VAPOUR-LIQUID EQUILIBRIA
SYSTEMS NITROGEN-METHANE-ETHANE
AT -151.1°F

by

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ABSTRACT

A forced-recirculation type apparatus for the determination of the vapour liquid equilibrium data at low temperature and high pressure conditions was designed and constructed for this study. A detailed description of the design is presented in the thesis.

Vapour-liquid equilibrium data were obtained for the binary and ternary mixtures of nitrogen methane and ethane at -151.1°F. The pressure range covered in this investigation was from 8 to 750 psi. In the correlation of the data, the experimental data were found to be self-consistent.

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SUMMARY

A brief presentation of the development and a comparison of the advantages and the disadvantages of the different experimental methods for the determination of vapour-liquid equilibrium data are made in this thesis.

A forced-recirculation type apparatus for the determination of vapour-liquid equilibrium data at low temperature and high pressure conditions was designed and constructed for this study. This apparatus is suitable for operating in the temperature and the pressure ranges from -320° F to 212° F and 0 psi to 1500 psi respectively. The temperature can be regulated and maintained within $\pm$ 0.02° F at -150° F.

Vapour-liquid equilibrium data were obtained for the binary and ternary mixtures of nitrogen methane and ethane at -151.1° F. The pressure range covered in the investigation was from 8 psi to 750 psi. In the correlation of the data, the experimental data were found to be self-consistent.

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NOMENCLATURE

A	=	cross sectional area
A_o	=	the constant of the B - W - R equation of state
$A_{i/j}$, $A_{j/i}$, $A_{k/j}$	=	Wilson's parameters, Eq. 1.3.2 (13)
AM	=	molal average molecular weight
B_o	=	the constant of the B - W - R equation of state
C_o	=	the constant of the B - W - R equation of state
C	=	total number of components in the system, Eq. 1.2.1 (1)
c	=	total number of components
d	=	density
E	=	internal energy
F	=	number of degrees of freedom, Eq. 1.2.1 (1)
°F	=	degrees of Fahrenheit
f	=	fugacity
G	=	Gibbs' free energy
g_{ij} or g_{ii}	=	the constants in the Wilson equation, which are proportional to the interaction energy between molecules i and j or i and i
h	=	the convection heat transfer coefficient
H	=	the enthalpy of the fluid

K_i = $\frac{y_i}{x_i}$, equilibrium vapourization constant of component i or called K-value

k = thermal conductivity

MABP = molal average boiling point

M_i = molecular weight of the component i

n_i = number of moles of component i

P = pressure

P = number of phases, Eq. 1.2.1 (1)

P_c = critical pressure

P_{cv} = convergence pressure, section 1.2.2

P_r = $\frac{P}{P_c}$, reduced pressure

P_{pc} = pseudocritical pressure

q_z = heat flux in z-direction

R = gas constant

R = outside diameter, Appendix B

$^\circ R$ = degrees of Rankine

S = entropy

T = temperature

T_a = actual temperature

T_c = critical temperature

T_r = $\frac{T}{T_c}$, reduced temperature

T_r = room temperature, Appendix B

V = volume

W = acentric factor

x_i, N = mole fraction of the component i in the liquid phase

y_i = mole fraction of the component i in the vapour phase

Z_i = mole fraction of the component i either in the liquid phase or in the vapour phase

α = the constant of the B - W - R equation of state

β = the constant of the B - W - R equation of state

β = dimensionless constant, Appendix B

γ = the constant of the B - W - R equation of state

γ = activity coefficient, Eq. 1.3.1 (10)

δ = solubility parameter, Eq. 1.3.2 (6)

Δ = difference

$\hat{\phi}_i = \frac{\hat{f}_i}{x_i P}$, fugacity coefficient of component i in the solution

$\phi_i = \frac{f_i}{P}$, fugacity coefficient of pure component i

ϕ = volume fraction, Eq. 1.3.2 (3)

ϕ = the name of a certain function, Eq. 1.2.1 (7)

ζ = local volume, Eq. 1.3.2 (10)

$\zeta = \frac{z}{L}$, dimensionless length, Appendix B

θ = $\frac{T - T_a}{T_r - T_a}$, dimensionless temperature, Appendix B

$\sum$ = summation

Subscripts

1, 2, i,
j or k = component 1, 2, i, j or k respectively

z = in z-direction

Superscripts

* = ideal state or zero pressure state

— = partial molal property

$\wedge$ = fluid properties (for fugacity or fugacity coefficient) in the solution, but it is not a partial molal property

V = vapour phase

L = liquid phase

E = excess property

M = mixing property

INTRODUCTION

Separation of the components of natural gas for petrochemical industry becomes increasingly important. Gases to be liquefied are frequently obtained as by-products from some parent sources and may contain very large amounts of impurities. Determining the methods of separation and removal of impurities are difficult since the systems are seldom ideal and may deviate considerably from some theoretical models. Practical necessities demand either more and accurate prediction methods or experimental determination of vapour-liquid equilibrium data.

During the past three decades many methods have been developed to meet the need. Briefly these may be classified into the following categories: (1) by means of the evaluation of activity or fugacity coefficients, (2) the use of the equation of state, (3) by means of the molecular theory, (4) the direct determination of phase compositions and presentation in the form of tables, graphical or analytical correlations.

A survey described under the title of "Literature Review" shows that all prediction methods have only limited success. Although it is generally known that thermodynamic properties may be conveniently derived from an equation of state, this method also has its limitations. For example one of the best known equations of state, the Benedict-Webb-

Rubin equation, in general, may be used to predict vapour liquid equilibrium, but it has been recognized even by Benedict himself that at low temperature it was not entirely satisfactory (71). Therefore it may be concluded that to date no single method has been successful in describing all the binary and multicomponent vapour-liquid equilibrium systems. Consequently further studies are still necessary.

In this study, attempts have been made to determine the vapour liquid equilibrium composition at a low temperature experimentally. The material presented here will include: a literature review, a design and construction of a forced-recirculation type apparatus for obtaining the vapour-liquid equilibrium data at a low temperature and a presentation of vapour-liquid equilibrium data of the binary and the ternary systems containing nitrogen, methane and ethane.

PART I. LITERATURE REVIEW

A complete literature survey up to October 1, 1959 has been conducted by Flynn (27). It contains a bibliography of the physical equilibria and related properties of some cryogenic systems, including the following components: hydrogen, helium, nitrogen, carbon dioxide, carbon monoxide, methane, ethane and propane. Annual reviews on the topic Thermodynamics (13, 14, 63, 64, 65) have also provided adequate information for the current papers.

In this report a brief review of the literature will be made concerning the experimental procedure and methods of correlation and prediction. Current papers will be quoted accordingly. The survey will be limited to the field related to the vapor-liquid equilibrium studies below ambient temperature.

1.1 EXPERIMENTAL METHODS

In the literature, various methods have been proposed for investigating vapour-liquid equilibrium. The acceptable methods may be classified as follows:

1.1.1 Dew-point and Bubble-point Method

Dew point is determined by introducing a known gas mixture into an equilibrium cell at constant temperature. The pressure is

observed as a dew point, at which first minute drops of liquid can be detected along the wall of the cell. Bubble-point is determined by introducing gas mixture step by step until the cell is filled with liquid. After each addition the pressure is observed as a bubble point at which the last bubble starts to disappear.

This method was developed many years ago and has been frequently employed. It has been used by Holst and Hamburger (34) for argon-nitrogen mixtures, by Bourbo and Ischkin (8) for argon-oxygen mixtures and by Steckel (66) for nitrogen-carbon monoxide mixtures. It has been developed to a considerable perfection by Sage and Lacey (60) who used it for mixtures of light hydrocarbons, chiefly above room temperature. It also has been introduced by Bloomer (10, 11, 12, 23, 25) into the field of cryogenic vapour-liquid studies for the systems nitrogen-methane, nitrogen-ethane, and methane-ethane. This method has the advantage that the phase compositions need not be analyzed, since the mixtures may be prepared with predeterminate composition. However, it must be applied with great care if accurate results are to be obtained. The major disadvantage of this type of apparatus is that the data can be obtained only for the binary systems.

1.1.2 Static Method

A mixture is placed in the equilibrium cell which is maintained at a constant temperature and is agitated in some way, usually by rocking the container. After a certain period of time the mixture should reach equilibrium. The pressure is then read and a portion of the vapour and liquid are withdrawn and analyzed.

The static method has been used by Verschoyle (77) for the binary systems nitrogen-hydrogen, carbon monoxide-hydrogen, and the ternary system nitrogen-carbon monoxide-hydrogen by Freeth and Verschoyle (28) for the hydrogen-methane mixtures and by Fedoritenko and Ruhemann (26) for the mixtures of nitrogen and helium.

It is a useful and fairly accurate method for high and moderate pressures especially when the temperature is above the critical point of one of the components. However, in this method no provision is made for keeping the pressure constant while the samples are being withdrawn. A drop in pressure during sampling, of course, disturbs the equilibrium.

1.1.3 Flow Method

A gas mixture is passed under steady state condition into the equilibrium cell where it is cooled and partially liquefied. The liquid

which is formed, and the vapour in equilibrium with the liquid are separated and removed continuously to the storage for analysis. The sample also can be analysed continuously.

This method has been used by Steckel and Zinn (66) for the system hydrogen-nitrogen-methane, by Ruhemann and Zinn (67) for the hydrogen-nitrogen carbon monoxide system, by Fedoritenko and Ruhemann (26) for the nitrogen and helium, by Ruhemann (57) for the methane-ethane mixtures and by Guter, Newitt and Ruhemann (29) for the system methane-ethylene and by Stutzman and Brown (73) for natural gas systems. The advantages of this method are as follows: (1) large quantities of samples of vapour and liquid can be obtained with a small experimental assembly, and (2) the intimate contact between the vapour and the liquid during condensation provides a rapid approach to equilibrium.

The principle difficulties encountered in this method are that the pressure and the temperature cannot be controlled well in the cell while rapid condensation occurs. Also in the critical region the separation of the two phases becomes difficult.

1.1.4 Distillation Tower Method

Chu, et al. (19) studied the system acetone-water and stated that a very close approach to phase equilibrium was attainable on a

distillation tray consisting of one bubble cap and operating under total reflux condition. Wang (78) based on this idea and constructed a still which consisted of a number of sieve plates in which the separation on each tray was expected to be equivalent to the performance of one theoretical plate. Wang studied the argon-oxygen system by means of this apparatus and found that the reproducibility of the data was within $\pm$ 2 per cent, on the logarithm relative volatility, over the entire composition range. The over-all accuracy of this method was estimated to be $\pm$ 3 per cent, prior to any correction. Indeed it is not accurate enough from the academic stand point, but it provides quick investigation which should draw much attention from the practical stand point. The author of this study expects that it is possible to modify this still or to estimate the efficiency of the still to bring it into operation. It will enable the gap to be shortened between the Academicians and the Engineers.

1.1.5 Forced-recirculation Method

Dodge and Dunber (22) inherited the idea of Inglis (35) and developed this forced-recirculation method. The vapour, distilled from the liquid, was recirculated back through the liquid by means of a mercury pump. In this way the liquid was stirred and equilibrium insured by continually bringing the vapour into contact with the liquid.

Dodge and Dunbar used this apparatus in the study of the oxygen and nitrogen system with great success. It is probably the most accurate and reliable one of all the existing methods and is widely adopted through the world. Briefly it has been used by Torocheshnikov (74) in studying the equilibrium of the carbon monoxide-nitrogen system. Aroyan and Katz (2) studied the system methane-hydrogen by means of this method and modified the circulation process by introducing an electromagnetic pump. Later this method was used by William and Katz (79) for the systems hydrogen-ethylene, hydrogen-ethane, hydrogen-propylene and hydrogen-propane, by Benham and Katz (5) for the systems hydrogen-methane, hydrogen-methane-propylene, hydrogen-methane-ethylene and ethane-ethylene-propylene, by Cosway and Katz (18) for the systems containing hydrogen, nitrogen, methane and ethane. Further modification was made by Harvey (32), Price and Kobayashi (50). They introduced a visible equilibrium cell and used bath liquid in the studies of the ternary system methane-ethane-propane (32, 50). It was also used by Toyama, Chappelear, Leland and Kobagashi (34) for the system carbon monoxide-methane. Similar apparatus were constructed by Brandt, Stroud and Deaton (9) and by Stein, Sterner and Geist (68). In this study the force-recirculation method was also chosen.

1.2 CORRELATION METHODS

1.2.1 Basic Theory of Correlation

According to the phase rule

$$P + F = C + 2 \qquad 1.2.1\ (1)$$

where F = number of degrees of freedom in the system,

C = number of components in the system,

P = number of phases present in the system.

The number of variables of a two-phase system is equal to the number of components.

A composition or a composition variable may be chosen in addition to the pressure and the temperature for describing the ternary system.

The composition variables employed in the literature may be summarized as follows:

$$K_i = y_i/x_i, \qquad 1.2.1\ (2)$$

$$MABP = \sum_{i=1}^{c} Z_i\,(NBP)_i, \qquad 1.2.1\ (3)$$

$$AM = \sum_{i=1}^{c} Z_i\,M_i, \qquad 1.2.1\ (4)$$

$$P_{pc} = \sum_{i=1}^{c} Z_i P_{c_i}, \qquad 1.2.1\ (5)$$

$$T_{pc} = \sum_{i=1}^{c} Z_i T_{c_i}. \qquad 1.2.1\ (6)$$

where

K_i = vaporization equilibrium constant of component "i", or called K-value

MABP = Molal average boiling point

Z_i = mole fraction of component i

x_i = mole fraction of component i in the liquid phase

y_i = mole fraction of component i in the vapour phase

AM = molal average molecular weight

M_i = molecular weight of the component i

P_{pc} = pseudo critical pressure

T_{pc} = pseudo critical temperature

c = total number of components

The functional relationship for a ternary system may be generalized as follows:

$$\phi\ (K_i, \theta, P, T) = 0 \qquad 1.2.1\ (7)$$

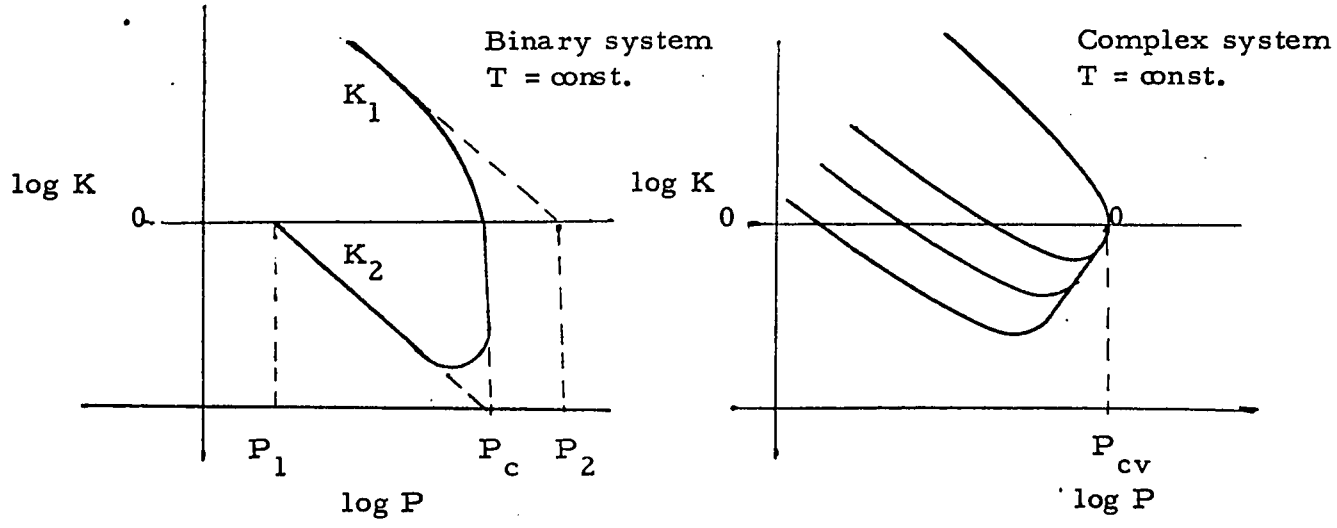
where θ may be a composition or a derived composition variable of any phase.

For a n-component system, the system may be described in a similar manner by n-2 variables in addition to the pressure and the temperature.

When Henry's law is applicable for the system concerned, one variable may be deducted accordingly.

1.2.2 Convergence Pressure Method

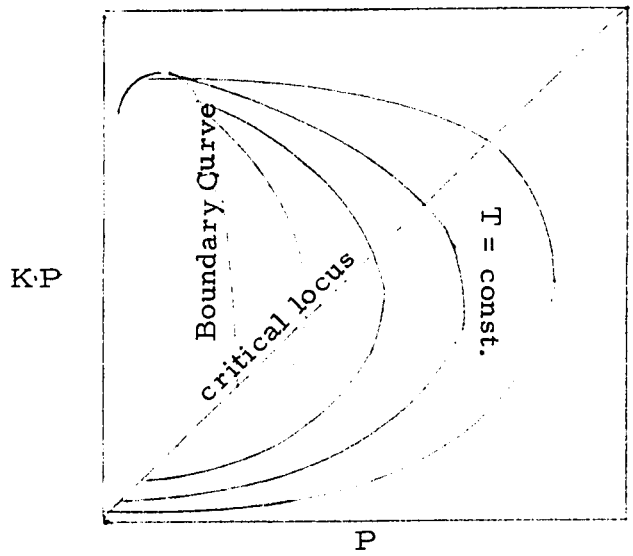
The plots of the logarithmic K-value as a function of the logarithm of the total pressure are frequently employed. A typical example of such a plot may be shown as follows:



The dotted lines in the plot for a binary system indicate the situation when Raoult's law is obeyed. The solid lines indicate a typical behaviour for hydrocarbons. Katz (36) first noted that the pressure at which the K-values for both constituents become unity is the critical pressure at the temperature in question. For a complex system, a similar behaviour is also observed, where the K-values converge to unity at the convergence pressure P_{cv}. If a system is at its critical isotherm the convergence pressure is equal to its critical pressure. By using the convergence pressure in addition to the temperature and the pressure it is very convenient for correlation K-values. It has been used extensively for complex hydrocarbon systems (41, 31, 30, 37, 43, 59, 83).

1.2.3 Sage-Reamer's Plot

Sage and Reamer (61) suggested that if the temperature and the pressure of a given system are well below the critical point, it was convenient to plot the product of the equilibrium constants and the pressure as a function of the pressure. Outside of the critical region this product changes only slightly with the pressure and to an even smaller extent with the temperature. The use of this product permits a relatively large amount of data to be included in a single diagram.



1.3 PREDICTION METHODS

Prediction methods available in the literature may be classified into three categories, namely: (1) by means of evaluating the activity or the fugacity coefficients, (2) by means of equations of state, (3) by means of a molecular theory. The last method should provide eventually the final answer to the problem in the discussion. Owing to its present limited applicability, it has been excluded from this survey.

For the sake of discussion it may be more convenient to begin with the presentation of the basic principles, then to be followed by the presentation of the different prediction methods.

1.3.1 Basic Theory of the Solution

Fugacity Coefficient

Fugacity at constant temperature for either gases or liquids may be defined by

$$dG_i = RT\, d\ln f_i \text{ (const. T)} \qquad 1.3.1\ (1)$$

with the condition that

$$\lim_{P \to 0} \frac{f}{P} = \frac{f_i^*}{P^*} = 1$$

For a constituent in the solution, one may proceed in an analogous manner

$$d\overline{G}_i = RT\, d\ln \hat{f}_i \text{ (const. T)} \qquad 1.3.1\ (2)$$

where $\hat{f}_i$ is called the fugacity of component i in the solution, and with the condition that

$$\lim_{P \to 0} \frac{\hat{f}_i}{x_i P} = \frac{\hat{f}_i^*}{x_i P^*} = 1$$

For the vapour phase, integration of equation 1.3.1 (2) at constant temperature and pressure from the state of pure component i to the state of y_i in the vapour gives

$$\overline{G}_i^{\,v} - G_i^{\,v} = RT \ln (\hat{f}_i^{\,v} / f_i^{\,v}) \qquad 1.3.1\ (3)$$

Similarly for the liquid phase gives

$$\bar{G}_i^L - G_i^L = RT \ln (f_i^L / f_i^L) \qquad 1.3.1\ (4)$$

At equilibrium

$$\bar{G}_i^V = \bar{G}_i^L ,$$

thus combination of Eq. 1.3.1 (3) and Eq. 1.3.1 (4) gives

$$G_i^V - G_i^L = -RT \ln \frac{\hat{f}_i^V f_i^L}{\hat{f}_i^L f_i^V} \qquad 1.3.1\ (5)$$

Integrating Eq. 1.3.1 (1) from vapour state to liquid state for the pure component gives

$$G_i^V - G_i^L = -RT \ln \frac{f_i^L}{f_i^V} \qquad 1.3.1\ (6)$$

Comparison of Eq. 1.3.1 (5) and Eq. 1.3.1 (6) gives

$$\hat{f}_i^V = \hat{f}_i^L \qquad 1.3.1\ (7)$$

Since $\hat{f}_i^V = y_i \hat{\phi}_i^V P$

and $\hat{f}_i^L = x_i \hat{\phi}_i^L P$

therefore

$$y_i \hat{\phi}_i^V P = x_i \hat{\phi}_i^L P \qquad 1.3.1\ (8)$$

or

$$K_i = \frac{y_i}{x_i} = \frac{\hat{\phi}_i^L}{\hat{\phi}_i^V} \qquad 1.3.1\ (9)$$

One may therefore evaluate the equilibrium vapourization constant K_i by knowing the fugacity coefficients.

Activity Coefficient

Furthermore, the activity coefficient may be defined as

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} \qquad 1.3.1\ (10)$$

or $$f_i^L = \gamma_i^L x_i f_i^L$$

and $$f_i^v = \gamma_i^v y_i f_i^v$$

therefore $$\gamma_i^L x_i f_i^L = \gamma_i^v y_i f_i^v \qquad 1.3.1\ (11)$$

$$K_i = \frac{\gamma_i^L}{\gamma_i^v} \frac{f_i^L}{f_i^v} \qquad 1.3.1\ (12)$$

By combining the activity and the fugacity coefficients the following relationship is obtained:

$$\hat{f}_i^v = y_i \hat{\phi}_i^v P = \hat{f}_i^L = \gamma_i^L x_i f_i^L \qquad 1.3.1\ (13)$$

or

$$K_i = \frac{\gamma_i^L f_i^L}{\hat{\phi}_i^v P} \qquad 1.3.1\ (14)$$

This is a convenient relationship to be used for evaluating K-values. Since f_i^L, the fugacity of pure component i, is generally available, $\hat{\phi}_i^v$, fugacity coefficient of the vapour phase, usually can be calculated by using an equation of state.

Excess Gibbs' Free Energy

If Eq. 1.3.1 (2) is integrated at constant temperature and composition for a pressure change from P* to P the result is

$$\overline{G}_i - \overline{G}_i^* = RT \ln \frac{\hat{f}_i}{x_i P^*} \qquad 1.3.1\ (15)$$

Similarly for a pure component i,

$$G_i - G_i^* = RT \ln \frac{f_i}{P^*} \qquad 1.3.1\ (16)$$

Subtracting Eq. 1.3.1 (16) from Eq. 1.3.1 (15) gives

$$\overline{G}_i - G_i - (\overline{G}_i^* - G_i^*) = RT \ln \frac{\hat{f}_i}{x_i f_i} \qquad 1.3.1\ (17)$$

and if Eq. 1.3.1 (4) is applied at zero pressure,

$$\overline{G}_i^* - G_i^* = RT \ln \frac{\hat{f}_i}{f_i^*}$$

or

$$= RT \ln \frac{x_i P^*}{P^*}$$

or

$$= RT \ln x_i \qquad 1.3.1\ (18)$$

Then

$$\overline{G}_i - G_i = RT \ln \gamma_i x_i \qquad 1.3.1\ (19)$$

The total Gibbs free energy of a solution is given by

$$n G = \sum_i n_i \overline{G}_i \qquad 1.3.1\ (20)$$

Combining Eq. 1.3.1 (19) and Eq. 1.3.1 (20) gives

$$nG = \sum_i n_i G_i + RT \sum_i n_i \ln \gamma_i x_i \qquad 1.3.1\ (21)$$

For an ideal solution $\gamma = 1$, Eq. 1.3.1 (21) reduces to

$$nG_{id} = \sum_i n_i G_i + RT \sum_i n_i \ln x_i \qquad 1.3.1\ (22)$$

Therefore the excess Gibbs free energy will be

$$nG^E = nG - nG_{id} = RT \sum_i n_i \ln \gamma_i \qquad 1.3.1\ (23)$$

Partially differentiating it with respect to n_i gives the relationship of the excess Gibbs free energy with the activity coefficient

$$\left(\frac{\partial nG^E}{\partial n_i}\right)_{T,\ P,\ n_j} = RT \ln \gamma_i \qquad 1.3.1\ (24)$$

This is the fundamental relationship used by all the solution models.

It is clear that γ_i is a measurement of nonideality of the liquid phase and is related to the excess Gibbs free energy as shown in equations 1.3.1 (23) and 1.3.1 (24). If one can find any means to express the excess Gibbs free energy, the activity coefficients of the various components can evidently be determined by the differentiation of G^E with respect to n_i. The liquid phase behaviour may therefore be defined. The general properties of the solution are listed as follows:

Type of Solution	$\bar{V}_1 - V_1$	$\bar{H}_1 - H_1$	$\bar{S}_1 - S_1$	γ_1
Ideal	0	0	$-R\ln x_1$	1
Non-ideal				
Regular	0	+	$-R\ln x_1$	> 1
Athermal	0	0	$> -R\ln x_1$ ($V_2 \gg V_1$)	< 1
Associated	$\pm$	+	$> -R\ln x_1$	> 1
Solvated	$\pm$	-	$< -R\ln x_1$	< 1

1.3.2 **Prediction Methods by Means of Evaluating Activity Coefficients**

Scatchard-Hildebrand equation (33)

The relationship between the excess Gibbs free energy, the excess enthalpy and the excess entropy is given by

$$\Delta G^E = \Delta H^E - T\Delta S^E \qquad 1.3.2\ (1)$$

Hildebrand assumed that for a regular solution $\Delta S^E = 0$, $\Delta V^E = 0$. Therefore for the binary system,

$$\Delta G^E = \Delta H^E = \Delta E^E = \phi_1 \phi_2 V (\delta_1 - \delta_2)^2 \qquad 1.3.2\ (2)$$

where $$\phi_1 = \frac{N_1 V_1}{V} \qquad 1.3.2\ (3)$$

$$\phi_2 = \frac{N_2 V_2}{V} \qquad 1.3.2\ (4)$$

$$V = N_1 V_1 + N_2 V_2 \qquad 1.3.2\ (5)$$

$$\delta_i = \left(\frac{\Delta H_i^v - RT}{V_i}\right)^{1/2} \quad , \; i = 1 \text{ or } 2 \qquad 1.3.2\,(6)$$

Differentiating Eq. 1.3.2 (2) with respect to n_1 and combining with Eq. 1.3.1 (24) gives:

$$RT \ln \gamma_1 = V_1 \phi_2^2 (\delta_2 - \delta_1)^2 \qquad 1.3.2\,(7)$$

Many methods have been proposed for evaluating the solubility parameter δ_i theoretically (33) and empirically (15, 48), and many applications have been found which were related to the solubility of gases (16, 42, 47, 49), to polymer solution (7) and to hydrocarbon systems (15, 48). The method proposed by Chao and Seader (15) may be considered as one of the most useful ones. They correlated the liquid phase fugacity coefficient and the solubility parameters of the hydrocarbons and employed Eq. 1.3.1 (14) for calculating the K-values.

Flory-Hoggin's Equation (33)

Flory-Hoggin assumed that for an athermal solution, $\Delta H^M = 0$ $\Delta V^M = 0$. Thus the Gibbs free energy of mixing may be represented by

$$\Delta G^M = -T\Delta S^M$$

Since, for an athermal mixing,

$$\Delta S^M = -R \sum_i x_i \ln \phi_i$$

Therefore $$\Delta G^M = RT \sum_i x_i \ln \phi_i \qquad 1.3.2\,(8)$$

For an ideal solution, $\Delta S^M = -R\sum_i x_i \ln x_i$. Hence

$$\Delta G^E = RT \sum_i x_i \ln \frac{\phi_i}{x_i} \qquad 1.3.2\ (9)$$

Wilson's Equation (80)

Wilson introduced the local volume concept which was defined by

$$\xi_i = \frac{x_i V_i e^{-g_{ii}/kT}}{\sum_j x_j V_j e^{-g_{ij}/kT}} \qquad 1.3.2\ (10)$$

and arrived at Eq. 1.3.2 (11)

$$\Delta G^E/RT = -\sum_i x_i \ln \sum_j x_j (V_j/V_i) e^{-(g_{ij} - g_{ii})/kT} \qquad 1.3.2\ (11)$$

where g_{ij} is a constant and proportional to the interaction energy between molecules i and j. It is clear that exponential terms in Eq. 1.3.2 (10) serve as a weight factor for the molar volume. If $g_{ii} = g_{ij}$, Wilson's equation will be reduced to the Flory-Huggin equation. Partially differentiating Eq. 1.3.2 (11) with respect to n_i gives

$$\ln \gamma_i = -\ln (1 - \sum_j x_j A_{j/i}) + 1 - \sum_j \left[x_j (1 - A_{i/j}) / (1 - \sum_k x_k A_{k/j}) \right] \qquad 1.3.2\ (12)$$

where $$A_{j/i} = 1 - (V_j/V_i)\, e^{-(g_{ji} - g_{ii})/kT} \qquad 1.3.2\ (13)$$

Wilson tested equation 1.3.2 (11) with highly polar mixtures with satisfactory results (80). Orye and Prausnitz used Eq. 1.3.2 (12) to study highly polar systems and concluded that Wilson's equation is the best two-parameter equation to describe the systems (44).

However, if we recall one of the assumptions, $\Delta H^M = 0$ made in the derivation of the Flory-Hoggin Equation, one may question the applicability of the Wilson Equation for systems having larger heats of mixing values.

1.3.3 Prediction by Means of an Equation of State

This is one of the most convenient methods for predicting vapour-liquid equilibrium provided one can find a suitable equation of state which can be used to describe both vapour and liquid phases.

There are many equations of state available in the literature. Two of them are generally considered to be adequate for this purpose. They are the equations of Benedict-Webb-Rubin (3) and modified Redlich-Kwong (53, 54, 55).

Benedict-Webb-Rubin's Equation

Benedict's equation of state is the best starting point for thermodynamic analysis of hydrocarbon mixtures because it furnishes

a close representation of the data. In principle it does not need the properties of the mixtures but it does require fairly extensive data for the pure substances and somewhat lengthy calculations. In fact it has been used in correlating experimental vapour liquid equilibrium data for many binary and ternary systems of light hydrocarbons (4), for the carbon monoxide-nitrogen binary system (62), for the carbon dioxide-propane binary system (20), for the nitrogen-methane binary system (71), for the methane-ethane-propane ternary system (51), for light hydrocarbon systems containing hydrogen (40), and most recently for the six binary systems methane-carbon dioxide, propane-carbon dioxide, n-butane-carbon dioxide, nitrogen-methane, methane-n-butane and ethane-n-butane (38).

Good agreement between the predicted values and experimental data was obtained for the light hydrocarbon systems (4), and after an adjustment of one of the parameters in the equation of state, satisfactory agreement was also obtained in the correlation of the binary nitrogen-methane system (70). The application of B - W - R equation of state to the correlation of K - value for the carbon monoxide-nitrogen system was satisfactory (62).

However, for the system carbon dioxide-propane, the K-values obtained for carbon dioxide were in error by 100 per cent. The methane-ethane-propane ternary system was also correlated by Price, Leland and Kobayashi (51) and found to be in great error at the lower temperatures where the density of the liquid phase was greatest. This conclusion agrees with Benedict's own opinion (71) who stated that for the nitrogen-methane system the agreement was not entirely satisfactory (71). He concluded that if a limited amount of data could be obtained to enable one to determine one of the mixing rule coefficients, the equation of state would be a powerful technique for advancing knowledge of thermodynamic properties of mixtures (71). In view of this conclusion it might be stated that the B - W - R equation could be a powerful correlation implement but not a perfect prediction means.

In a recent paper Lin and Naphtal (38) modified the B - W - R equation of state and reduced the maximum deviation to 5.8%. They suggested that in order to predict the vapourization equilibrium constant of the components in a mixture, the equation should be able to represent the P - V - T behaviour for the pure components in the states of superheated liquid and subcooled vapour which were known to be unstable.

Lin's work indicates that a new approach could be followed if one wishes to obtain good results. Thus one should not be satisfied by the available forms of the equation of state and should improve the existing one or search for a new equation.

The modified form of the B - W - R equation proposed by Lin and Naphtal is given as follows:

$$P = RTd + (B_o RT - A_o - C_o/T^{\beta})\, d^2 + (bRT - a)\, d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2) \exp(-\gamma d^2)$$

Strobridge (72) made another modification by using sixteen adjustable coefficients and obtained a better fit in P - V - T behaviour even to high density regions. This modification was specifically derived (72) for representing the nitrogen data but it was subsequently used to represent P - V - T properties for other cryogenic fluids. For example, the coefficients for this equation were determined from experimental data or derived data for helium, para hydrogen, argon, neon and oxygen. In the case of carbon monoxide, coefficients were calculated from the nitrogen coefficients. In general this modification showed a progress in the application to the low temperature region. However, it has been pointed out (70) that caution should be taken if it is used in the critical region. It seems reasonable to assume that this modified equation

may be used to predict vapour liquid equilibrium behaviour of the cryogenic fluid systems.

Redlich-Kwong Equation of State (53)

Three modifications were made recently for the Redlich-Kwong equation of state (62, 63, 64). The original form of the two parameters was found (53) to represent P - V - T data with good precision, even at high gas densities. Enthalpy data were also well represented by means of this equation (24). The first modification was made by Redlich and Dunlop (54). A superposition of a deviation function, containing, in addition, a third parameter - acentric factor, led to appreciable improvement. However, the application was restricted to the gaseous state. Recently an important modification (55) was made by Redlich, Ackerman, Gunn, Jacobson and Lau. The application of the new improvement was extended to the region of liquid state and to represent vapour pressures. Three parameters, T_c, P_c, W have been retained but the methods for combining parameters for mixtures were changed. Tests of this improvement in the properties of compressibilities and fugacities were made for the binary systems methane-n-pentane and n-butane-carbon dioxide, with good agreement (55).

Another modification was made by Wilson (82) based on the fact that the original equation did not represent vapour pressure well. He simply introduced a temperature dependence to one of the parameters with sound improvement in the low temperature region. A comparison between experimental and predicted vapour liquid data was made for the nitrogen-methane and the helium-hydrogen systems with satisfactory results (82).

PART II DESIGN AND CONSTRUCTION OF AN APPARATUS FOR THE DETERMINATION OF VAPOUR-LIQUID EQUILIBRIUM DATA AT LOW TEMPERATURES

A forced-recirculated apparatus has been designed and constructed in this study for the determination of vapour-liquid data at low temperatures and high pressures. It consists of a feed measuring and charging device, an equilibrium cell, a recirculation pump, a closed recirculation loop, a constant temperature bath and its control system, a set of sampling facilities, and temperature and pressure measuring devices. Detailed descriptions of this apparatus are given as follows:

2.1 FEED MEASURING AND CHARGING DEVICE

Three gas storage tanks have been connected in parallel to form a feed-supply system. A vacuum pump has been installed and connected to the system, the equilibrium cell and the gas storage tanks. The system can be evacuated and flushed with hydrocarbon alternately before filling. Vacuum can be detected by an attached McLeod gauge. A schematic diagram of the forced-recirculation apparatus is shown in Figure 1. For the purpose of evaluating the quantity of the charge one pressure gauge has been installed.

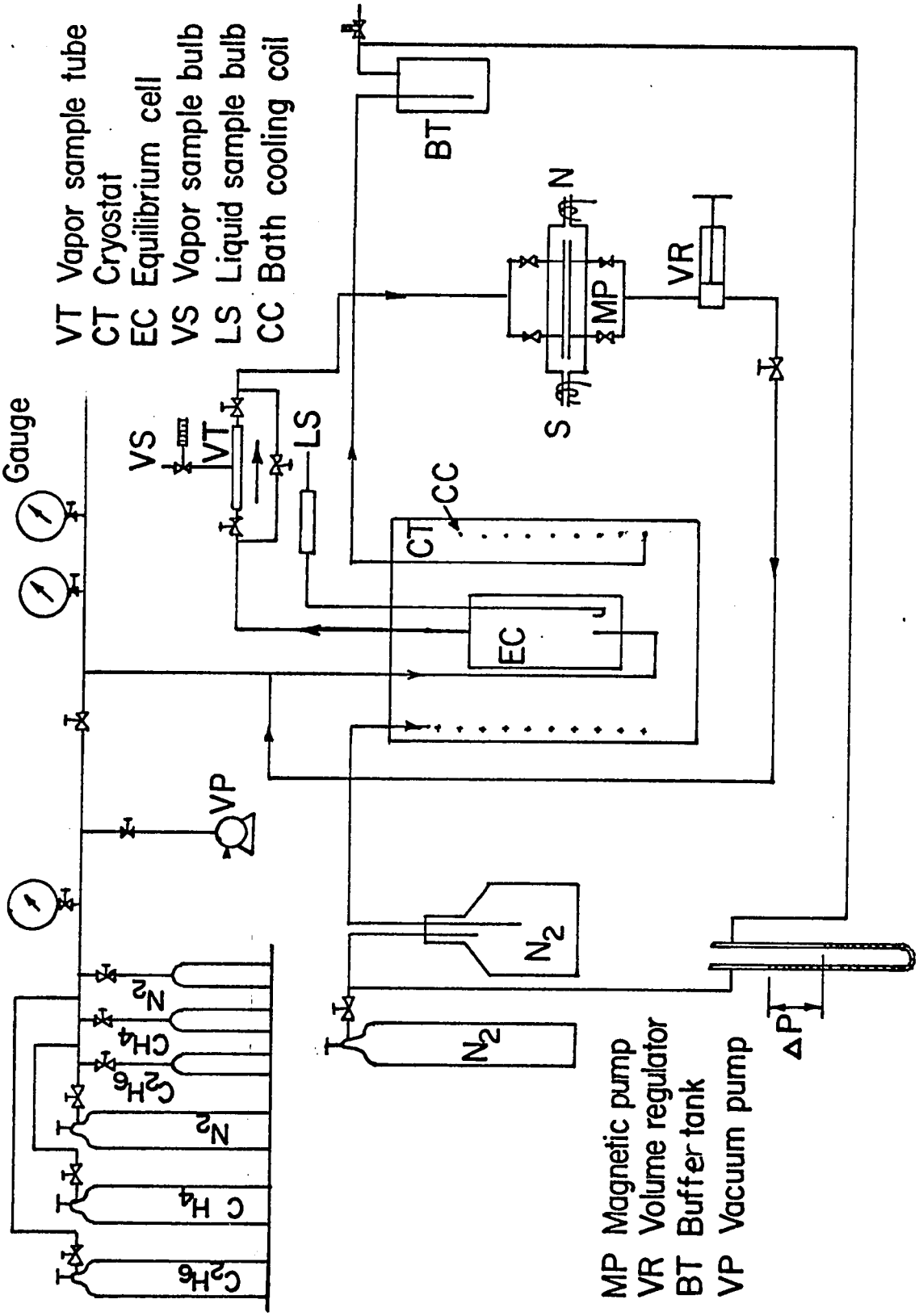


Fig. 1 The schematic diagram of the forced-recirculation apparatus.

Charge procedure: The heavier component is first introduced to the cell then followed by a lighter component. The lightest component is introduced through a pressure regulator, which is designed in such a manner that data can be obtained at constant temperature and pressure. Therefore the uncertainty associated with the interpolation of data can be avoided.

2.2 EQUILIBRIUM CELL

A schematic diagram of the equilibrium cell is shown in Figure 2. The cell is made of 306 stainless steel tubing of 3/8" in diameter. The top end is sealed by a Swagelok connection, and the bottom end is welded with a 1/8" Autoclave joint, which is connected to the cooling coil of the vapour inlet line. Through the Swagelok connection on the top of the cell is a drilled hole. Into this drilled hole a 3/16" diameter tubing is inserted to provide a vapour outlet and a cold chamber for a thermocouple. Two protective type thermocouples of 1/16" in diameter, which were supplied by the Thermo-Electric Company, are installed inside the cell. One is extended to the upper quarter part of the cell via the vapour outlet tubing, and the other is extended to the lower quarter part of the cell. These can be used to measure the temperatures in the vapour phase and the liquid phase respectively.

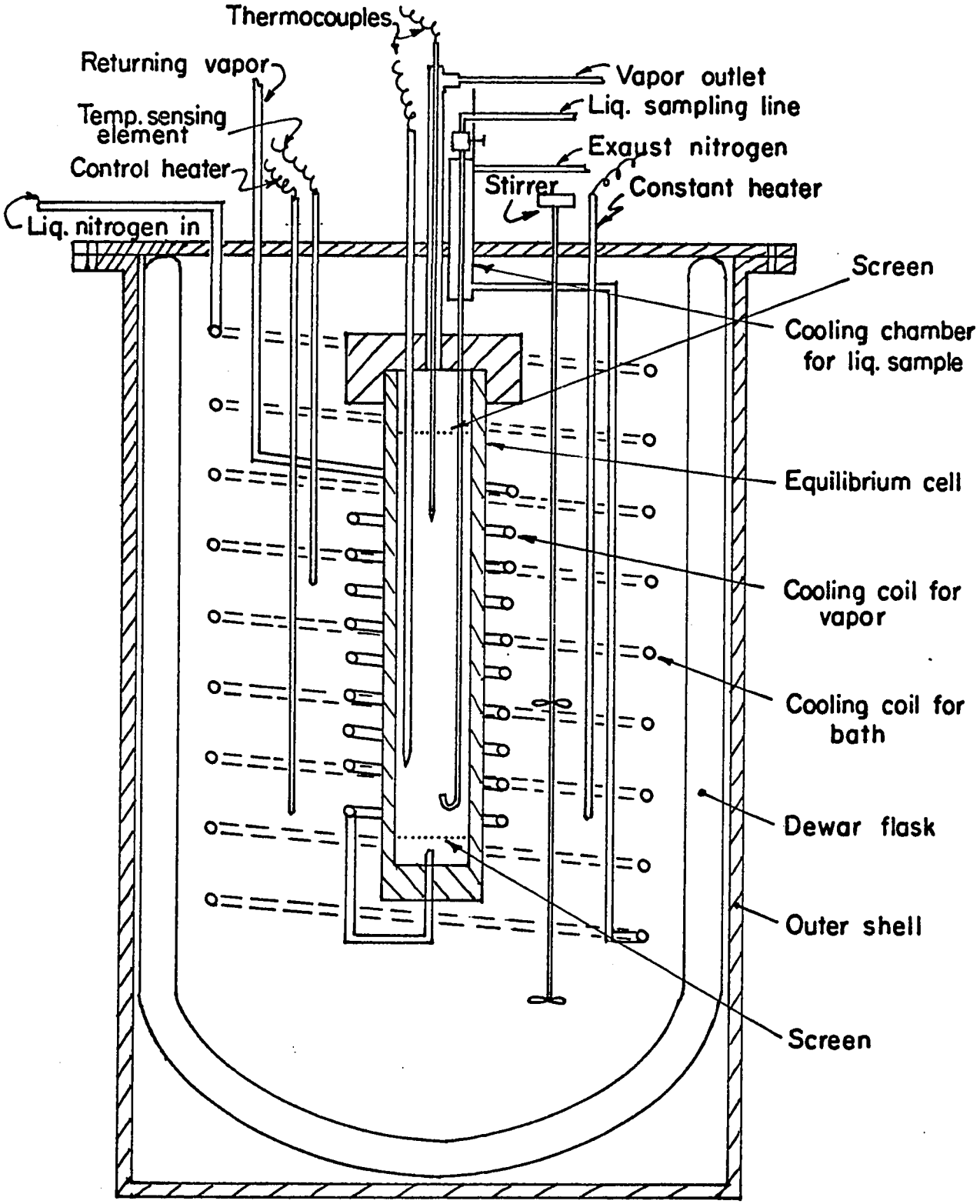


Fig. 2 The schematic diagram of the equilibrium cell and the cryostat.

A liquid sampling tubing of 1/16" in diameter also is inserted through the top of the cell and extended to the lower part of the cell. The recirculating vapour enters through the hole at the bottom and passes through a screen which distributes the vapour bubbles to the liquid phase. Near the top of the cell an additional screen is furnished to eliminate liquid entrainment. The equilibrium cell is immersed in the cryostat which contains the bath liquid.

2.3 RECIRCULATION PUMP

In this study an electromagnetic circulating pump has been built for recirculating the vapour through the equilibrium cell in a closed system. The design is similar to that reported by Sterner (69) but with several modifications. The pump is essentially a double acting plunger pump with four check valves in the body, two inlets and two outlets. One permanent magnetic piston rod which travels inside the cylinder is driven by the electromagnetic coils on both ends. Both magnetic coils are energised by charging D. C. current but in opposite polarity. The action is that one pulls the piston and the other pushes. The polarity is reversed every second.

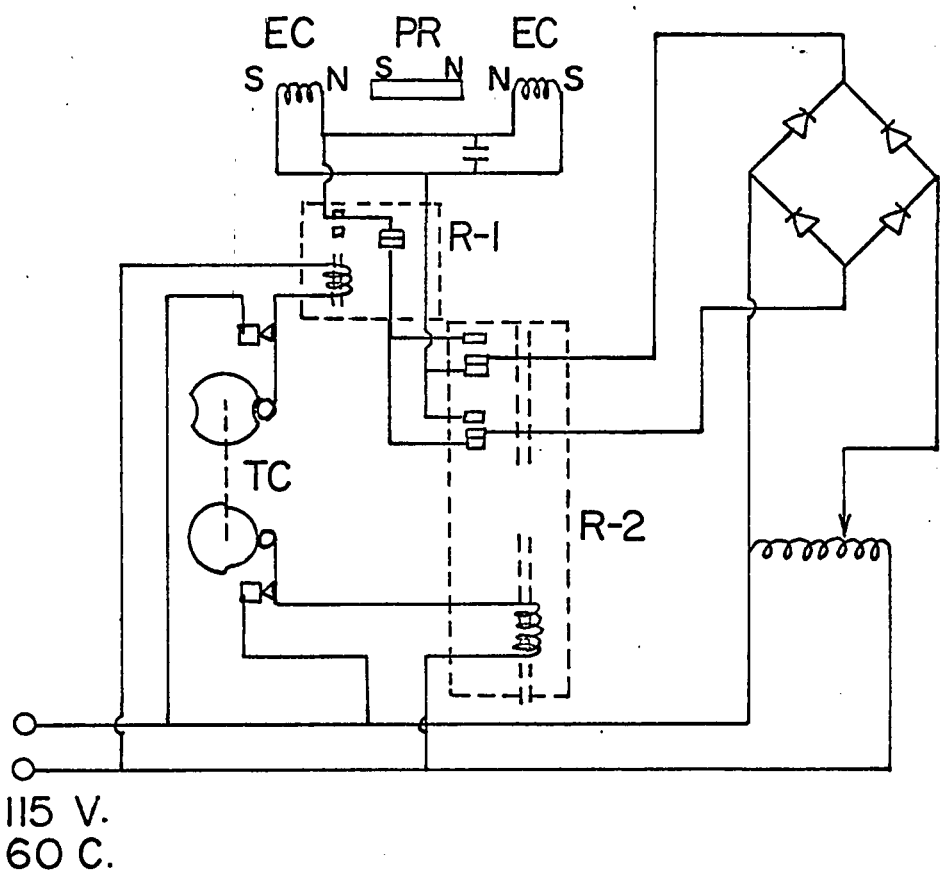
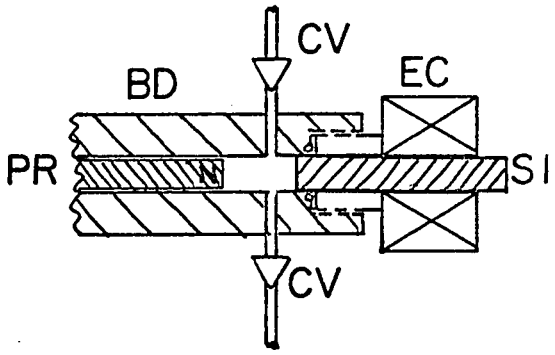


Fig. 17 The electric circuit of the electromagnetic pump.



EC Electromagnetic coil
PR Piston rod
R-1 On-off relay
R-2 Reversing relay
TC Timing cam
CV Poppet check valve
BD Pump body
S1 Soft iron rod

Fig. 18 The cross section of one portion of the electromagnetic pump.

The performance test of this pump has shown the following results. For the purpose of comparison Sterner's data are included.

	This work	Sterner
1. Pressure difference could be developed, psi	6.3	3
2. Circulation rate with pulse per second, cc/min	56	25

Major modifications are described as follows:

1. The piston ring has been replaced with a Teflon bushing to cover the piston rod which can provide a better seal. The work can be done by inserting a magnetic bar into the Teflon bushing and machining off the surface until the required diameter has been reached.

2. The Alnico 1 piston rod has been replaced by Alnico 5 to get longer and better service. Alnico 1 piston rod becomes demagnetized easily after a few days' service.

3. The ball type check valves were replaced by NUPRO check valves to reduce back pressure to a minimum or to a negligible value. NUPRO check valves were supplied by Nuclear Products Company, Cleveland, Ohio.

4. An adjustable motor has been selected to drive the timing cam in which the flow rate can be regulated more easily.

5. The resistance in the electromagnetic coils has been reduced to 19 ohms to decrease the voltage required across the circuit. This in turn reduces the spark problem, prolongs the life of the relays, and therefore a smooth operation has been achieved.

The advantages of using an electromagnetic pump are the following: operation of the pump makes no change in the total volume of the system, no moving parts extend outside the body, leakage which used to be a serious problem for high pressure operation is easily prevented.

Before constructing this pump, extensive efforts were made to locate the commercial product but they were not successful.

2.4 RECIRCULATION LOOP

With reference to Figure 1, the recirculation loop consists of a circulation pump, a volume regulator, a sampling loop, a cooling coil and an equilibrium cell. This loop provides a path which allows the withdrawal of the vapour from the vapour phase. When the vapour passes through the volume regulator, the sampling loop, it is heated up to the room temperature, but it is cooled to the bath temperature when it passes through the cooling coil, inside the cryostat before returning to the cell to avoid the temperature difference which may disturb the equilibrium.

2.5 CRYOSTAT AND ITS TEMPERATURE CONTROL SYSTEM

A Dewar flask of 5 liters in capacity is used as a cryostat. Isopentane is chosen as the bath liquid. The temperature may be controlled to within $\pm$ 0.01° F at -150° F. It is shown in Figure 2 that a refrigeration coil, a stirrer, two heating elements and a resistant type temperature sensing element have been installed inside the cryostat. Liquid nitrogen has been chosen as a refrigerant which is supplied under pressure through the refrigeration coil, made of 1/4" copper tubing and immersed in the cryostatic bath. The refrigerant - nitrogen, after vapourisation is led through a five gallon buffer tank, a needle valve and then to the open air. The pressure difference between the up stream and the down stream section of the system can be read and controlled by a manometer and an outlet needle valve. With these installations the refrigerant vapourization rate can be adjusted to a desired level, since the flow rate of the refrigerant is proportional to the square root of the pressure difference between the up stream and the down stream. In case of a pressure fluctuation, the higher pressure difference will increase the flow rate of the refrigerant and hence increase the vapourisation rate. Consequently the higher vapourisation rate will develop higher pressure in the buffer tank and thus reduce the pressure difference between them. Therefore the system can automatically be

regulated and the refrigerant flow rate be maintained at the desired level. The temperature can be controlled to $\pm$ 0.2° F. More accurate control, $\pm$ 0.02°F has been achieved by turning on the constant heater, regulated by a powerstat and the controlled heater, which in turn is regulated by a proportional type temperature controller.

2.6 SAMPLING FACILITIES AND PROCEDURES

After the system reaches equilibrium and temperature and pressure are recorded, the vapour sample may be trapped in the vapour sampling tube. A portion of the liquid in the cell may be withdrawn through the liquid sampling tubing of 1/16" in diameter. This tubing is extended into the cell through a cooling chamber to a point near the bottom of the cell. The cooling chamber is cooled by the exhausted refrigerant, after vapourization in the refrigeration coil. The cooling chamber may be considered to be at the same temperature as that in the cryostatic bath.

The sampling of liquid is quite critical and has a considerable effect on the accuracy of the results.

Difficulty has been encountered and many suggestions have been made by different investigators (2), (22), (81). It seems that most of them have partially solved the problem but none of them have reported

the technique in sufficient detail. A test run of this apparatus has indicated that either a sudden change of temperature or pressure may cause a fractionating effect inside the sampling tube, thus affecting the liquid sampling. To solve this problem, the exhaust refrigerant is introduced into a cooling chamber to keep the sampling tubing as cold as the cryostatic bath. Furthermore, a needle valve and a three way valve have been installed in between the liquid sampling tubing and the sampling bulb. By opening the needle valve slowly, the first portion of the sample is used to purge the line and to bubble through water in a small flask. The sampling rate thus can be checked and adjusted as required to minimize the sudden pressure change during the sampling process. It is reasonable to assume that this method allows a near ideal plug flow of liquid sample through the tubing and a total vapourisation of the sample after it has passed through the needle valve which is exposed to ambient surrounding. Moreover, while the liquid sample is withdrawing the system pressure can be maintained by adjusting the screw on the system volume regulator. Both the liquid and vapour samples are finally collected in a 10 c.c. sampling bulb at 25 psig. In addition the entire system can be evacuated to 0.1 mm. Hg. before the filling.

2.7 TEMPERATURE AND PRESSURE MEASUREMENT

The temperature at equilibrium can be measured by a potentiometer, Tinsley type 4025, and a protective type copper-constantan thermocouple which extends to the vapour section inside the cell. Crushed ice has been used as a reference junction. Calibration of the thermocouple has been accomplished by the measurement of the vapour pressure of Research grade methane. Previously the thermocouple was calibrated against a standard platinum resistance thermometer. It was found that there was a 1.1°F difference at -150°F between the two methods. The vapour pressure measurement is thought to be more reliable since in previous calibration heat may conduct through the protecting tube of the thermocouple and cause serious error. A discussion of this error will be given in Appendix B.

It has been reported (81) that the measurement of the vapour pressure of oxygen should be chosen as a primary standard for calibration of the thermocouple. In this study the system temperature is above the critical temperature of oxygen. Therefore methane has been chosen as a secondary standard for the calibration.

The pressure can be measured by either one of the two Bourdon-type test gauges. The range of one gauge is 0 - 600 psig

with 2 psi per division and the other, 0 - 1500 psig with 5 psi per division. These gauges had been previously tested against a dead-weight tester in the laboratory of the Mining Branch, Ottawa.

The calibration curves of the thermocouple and the pressure gauges are both shown in Appendix C.

PART III EXPERIMENTAL DETAILS

The existing vapour-liquid equilibrium data for the system containing nitrogen methane ethane are listed in Table 1.

The conditions investigated in this study are listed below:

System	Temperature °F	Pressure psia	No. of Runs
N_2 - CH_4	-151.1	36 - 750	10
N_2 - C_2H_6	-151.1	10 - 500	8
CH_4 - C_2H_6	-151.1	10 - 350	12
N_2 - CH_4 - C_2H_6	-151.1	200	7
N_2 - CH_4 - C_2H_6	-151.1	300	8
N_2 - CH_4 - C_2H_6	-151.1	400	7

3.1 MATERIALS

The materials used in this study were obtained from Matheson of Canada, Ltd., Whitby, Ontario. Their minimum purities are listed as follows:

	Minimum Purity, mol %	
	Research Grade	CP Grade
Nitrogen	99.999	99.7
Methane	99.99	99.0
Ethane	99.9	99.0

These materials were used in this study without any further purification.

Table 1

Sources of Vapour-Liquid Equilibrium Data Containing Nitrogen, Methane and Ethane

System	Reference	Approx. Temp. Range, °F	Approx. Press. Range, psia
Nitrogen-Methane	(75)	-298 to -220	15 to 150
Nitrogen-Methane	(17)	-280 to -150	15 to 650
Nitrogen-Methane	(12)	-295 to -117	15 to 735
Nitrogen-Methane	(39)	-298 to -259	14.7
Nitrogen-Methane	(25)	-291 to -124	14.7 to 700
Nitrogen-Ethane	(25)	-260 to 40	14
Nitrogen-Ethane	(52)	-200 to 50	100 to 1300
Nitrogen-Ethane (3 points in total)	(18)	-200° F and -100° F	500 and 1000
Methane-Ethane	(25)	-200 to 32	8 to 970
Methane-Ethane	(57)	-120 to -10	74 to 295
Nitrogen-Methane-Ethane (5 points in total)	(18)	-200° F and -100° F	500 and 1000

3.2 OPERATING PROCEDURES

Routine operation of the equilibrium apparatus started with the cell at room temperature and the entire system under vacuum. First a relatively larger than normal amount of refrigerant was forced through the refrigeration coil inside the cryostat to attain a nearly desired temperature. Then the cryostat was filled with bath liquid - isopentane, the stirrer was turned on and the system was allowed to cool down. As soon as the desired temperature was reached, then the refrigerant vapourization rate reduced to a certain level, which was a little more than needed to maintain the system temperature. The temperature controller was then turned on, the constant heater load was adjusted to secure the optimum control.

Precalculated quantities of hydrocarbons were introduced into the system and liquefied inside the cell, the lightest component, nitrogen, was introduced through the circulation loop. The return line from the volume regulator was closed and nitrogen was allowed to bubble slowly through the liquid hydrocarbon. The charging valve was kept open with the pressure regulator preset at a certain value. As soon as the desired pressure was reached, the circulation was

continued for 10 to 15 minutes, then the charging valve was closed while circulation was continued. With this procedure it was found that the pressure usually could be maintained at a level within $\pm$ 1 psi through the run. The advantage of this technique was that equilibrium could be reached one hour sooner than the case where a premixed mixture was introduced for each run.

After two or more hours of operation, the circulation was stopped for a short while and the temperature and pressure were recorded. The circulation was resumed, the sample was then taken and analyzed for composition.

3.3 TIME REQUIRED TO REACH EQUILIBRIUM

A rough indication for equilibrium was given by the pressure gauge but this was not a sensitive means. During the test run period of this study a few samples were collected after one hour of circulation and analyzed for composition. The composition was found to be constant within the experimental error. The time required for reaching equilibrium varies from the two-eight hours, reported by Benhum for hydrogen, nitrogen, hydrocarbon systems (5) to six minutes, reported by Wilson for argon-oxygen-nitrogen system (81).

3.4 ANALYTICAL METHOD

The mass spectrometric method, in general, is supposed to be the best method for this type of study but no such instrument was available here at the moment. Therefore the best choice for composition analysis was by means of gas chromatography. A Type-J column six feet long, filled with 28 - 30 mesh silica gel was used and provided satisfactory service. A retention time of six to eight minutes was required for complete separation of the components, nitrogen methane and ethane. Wagner and Weber (84) suggested that the peak area ratios could be plotted against the composition ratio of a known sample. This method was recently modified by Deshpande and Lu (21). Weber's method has shown several advantages over the traditional methods, where usually a knowledge of the absolute peak areas was required. Should any fluctuations occur in detector current, temperature, pressure of the column, carrier gas flow rate, sample quantity, recorder performance, etc., the error would be compensated and would not affect the final result if the ratio plot method was chosen.

A Perkin Elmer Model C Vapour Fractometer combined with a Leeds and Northrup Model 6000 S potentio-recorder and a Perkin Elmer Model 194 automatic integrator were used throughout this

study. In general reproducibility was good to $\pm$ 0.5 mol per cent. The accuracy could be improved by repeating the analysis four to five times for one sample then taking the average.

In the case where one constituent in the sample was extremely low, for instance the nitrogen content in the liquid phase, and the ethane content in the vapour phase, repeated analysis method was used to achieve accuracy.

The calibration curves for the binary and the ternary mixtures are shown in Appendix D.

3.5 RESULTS AND CORRELATIONS

A total of fifty-two experimental points have been obtained in this study.

The plots of pressure as a function of the phase composition at constant temperature for the binary systems nitrogen-methane, nitrogen-ethane and methane-ethane are shown in Figures 3, 5, 7 respectively.

The correlation plots of the equilibrium vapourization constant, K, as a function of pressure for the binary systems nitrogen-methane, nitrogen-ethane and methane-ethane are shown in Figures 4, 6, 8 respectively.

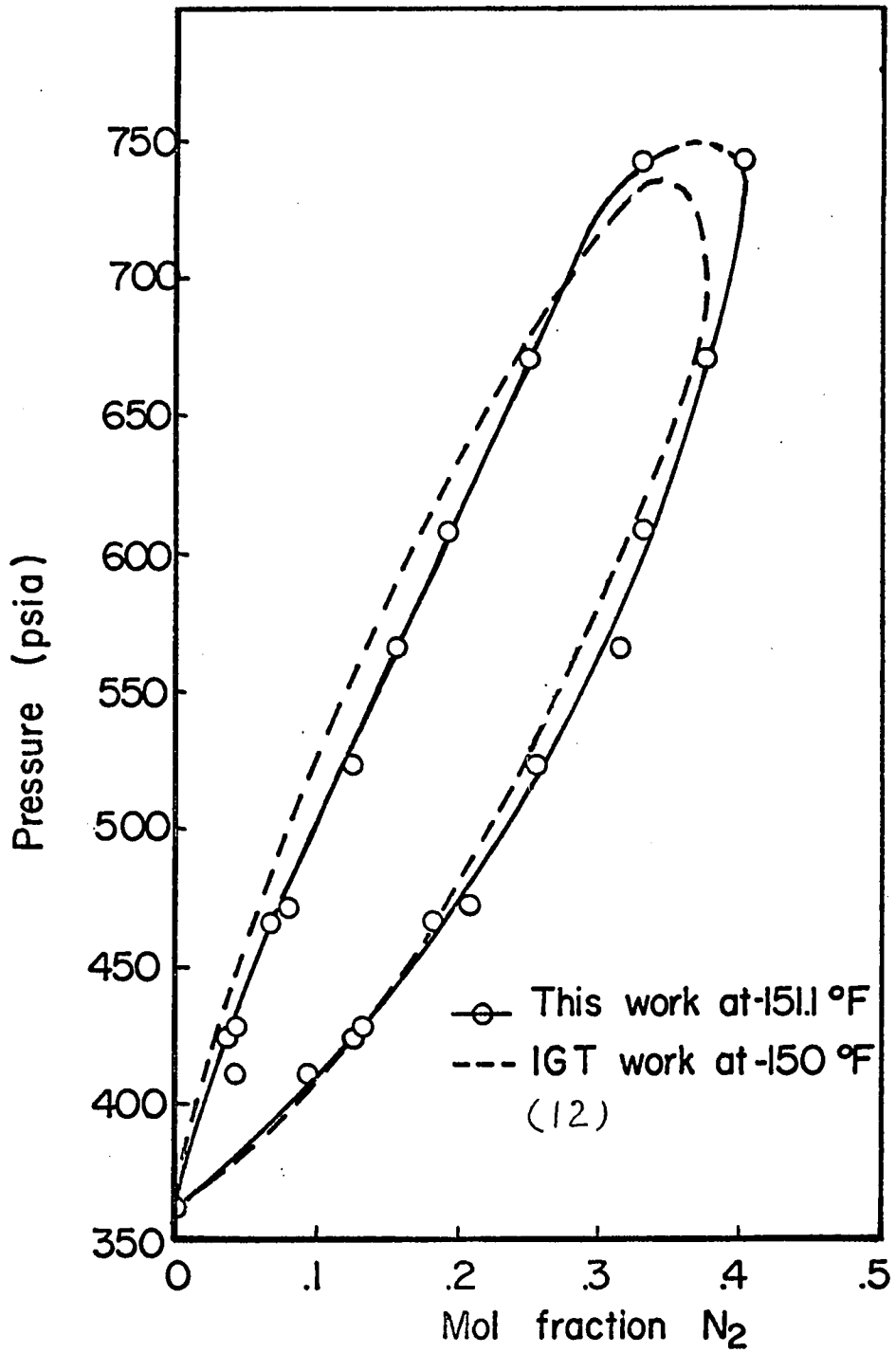


Fig. 3 The p-x-y diagram of the nitrogen-methane system at -151.1 °F.

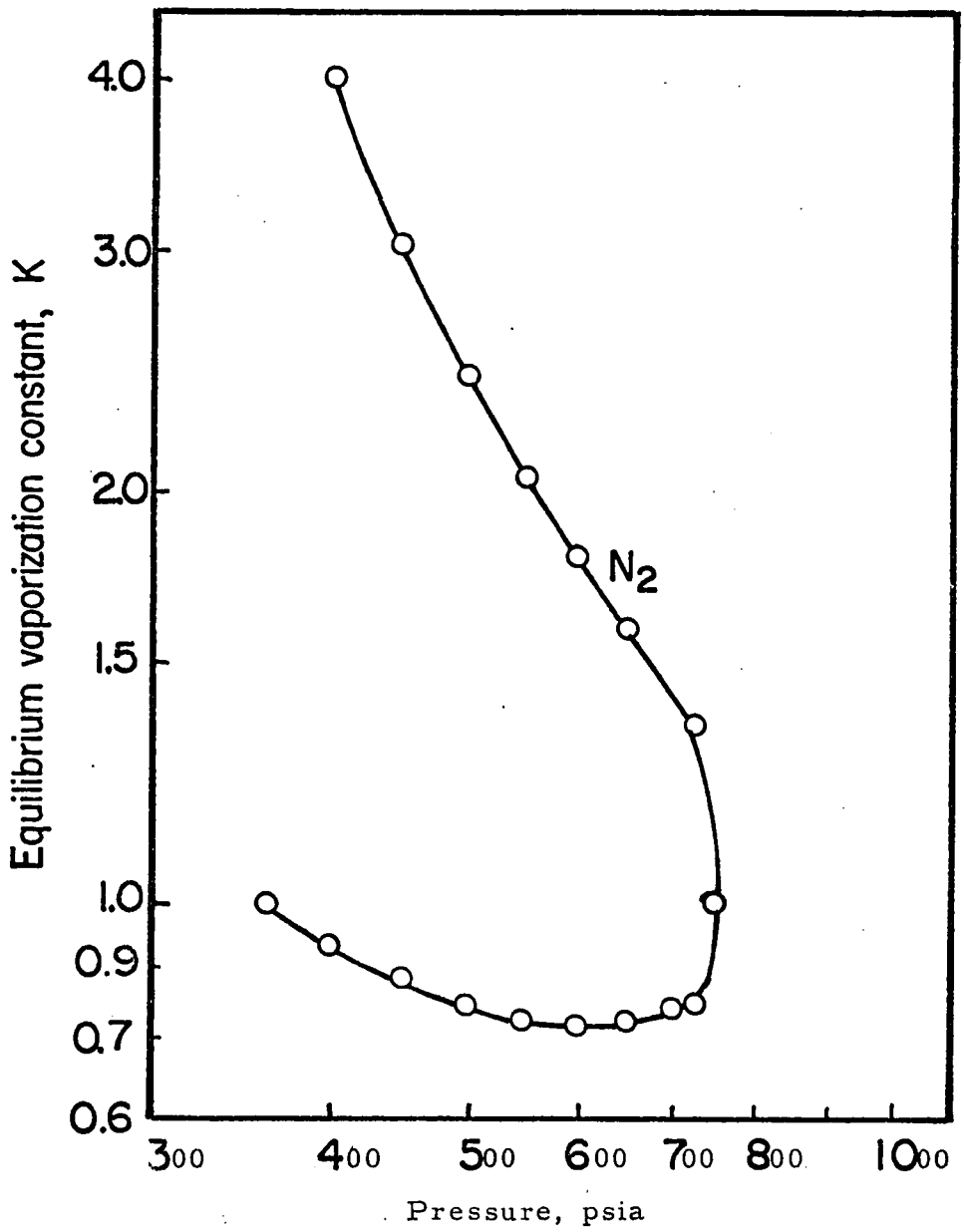


Fig. 4 The K-P diagram of the nitrogen-methane system.

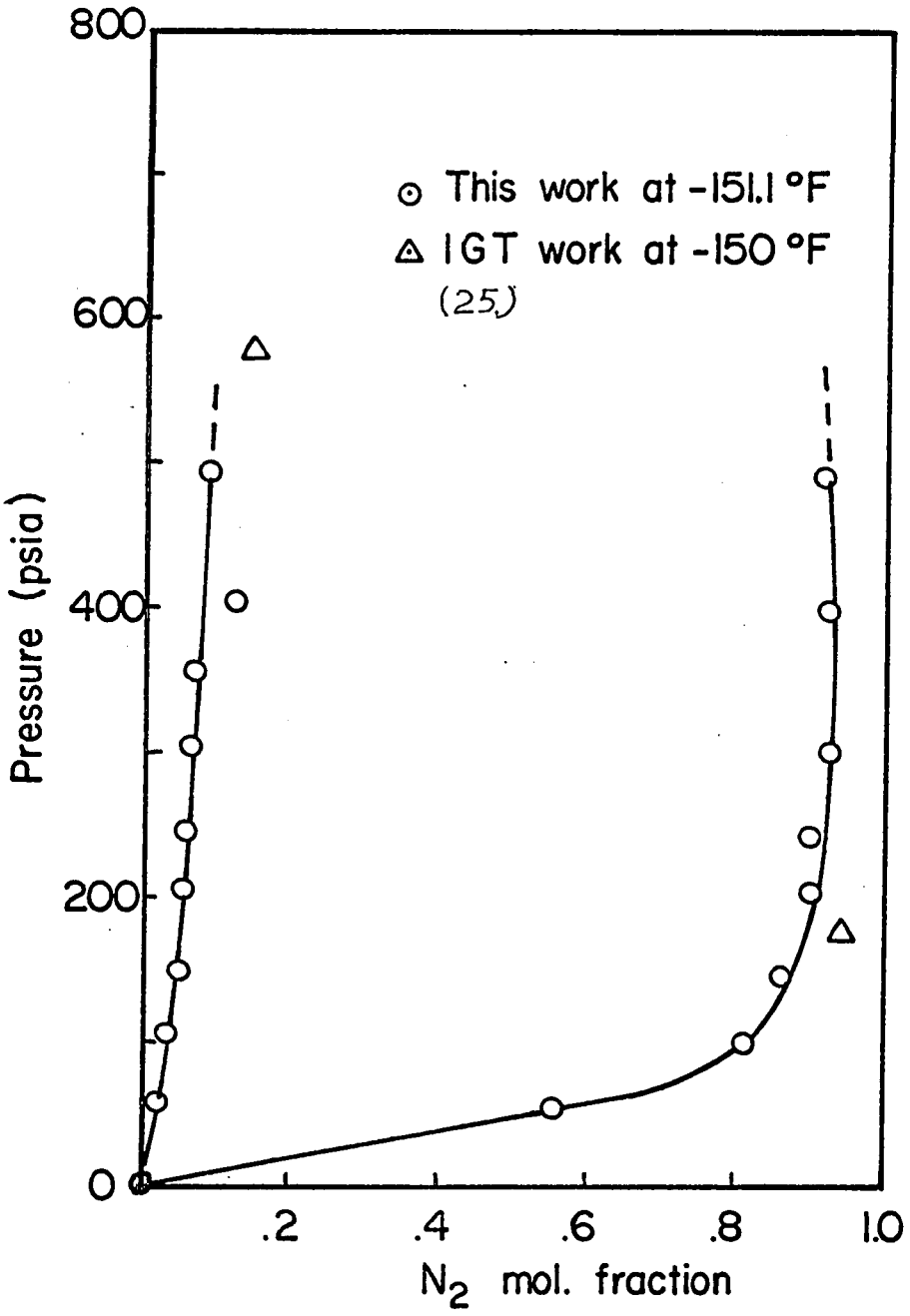


Fig. 5 The P-x-y diagram of the ethane-nitrogen system at -151.1 °F.

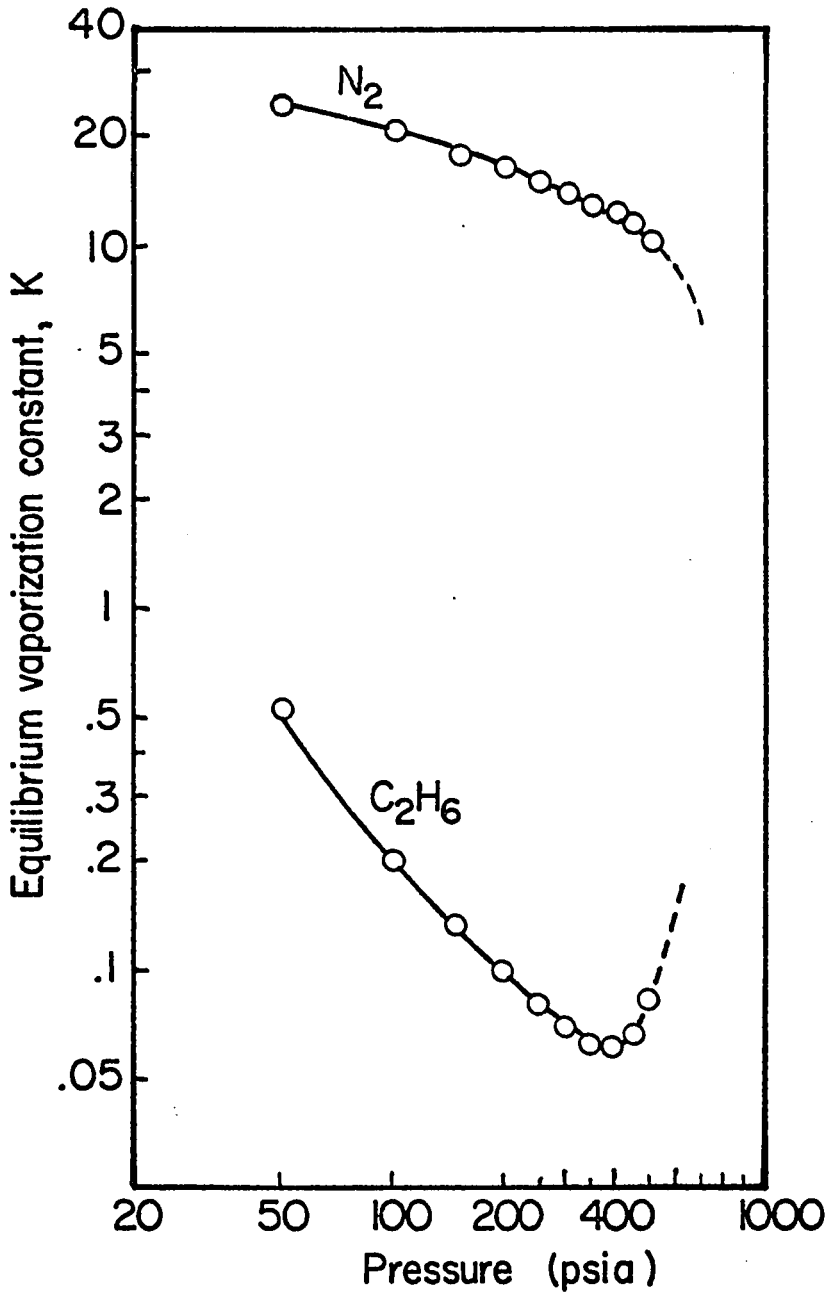


Fig. 6 The K-P diagram of the ethane-nitrogen system at -151.1 °F.

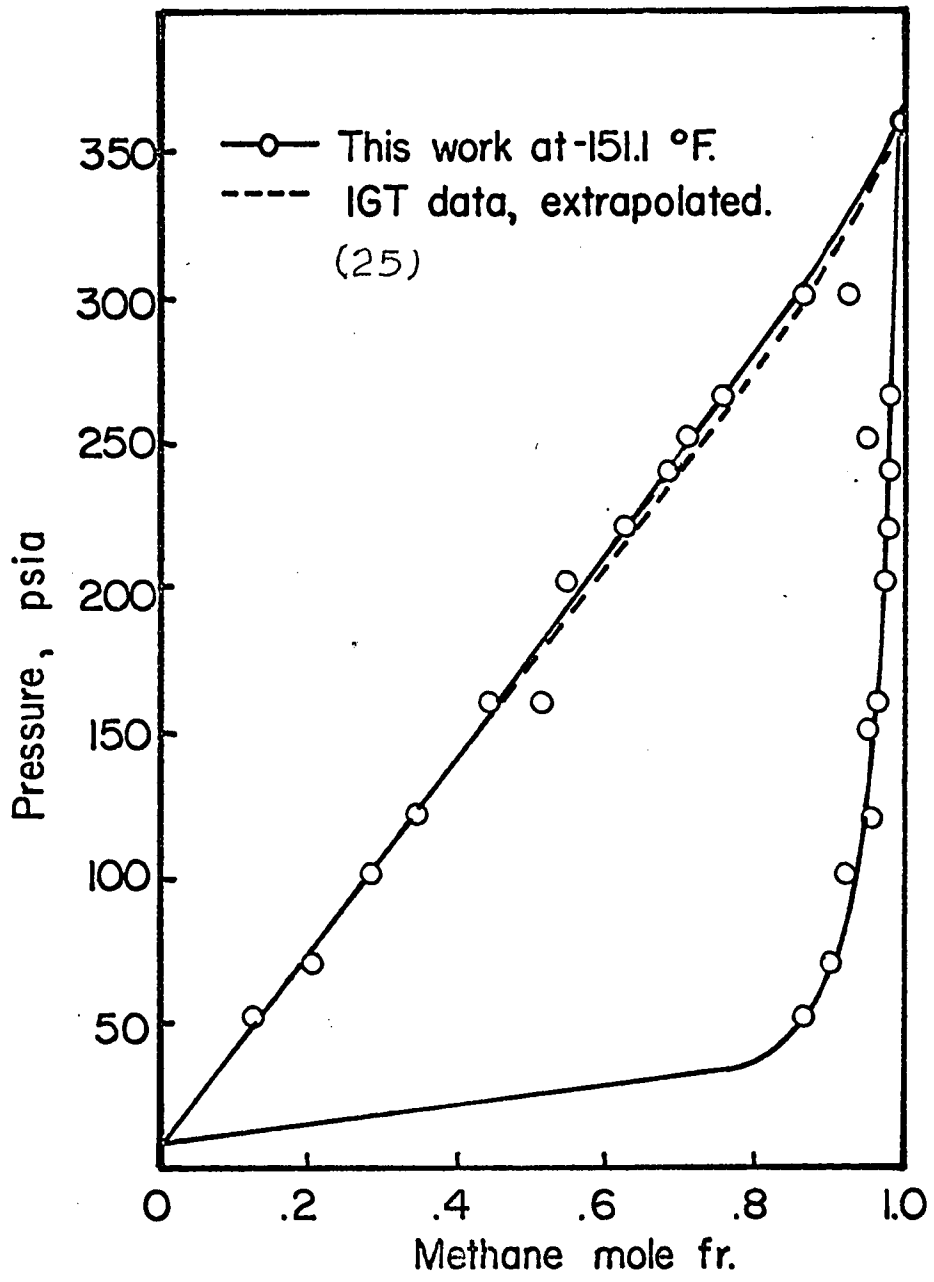


Fig. 7 The P-x-y diagram of the methane-ethane system.

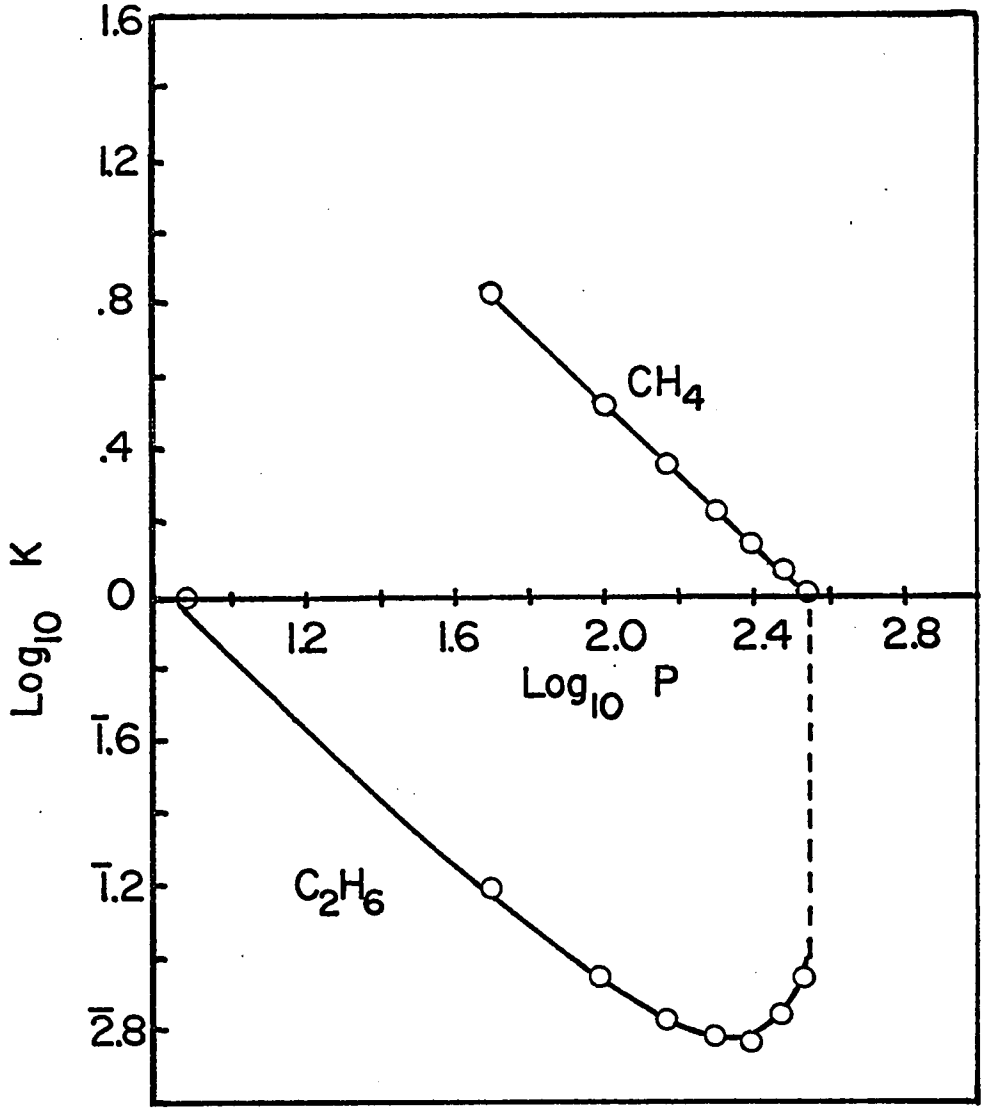


Fig. 8 The K-P diagram of the Methane-Ethane system as a function of pressure at -151.1 °F.

Figures 9, 10, 11 are conventional triangular composition diagrams for the ternary system nitrogen-methane-ethane at constant temperature, -151.1° F, and pressures of 200, 300 and 400 psia respectively.

Figure 12 gives the correlation of equilibrium vapourisation constant K as a function of mole per cent of methane in the liquid phase.

From Figure 12, the equilibrium vapourization constant could be read and replotted in Figure 13, as a function of pressure with mole per cent of methane in the liquid phase as the parameter.

The data taken from Figure 12 are replotted in Figures 9, 10, 11 in the dash lines which show that self consistency has been obtained for these correlations.

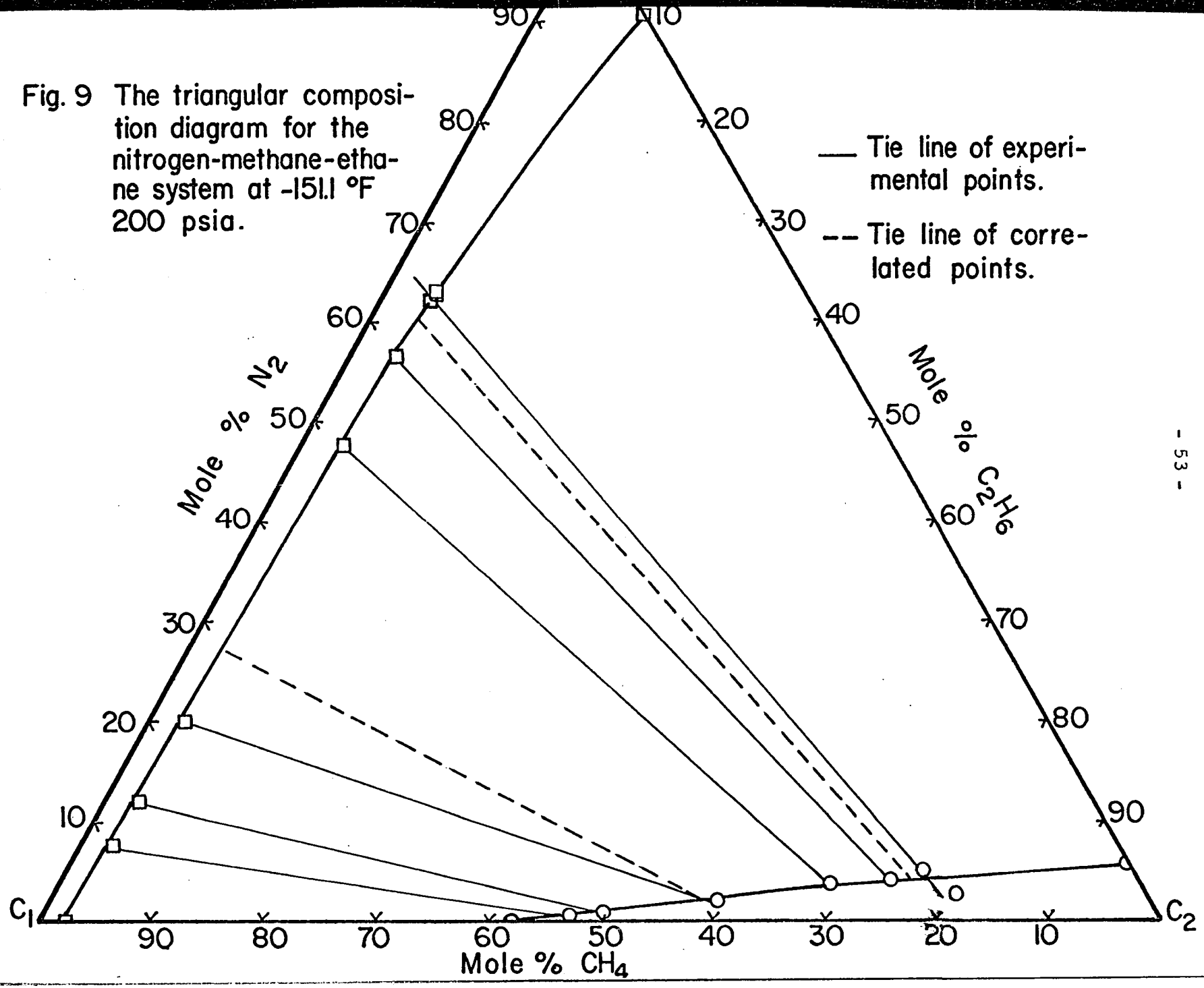


Fig. 9 The triangular composition diagram for the nitrogen-methane-ethane system at -151.1 °F 200 psia.

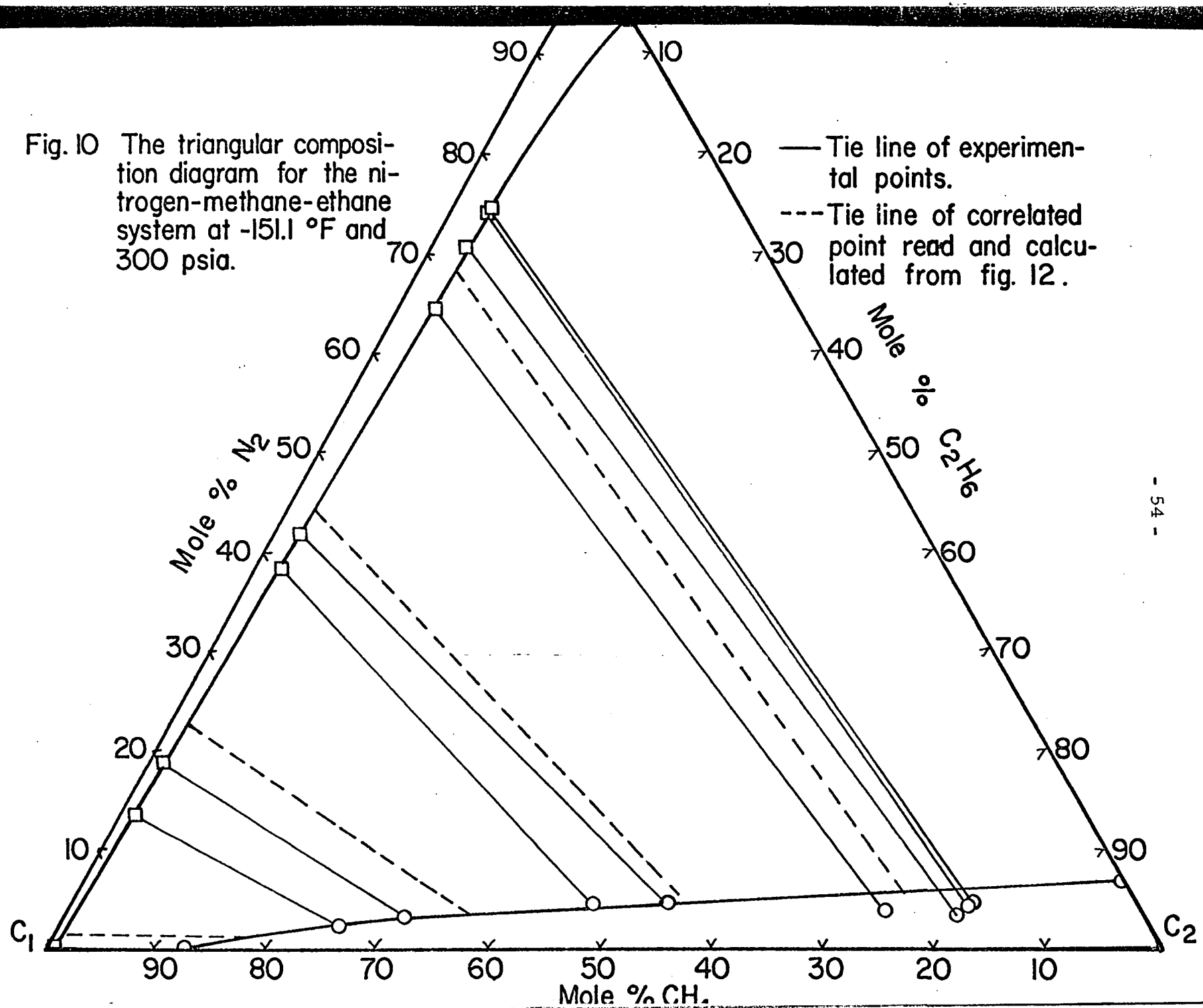


Fig. 10 The triangular composition diagram for the nitrogen-methane-ethane system at -151.1 °F and 300 psia.

—— Tie line of experimental points.

--- Tie line of correlated point read and calculated from fig. 12.

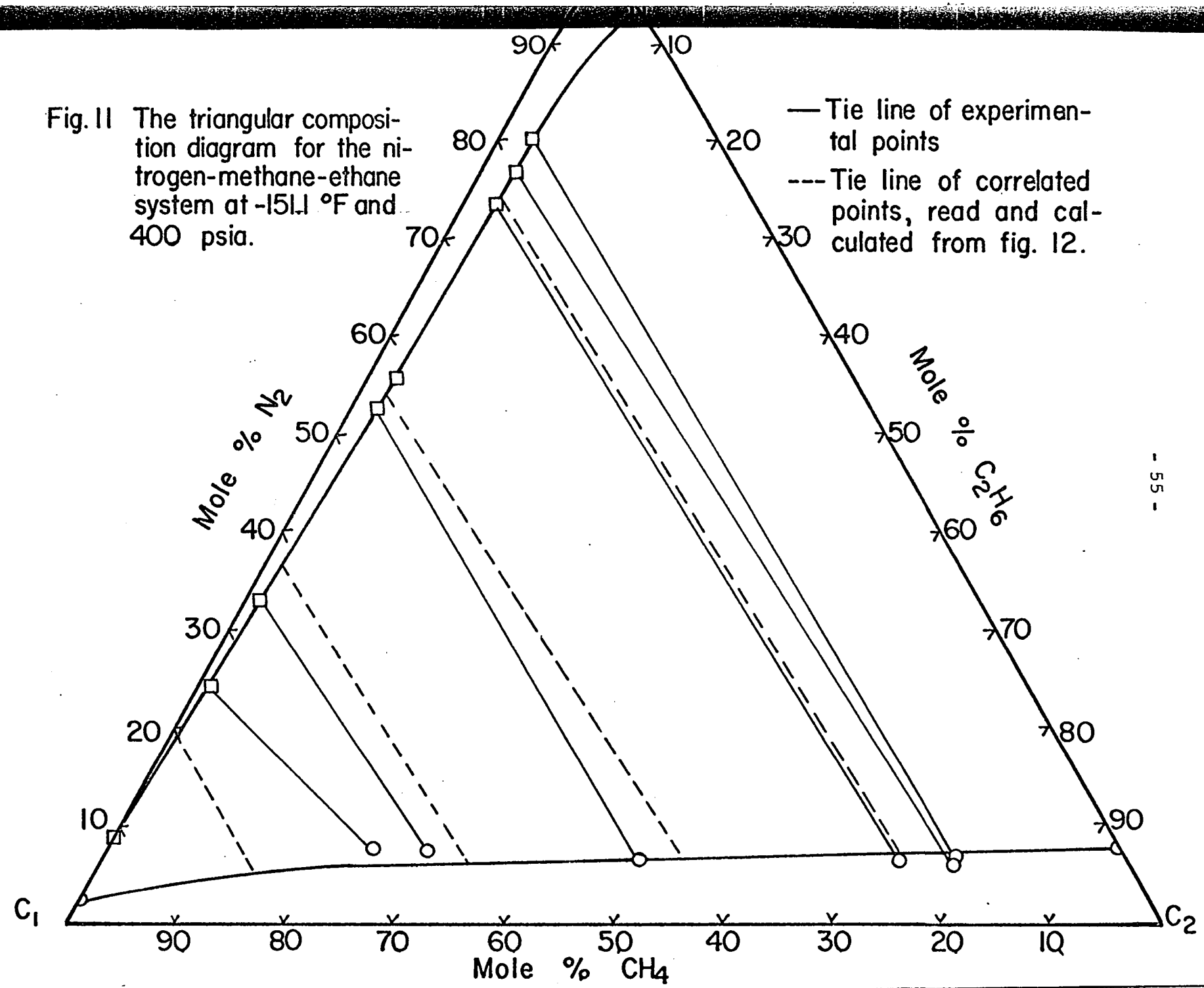


Fig. 11 The triangular composition diagram for the nitrogen-methane-ethane system at -151.1 °F and 400 psia.

— Tie line of experimental points

--- Tie line of correlated points, read and calculated from fig. 12.

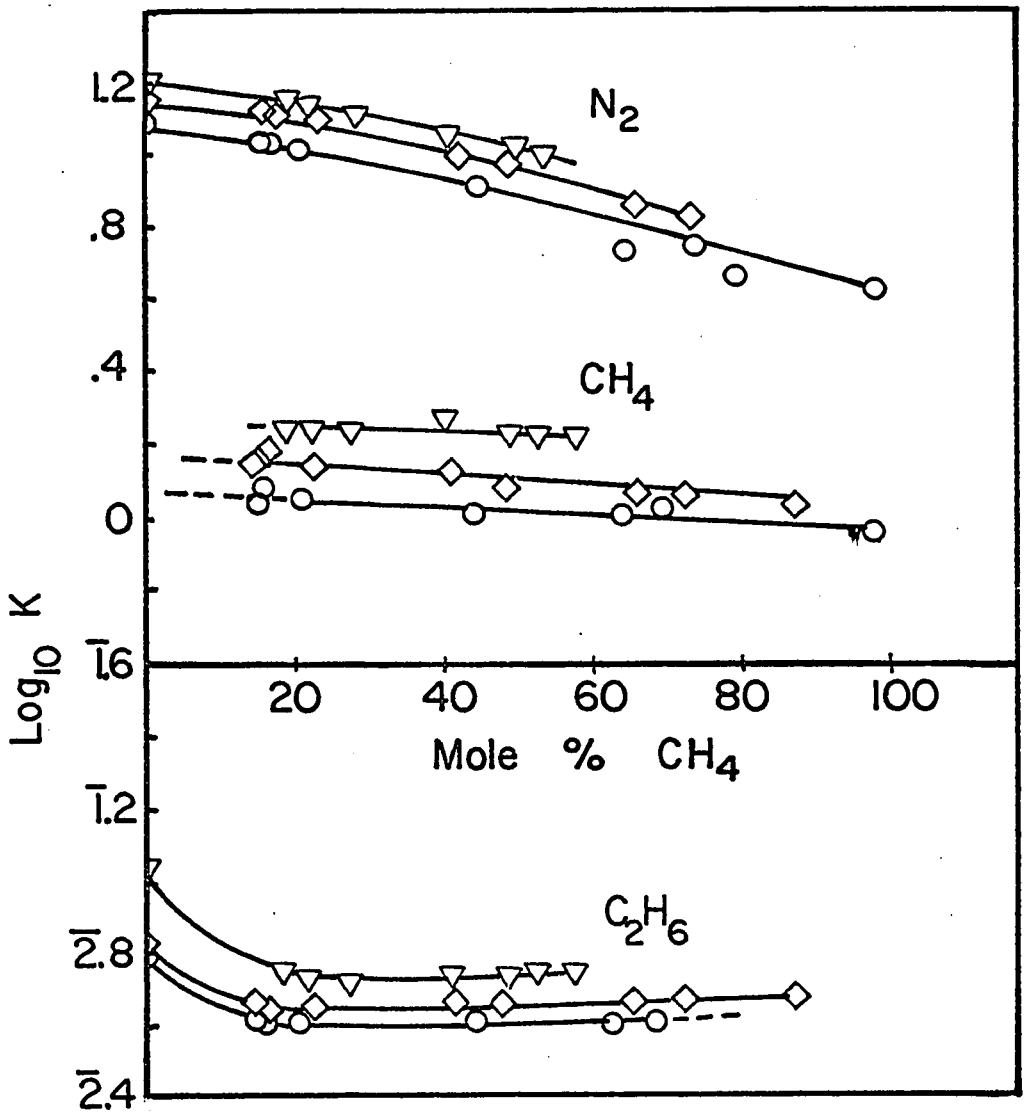


Fig. 12 Equilibrium vaporization constants for constituents in the nitrogen-methane-ethane system at -151.1 °F as a function of the mole percent CH_4 in the liquid phase.

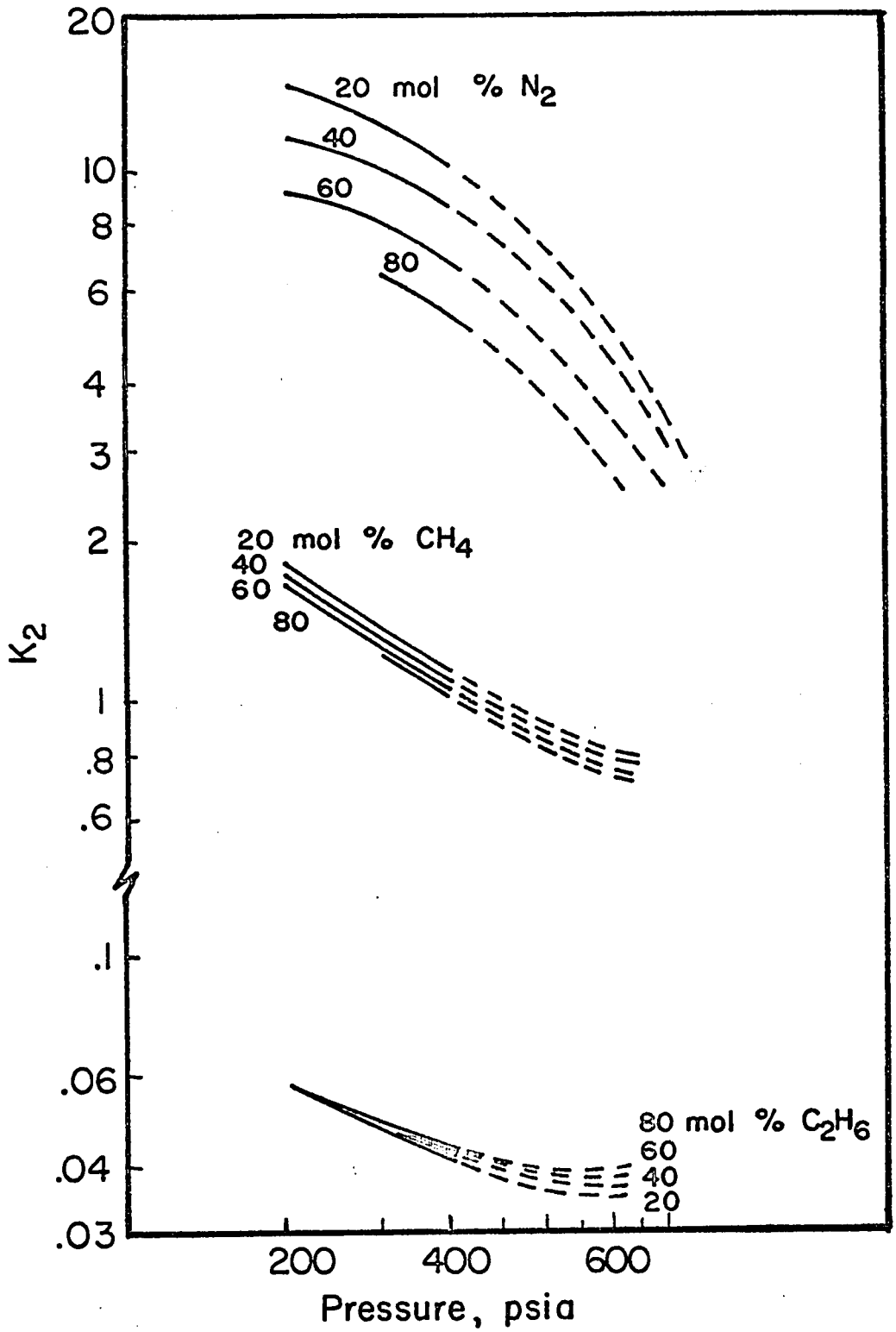


Fig. 13 Equilibrium vaporization constants of the $N_2 - CH_4 - C_2H_6$ system as a function of pressure at -151.1 °F and constant mole % CH_4 in the liquid as a parameter.

PART IV DISCUSSION AND CONCLUSIONS

4.1 SYSTEMS CONTAINING METHANE

Nitrogen, methane and ethane are considered near the simple fluid. Their acentric factors are reported as 1.040, 1.013 and 1.105 respectively by Pizer (45).

The acentric factor is defined (45) by

$$W = - \log P_r - 1.000$$

with P_r, the reduced pressure (P/P_c) at reduced temperature, $T_r = 0.7$. For a simple fluid the acentric factor is unity. The results of this experimental work indicate that the solutions of these components are not so simple. Among the systems studied, only one pair, the methane-ethane system may be considered nearly ideal. The nonideality of the system containing methane has been noted (15) for some time but so far no answer is available. The result of this study would be helpful for the explanation, if the range of investigation could be extended with respect to temperature and pressure.

4.2 PERFORMANCE OF THE APPARATUS

The performance of the apparatus is usually determined by comparing the experimental results with the literature data. The

same approach has been taken in this study. For the methane-ethane system the data of Ellinton (25) are plotted in Figure 7. The agreement is excellent. The plot for the nitrogen-methane system of Figure 3 shows a systematic error when the work of Bloomer (12) and Cines (17) are compared. This is most likely due to different chemicals used in the beginning of this study and it will be discussed later. For the nitrogen-ethane system very few points in the same range have been reported (31) and so comparison of the results is difficult. Furthermore, Bloomer and Ellinton's work (12, 25) was carried out by using the dew point method. For comparison purpose, data collected by different methods are more beneficial because systematic errors of the methods themselves may be avoided.

4.3 CONSISTENCY TEST

A thermodynamic consistency test has not been carried out since the method available (1) for a system with one component above its critical point requires P - V - T data. These data are not yet completely available.

4.4 EFFECT OF IMPURITIES OF CHEMICALS

The chemicals used for this study are of research grade quality except that for the nitrogen-methane system which was collected

in or before October 1965, in that period C.P. grade chemicals were used. Systematic error of the data of nitrogen-methane system between this work and literature may be due to the impurity in the C.P. grade chemicals. A total of eighteen runs of the ternary system, collected in that period showed scattering and have been discarded completely.

4.5 USEFUL EXPERIENCE IN THE DESIGN AND CONSTRUCTION OF THE APPARATUS

In a review of this work one may discover that to collect data at low temperature is a time-consuming operation but to construct such an apparatus is far more difficult than to collect the data. Although the forced-recirculation type apparatus was introduced several decades ago by Dodge and Dunbar (25) experimental techniques were still not perfected. Furthermore, detailed descriptions of the design and operating procedure are usually lacking. This report, which has a complete description of the experience for designing and constructing such an apparatus, would be useful to those who are going to work in this or a related field.

APPENDIX A

Experimental and Smoothed Data of the Systems Containing Nitrogen, Methane and Ethane

Table 2

Experimental Data of the Nitrogen-Methane System at Temperature - 151.1°F

Run Number	Pressure psia	Composition, N_2 mol. fr.	
		Liquid	Vapor
1015 C	411.2	.0434	.09174
824 B	424.2	.0387	.1266
901 C	427.7	.0440	.1342
1015 B	467.2	.06604	.1812
902 A	471.7	.0796	.2095
825 B	522.7	.1274	.2560
901 A	564.7	.1507	.3162
1016 A	607.7	.1948	.3341
901 B	670.7	.2515	.3758
826 B	743.7	.3318	.4030

Table 3

Smoothed Data of the Nitrogen-Methane System at Temperature - 151.1°F

Pressure psia	Composition, N_2 mol. fr.		Equilibrium Constant	
	Liquid	Vapor	K_{N_2}	K_{CH_4}
362	0	0	-	1.000
400	.0207	.0833	4.024	.9361
450	.0555	.168	3.027	.8809
500	.0975	.237	2.431	.8454
550	.1415	.292	2.064	.8247
600	.186	.333	1.790	.8194
650	.230	.366	1.591	.8234
700	.277	.393	1.424	.8400
725	.300	.405	1.350	.8500
750	.375	.375	1.000	1.000

Table 4

Experimental Data of the Nitrogen-Ethane System at Temperature - 151.1°F

Run Number	Pressure psia	Composition, N_2 mol. fr. Vapor	Liquid
1018	56.2	.5564	.02495
1021 A	104.7	.8140	.03795
1019 B	149.2	.8665	.05210
1020 A	204.7	.9081	.05823
1021 C	304.7	.9300	.06228
1022 A	355.7	-	.07307
1020 B	403.7	.9254	.1213
1022 C	494.7	.9184	.08764

Table 5

Smoothed Data of the Nitrogen-Methane System at Temperature - 151.1°F

Pressure psia	Composition, N_2 mol. fr.		Equilibrium Constant	
	Liquid	Vapor	K_{N_2}	$K_{C_2H_6}$
7.38	0	0	-	1.0
50	.020	.488	24.40	.5224
100	.037	.807	21.81	.2004
150	.050	.872	17.44	.1347
200	.056	.905	16.16	.1006
250	.061	.924	15.15	.08094
300	.067	.936	13.97	.06860
350	.072	.942	13.08	.06250
400	.076	.942	12.39	.06277
450	.081	.938	11.58	.06746
500	.089	.923	10.37	.08452

Table 6

Experimental Data of the Binary Methane-Ethane System at Temperature - 151.1°F

Run Number	Pressure psia	Composition, CH_4 mol. fr. Vapor	Liquid
60222-1	51.7	0.8690	0.1244
60223-1	70.2	0.9024	0.2108
60223-2	101.2	0.9255	0.2872
60223-3	130.9	0.9603	0.3491
60223-4	161.2	0.9623	0.5176 (high)
60224-1	201.5	0.9752	0.5486
60224-2	251.7	0.9494 (low)	0.7093
60225-1	219.7	0.9799	0.6251
60225-2	301.7	0.9242 (low)	0.8602
60301-1	158.2	0.9661	0.4453
60304-1	263.2	0.9867	0.7544
60303-1	242.2	0.9811	0.6853

Table 7

Smoothed Data of Binary Methane-Ethane System at Temperature 151.1°F

Pressure psia	Composition, mol. fr. CH_4		$\log_{10} K$	
	Liquid	Vapor	CH_4	C_2H_6
8	0.000	0	-	0
50	.127	.865	0.8332	$\bar{1}$.1892
100	.277	.935	0.5283	$\bar{2}$.9538
150	.423	.961	0.3564	$\bar{2}$.8298
200	.570	.974	0.2328	$\bar{2}$.7816
250	.715	.983	0.1383	$\bar{2}$.7757
300	.859	.990	0.0618	$\bar{2}$.8507
350	.978	.998	0.0088	$\bar{2}$.9586
361	1.000	1.000	0.0000	-

Table 8

Experimental Data of the Ternary Nitrogen-Methane-Ethane System at Temperature -151.1°F

Run No.	Pressure psia	Composition Liquid mol. fr. N_2	CH_4	C_2H_6	Composition Vapor mol. fr. N_2	CH_4	C_2H_6
-	200	.0560	0	.9440	.9050	0	.0950
1110A	199.7	.04082	.2201	.7391	.5628	.3956	.04158
1112A	198.7	.02853	.1686	.8029	.6222	.3368	.04109
1114A	199.2	.009581	.4957	.4948	.1200	.8497	.03357
1116A	200.3	.04912	.1873	.7636	.6241	.3331	.04288
1117A	198.5	.03694	.2751	.6900	.4788	.4838	.03748
60301-2	196.7	.01901	.3888	.5922	.2000	.7661	.03385
60302-2	200.2	.00542	.5258	.4687	.0742	.8937	.03213
-	200	0	.5800	.4200	0	.977	.02300

Table 8 (Continued)

Run No.	Pressure psia	Composition Liquid mol. fr. N_2	CH_4	C_2H_6	Composition Vapor mol. fr. N_2	CH_4	C_2H_6
-	300	.0670	0	.9330	.9360	0	.06400
1111 A	299.7	.03361	.1648	.80164	.7065	.2634	.03008
1112 B	299.7	.04383	.1446	.8116	.7417	.2261	.03213
1114 B	298.7	.04599	.4182	.5358	.4193	.5564	.02436
1116 B	300.2	.04360	.1482	.8082	.7443	.2220	.03371
1117 B	298.5	.03811	.2259	.7359	.6457	.3208	.03350
60302-2	300.7	.04622	.4832	.4706	.3843	.5915	.02421
60303-2	302.7	.03092	.6674	.3016	.1884	.7954	.01625
60304-2	301.2	.02511	.7213	.2535	.1364	.8498	.01387
-	300	0	.8750	.1250	0	.990	.0100

Table 8 (Continued)

Run No.	Pressure psia	Composition Liquid mol. fr. N_2	CH_4	C_2H_6	Composition Vapor mol. fr. N_2	CH_4	C_2H_6
-	400	.07600	0	.924	.9420	0	.0580
1111 B	399.7	.05924	.1564	.7843	.7693	.1989	.03180
1114 C	399.7	-	-	-	.5599	.4148	.02533
1116 C	401.2	.06841	.1503	.7813	.8030	.1669	.03011
1117 C	401.7	.06195	.2071	.7309	.7391	.2330	.02786
60302-3	401.2	.06417	.4455	.4903	.5279	.4504	.02167
60302-3	400.7	.07453	.6324	.2931	.3804	.6025	.01714
60304-3	400.7	.07475	.6805	.2448	.3329	.6511	.01602
-	400	.0207	.9793	0	.0833	.9167	0

Table 9

Smoothed Data of the Ternary Nitrogen-Methane-Ethane System at Temperature -151.1° F

Composition Liquid mol. fr.			Composition Vapor mol. fr.			$\log_{10} K$		
N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6
200 psia								
.056	.000	.944	.905	.000	.095	1.2084	-	$\bar{1}$.0027
.043	.187	.770	.623	.333	.044	1.1610	.2506	$\bar{2}$.7570
.040	.221	.739	.565	.395	.040	1.1500	.2522	$\bar{2}$.7334
.037	.277	.686	.478	.485	.037	1.1113	.2432	$\bar{2}$.7320
.018	.402	.580	.202	.766	.032	1.0500	.2799	$\bar{2}$.7417
.0115	.495	.4965	.121	.856	.028	1.0220	.2378	$\bar{2}$.7512
.0075	.530	.4625	.077	.897	.026	1.0116	.2284	$\bar{2}$.7499
.000	.580	.420	.000	.977	.023	-	.2264	$\bar{2}$.7385

Table 9 (Continued)

Composition Liquid mol. fr.			Composition Vapor mol. fr.			$\log_{10} K$		
N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6
300 psia								
.067	.000	.933	.936	.000	.064	1.1452	-	$\bar{2}$.8368
.057	.145	.798	.752	.212	.036	1.1206	.1650	$\bar{2}$.6533
.056	.150	.794	.745	.219	.036	1.0239	.1644	$\bar{2}$.6565
.054	.170	.776	.701	.265	.034	1.1133	.1928	$\bar{2}$.6416
.051	.230	.719	.646	.322	.032	1.1028	.1461	$\bar{2}$.6485
.042	.418	.540	.419	.556	.024	.9989	.1239	$\bar{2}$.6478
.040	.483	.477	.385	.593	.022	.9834	.0892	$\bar{2}$.6639
.026	.664	.310	.187	.798	.015	.8568	.0799	$\bar{2}$.6847
.020	.730	.250	.137	.851	.012	.8357	.0667	$\bar{2}$.6812
.000	.875	.125	.000	.994	.006	-	.0554	$\bar{2}$.6812

Table 9 (Continued)

Composition Liquid mol. fr.			Composition Vapor mol. fr.			$\log_{10} K$		
N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6	N_2	CH_4	C_2H_6
400 psia								
.076	.000	.924	.942	.000	.058	1.0932	-	$\bar{2}$.7978
.073	.152	.775	.800	.1675	.0325	1.0399	0.0422	$\bar{2}$.6226
.071	.160	.769	.770	.199	.031	1.0353	0.0947	$\bar{2}$.6054
.070	.208	.722	.734	.2365	.0295	1.0206	0.0558	$\bar{2}$.6113
.064	.445	.491	.527	.453	.020	0.9156	0.0076	$\bar{2}$.6099
.060	.641	.299	.333	.655	.012	0.7443	0.0094	$\bar{2}$.6034
.060	.691	.249	.243	.747	.010	0.6075	0.0338	$\bar{2}$.6038
.0207	.9793	.000	.0833	.9167	.000	0.6046	$\bar{1}$.9713	-

APPENDIX B

Estimation of Error in the Calibration of Thermocouples

Two thermocouples of the protective type with stainless steel shell were calibrated in the Calorimetric Laboratory of the Chemistry Department, University of Ottawa, by comparing with a standard platinum resistance thermometer in baths of liquid nitrogen and of dry ice. Later the same thermocouples were re-calibrated by the measurement of vapour pressure of research grade methane. The results showed that the first method gave values 1.1° F higher than the second. The reason may be given in the following section by a mathematical approximation.

A thermal energy balance on a segment Δz of the shell of the thermocouple gives

$$q_z/_z \cdot A - q_z/_{z+\Delta z} \cdot A - h\, 2\pi R \Delta z (T - T_a) = 0 \qquad (1)$$

where q_z = heat flux in z direction, Btu/ft^2 - hr

A = cross-sectional area of the shell, in ft^2

h = convection heat transfer coefficient, in Btu/ft^2 - hr

R = outside diameter of the shell, in ft

T = Temperature reading by thermocouple

T_a = actual temperature.

Simplifying Eq. (1) gives

$$-\frac{dq_z}{dz} = \frac{2\pi Rh}{A}(T - T_a) \qquad (2)$$

Inserting the Fourier law, $q_z = -k\frac{dT}{dz}$ gives

$$\frac{d^2T}{dz^2} = \frac{2\pi Rh}{Ak}(T - T_a)$$

k = thermal conductivity of the shell, Btu/ft - hr

$\theta = \frac{T - T_a}{T_r - T_a}$, dimensionless temperature,

$\zeta = \frac{z}{L}$, dimensionless length,

$\beta^2 = \frac{2\pi Rh L^2}{Ak}$, dimensionless constant,

where L = depth of immersion in ft

T_r = room temperature during calibration in °R

Substituting into Eq. (2) gives

$$\frac{d^2\theta}{d\zeta^2} = \beta^2\theta$$

with the assumption that

(1) $\theta / _{\zeta = 1} = 1$

(2) $\frac{d\theta}{d\zeta} / _{\zeta = 1} = 0$

The thermocouple shell has a cone shape at the end and may be assumed to have no temperature gradient across the end. Then this ordinary differential equation will have the solution (6)

$$\theta = \frac{\cosh \beta (1 - \xi)}{\cosh \beta}$$

or

$$\frac{T - T_a}{T_r - T_a} = \frac{\cosh \beta (1 - \xi)}{\cosh \beta}$$

For a thermocouple with the following dimensions

outside diameter $R_1 = \frac{1}{16} \times \frac{1}{12}$ ft

inside diameter $R_2 = \frac{1}{32} \times \frac{1}{12}$ ft

$h = 10$ Btu/ft^2 - hr

$k = 10$ Btu/ft - hr - °R

$L = \frac{4}{12}$ ft

The values of β may be given by

$$\beta = \sqrt{\frac{2 \left(\frac{1}{16} \times \frac{1}{12}\right) (10) \left(\frac{4}{12}\right)^2}{\frac{1}{144} \left(\frac{1}{16^2} - \frac{1}{32^2}\right) (10)}}$$

or $= 7.4$

or $\cosh \beta \doteq 800$

where $T_r = 535°R$

$T = 140°R$ (Liquid nitrogen)

$= 351°R$ (dry ice)

At $\xi = 1$, $\cosh \beta (1 - \xi) = 1$

Therefore, for liquid nitrogen bath $T_a = 138.2°R$

and for dry ice bath $T_a = 350.8°R$

Hence the errors are 1.8°R and 0.2°R for the nitrogen and the dry ice bath respectively.

Since the heat conductivity of the shell of the standard thermometer, 0.4 Btu/ft - °R - hr (quarts) is very small compared to the heat conductivity of the shell of the thermocouple, 10 Btu/ft - °R - hr (stainless steel) thus it may be neglected. Therefore it agrees fairly well with the experimental discrepancy.

APPENDIX C

Calibration Curves For the Thermocouple and the Pressure Gauges

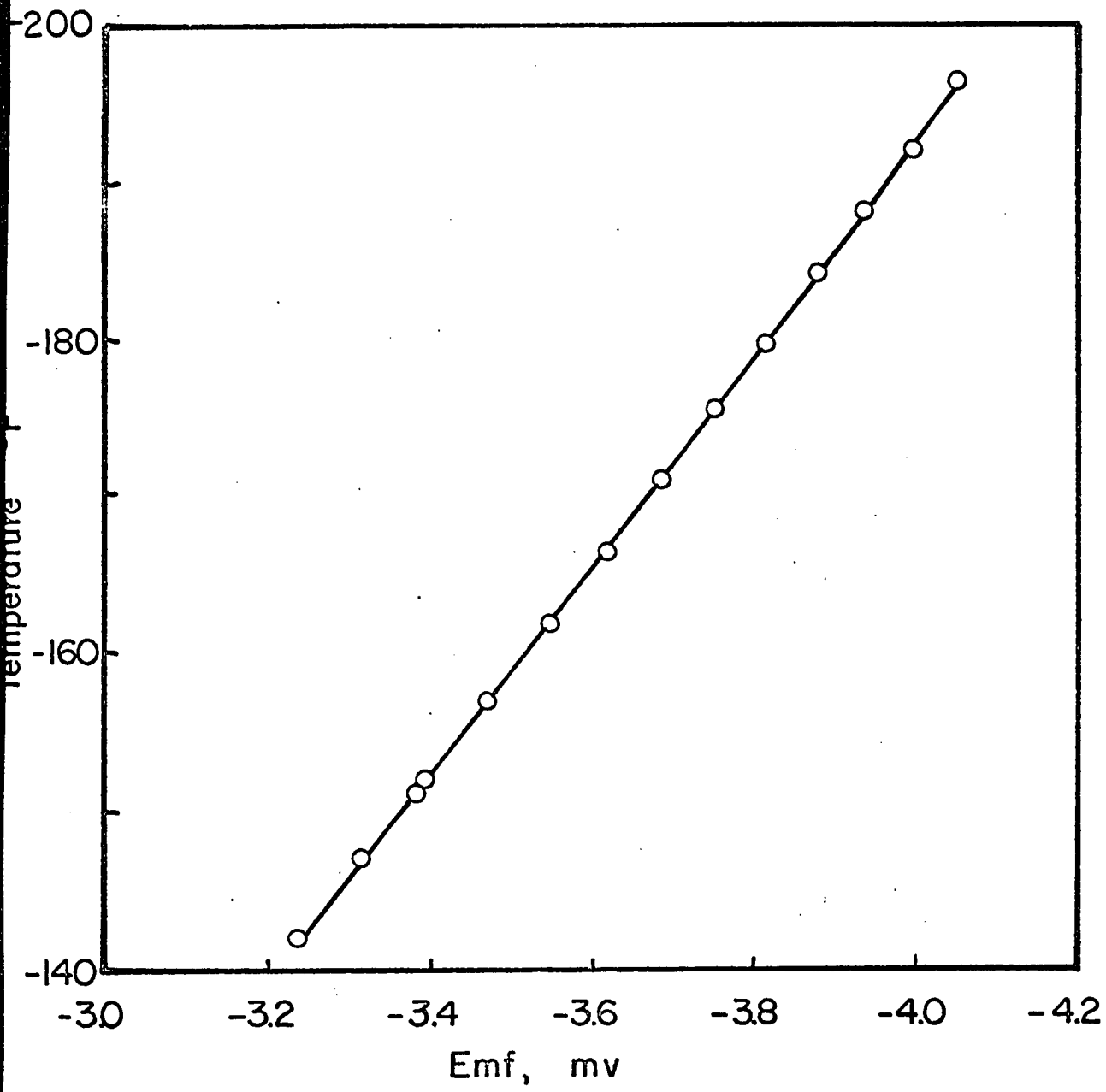


Fig. 14 The calibration curve of the copper-constantan thermocouple (No. 1).

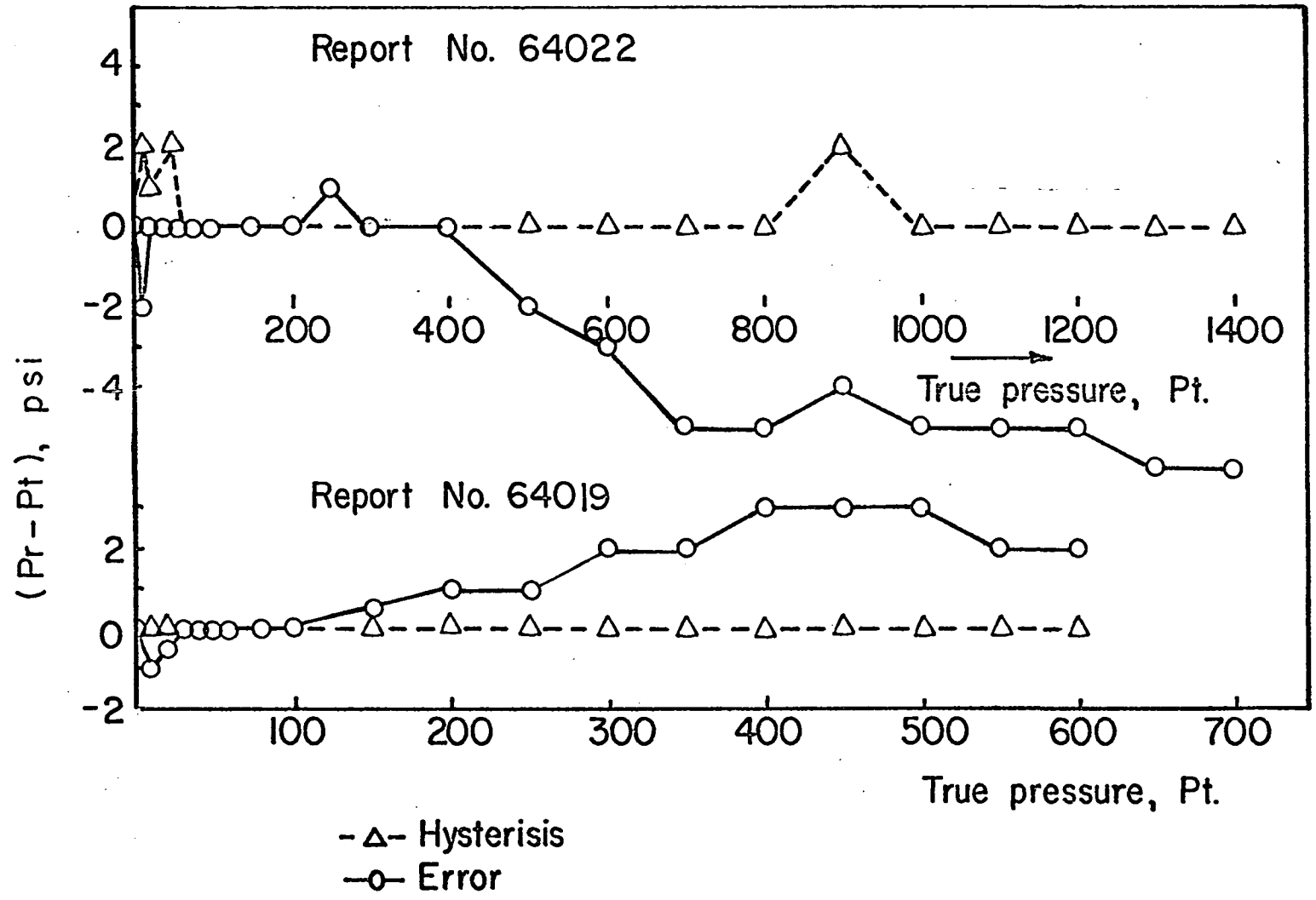


Fig. 15 Calibration plots of the pressure gauge, data taken from report no. 64019, 64022 of Mines Branch, Division of fuel and mining practice, High pressure chemistry Section, Ottawa.

APPENDIX D

Calibration Curves of Vapour Fractometer for the Binary and the Ternary Mixtures

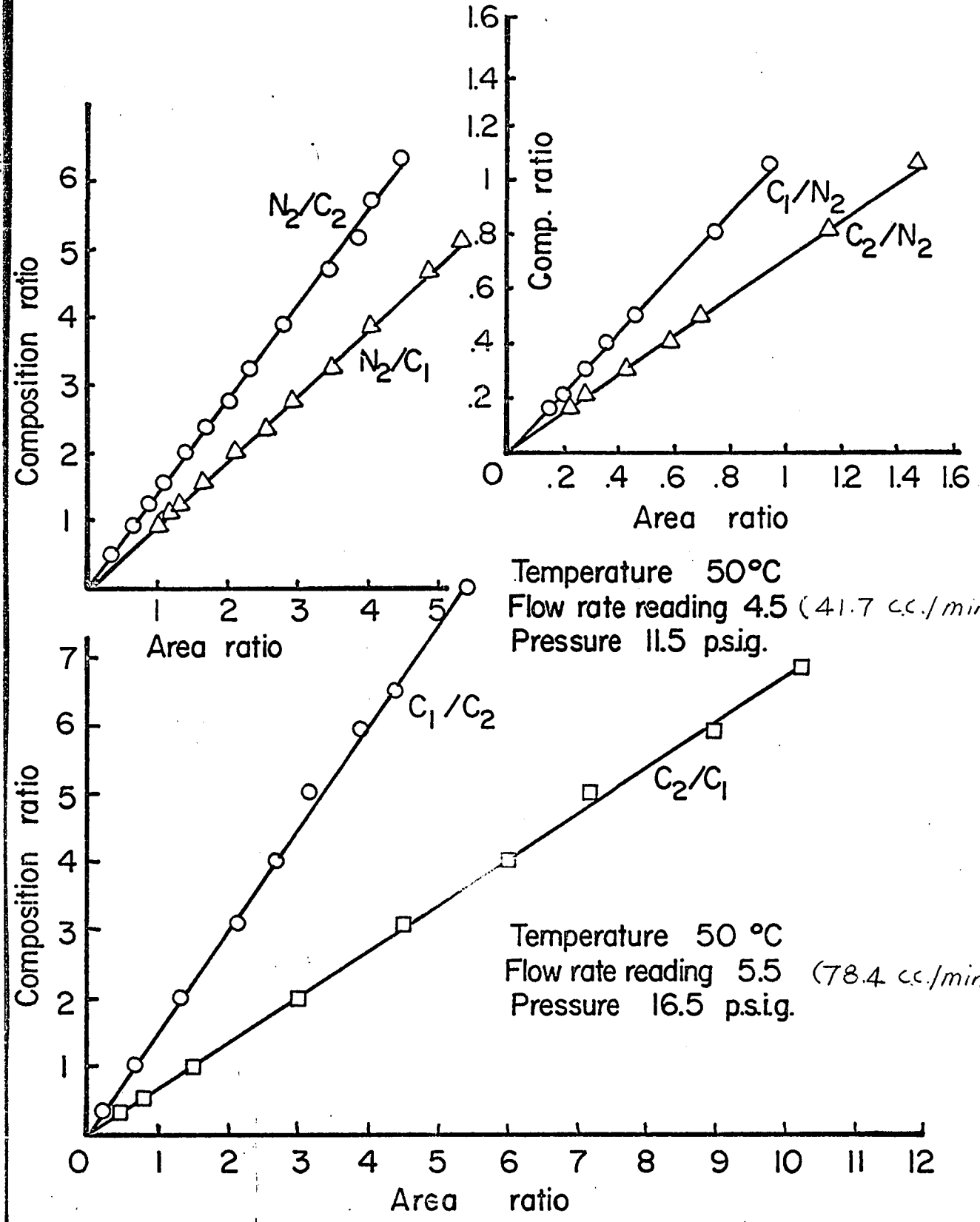


Fig. 16 Calibration curves of vapor fractometer

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