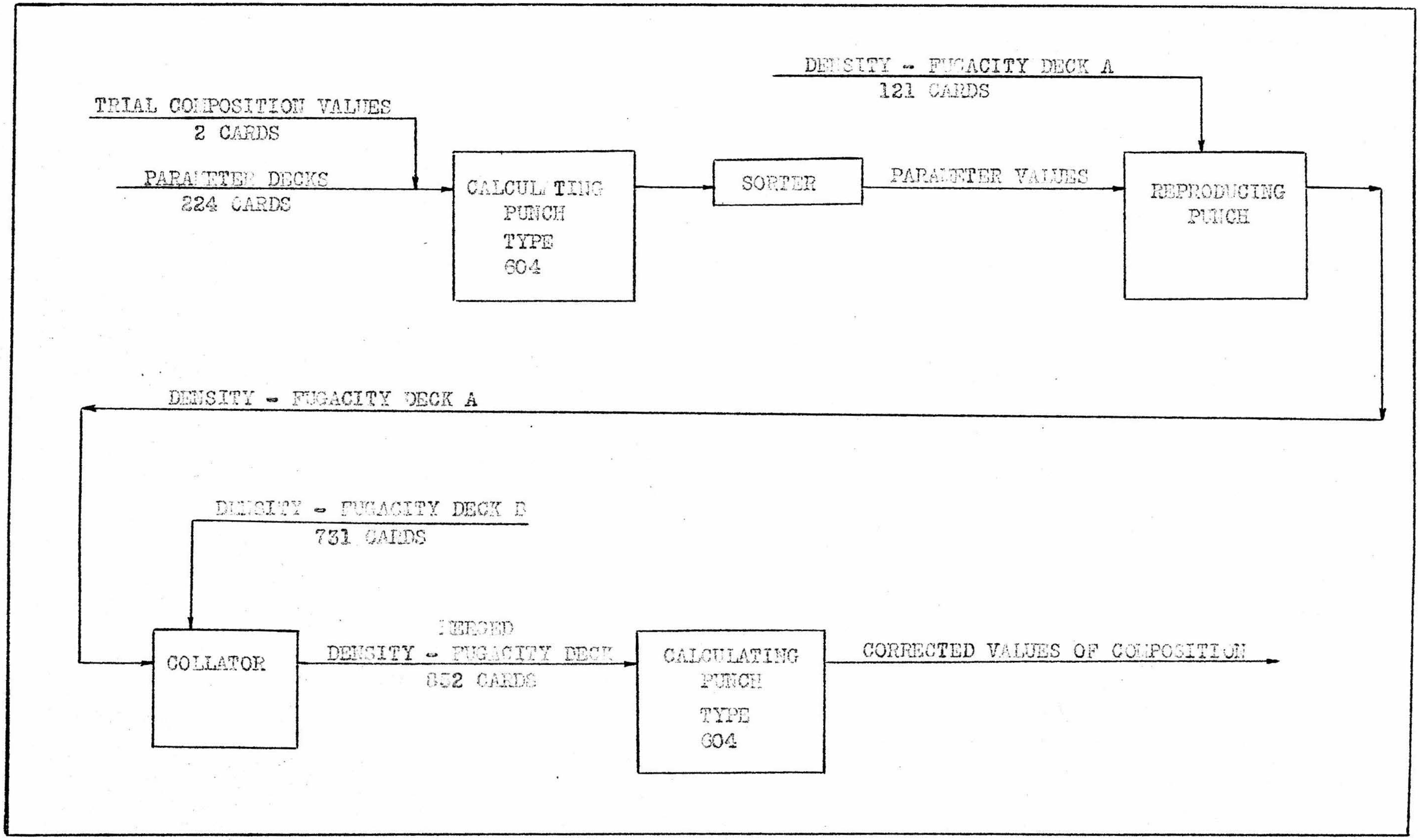
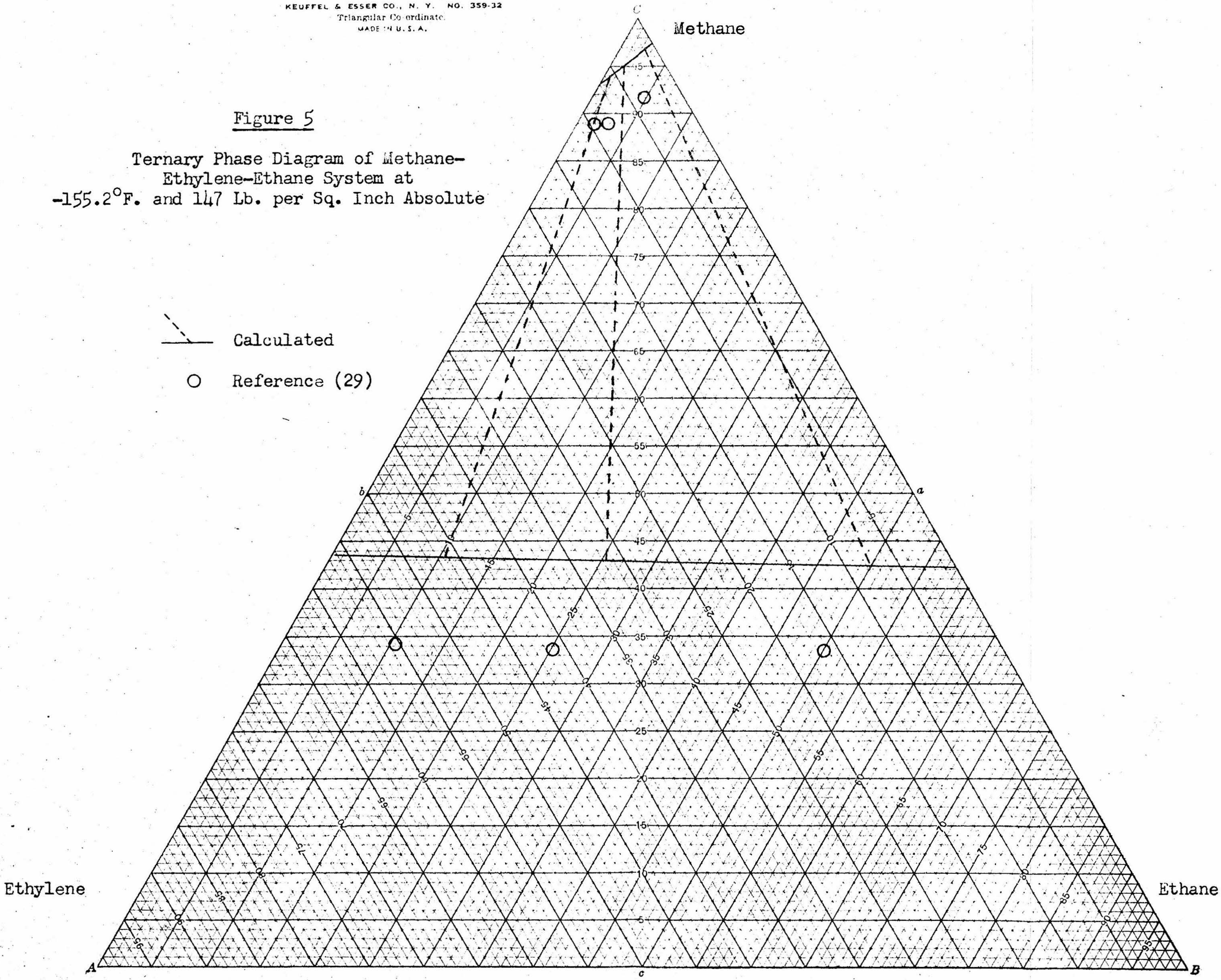


Figure 4

Schematic Diagram of Machine Operations
for Calculation of Coexisting Phases in Ternary Hydrocarbon System

Figure 5

Ternary Phase Diagram of Methane-Ethylene-Ethane System at -155.2°F. and 147 Lb. per Sq. Inch Absolute



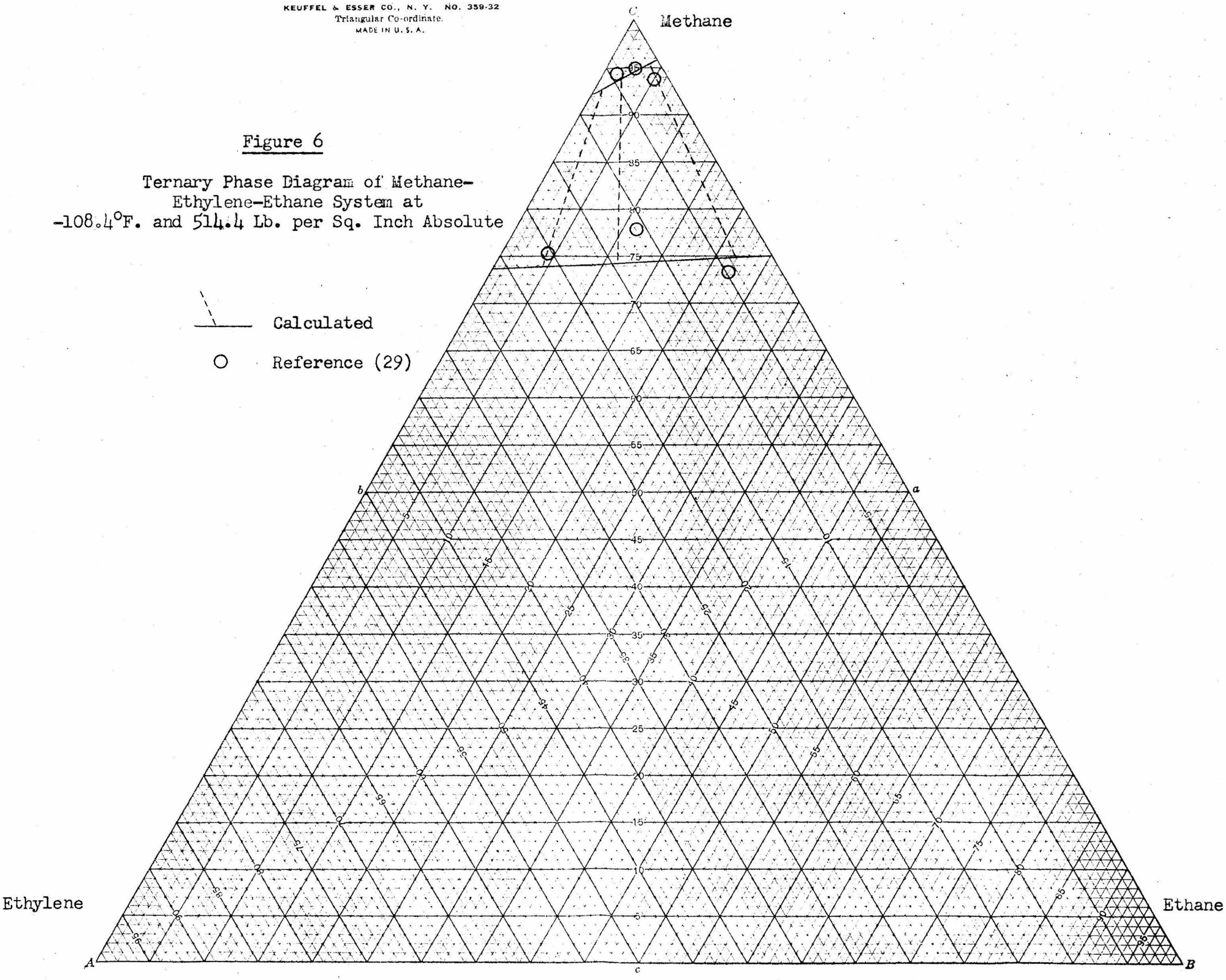


Figure 6

Ternary Phase Diagram of Methane-Ethylene-Ethane System at -108.4°F. and 514.4 Lb. per Sq. Inch Absolute

Figure 7

Ternary Phase Diagram of Methane-Ethylene-Ethane System at 32°F. and 734.8 Lb. per Sq. Inch Absolute

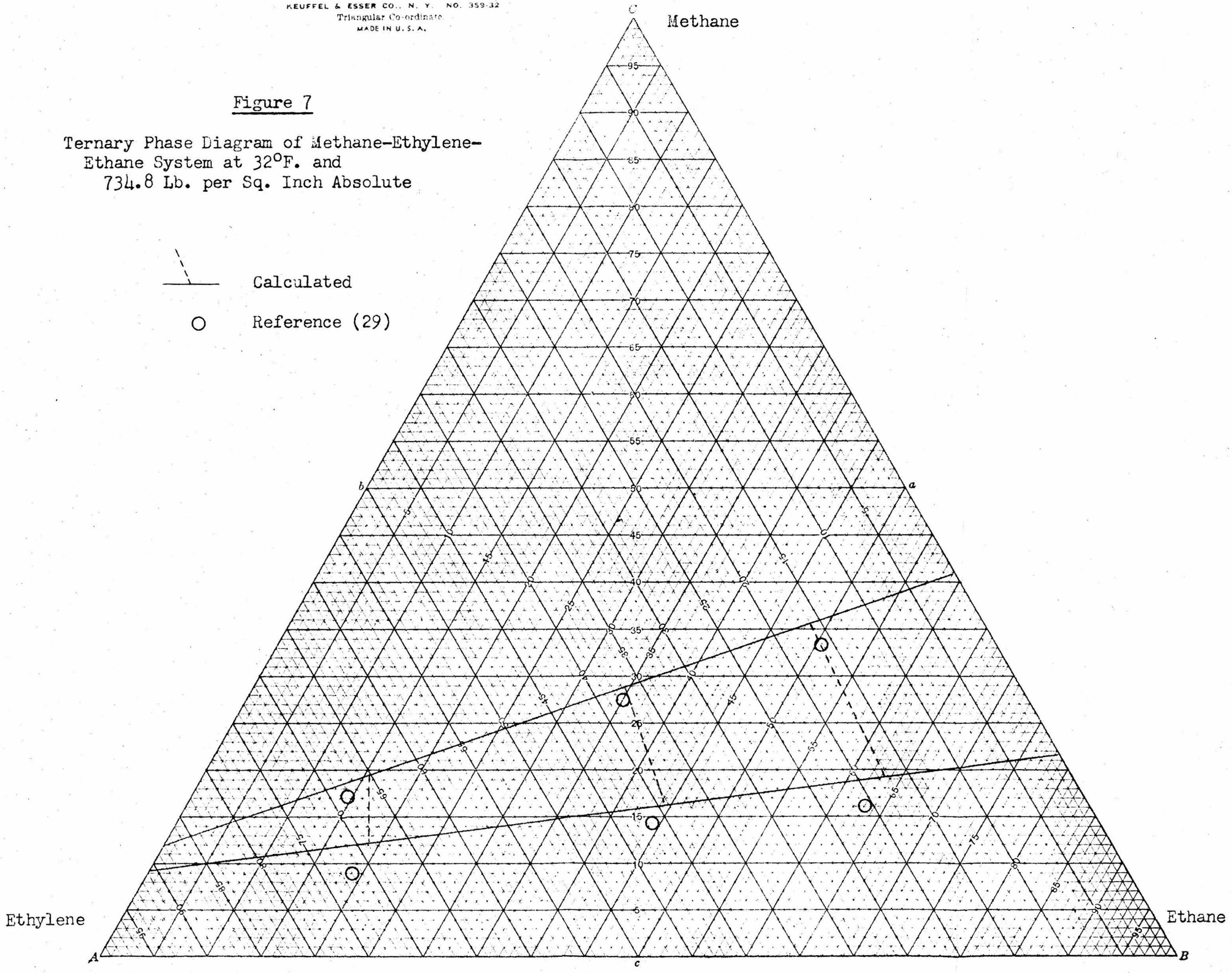
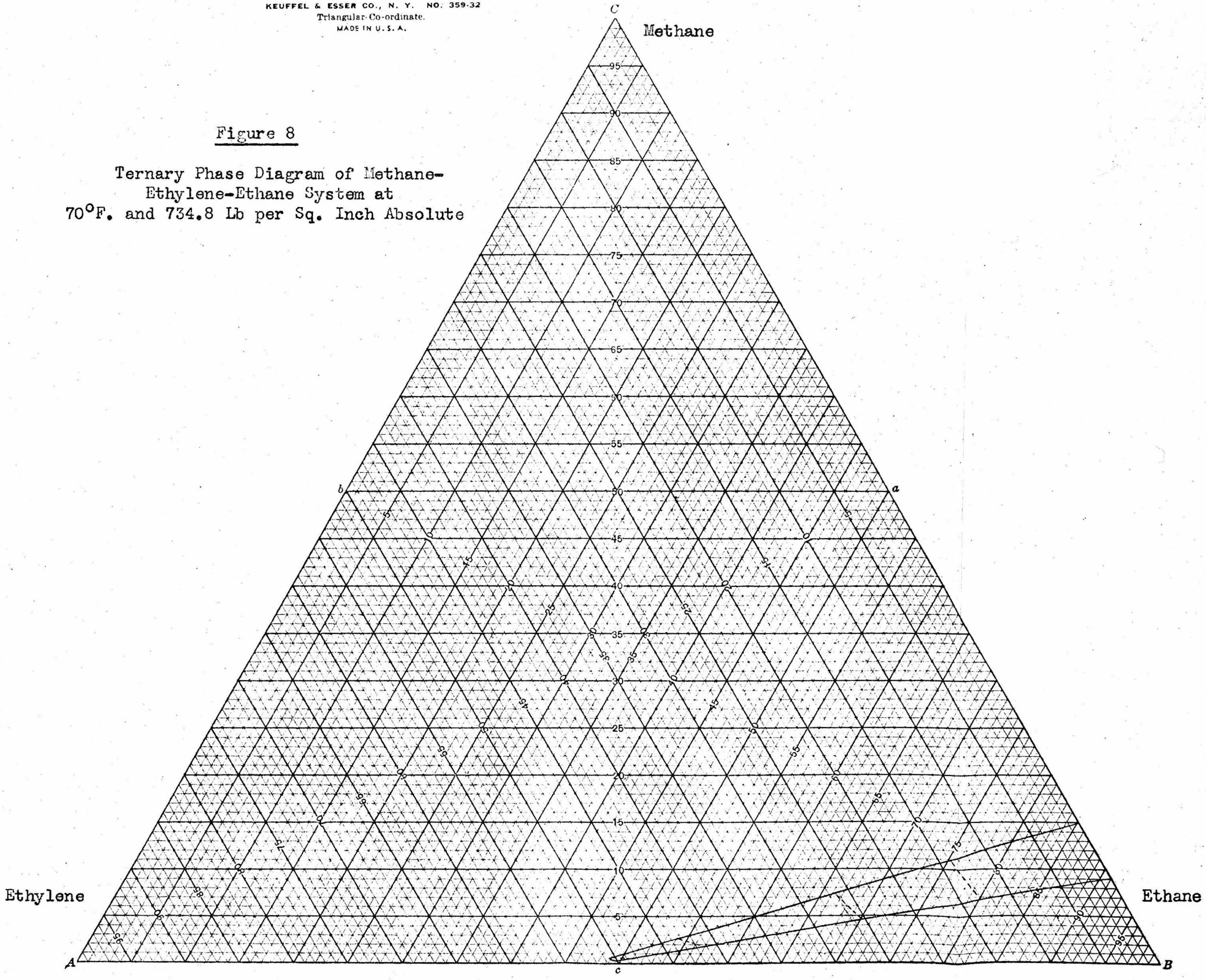


Figure 8

Ternary Phase Diagram of Methane-
Ethylene-Ethane System at
70°F. and 734.8 Lb per Sq. Inch Absolute



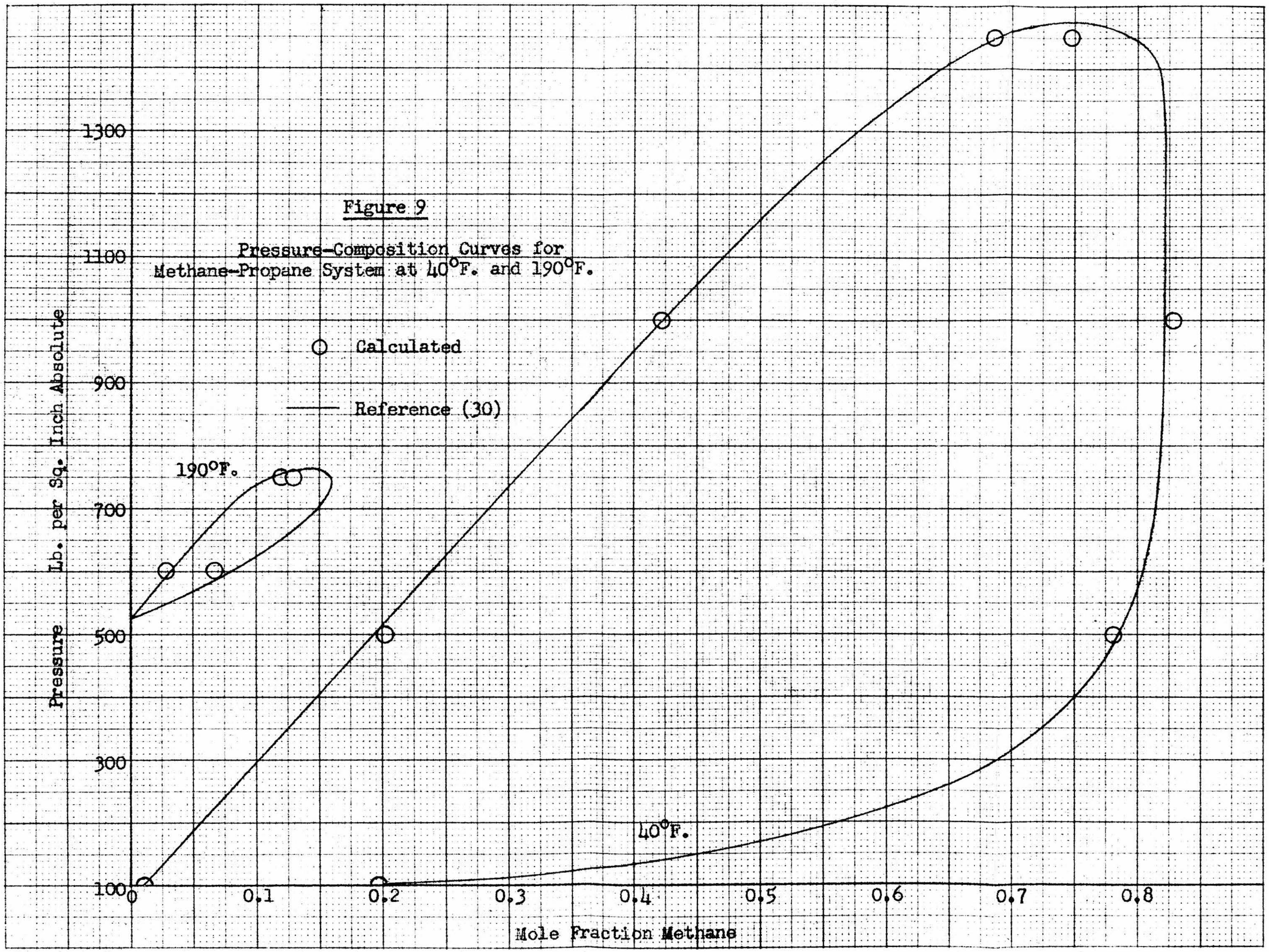


Figure 9

Pressure-Composition Curves for
Methane-Propane System at 40°F. and 190°F.

Appendix

Appendix I

Derivations of Thermodynamic Relations for Entropy, Enthalpy, and Fugacities of Real Gas Mixtures

1. Enthalpy

In order to derive an expression for the enthalpy with molal volume and temperature as independent variables it is convenient to first treat the internal energy. Since the internal energy is a state variable we may write

$$E - E_o = \int_{T_o}^{T} \left(\frac{\partial E}{\partial T}\right)_{V,n} dT + \int_{V_o}^{V} \left(\frac{\partial E}{\partial V}\right)_{T,n} dV \tag{1}$$

Substituting the definition

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,n} \tag{2}$$

and the thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P \tag{3}$$

into Equation 1 we obtain

$$E - E_o = \int_{T_o}^{T} C_v \, dT + \int_{V_o}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P\right] dV \tag{4}$$

For a mixture at infinite attenuation

$$E^* = \sum_k n_k E_k^* \tag{5}$$

$$C_v^* = \sum_k n_k C_{Vk}^* \tag{6}$$

Choosing the path of integration in Equation 4 so that the temperature of the system is changed at infinite attenuation, and substituting Equation 5, we obtain

$$E = \sum_k n_k E^*_{ok} + \int_{T_0}^{T} n_k C^*_{vk}\, dT + \int_{\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P\right] dV \tag{7}$$

The equation for enthalpy is obtained from Equation 7 by substituting the relations

$$H = E + PV \tag{8}$$

$$(P^* V^*) = RT \tag{9}$$

$$C^*_p - C^*_v = R \tag{10}$$

This substitution gives

$$H = \sum_k n_k\left[H^*_{ok} + \int_{T_0}^{T} C^*_{pk}\, dT\right] + \int_{V}^{\infty} \left[P - T\left(\frac{\partial P}{\partial T}\right)_{V,n}\right] dV + PV - RT \tag{11}$$

2. Entropy

The treatment of entropy in a manner identical to enthalpy results in an improper integral. This difficulty is circumvented by addition and subtraction of a term. The following derivation is adapted from Beattie (13). From the thermodynamic relations

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \tag{12}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{13}$$

the general expression for an entropy change of a system of invariant composition may be written

$$S - S_o = \int_{V_o}^{V} \left(\frac{\partial P}{\partial T}\right)_{V,n} dV + \int_{T_o}^{T} \frac{C_v}{T}\, dT \tag{14}$$

Since entropy is a state variable, it is possible to choose any integration path. For the present purposes it is expedient to use a three-step path, first changing volume from V_o to V^* at temperature T_o, then changing the temperature from T_o to T at conditions of infinite attenuation and finally changing the volume from V^* to V at temperature T. The expression thus obtained is

$$S - S_o = {}_{T_o}\!\int_{V_o}^{V^*} \left(\frac{\partial P}{\partial T}\right)_{V,n} dV + \int_{T_o}^{T} \frac{C_V^*}{T}\, dT + {}_{T}\!\int_{V^*}^{V} \left(\frac{\partial P}{\partial T}\right)_{V,n} dV \qquad (15)$$

The integral expression R dV/V is now subtracted to each integral and the equivalent integrated expression added, giving

$$S - S_o = \int_{V_o}^{V^*} \left[\left(\frac{\partial P}{\partial T}\right)_{V,n} - \frac{R}{V}\right] dV + \int_{T_o}^{T} \frac{C_V^*}{T}\, dT + \int_{V^*}^{V} \left[\left(\frac{\partial P}{\partial T}\right)_{V,n} - \frac{R}{V}\right] dV + R \ln \frac{V}{V_o} \qquad (16)$$

At infinite attenuation the ideal solution laws apply, and we may write

$$S_o^* = \sum_k n_k S_k^* - \sum_k n_k R \ln \frac{n_k R T_o}{V^*} \qquad (17)$$

Integrating between the states (T_o, V_o) and (T_o, V^*)

$$S_o - S_o^* = -\int_{V_o}^{V^*} \left[\left(\frac{\partial P}{\partial T}\right)_{V,n} - \frac{R}{V}\right] dV + R \ln \frac{V_o}{V^*} \qquad (18)$$

Combining Equations 17 and 18

$$S_o = -\int_{V_o}^{V^*} \left[\left(\frac{\partial P}{\partial T}\right)_{V,n} - \frac{R}{V}\right] dV + R \ln \frac{V_o}{R T_o} + \sum_k n_k S_{ok}^* - R \sum_k n_k \ln n_k \qquad (19)$$

Also at infinite attenuation

$$C_{Pk}^{*} = \sum_k n_k C_{pk}^{*} \tag{20}$$

$$C_V^{*} = C_p^{*} - R \tag{21}$$

Substituting Equations 19, 20, and 21 in Equation 16

$$S = \sum_k \int_{T_0}^{T} \frac{n_k C_{pk}^{*}}{T}\, dT + \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T}\right)_{V,n} - \frac{R}{V} \right] dV - R \ln \frac{T}{T_0} + R \ln \frac{V_0}{RT_0} + \sum_k n_k S_{ok}^{*} - R \sum_k n_k \ln n_k \tag{22}$$

Rearranging Equation 22 we obtain

$$S = \sum_k n_k \left[S_{ok}^{*} + R \ln \frac{V}{n_k RT} + \int_{T_0}^{T} C_{pk}^{*}\, dT \right] + \int_{V}^{\infty} \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV \tag{23}$$

3. Fugacity

The free energy may be written

$$F = H - TS \tag{24}$$

Combining Equations 11 and 23

$$F = \sum_k n_k \left[H_{ok}^{*} - TS_{ok}^{*} + \int_{T_0}^{T} C_{pk}^{*}\, dT - \int_{T_0}^{T} C_{pk}^{*}\, dT - RT \ln \frac{V}{n_k RT} \right] + \int_{V}^{\infty} \left[P - T\left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV - \int_{V}^{\infty} \left[\frac{RT}{V} - T\left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV + PV - RT \tag{25}$$

Rearranging

$$F = \sum_k n_k \left[H_{ok}^{*} - T S_{ok}^{*} - RT \ln \frac{V}{n_k RT} \right] + \int_{V}^{\infty} \left[P - \frac{RT}{V} \right] dV + PV - RT \qquad (26)$$

Writing Equation 26 in total quantities

$$\underline{F} = \sum_k m_k \left\{ H_{ok}^{*} - T S_{ok}^{*} - RT \ln \frac{\underline{V}}{m_k RT} \right] + \int_{\underline{V}}^{\infty} \left[P - \frac{m RT}{\underline{V}} \right] d\underline{V} + P\underline{V} - mRT \qquad (27)$$

where

$$m = \sum_k m_k \qquad (28)$$

The chemical potential may be written

$$\mu_k = \left(\frac{\partial [\underline{F} - P\underline{V}]}{\partial m_k} \right)_{T, V, m_i} \qquad (29)$$

Differentiating the term $(\underline{F} - P\underline{V})$ in Equation 27

$$\mu_k = H_{ok}^{*} - T S_{ok}^{*} - RT \ln \frac{\underline{V}}{m_k RT} + RT + \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial m_k} \right)_{T, \underline{V}, m_i} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \qquad (30)$$

Rearranging

$$\mu_k = \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial m_k} \right)_{T, \underline{V}, m_i} - \frac{RT}{\underline{V}} \right] d\underline{V} - RT \ln \frac{\underline{V}}{m_k RT} + H_{ok}^{*} - T S_{ok}^{*} \qquad (31)$$

The fugacity is defined by the expression

$$\mu_k = RT \ln f_k + B(T) \qquad (32)$$

where

$$\beta(T) = \mu_k^* = H_{ok}^* - TS_{ok}^* \tag{33}$$

Substituting Equations 32 and 33 in Equation 31 we obtain the fugacity expression

$$RT \ln f_k = RT \ln \frac{m_k RT}{\underline{V}} + \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial m_k} \right)_{T, \underline{V}, m_i} - \frac{RT}{\underline{V}} \right] d\underline{V} \tag{34}$$

Appendix II

Derivations of Equations for Entropy, Enthalpy, and Fugacities from the Benedict Equation of State

1. Enthalpy

The thermodynamic expression for enthalpy derived in Appendix I is

$$H = \sum_k n_k \left[H^*_{0k} + \int_{T_0}^{T} C^*_{p_k}\, dT \right] + \int_V^\infty \left[P - T\left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV + PV - RT \qquad (11)$$

The Benedict Equation of state is

$$P = \frac{RT}{V} + \left[B_0 RT - A_0 - \frac{C_0}{T^2} \right] \frac{1}{V^2} + \left[bRT - a \right] \frac{1}{V^3} + \frac{c}{T^2 V^3} (1 + \gamma/V^2) \exp(-\gamma/V^2) + \frac{a\alpha}{V^6} \qquad (35)$$

Differentiating Equation 35 with respect to temperature at constant volume and composition

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{R}{V} + \left[B_0 R + \frac{2C_0}{T^3} \right] \frac{1}{V^2} + \frac{bR}{V^3} - \frac{2c}{T^2 V^3} (1 + \gamma/V^2) \exp(-\gamma/V^2) \qquad (36)$$

Multiplying Equation 36 by T and subtracting from Equation 35

$$P - T\left(\frac{\partial P}{\partial T}\right)_{V,n} = -\left[A_0 + \frac{3C_0}{T^2} \right] \frac{1}{V^2} - \frac{a}{V^3} + \frac{a\alpha}{V^6} + \frac{3c}{T^2 V^3} \exp(-\gamma/V^2) + \frac{3c\gamma}{T^2 V^5} \exp(-\gamma/V^2) \qquad (37)$$

Integrating Equation 37

$$\int_V^\infty \left[P - T\left(\frac{\partial P}{\partial T}\right)_{V,n} \right] dV = -\left[A_0 + \frac{3C_0}{T^2} \right] \frac{1}{V} - \frac{a}{2V^2} + \frac{a\alpha}{5V^5} + \frac{3c}{\gamma T^2} \left[1 - \exp(-\gamma/V^2) \right] - \frac{3c}{2T^2 V^2} \exp(-\gamma/V^2) \qquad (38)$$

Multiplying Equation 35 by V and subtracting RT

$$PV-RT=\left[B_oRT-A_o-\frac{C_o}{T^2}\right]\frac{1}{V}+\left[bRT-a\right]\frac{1}{V^2}$$

$$+\frac{c}{T^2V^2}\left(1+\gamma/V^2\right)exp\left(-\gamma/V^2\right)+\frac{a\alpha}{V^5} \tag{39}$$

Adding Equations 38 and 39 and substituting in Equation 11

$$H=\sum_k n_k\left[H_{ok}^{*}+\int_{T_o}^{T}C_{pk}^{*}\,dT\right]+\left[B_oRT-2A_o-\frac{4C_o}{T^2}\right]\frac{1}{V}+\left[2bRT-3a\right]\frac{1}{2V^2}$$

$$+\frac{6a\alpha}{5V^5}+\frac{c}{T^2V^2}\left[3\frac{1-exp(-\gamma/V^2)}{\gamma/V^2}-\frac{exp(-\gamma/V^2)}{2}-\frac{\gamma}{V^2}exp(-\gamma/V^2)\right] \tag{40}$$

2. Entropy

The thermodynamic expression for entropy derived in Appendix I is

$$S=\sum_k n_k\left[S_{ok}^{*}+R\ln\frac{V}{n_kRT}+\int_{T_o}^{T}\frac{C_{pk}^{*}}{T}\,dT\right]$$

$$+\int_V^{\infty}\left[\frac{R}{V}-\left(\frac{\partial P}{\partial T}\right)_{V,n}\right]dV \tag{23}$$

Rearranging Equation 36 and integrating

$$\int_V^{\infty}\left[\frac{R}{V}-\left(\frac{\partial P}{\partial T}\right)_{V,n}\right]dV=-\left[B_oR+2\frac{C_o}{T^3}\right]\frac{1}{V}-\frac{bR}{2V^2}$$

$$+\frac{2c}{T^3V^2}\left[\frac{1-exp(-\gamma/V^2)}{\gamma/V^2}-\frac{exp(-\gamma/V^2)}{2}\right] \tag{41}$$

Substituting this equation in Equation 23

$$S = \sum_k n_k \left[S_{ok}^{*} + R \ln \frac{V}{n_k RT} + \int_{T_0}^{T} \frac{C_{pk}^{*}}{T} dT \right] - \left[B_0 + \frac{2C_0}{T^3} \right] \frac{1}{V}$$

$$- \frac{bR}{2V^2} + \frac{2c}{T^3 V^2} \left[\frac{1 - \exp(-\gamma/V^2)}{\gamma/V^2} - \frac{\exp(-\gamma/V^2)}{2} \right] \qquad (42)$$

3. <u>Fugacity</u>

The thermodynamic expression for the fugacity of a component in a mixture as derived in Appendix I is

$$RT \ln f_k = RT \ln \frac{m_k RT}{\underline{V}} + \int_{\underline{V}}^{\infty} \left[\left(\frac{\partial P}{\partial m_k} \right)_{T,\underline{V},m_i} - \frac{RT}{\underline{V}} \right] d\underline{V} \qquad (34)$$

Writing the Benedict equation of state with total quantities

$$P = \frac{mRT}{\underline{V}} + \left[B_0 RT - A_0 - \frac{C_0}{T^2} \right] \frac{m^2}{\underline{V}^2} + \left[bRT - a \right] \frac{m^3}{\underline{V}^3}$$

$$+ \frac{c m^3}{T^2 \underline{V}^3} \left(1 + \frac{\gamma m^2}{\underline{V}^2} \right) \exp\left(\frac{-\gamma m^2}{\underline{V}^2} \right) + \frac{a \alpha m^6}{\underline{V}^6} \qquad (43)$$

The parameters in this equation may be written

$$B_0 = \sum_k \frac{m_k B_{ok}}{m} \qquad (44)$$

$$A_0 = \left[\frac{\sum_k m_k A_{ok}^{1/2}}{m} \right]^2 \qquad (45)$$

$$C_0 = \left[\frac{\sum_k m_k C_{ok}^{1/2}}{m} \right]^2 \qquad (46)$$

$$b = \left[\frac{\sum_k m_k b_k^{1/3}}{m} \right]^3 \qquad (47)$$

$$a = \left[\frac{\sum_k m_k a_k^{1/3}}{m} \right]^3 \tag{48}$$

$$c = \left[\frac{\sum_k m_k c_k^{1/3}}{m} \right]^3 \tag{49}$$

$$\gamma = \left[\frac{\sum_k m_k \gamma_k^{1/2}}{m} \right]^2 \tag{50}$$

$$\alpha = \left[\frac{\sum_k m_k \alpha_k^{1/3}}{m} \right]^3 \tag{51}$$

where

$$m = \sum_k m_k \tag{52}$$

Differentiating Equation 43 with respect to m_k

$$\begin{aligned}
\left(\frac{\partial P}{\partial m_k}\right)_{\underline{V},T,m_i} = {} & \frac{RT}{\underline{V}} + 2\left[B_0 RT - A_0 - \frac{C_0}{T^2}\right]\frac{m}{\underline{V}^2} + 3\left[bRT - a\right]\frac{m^2}{\underline{V}^3} \\
& + \frac{6a\alpha m^5}{\underline{V}^6} + \frac{3cm^2}{T^2\underline{V}^3}\left[1 + \frac{\gamma m^2}{\underline{V}^2}\right]\exp\left(-\frac{\gamma m^2}{\underline{V}^2}\right) + \frac{2\gamma c m^4}{T^2\underline{V}^5}\exp\left(-\frac{\gamma m^2}{\underline{V}^2}\right) \\
& - \frac{2\gamma c m^4}{T^2\underline{V}^5}\left(1 + \frac{\gamma m^2}{\underline{V}^2}\right]\exp\left(-\frac{\gamma m^2}{\underline{V}^2}\right) + \Bigg\{\left[B_{0k} - B_0\right]RT - 2A_0^{1/2}\left[A_{0k}^{1/2} - A_0^{1/2}\right] \\
& - \frac{2C_0^{1/2}}{T^2}\left[C_{0k}^{1/2} - C_0^{1/2}\right]\Bigg\}\frac{m}{\underline{V}^2} + \left\{3b^{2/3}\left[b_k^{1/3} - b^{1/3}\right]RT - 3a^{2/3}\left[a_k^{1/3} - a^{1/3}\right]\right\}\frac{m^2}{\underline{V}^3} \\
& + \left\{3a\alpha^{2/3}\left[\alpha_k^{1/3} - \alpha^{1/3}\right] + 3\alpha a^{2/3}\left[a_k^{1/3} - a^{1/3}\right]\right\}\frac{m^5}{\underline{V}^6} \\
& + \frac{3c^{2/3}m^2\left[c_k^{1/3} - c^{1/3}\right]}{T^2\underline{V}^3}\left[1 + \frac{\gamma m^2}{\underline{V}^2}\right]\exp\left(-\frac{\gamma m^2}{\underline{V}}\right) \\
& + \frac{2cm^4\gamma^{1/2}}{T^2\underline{V}^5}\left[\gamma_k^{1/2} - \gamma^{1/2}\right]\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right) \\
& - \frac{2\gamma^{1/2}cm^4}{T^2\underline{V}^5}\left[1 + \frac{\gamma m^2}{\underline{V}^2}\right]\left[\gamma_k^{1/2} - \gamma^{1/2}\right]\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right)
\end{aligned} \tag{53}$$

Rearranging and integrating

$$
\begin{aligned}
\int_{\underline{V}}^{\infty}\left[\left(\frac{\partial P}{\partial m_k}\right)_{T,\underline{V},m_i}-\frac{RT}{\underline{V}}\right]d\underline{V} = {} & \left[(B_o+B_{ok})RT-2(A_oA_{ok})^{1/2}-\frac{2(C_oC_{ok})^{1/2}}{T^2}\right]\frac{m}{\underline{V}} \\
& +\frac{3}{2}\left[(b^2b_k)^{1/3}RT-(a^2a_k)^{1/3}\right]\frac{m^2}{\underline{V}^2}+\frac{3}{5}\left[a(\alpha^2\alpha_k)^{1/3}+\alpha(a^2a_k)^{1/3}\right]\frac{m^5}{\underline{V}^5} \\
& +\frac{3(c^2c_k)^{1/3}}{2\gamma T^2}\left[1-\exp\left(-\frac{\gamma m^2}{\underline{V}^2}\right)\right]+\frac{3(c^2c_k)^{1/3}}{2\gamma T^2} \\
& -\frac{3(c^2c_k)^{1/3}m^2}{2T^2\underline{V}^2}\exp\left(-\frac{\gamma m^2}{\underline{V}^2}\right)-\frac{3(c^2c_k)^{1/3}}{2T^2\gamma}\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right) \\
& -\frac{c(\gamma\gamma_k)^{1/2}m^4}{T^2\underline{V}^4}\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right)+\frac{2c}{T^2}\left(\frac{\gamma_k}{\gamma}\right)^{1/2}\frac{m^2}{\underline{V}^2}\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right) \\
& -\frac{2c\gamma_k^{1/2}}{T^2\gamma^{3/2}}\left[1-\exp\left(\frac{-\gamma m^2}{\underline{V}^2}\right)\right]
\end{aligned}
\tag{54}
$$

Substituting Equation 54 in Equation 34 and rearranging we obtain the expression for the fugacity of a component in a mixture

$$
\begin{aligned}
RT\ln f_k = {} & RT\ln\frac{n_kRT}{V}+\left[(B_o+B_{ok})RT-2(A_oA_{ok})^{1/2}-\frac{2(C_oC_{ok})^{1/2}}{T^2}\right]\frac{1}{V} \\
& +\frac{3}{2}\left[RT(b^2b_k)^{1/3}-(a^2a_k)^{1/3}\right]\frac{1}{V^2}+\frac{3}{5}\left[a(\alpha^2\alpha_k)^{1/3}+\alpha(a^2a_k)^{1/3}\right]\frac{1}{V^5} \\
& +\frac{3(c^2c_k)^{1/3}}{T^2V^2}\left[\frac{1-\exp(-\gamma/V^2)}{\gamma/V^2}-\frac{\exp(-\gamma/V^2)}{2}\right] \\
& -\frac{2c}{T^2V^2}\left(\frac{\gamma_k}{\gamma}\right)^{1/2}\left[\frac{1-\exp(-\gamma/V^2)}{\gamma/V^2}-\exp(-\gamma/V^2)-\frac{\gamma}{2V^2}\exp(-\gamma/V^2)\right]
\end{aligned}
\tag{55}
$$

II

ISOBARIC HEAT CAPACITIES OF N-HEXANE, METHYLCYCLOPENTANE, AND N-OCTANE AT THE BUBBLE POINT

Appendix III

Directions for Coding of Cards for Sequential Calculations

The principles of calculations using the general purpose control panels on the Electronic Calculating Punch, Type 604, are explained in Sections III-B and III-C. Coding of a problem consists of designating the proper "X" or "12" punches and value, if any, to be placed in each card of a sequence or deck so that the desired solution is obtained when the deck is passes through the Type 604. To code a problem one must know the function of each code punch and the order in which operations occur during a calculate cycle, e.g., multiplication occurs before division, etc. The planning of the calculate section of the general purpose control panel is shown in Table I. The functions of the code punches are summarized in Table II. In cases where a single operation such as addition is desired during a card cycle, the proper coding will be obvious from a study of these tables. However, because it was desirable to achieve a maximum of efficiency, i.e., fewest cards for a given calculation, it was found expedient to introduce the complication of combination code punching (see Table II). In this manner a wider selection of operations during a single card cycle is possible.

A complete explanation of all the functions of the general purpose control panel would not be possible in a discussion of reasonable length. It is felt that a person familiar with the Type 604 can obtain from Tables I and II and from the wiring diagram of

Figure 3 a working knowledge of the coding procedure. The explanation of special features given below should aid in this objective.

1. Factor transfer. It is often desirable to transfer the counter number to a Factor Storage space as, for example, when the counter number is to be squared. Such an operation may be done most readily by reading the rounded value of the counter number into Factor Storage 1-2 on the first program. Code punches in columns 6 and 7 will give this result. Since punches in 6 or 7 cause addition or subtraction respectively, it follows that an addition or subtraction cannot be done during the same card cycle as the transfer.

2. Accumulative multiplication. The sum of two products involving four different factors may be made on two successive card cycles by use of this feature. The product of a multiplication during the first cycle is transferred to General Storage 1-2 in program 24. This is caused by a code punch in column 4 if one is not also present in 5. A new factor is also caused to be put in the counter by this coding. In the following card cycle a second multiplication may be performed and the two products added at program 23 by use of code punches in columns 1, 2, and 3.

3. Exponential Feature. The procedure for calculating e^x involves introducing as the card factor on a series of cards the values of $e^{X/2}$, $e^{X/4}$, $e^{X/8}$, ..., where X is the maximum value of x. During the initial card cycle the value of x is doubled and the value $2x - X$ calculated in programs 6 to 8. This value is "balance tested"

in program 9. If the value is positive the counter number is multiplied by $e^{X/2}$ during the multiplication programs and the value 2x - X transferred to General Storage in program 9. If the value is negative the multiplication is suppressed and the value of 2x is calculated and transferred to General Storage 1-2 in programs 8 and 9. The process is repeated on the succeeding card using the values $e^{X/4}$ and 2x - X or 2x as the case may be. In this manner the exponent may be calculated to any desired accuracy. The above operations take place when code punches are in columns 3, 6, and 7.

4. Card Storage. The principles of card storage are outlined in Section III-C. However, because there are eight eight-digit storage spaces on the cards and only sufficient selector capacity to transfer values from four of these spaces to the storage of the machine, it was necessary to introduce some complicating expedients. A value to be stored is punched (when a code punch is in column 13) into columns 17 to 24 of a card. It is punched from this card into columns 25 to 32 of the next card and so on. In this manner a number moves across the cards, completing a cycle after eight cards. When it is desired to transfer a number from card storage to the machine for use during the calculate cycle, a code punch is placed in column 12 and in the proper combination of 9, 10, and 11 as shown in Table II. If the number is not in any of the groups of columns shown in Table II, it is necessary to delay the read-in one card cycle at which time the number necessarily will be in one of these groups. A number is dropped from card storage by punching a number from the

machine into columns 17 to 24 when the number to be dropped is in 73 to 80.

To facilitate coding it was found convenient to number cards in a mode of 8 (see Tables III to VI) so that a particular stored number would be in the same position on all cards with an identical units number. The adoption of the "punch index" listed in Tables III to VI was also for convenience in coding. Punch index is defined as (7 minus the units number of card containing instruction to punch). For example, a number which is caused to be punched by a code punch in column 13 of card 3041 has the punch index 7 - 1 or 6. The punch index serves to "locate" a number in card storage when it is desired to read it into the machine. Number the card storage column groups 17 to 24, 25 to 32, etc., as 1, 2, .., 8, a stored value may be located on a card by the formula, (units number of card + punch index = storage space). For example, in card 3090, a value with punch index 6 would be in storage space 6 or columns 57 to 64. Although this scheme may appear complicated, it is of considerable aid in coding problems.

Appendix IV

Preparation of Parameter Calculation Decks for Different Ternary Mixtures

The card deck for calculation of parameters in the Benedict equation is described in Table III. This particular deck is for the methane-ethylene-ethane system. Preparation of a deck for any other ternary mixture of components for which parameters are available may be done by a routine punched card procedure which will be described. The appropriate fractional powers of the parameter values for each compound are key punched in columns 17 to 24 on a series of cards and the cards filed. These cards are numbered in columns 4 to 6 with the card number corresponding to the cards on which the values should appear as card factors in the parameter calculation deck (Table III). To obtain a deck for a different ternary, the cards containing powers of the parameter values and an existing calculation deck are run through the Collator, selecting all calculation cards which have numbers in columns 4 to 6 identical to the parameter value cards. The calculation cards are then reproduced, first leaving out the card factor value, and then punching the new parameter values into the card factor space. The entire parameter calculation deck can then be merged on the Sorter. It is now ready for calculations on the new ternary mixture.

I

Introduction

Experimental measurements of the heat capacities of n-hexane, methylcyclopentane, and n-octane in the liquid phase have been reported in the literature. The studies by Parks et al (1), Huffman et al (2), and Douslin and Huffman (3) established the behavior of n-hexane in the liquid phase at temperatures below 80°F. There are available (2,4) measurements of methylcyclopentane in the liquid phase at temperatures below 80°F. Data on n-octane were obtained by Parks et al (1), Huffman et al (2), and Osborne and Ginnings (5) which established the heat capacity at temperatures up to 95°F. The work reported in this part of the present thesis includes measurements of the isobaric heat capacity of the bubble-point liquid from 80° to 200°F. for these three hydrocarbons.

Measurements were made in the two-phase region with a constant-volume calorimeter (6,7,8,9). A measured quantity of energy was added electrically to the calorimeter and contents, and the change in temperature noted. This procedure was repeated throughout the temperature interval between 80° and 200°F. for the hydrocarbons investigated. Measurements were made on two different quantities of each hydrocarbon. A thermodynamic analysis of this process has been presented (9) and leads to the following equation relating the experimentally measured quantities to the isobaric heat capacities at bubble point:

$$C_{Pb} = \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2}\left(\frac{V_d - V_b}{V_d}\right) + T\left(\frac{\partial V}{\partial T}\right)_{Pb}\left(\frac{dP''}{dT}\right) +$$

$$T\left(\frac{dP''}{dT}\right)\left[\frac{V_d \frac{dV_b}{dT} - V_b \frac{dV_d}{dT}}{V_d}\right] + \frac{V_b}{V_d}\left[C_{Pd} - T\left(\frac{\partial V}{\partial T}\right)_{Pd}\frac{dP''}{dT}\right] \qquad (1)$$

The experimentally determined quantities $Q_1/\Delta T$ and $Q_2/\Delta T$ represent the net energy required per unit temperature change of the calorimeter bomb and contents for the large and small samples of each hydrocarbon studied, and for the small temperature intervals used they were taken as equal to q_1/dT and q_2/dT for the mean value of temperature in the interval. The other terms of Equation 1 serve to relate the isobaric heat capacity at bubble point to the isochoric measurements.

II

Materials

The n-hexane was obtained from the Phillips Petroleum Company and was reported to contain over 99 mole % n-hexane. This material was subjected to two distillations in a 30-plate column at a reflux ratio of approximately 5 to 1. At least 10% of the initial overhead and a similar quantity of material remaining in the kettle were discarded in each fractionation. The variation of the temperature at the top of the column was observed to be less than 0.1°F. during the fractionation of the sample. The refractive index as measured on an Abbe refractometer at 77°F. was 1.3722 for the D-lines of sodium as compared with a critically chosen value of 1.37226 (10).

The methylcyclopentane likewise was obtained from the Phillips Petroleum Company and was reported to contain more than 99 mole % methylcyclopentane. This material was first fractionated in a 30-plate glass column at a reflux ratio of 5 to 1, discarding about 10% of the initial overhead and a like amount of material remaining in the kettle. The intermediate overhead liquid was passed through a 1-inch diameter column packed for a distance of 5 feet with silica gel supplied by the Davison Chemical Corporation and identified as 659528 - 2000. The initial 80% of the effluent was collected and passed through a second column of the gel, the first 80% of this sample then being treated in the same manner a third time. The partially purified methylcyclopentane thus obtained was subjected to a second distillation identical to the first. Independent measurements made at the California Research Corporation upon a sample of the purified methylcyclopentane indicated a refractive index at 68°F. of 1.40973 and a freezing point of -224.39°F. The corresponding critically chosen values (10) are 1.40970 and -224.40°F.

The n-octane used was supplied by the Eastman Kodak Company and was identified as the "white label" grade. This material was fractionated in the same manner as was the n-hexane. The variation of the temperature at the top of the column was observed to be less than 0.1°F. during the isobaric fractionation process. The refractive index of the product was 1.3951 at 77°F. as compared with a reported value (10) of 1.39508.

In all cases the samples were stored over sodium following purification. Noncondensable gases were removed from each sample by repeated solidification at liquid air temperature and low pressure immediately before adding it to the calorimeter bomb.

III

Apparatus and Procedure

The calorimetric equipment used in these studies was substantially the same as that employed in earlier investigations at this laboratory and has been described in some detail (7,8). The calorimeter bomb consisted of a cylindrical steel container provided with hemispherical closures within which the hydrocarbon liquid was confined. The volume of the container was 0.0142 cubic foot. Energy was added electrically to the interior of the calorimeter by means of a glass-insulated constantan wire encased within a stainless steel tube approximately 0.05 inch in diameter. The ends of the steel tube were brought through the wall of the calorimeter and were sealed to it at the point of egress. The quantity of energy added electrically to the calorimeter was determined by conventional volt box and standard resistance techniques. A Leeds and Northrup Type K potentiometer was employed to measure the electromotive force applied and the current flowing through the calorimeter heater. All of the electrical measuring devices were carefully calibrated and it is believed that the determination of the rate of energy addition introduced no significant uncertainty in the results.

In order to decrease thermal transfers to and from the calorimeter, it was surrounded by a metal jacket and the intervening space evacuated. The jacket was submerged in an agitated oil bath and provisions were made for automatically maintaining the average temperature of the interior surface of the jacket at substantially that of the exterior surface of the calorimeter. Measurements were carried out to establish the thermal transfer between the calorimeter and the wall of the jacket as a function of the measured temperature difference. This operation was accomplished by adding a measured quantity of energy to the calorimeter while holding the temperature of the jacket constant. The temperature difference was then determined as a function of time until the temperature of the calorimeter returned to its initial value. These calibrations were made at several temperatures in order to obtain the variation in the rate of thermal transfer with change in the temperature of the calorimeter. The energy transfers between the calorimeter and the wall of the jacket were in almost all cases less than 1% of the total energy added to the system. It is believed that such transfers were measured with sufficient accuracy to ensure that the resulting uncertainty in the value of the net energy added to the calorimeter was not greater than 0.07%.

The experimental procedure involved adding to the calorimeter a known weight of the particular hydrocarbon under investigation and the determination of the net energy required to raise the temperature of the calorimeter and contents through a known small temperature interval. For the temperature interval of a single measurement, it was assumed that the quantity $\underline{Q}/(T_B - T_A)$ was equal to the value $\underline{Q}/dT$ at the mean of the initial and final temperatures. As a check on the results, two series of measurements over the temperature range investigated were made on different days. Additional material was then added to the calorimeter and the sequence of measurements repeated.

The quantity of energy added electrically was adjusted to yield a temperature rise of approximately 6°F. between the initial and final states. Energy was added to the calorimeter for either 500 or 700 seconds for each measurement. The longer heating period was used when the larger of the two quantities of hydrocarbon was in the calorimeter. The uncertainty in the determination of the total energy added to the equipment was less than 0.05%. An effort was made to carry out each set of determinations in accordance with an established procedure. The time necessary for the attainment of equilibrium after the addition of energy was used as the conditioning period for the next step. The temperature of the contents of the calorimeter was measured with a precision of ± 0.005°F. at the beginning of the energy addition and at the end of the period required for the attainment of equilibrium. The uncertainty in the measurement of temperature rise was not greater than 0.25%.

The samples were added to the calorimeter by weighing bomb methods (11) with a precision of ± 0.00001 pound. A check of the weight of sample in the calorimeter was obtained by weighing the material withdrawn after completing a set of measurements on a hydrocarbon. It is believed that the uncertainty in the sample weight made a negligible contribution to the probable error of the measured heat capacity.

IV

Supplementary Calculations

In order to obtain the isobaric heat capacity at the bubble point from the experimentally measured quantities, the terms of Equation 1 must be evaluated. The volumetric data and isobaric heat capacity values for the dew-point gas required as correction terms were available primarily from experimental information. Volumetric and vapor pressure data for n-hexane were based on measurements by Young (12). In order to obtain the specific volume of the dew-point gas at temperatures lower than those covered by this experimental work, the Clapeyron equation was employed:

$$\frac{dP''}{dT} = \frac{\Delta H}{T\,\Delta V} \tag{2}$$

Values of the enthalpy change upon vaporization for n-hexane at temperatures below 140°F. were estimated from the relation proposed by Nutting (13):

$$\Delta H = \beta\left(T_c - T\right)^n \tag{3}$$

The constants of Equation 3 for n-hexane were determined from experimental measurements of the heat of vaporization at 77°F. and at the normal boiling point (10). The value of the critical temperature determined by Kay (14) was used in the calculations. Agreement within 1% was found between the specific volumes at dew point calculated in this way and Young's experimental values (12). The heat capacity of the dew-point gas for n-hexane was estimated from values of the isobaric heat capacity at one atmosphere and at zero pressure as given by Waddington and Douslin (15). The isobaric volume-temperature derivative at dew point was calculated from an equation of state derived by these authors (15) from thermal measurements.

The specific volume for methylcyclopentane at bubble point was obtained from Timmermans et al (16). The vapor pressure was obtained from the compilations of Rossini et al (10). Vapor pressure and bubble-point volume values for n-octane were obtained by Young (13). For both methylcyclopentane and n-octane, the specific volumes of the dew-point gas was calculated from the Clapeyron equation by the procedure described for n-hexane. Values of the heat capacity of the dew-point gas were estimated from the heat capacity at infinite attenuation as reported by Souders et al (17) for methylcyclopentane and from a recent compilation (10) for n-octane. Values of the isobaric volume-temperature derivative at dew point were determined for methylcyclopentane and n-octane from the law of corresponding states. The accuracy of the partial derivative so obtained is probably low, but the term of Equation 1 containing this quantity amounted to no more than 0.3% of the heat capacity and consequently a large error in this derivative would not influence the final result significantly.

V

Experimental Results

The experimental values obtained for the heat capacity of the calorimeter bomb and contents at several temperatures for two different quantities of each hydrocarbon are presented in Table I. Figures 1, 2, and 3 show these values as a function of temperature for n-hexane, methylcyclopentane, and n-octane respectively. For each quantity of a hydrocarbon in the calorimeter two sets of data are shown. These represent measurements taken on different days. The average deviation of the experimental points from the corresponding smooth curves drawn for each substance and expressed as a percentage of the difference in heat capacity between the two curves is 0.6% in the case of n-hexane, 0.4% for methylcyclopentane, and 0.5% for n-octane.

In order that the magnitude of the correction terms of Equation 1 as established may be more readily evaluated, they have been combined into a single term. This term is defined by the following expression:

$$C = \frac{C_{Pb} - \left[\dfrac{\dfrac{q_1}{dT} - \dfrac{q_2}{dT}}{m_1 - m_2}\right]}{C_{Pb}} \qquad (4)$$

The value of this quantity as a function of temperature for each of the compounds investigated is presented in Figure 4. The corrections are of relatively small magnitude and do not appear to contribute to the uncertainty of the recorded isobaric heat capacities by more than 0.15%.

Values of the isobaric heat capacity at bubble point for n-hexane, methylcyclopentane, and n-octane are recorded in Table II. These values were obtained from the information presented in Table I by solution of Equation 1. A consideration of the accuracy of the individual quantities involved indicates a probable error in the tabulated values of approximately 0.7%.

The heat capacities are presented graphically in Figures 5 and 6, which also include earlier measurements for comparison. Most of these measurements were made at temperatures below 80°F. but can be compared with short extrapolations of the present work. Good agreement was realized with the results obtained by other investigators in the cases of n-hexane (1,2,3) and of methylcyclopentane (2,4).

The values of isobaric heat capacity shown in Figure 6 and attributed to Osborne and Ginnings (5) for n-octane were calculated from the volumetric corrections developed in this work and from their values of $(\underline{Q}_1-\underline{Q}_2)/\Delta T \Delta m$ for an isochoric system. The correction was less than 0.1% of the reported heat capacity. The data of Osborne and Ginnings (5) are about 1.3% higher than the information obtained in this study. Values reported for the isobaric heat capacity of liquid n-octane by Parks et al (1) and by Huffman et al (2) appear to be in close agreement with the present measurements. The discrepancies between the extrapolated data of this study and published data are believed to be less than the estimated combined uncertainties of the various sets of measurements except in the case of the results of Osborne and Ginnings (5).

Nomenclature

C_p	Isobaric heat capacity, B.t.u. per lb. per °R.
H	Enthalpy change during isobaric-isothermal vaporization, B.t.u. per lb.
m	Weight of material in calorimeter, lb.
P	Pressure, lbs. per sq. inch absolute
$\underline{Q}$	Heat associated with process, B.t.u.
$\underline{q}$	Heat associated with infinitesimal change in state, B.t.u.
T	Temperature, °R.
V	Specific volume, cu. ft. per lb.
β	Constant of proportionality in Equation 3

Subscripts

A,B	Refers to state A and state B
b	Refers to bubble-point conditions
c	Refers to critical state
d	Refers to dew-point conditions
1,2	Refers to conditions with different quantities of sample in calorimeter

Superscript

$''$	Refers to two-phase state

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List of Tables

TABLE I.

Heat Capacity of Calorimeter and Contents

n-Hexane

0.04443 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
79.60	0.3047	76.07	0.3024
87.33	0.3061	83.43	0.3050
94.85	0.3075	90.68	0.3069
102.25	0.3086	97.80	0.3076
109.59	0.3117	104.82	0.3103
116.85	0.3135	111.72	0.3140
124.28	0.3126	118.56	0.3124
131.46	0.3139	125.38	0.3127
138.56	0.3166	132.15	0.3150
145.61	0.3181	138.88	0.3167
152.64	0.3191	145.57	0.3180
159.65	0.3210	152.26	0.3190
166.63	0.3220	158.94	0.3200
173.58	0.3254	165.58	0.3238
180.48	0.3258	172.17	0.3248
187.40	0.3270	178.74	0.3247
194.26	0.3307	185.30	0.3269
201.05	0.3327	191.80	0.3293
		198.23	0.3320

---

[a] Weight of material in calorimeter.

TABLE I. (Cont.)

n-Hexane

0.35573 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
78.31	0.4690	124.10	0.4893
85.78	0.4761	130.31	0.4913
92.40	0.4784	136.49	0.4919
98.92	0.4785	142.64	0.4964
105.38	0.4819	148.81	0.4987
111.76	0.4861	155.05	0.5001
118.09	0.4878	161.24	0.5031
124.40	0.4893	167.37	0.5088
130.65	0.4908	173.49	0.5091
136.89	0.4927	179.64	0.5064
143.13	0.4972	185.75	0.5113
149.31	0.4991	191.75	0.5205
155.44	0.5008	197.71	0.5197
161.55	0.5040		
167.66	0.5053		

TABLE I. (Cont.)

Methylcyclopentane

0.01763 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
86.24	0.2883	119.40	0.2954
93.88	0.2896	126.03	0.2979
101.26	0.2927	132.65	0.2985
108.35	0.2934	139.26	0.2983
115.27	0.2960	145.77	0.3026
121.96	0.2975	152.06	0.3041
128.53	0.2987	158.30	0.3038
135.07	0.2992	164.67	0.3046
141.58	0.3003	171.08	0.3081
148.05	0.3025	177.48	0.3097
154.46	0.3042	183.84	0.3104
160.90	0.3044	190.18	0.3118
167.16	0.3076		

TABLE I. (Cont.)

Methylcyclopentane

0.41089 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
85.60	0.4639	118.53	0.4796
92.47	0.4692	124.90	0.4859
99.18	0.4728	131.19	0.4854
105.71	0.4759	137.46	0.4875
112.12	0.4792	143.67	0.4926
118.65	0.4819	149.88	0.4947
125.04	0.4804	156.08	0.4971
131.36	0.4871	162.21	0.4988
137.61	0.4882	168.33	0.5056
143.82	0.4918	174.47	0.5047
150.00	0.4952	180.59	0.5083
156.15	0.4968	186.68	0.5104
162.27	0.5000	192.73	0.5149
168.34	0.5031	198.73	0.5182

TABLE I. (Cont.)

n-Octane

0.057545 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
77.32	0.3109	132.98	0.3221
84.44	0.3110	139.65	0.3247
91.33	0.3142	146.26	0.3265
105.80	0.3167	152.84	0.3271
112.49	0.3193	159.40	0.3276
119.19	0.3205	165.93	0.3307
125.85	0.3229	172.39	0.3319
132.48	0.3229	178.84	0.3312
139.08	0.3235	185.30	0.3325
145.65	0.3250	191.70	0.3349
152.20	0.3274	198.11	0.3368
158.72	0.3279		
165.22	0.3287		
171.68	0.3325		

TABLE I. (Cont.)

n-Octane

0.45042 lb.[a]

Measurement A		Measurement B	
Temperature, ° F.	q/dT B.t.u./° R.	Temperature, ° F.	q/dT B.t.u./° R.
81.65	0.5165	118.30	0.5335
88.40	0.5238	124.29	0.5360
94.94	0.5244	130.42	0.5354
101.34	0.5241	136.73	0.5383
107.66	0.5294	142.99	0.5439
114.01	0.5319	149.20	0.5431
120.38	0.5350	155.41	0.5446
126.70	0.5374	161.56	0.5493
132.99	0.5388	167.70	0.5522
139.24	0.5417	173.81	0.5555
145.45	0.5448	179.89	0.5574
151.62	0.5480	185.94	0.5603
157.83	0.5478	191.97	0.5642
164.04	0.5536	197.99	0.5632

TABLE II.

Isobaric Heat Capacities of n-Hexane, Methylcyclopentane, and n-Octane at Bubble Point

Temperature, °F.	n-Hexane	Methylcyclopentane	n-Octane
80	0.5435[a]	0.4516	0.5255
90	0.5496	0.4577	0.5304
100	0.5559	0.4639	0.5353
110	0.5624	0.4702	0.5403
120	0.5690	0.4766	0.5453
130	0.5757	0.4830	0.5504
140	0.5825	0.4895	0.5555
150	0.5894	0.4961	0.5606
160	0.5963	0.5028	0.5658
170	0.6033	0.5096	0.5711
180	0.6106	0.5165	0.5764
190	0.6182	0.5235	0.5819
200	0.6261	0.5305	0.5875

[a] Isobaric heat capacity at bubble point, B.t.u. per lb. per °R.

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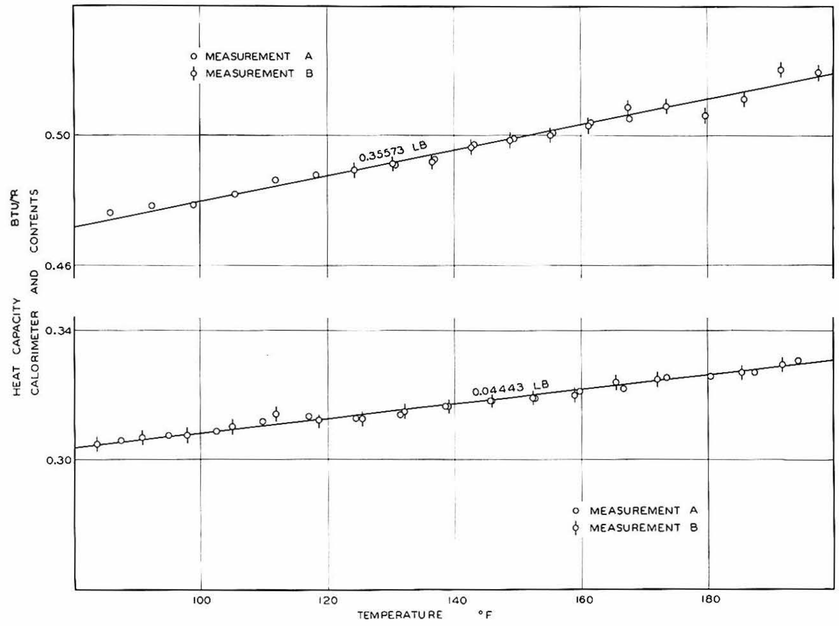


Figure 1. Experimental Results for n-Hexane

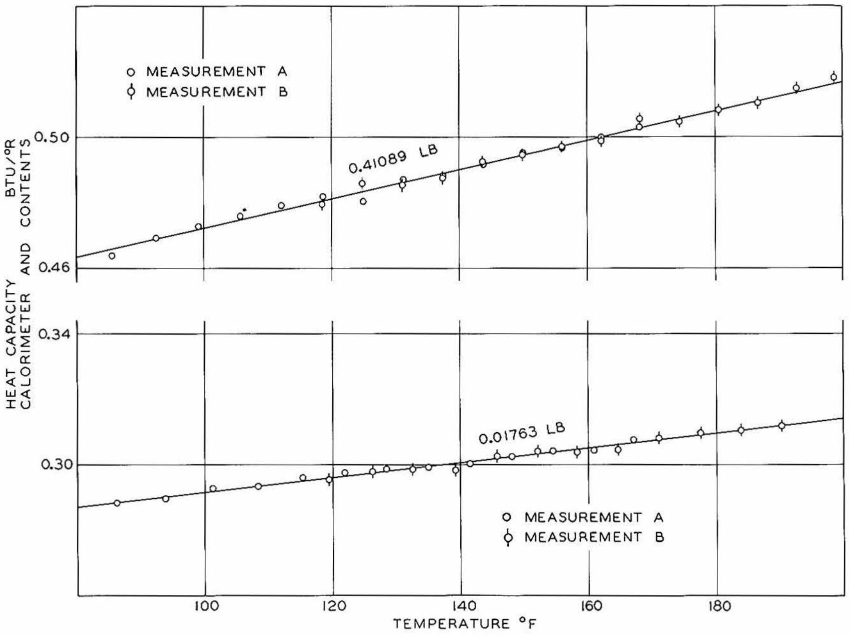


Figure 2. Experimental Results for Methylcyclopentane

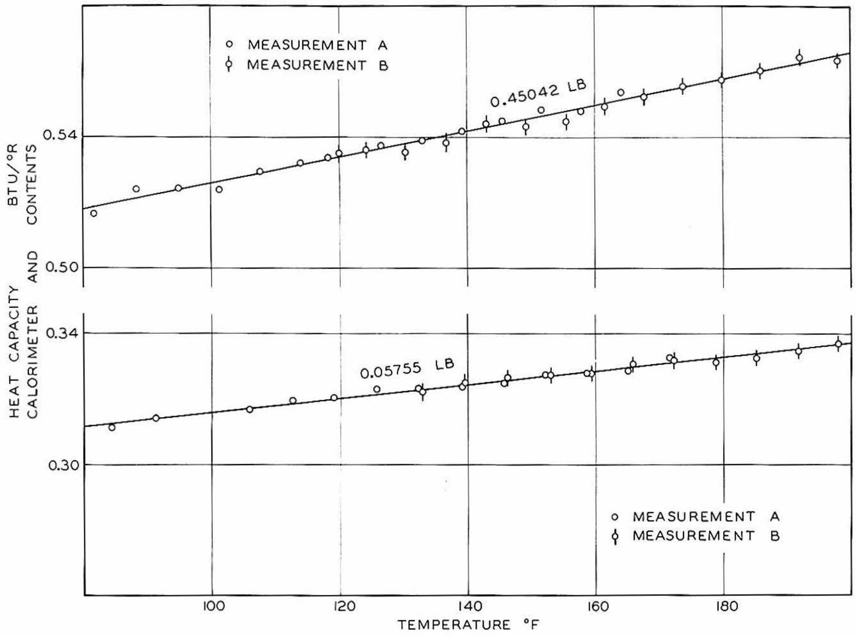


Figure 3. Experimental Results for n-Octane

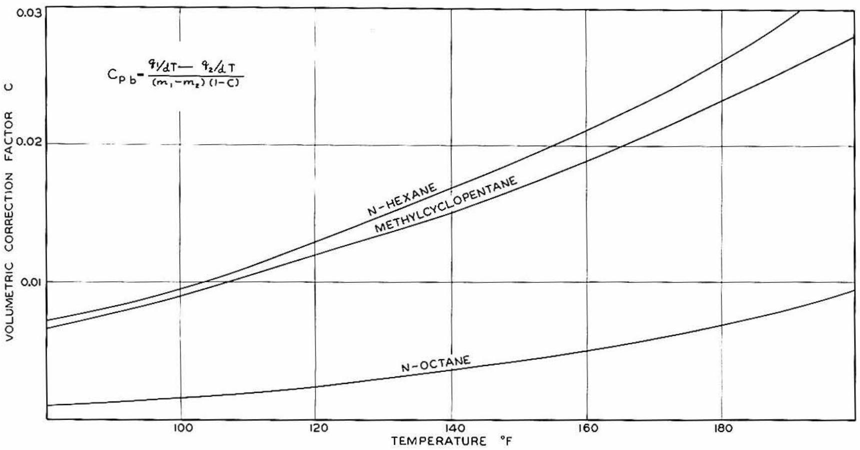


Figure 4. Volumetric Correction, Expressed as Fraction of Heat Capacity

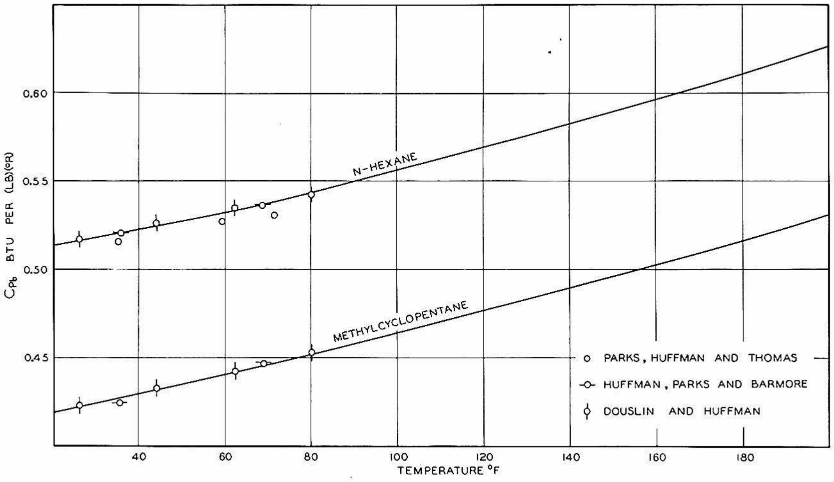


Figure 5. Isobaric Heat Capacity of n-Hexane and Methylcyclopentane at Bubble Point

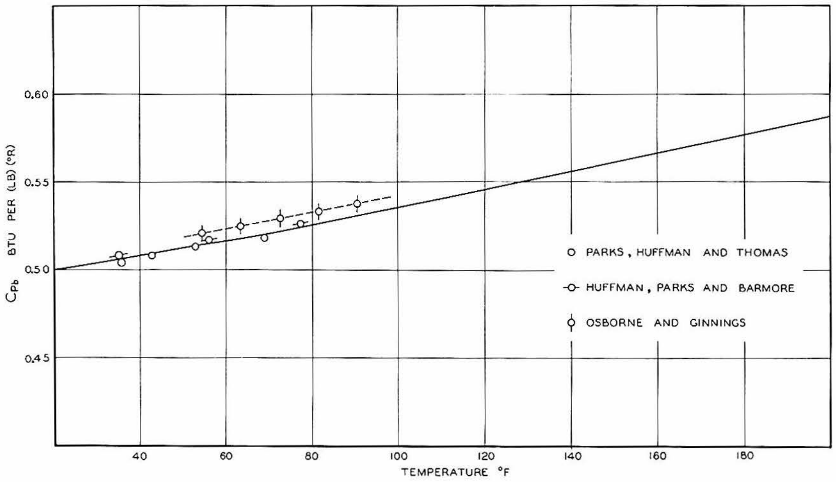


Figure 6. Isobaric Heat Capacity of n-Octane at Bubble Point

Propositions submitted by Thomas Joseph Connolly

Ph.D. Oral Examination, May 24, 1950, 1:00 P.M., Crellin Conference Room
Committee: Professors Sage (Chairman), Badger, Bates, Frankel,
Kirkwood, and Lacey

Chemical Engineering

1. In order to facilitate the calculations involved in the design of multicomponent distillation columns Underwood (1) and Gilliland (2) have derived relationships in terms of component concentrations as a criterion of the optimum feed plate. Both of these relationships may be shown to give erroneous answers in some cases. This result arises from errors in certain assumptions in their derivations.

2. Certain low temperature fractional crystallization processes might be facilitated by throttling a cooling medium such as CO_2 at high pressure directly into the crystallizing medium. This would eliminate heat transfer surfaces which may become reduced in efficiency due to coating with crystals. Such an expedient should lend itself to a continuous process as opposed to batch and offer the advantages generally attached thereto.

3. Stockmayer (3) has proposed that a second virial coefficient of the form

$$B(T) = B_o - A/RT \exp(D/T^2)$$

be applied to polar gases in mixture with non-polar gases. It is recommended that a second virial coefficient of this form be incorporated in the Benedict equation (4) and parameters for H_2S evaluated. This equation together with existing equations for hydrocarbons could be used for calculations of properties of H_2S - hydrocarbon systems. The applicability of such an equation could be tested by comparison of calculation results with existing data from this laboratory.

4. An accurate and relatively simple equation relating the isobaric heat capacity at the bubble point to isochoric calorimetric measurements on pure substances in the two-phase region is

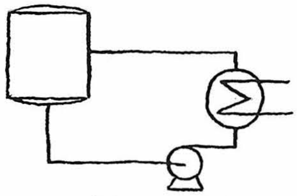
$$C_{Pb} = \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2} + \frac{\Delta\beta}{\Delta T} - V_b \frac{dP''}{dT} + T \frac{dV_b}{dT} \frac{dP''}{dT}$$

(See Nomenclature in Part II of thesis)

$$\beta = T V_b \frac{dP''}{dT}$$

This relationship offers the advantage that the correction terms require only a knowledge of the vapor pressure and bubble-point specific volume in the temperature range studied.

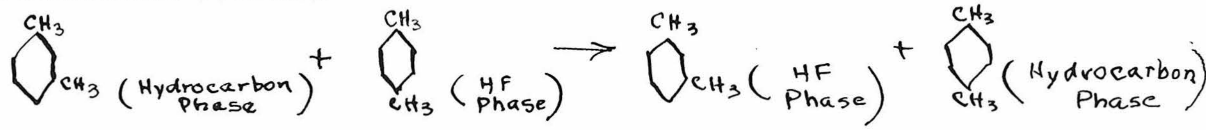
5. In a batch heating or cooling process of the type



where the heating or cooling medium is a single phase fluid, the log mean temperature difference correction for multipass heat exchangers (5) may be applied. This correction can be shown to be constant with time providing that flow rates and entering temperature of the heating or cooling medium remain constant.

Chemistry

6. It has been reported (6) that when BF_3 is introduced to a two-liquid phase mixture of HF and certain alkylaromatic hydrocarbons, a transfer of the hydrocarbon to the HF phase occurs. This phenomenon offers a good possibility of a process for separation of meta- and para-xylene since the transfer of xylene to the HF phase is selective for meta-xylene. A study to determine whether the kinetics of the metathesis reaction



are favorable would be interesting. If such is the case, a liquid-liquid multistage extraction process using reflux at both "raffinate" and "extract" ends of the stages could be designed to obtain good yields of high purity isomers.

7. In binary solutions of miscible liquids where one or both of the constituents are capable of forming hydrogen bonds, the formation of constant boiling mixtures can be closely related to the hydrogen bonding characteristics of the constituents. For a given mixture, qualitative predictions can be made as to the existence and type of azeotrope (maximum or minimum) from consideration of the type and strength of the hydrogen bonds.

8. A. B. Cox (7) has proposed what appears to be an accurate and unique equation of state

$$P^{1/3} = \frac{A}{V^{1/3}} + \frac{B}{V^{4/3}} + \frac{C}{V^{8/3}}$$

where the integral powers of the cube root of the volume arise from conventional treatment of PVT data rather than any preconceived form. The parameters A, B, and C are functions of temperature. It has been noted that the values of some of the constants in the parameter functions change abruptly at certain states in the single phase region. The changes appear to occur at a definite value of the specific volume for a given substance and are uneffected by relatively large changes in pressure and temperature. It is suggested that if these observations can be checked, the data should be considered for possible significance to the study of molecular interactions.

Mechanical Engineering

9. The temperature distribution in a thermal explosion of a combustible gaseous mixture can be predicted by a solution of a non-linear differential equation of the following type:

$$C\rho \frac{\partial T}{\partial \theta} = K \frac{\partial^2 T}{\partial x^2} - Q \frac{\partial n}{\partial \theta}$$

The first term on the right hand side of the equation represents cooling by conduction, the second term heating by chemical reaction. To obtain the temperature distribution in an explosive mixture Jost (8) approximates the solution of the above equation by a consideration of only the heat conduction term. A solution neglecting the heat generation term is appreciably in error and it is recommended that a more exact solution of the equation be obtained by the numerical method of Crank and Nicholson (9).

10. It is suggested that more reproducible and significant measurements of the ignition temperature of gaseous mixtures can be made by means of an adiabatic compression device than be some of the conventional techniques (8).

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