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MEASUREMENT OF SOLID-VAPOR PHASE EQUILIBRIA FOR
THE ARGON-NEOPENTANE SYSTEM

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by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

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ABSTRACT

A gas chromatograph sampling system was designed and constructed to be used in conjunction with existing equipment in order to make accurate measurements of a solid-vapor equilibrium system. The apparatus was then used to take equilibrium data on the argon-neopentane system at temperatures from 200⁰K to 258⁰K and over the pressure range 3.5 atmospheres to 80 atmospheres.

The equilibrium apparatus consisted of a copper equilibrium cell suspended in a constant temperature bath. The bath temperature was controlled by using excess liquid nitrogen refrigeration balanced with a proportionally controlled heater. The neopentane was placed in the cell, the unit was cooled and pressurized to the desired conditions, and argon gas was passed through the cell. Pressures within the cell were measured with one of three bourdon-tube gauges having ranges of 0-100 psig and 0-100 atmospheres. Temperatures were measured with a Leeds and Northrup platinum resistance thermometer. Equilibrium vapor from the cell was then analyzed in a gas chromatograph.

Data taken on the apparatus were analyzed to determine values of the interaction second virial coefficient, B_{12} . The values ranged from -110.74 cc/gmole at 257.906⁰K to -289.48 cc/gmole at 199.618⁰K. Of the mixing rules studied, the rule proposed by Duncan and Hiza (1970) most closely predicted the experimental k_{12} values.

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INTRODUCTION

Phase equilibrium is a fact of life. Its presence is felt in our daily life and in just about every industrial process one can imagine. In order to make wise use of the phenomenon, it is essential that we be able to predict when and to what degree it will occur in a given system. In order to make these predictions we rely on thermodynamics. This section presents a basic overview of the purposes for the research and the thermodynamic methods used to convert the raw data into useable information. A more detailed discussion of the thermodynamic equations is given in the "Theory" section of this report and an excellent presentation may be found in Molecular Thermodynamics of Fluid-Phase Equilibria by J. M. Prausnitz.

A fundamental criterion necessary for solid-vapor equilibrium is,

$$f_1^V = f_1^S \quad (1)$$

where f_1^V = the fugacity of component 1 in the vapor phase,

and f_1^S = the fugacity of component 1 in the solid phase.

For the present we may call the fugacity a measure of non-ideal behavior.

The following definition is made:

$$\phi^V = f_1^V / y_1 P \quad (2)$$

where ϕ^V = the fugacity coefficient,

f_1^V = the fugacity of component 1 in the vapor phase,

y_1 = the mole fraction of component 1 in the vapor phase, and
 P = the system pressure.

Thermodynamics can be used to show that for a solid-vapor system in which the solid phase is assumed to be pure, the following relation holds:

$$y_1 \phi_1 P = f \text{ (pure component 1 properties)} \quad (3)$$

Since the properties of the pure component can be determined, and P and y_1 can be measured, the only unknown quantity left is ϕ_1 , the fugacity coefficient of component 1 in the mixture. It can be shown that,

$$\phi_1 = f(T, P, v, y_1, \text{ and } R) \quad (4)$$

where T = the system temperature

P = the system pressure,

v = the molar volume,

y_1 = the mole fraction component 1, and

R = the appropriate gas constant.

However, in order to evaluate ϕ_1 from such an equation, a mathematical expression relating pressure, temperature, and volume is needed. In order to arrive at such an expression, investigators have employed two different methods of approaching the problem. One method has been to obtain pressure, temperature, and volume data on several systems and then use this data in elaborate equations to "back out" values of equation-of-state constants peculiar to that particular system. Since the constants are determined solely by empirical means they have no physical significance. They just happen to make the equation work.

The second method is based on the reasoning that the way a system behaves is determined ultimately by the system temperature, the pressure,

and some qualities inherent in the nature of the molecules involved. This method of prediction also has its drawbacks, the most obvious of which is the extreme complexity of the molecular interactions. Molecular characteristics may be quantized and combined in such a way as to predict the behavior of several one-component systems but the expression may not hold when applied to a two-component mixture due to the complex interaction of two unlike molecules.

Equations of state seek to predict the exact relation between temperature, pressure, and volume in a system. However, most of these equations are empirical in nature and the constants have little if any physical significance as related to molecular properties. These equations are developed for a pure component and are then extended to mixtures by using mixing rules to determine the appropriate values of the constants. These mixing rules have no physical basis and often do not apply to more than a few systems.

The virial equation of state alleviates these difficulties by using constants and mixing rules which have theoretical significance. The equation is expressed as follows:

$$Pv/RT = 1 + B/v + C/v^2 + D/v^3 + \dots,$$

where P = the system pressure,

v = the molar volume of the gas,

R = the appropriate gas constant,

T = the system temperature,

B = the second virial coefficient,

C = the third virial coefficient, and

D = the fourth virial coefficient.

The virial coefficients are not functions of pressure and for pure component systems are functions of temperature only. They are theoretically based on the intermolecular forces which exist in a real system. When applied to an ideal gas, which by definition has none of these forces, the equation reduces to $Pv = RT$, the ideal gas law. It is then apparent that the terms involving the virial coefficients are simply corrections to the ideal gas law to account for intermolecular attractions. The second virial coefficient accounts for interaction between two molecules, the third virial coefficient accounts for interaction between three molecules, and so on. As the system pressure increases, the mean free path of the molecules decreases, and thus three-molecule interactions become more likely. Also, the molar volume will decrease and the third term in the equation will increase. From this reasoning it follows that the expression, when applied to low pressures, may be truncated after the second term, whereas for higher pressures the third term must be included.

In order to extend the equation to binary mixtures at moderate pressures, a value of B must be used which accounts for all three types of two-molecule interactions (1-1, 2-2, and 1-2). Statistical mechanics has shown this value to be,

$$B_{\text{mix}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}, \quad (6)$$

where y_1 = mole fraction of component 1,

y_2 = mole fraction of component 2,

B_{11} = virial coefficient associated with 1-1 type interactions,

B_{22} = virial coefficient associated with 2-2 type interactions,

B_{12} = virial coefficient associated with 1-2 type interactions,

Applying the virial equation of state for a mixture to equation 1, it is found that,

$$\ln \phi = f(v_{\text{mix}}, y_1, y_2, B_{11}, B_{12}, Z_{\text{mix}}), \quad (7)$$

where v_{mix} = molar volume of the mixture,

y_1 = mole fraction of component 1 in the vapor,

y_2 = mole fraction of component 2 in the vapor,

B_{11} = virial coefficient for interaction of molecule 1 with molecule 1,

B_{12} = virial coefficient for interaction of molecule 1 with molecule 2,

Z_{mix} = compressibility factor for the mixture.

The problem is now one of determining the value of B_{11} and B_{12} . B_{11} is often available in the literature and both B_{12} and B_{11} may be found by using generalized correlations based on corresponding states. These correlations are based on the reasoning that two different components, if at the same reduced temperature and reduced pressure will behave similarly. Correlations relating second virial coefficients to reduced properties of pure components can be extended to apply to mixtures if the values of the reduced properties can be determined. Mixing rules can be applied to determine critical properties of the mixture and the correlations used to determine the value of the second virial coefficient, B_{12} . A mixing rule used to find the critical temperature is as follows:

$$T_{c12} = (T_{c1} T_{c2})^{1/2} (1 - K_{12}), \quad (8)$$

where T_{c12} = the critical temperature of the mixture,

T_{c1} = the critical temperature of component 1,

T_{c2} = the critical temperature of component 2, and

k_{12} = a correction factor.

The correction factor, k_{12} , is in turn related to the various characteristics of the molecules involved. Several expressions have been formulated to predict the value of k_{12} , however more experimental data are necessary if improvements are to be made in these expressions.

Herein lies the purpose of the present research. The experimental apparatus was designed to enable the investigator to determine the temperature, pressure, and composition of a binary mixture at equilibrium. In the first system analyzed, gaseous neopentane was injected into an equilibrium cell and cooled with liquid nitrogen until the neopentane solidified on the trays within the cell. Argon gas was then passed over the neopentane at a known pressure until equilibrium was reached. The equilibrium vapor was then analyzed on a gas chromatograph. Using the data obtained from the experiments and various thermodynamic equations of the general form:

$$B_{12} = (y_1, y_2, P, T, B_{11}, \text{ and } B_{22}), \quad (9)$$

Values of B_{12} for the argon-neopentane equilibrium system were determined. These values of B_{12} were then compared to existing generalized correlations and the appropriate value of k_{12} was calculated. This information, in conjunction with a detailed knowledge of the argon and neopentane molecules will enable future investigators to more exactly explain intermolecular interactions, and therefore phase equilibria, using fundamental molecular properties.

THEORY

An early thermodynamicist, J. W. Gibbs, reasoned that when two phases are brought into contact, they tend to a state of equilibrium in order to make some quantity identical in both phases. This abstract quantity he termed the "chemical potential", μ . If the different phases have different values of μ , they tend to rearrange themselves until the values are equal. Therefore a necessary condition for phase equilibrium is,

$$\mu_i^\alpha = \mu_i^\beta \quad (10)$$

where μ_i^α = the chemical potential of component i in the α phase, and

μ_i^β = the chemical potential of component i in the β phase.

Later, G. N. Lewis related the abstract term "chemical potential" to something measurable through the equation,

$$\mu_i - \mu_i^0 = RT \ln \frac{P}{P^0} \quad (11)$$

where μ_i = the chemical potential at the given conditions

μ_i^0 = the chemical potential at some standard conditions,

R = the appropriate gas constant,

T = the absolute temperature,

P = the system pressure, and

P^0 = a standard pressure.

Lewis, then, found that the abstract chemical potential is related to a simple logarithmic function of pressure, an easily measured quantity.

Lewis had used the ideal gas law to develop Equation (11) and therefore to extend the relation to non-ideal situations, he introduced another term called "fugacity", f . His new relation then became

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0} \quad (12)$$

where f_i = fugacity of component at the given conditions,

f_i^0 = fugacity of component at a standard state,

and applied to all phases of any composition, whether ideal or not. For a component in an ideal gas mixture, the fugacity equals the partial pressure ($y_i P$). Since ideal behavior is approached by all systems at very low pressures,

$$\frac{f_i}{y_i P} \longrightarrow 1.0 \quad \text{as} \quad P \longrightarrow 0$$

The ratio f_i/f_i^0 is termed the "activity" and provides a measure of the difference between a component's chemical potential at a given state and its chemical potential at its standard state, provided the temperatures are the same.

When Equation (12) is combined with Equation (10) it can be shown that,

$$f_i^\alpha = f_i^\beta \quad (13)$$

where f_i^α = fugacity of component i in the α phase, and

f_i^β = fugacity of component i in the β phase.

When dealing with solid-vapor equilibrium systems, it is usually assumed that the solubility of the gaseous component in the condensed phase is negligible.

Therefore the statement can be made that the fugacity of the component in

the solid phase will be exactly equal to the fugacity of the pure component at the given temperature and pressure. If we term this fugacity f_i^C , the following relation holds:

$$f_i^\alpha = f_i^C, \quad (14)$$

if α is the solid phase and the superscript c implies "condensed phase". From fundamental thermodynamic considerations it can be shown that the following expression holds:

$$RT \ln \frac{f_i^C}{P} = \int_0^P \left(v_i^C - \frac{RT}{P} \right) dP, \quad (15)$$

where R = appropriate gas constant,

T = the absolute temperature,

f_i^C = pure component fugacity at system conditions,

P = the system pressure, and

v_i^C = the molar volume.

If we divide the integration in Equation (15) into two separate integration procedures we have the following:

$$RT \ln \frac{f_i^C}{P} = \int_0^{P_i^0} \left(v_i - \frac{RT}{P} \right) dP + \int_{P_i^0}^P \left(v_i^C - \frac{RT}{P} \right) dP, \quad (16)$$

where P_i^0 = the saturation pressure, and

v_i = the molar volume of vapor.

Since the fugacity of the saturated vapor (the first term on the right hand side) is the same as the fugacity of the solid phase, Equation (15)

can be written as

$$RT \ln \frac{f_i^C}{P} = RT \ln \frac{f_i^O}{P_i^O} + \int_{P_i^O}^P v_i^C dP - RT \ln \frac{P}{P_i^O} \quad (17)$$

Performing the indicated integration assuming v_i^C is not a function of pressure, the following equation results:

$$RT \ln \frac{f_i^C}{P} = RT \ln \frac{f_i^O}{P_i^O} + v_i^C(P - P_i^O) - RT \ln \frac{P}{P_i^O} \quad (18)$$

The term "fugacity coefficient" may be defined at saturation by the relation

$$\phi_i^O = \frac{f_i^O}{P_i^O} \quad (19)$$

Substituting Equation (19) into Equation (18) and rearranging yields

$$f_i^C = P_i^O \phi_i^O \exp \frac{v_i^C (P - P_i^O)}{RT} \quad (20)$$

Again from fundamental thermodynamics the following equation can be derived:

$$RT \ln \frac{f_i}{P} = \int_v^\infty \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T, v, n_j} - \frac{RT}{v} \right\} dv - RT \ln Z \quad (21)$$

where y_i = mole fraction of component i in the vapor phase,

v = system volume,

n_i = number of moles of component i ,

n_j = number of moles of component j , and

Z = compressibility factor of the mixture.

Equation (21) can be solved only if the integral can be evaluated and to do this a relation between pressure, temperature and volume is required. Such information may be acquired either directly from experimental data or by an appropriate equation of state. Unfortunately, accurate P-V-T data are not as plentiful as one might imagine, so equations of state must be relied on quite heavily.

As mentioned in the "Introduction", equations of state may be formulated either by strict theoretical considerations or by mere empiricism. Empirical equations are much more plentiful and in many cases the values of the constants are easily found in the literature. However, if the system under investigation has not been previously studied, there is no guarantee that the equations will even apply.

The most logical, though not always the most convenient, type of equation of state to use is one which is based on the physical characteristics of molecules involved. Ideally, all pertinent characteristics of molecules can be quantized and the values mathematically related in such a way as to predict the value of any one of the P-V-T variables, given the other two. The virial equation of state is such a relation.

$$Z = \frac{PV}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} \dots, \quad (22)$$

where Z = compressibility factor,

P = system pressure,

v = molar volume,

R = the appropriate gas constant,

T = absolute temperature,

B = second virial coefficient,

C = third virial coefficient, and

D = fourth virial coefficient.

The coefficients are designed to be functions of temperature only. The compressibility factor is sometimes defined by a power series expansion in the pressure as well.

This form is:

$$Z = \frac{Pv}{RT} = 1 + B^i P + C^i P^2 + D^i P^3 + \dots \quad (23)$$

The coefficients B^i , C^i , D^i , etc. are also dependent on temperature only. Comparing the two forms of the equation, the coefficients can be related by the following expressions:

$$B^i = B/RT \quad (24)$$

$$C^i = C - B^2 / (RT)^2, \text{ and} \quad (25)$$

$$D^i = \frac{D - 3BC + 2B^3}{(RT)^3} \quad (26)$$

Values of the coefficients B and C for mixtures may be determined by many procedures, only two of which will be discussed here. The first method is to use low pressure P-V-T data along with the definitions:

$$B = \lim_{\rho \rightarrow 0} \left\{ \frac{\partial Z}{\partial \rho} \right\}_T \quad (27)$$

where ρ = density, and

$$C = \lim_{\rho \rightarrow 0} \frac{1}{2} \left\{ \frac{\partial^2 Z}{\partial \rho^2} \right\}_T \quad (28)$$

The virial equation may be rewritten in the form:

$$v \left(\frac{Pv}{RT} - 1 \right) = B + \frac{C}{v} + \dots \quad (29)$$

By using the low pressure data, isotherms can be plotted on a graph of $\left(\frac{Pv}{RT} - 1 \right)v$ versus $\rho = \frac{1}{v}$ and the curves extrapolated to the $\rho = 0$ axis. The intercept with the $v \left(\frac{Pv}{RT} - 1 \right)$ axis will be the value of B and the slope of the line will be C.

The second procedure involves using solid-vapor equilibrium data for the system under investigation. Thermodynamic equations have been derived to predict phase equilibrium values knowing the appropriate constants in a given equation of state. It therefore follows that if we take laboratory data to determine the phase equilibrium values, the equation of state constants can be "backed out" of the thermodynamic equation.

In the present research the second method of analysis has been used. The equation of state chosen was the virial equation due to its physically significant constants. It has been determined by statistical mechanics that the second virial coefficient provides a measure of the non-ideality caused by the interaction of two molecules. Likewise, the third virial coefficient accounts for three-molecule interactions, and so forth. When examining a pure component system, the only type of two-molecule interaction is between two molecules of the same component. However, in a binary mixture, there are three possible types of two-molecule interactions (1-1, 1-2, and 2-2). Similarly, there are four types of three-molecule interactions (1-1-1, 1-1-2, 1-2-2, and 2-2-2). Therefore when referring to the behavior of a mixed system, the value of B or C used in the equation of state will have to be some combination of the individual

values of the constant provided by each type of interaction. Again by statistical mechanics it has been shown that these mixing rules are as follows:

$$B_{\text{mix}} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}, \quad (30)$$

and

$$C_{\text{mix}} = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222}. \quad (31)$$

If we combine Equation (23) with Equation (24) to yield,

$$Z = \frac{Pv}{RT} = \frac{BP}{RT}, \quad (32)$$

we may use Equation (30) to arrive at a form:

$$V = (n_1 + n_2) \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)}, \quad (33)$$

where n_1 = the number of moles of component 1, and

n_2 = the number of moles of component 2.

It has been shown (Abbott & Van Ness, 1972, p. 244) that this equation may be rewritten in the form:

$$f_1^\alpha = y_1 P \exp \left\{ B_{11} + y_2^2 (2B_{12} - B_{11} - B_{22}) \right\}. \quad (34)$$

When applied to a solid-vapor system, Equation (14) and Equation (20) may be combined with Equation (34) to yield the following:

$$y_1 P \exp \frac{P}{RT} \left\{ B_{11} + y_2^2 (2B_{12} - B_{11} - B_{22}) \right\} = P_{1,1}^0 \exp \frac{v_1^c (P - P_1^0)}{RT} \quad (35)$$

From the previous discussion we know that,

$$RT \ln \frac{f_i^0}{p_i^0} = \int_0^{p_i^0} \left(v_i - \frac{RT}{P} \right) dP, \quad (36)$$

or,

$$\phi_i^0 = \exp \frac{1}{RT} \left\{ \int_0^{p_i^0} \left(v_i - \frac{RT}{P} \right) dP \right\}. \quad (37)$$

If the virial equation in the form of Equation (32) is now applied, the following relation holds:

$$\phi_1^0 = \exp \left(\frac{B_{11} p_1^0}{RT} \right). \quad (38)$$

This equation may now be substituted into Equation (35) and the result rearranged to yield:

$$\ln \frac{y_1^P}{p_1^0} = \frac{B_{11} p_1^0}{RT} + \frac{v_1^C (P - p_1^0)}{RT} - \frac{P}{RT} \left\{ B_{11} - y_2^2 (2B_{12} - B_{11} - B_{22}) \right\}. \quad (39)$$

The term y_1^P / p_1^0 is called the "enhancement factor" and measures the ratio of how much partial pressure a component actually exerts in a mixture to how much pressure it would exert if the mixture were ideal.

Equation (39) may be rearranged and solved for B_{12} to obtain:

$$B_{12} = \frac{1}{2Py_2^2} \left\{ B_{11} p_1^0 + v_1^C (P - p_1^0) - P [B_{11} + y_2^2 (-B_{11} - B_{22})] \right\} - \frac{RT}{2Py_2^2} \ln \frac{y_1^P}{p_1^0}. \quad (40)$$

If we know the system temperature and pressure we can obtain values of B_{11} and B_{22} in the literature or from generalized correlations. Values of the molar volume and vapor pressure may be found in a similar way. Then if we analyze the vapor to determine the composition, we can calculate

by Equation (40) the value of B_{12} .

At this point it may be advantageous to stand back and see where our calculations have led us and review where we wanted to go in the first place. Thus far we have shown that in order to predict phase equilibrium behavior of a binary mixture using the virial equation of state we must know an applicable value of B to use in the equation. In order to find this value we must know the value of B for both pure components and an "interaction coefficient", B_{12} . Our goal is to be able to calculate the value of B_{12} from fundamental molecular considerations and then use it to determine phase equilibrium behavior. However in order to develop relations for calculating B_{12} , theoreticians must have at their disposal experimental B_{12} values. The previous discussion has simply shown what laboratory data must be taken and how it must be combined to determine B_{12} values.

Program I in Appendix I was designed to calculate B_{12} values from Equation (40) after the appropriate values of the variables on the right hand side of the equation were supplied. Another method by which B_{12} values were obtained from the experimental data was one proposed by Canfield and Chiu (1967, page 741). The following equation was developed from the virial equation of state containing the second and third virial coefficients:

$$\frac{1}{y_1^2 P} \left[RT \ln \left(\frac{E_2}{\gamma_2^c x_2} \right) - v_2^c (P - P_2^0) + (1 - y_1^2) B_{22} P \right. \\ \left. - B_{22} P_2^0 - \frac{(C_{222} - B_{22}^2) P_2^0{}^2}{2 RT} \right] = (B_{11} - 2B_{12}) + \left\{ \frac{P}{2RT y_1^2} \right. \\ \left. \left[- 3C_{112} y_1^2 - 6C_{122} y_1 y_2 - 3C_{222} y_2^2 + (2C_{111} + 4B_{11} B_{12}) y_1^3 \right] \right.$$

$$\begin{aligned}
& + (6C_{112} + 8B_{12}^2 + 4B_{11}B_{12})y_1^2y_2 + (12 B_{12}B_{22} + 6C_{122})y_1y_2^2 \\
& + (2C_{222} + 4B_{22}^2)y_2^3 - 3B_{11}y_1^4 - 12 B_{11}B_{12} y_1^3y_2 \\
& - (12 B_{12}^2 + 6 B_{11}B_{22})y_1^2y_2^2 - 12 B_{22}B_{12}y_1y_2^3 - 3 B_{22}^2y_2^4 \Big] \Big\},
\end{aligned} \tag{41}$$

where,

$$\gamma_2^c = \frac{f_2^c}{f_2^{0c}}$$

f_2^c = the fugacity of component 2 in the solid phase,

f_2^{0c} = the fugacity of pure component 2 in the solid phase.

E = the enhancement factor.

The entire left hand side of Equation (41) is defined to be "ERT" and the entire right hand side abbreviated to the form:

$$(B_{11} - 2 B_{12}) + OP, \tag{42}$$

where O = a function dependent on virial coefficients and compositions.

Therefore, the final form of the equation is as follows:

$$ERT = (B_{11} - 2 B_{12}) + OP. \tag{43}$$

If a plot of "ERT" versus "P" is made for an isotherm, the curve can be extrapolated to an "optimum extrapolation pressure" (in our case the vapor pressure of neopentane) to determine the value of $(B_{11} - 2 B_{12})$. Using this value of ERT, the corresponding value of B_{12} can be determined. However, as explained by Canfield and Chiu (1967, p. 745), the extreme sensitivity of the function to uncertainties in several variables

at low pressures precludes the use of some low pressure data points. In the present investigation, the pressure below which the data was ignored was chosen to be 20 atmospheres, based on a judicious examination of the data. If all the values on the right hand side of Equation (41) are known, this method provides a convenient graphical technique to determine B_{12} values.

Using two techniques we have now calculated B_{12} values from experimental phase equilibrium data. However, we are still only halfway to our final goal of relating phase equilibrium to basic molecular properties. We must now find an equation which can predict these values using only molecular properties.

One method of predicting B_{12} values is to apply the Theory of Corresponding States. It has long been known that two different pure components, when at the same reduced temperature and pressure, behave similarly. Therefore, the behavior of different components can be "generalized" by considering the conditions not in terms of absolute temperatures and pressures, but rather in terms of reduced temperatures and pressures. These generalizations may be applied to virial coefficients. It has been shown (Prausnitz, 1969, p. 122) that the following relations holds for many simple molecules:

$$\frac{B_{11}}{v_c} = f\left(\frac{T}{T_c}\right), \quad (44)$$

where B_{11} = second virial coefficient of a pure component,

v_c = the critical volume,

T = absolute temperature, and

T_c = critical temperature.

This form was expanded by McGlashan, Potter, and Womold (1964) to include a third variable, n . The following relation has been shown to apply for a wide range of simple hydrocarbons and inert gases:

$$\frac{B_{11}}{v_c} = 0.430 - 0.886 \left(\frac{T}{T_c}\right)^{-1} - 0.694 \left(\frac{T}{T_c}\right)^{-2} - 0.0375 (n-1) \left(\frac{T}{T_c}\right)^{-4.5}, \quad (45)$$

where n = the number of carbon atoms.

It has been proposed by Pitzer and Curl (1957) that the inclusion of another variable, the acentric factor, ω , significantly improves the predictive capabilities of the Corresponding States Theory. The acentric factor is defined as follows:

$$\omega = -\log_{10} \left(\frac{P^S}{P_c} \right)_{\frac{T}{T_c} = 0.7} - 1.000 \quad (46)$$

where ω = acentric factor

P^S = the saturation vapor pressure,

P_c = the critical pressure,

T = absolute temperature, and

T_c = the critical temperature.

The proposed equation is as follows:

$$\begin{aligned} \frac{B_{11}P_c}{RT_c} = & (0.1445 + 0.073 \omega) - (0.330 - 0.46 \omega) \left(\frac{T}{T_c}\right)^{-1} - (0.1385 + 0.50 \omega) \left(\frac{T}{T_c}\right)^{-2} - (0.0121 + 0.097 \omega) \left(\frac{T}{T_c}\right)^{-3} \\ & - (0.0073 \omega) \left(\frac{T}{T_c}\right)^{-8}. \end{aligned} \quad (47)$$

Each of the above equations has been shown to apply to a wide variety of pure components, and they should apply to mixtures as well. In order to make such an extension, the values of the variables in the equations must be representative of the mixture rather than of either of the pure components. In order to determine these values, "mixing rules" are used. These rules dictate how the values of the pure component variables should be combined to arrive at a value applicable to the mixture. The accepted rule for the value of n_{12} to be used in Equation (45) is,

$$n_{12} = \frac{1}{2} (n_1 + n_2) \quad (48)$$

A proposed method of calculating P_{c12} (Prausnitz, 1969, p. 129) to be used in Equation (47) is

$$P_{c12} = \frac{Z_{c12}^{RT} c_{12}}{v_{c12}} \quad (49)$$

where Z_{c12} = compressibility factor of the mixture at the critical subject to Equation (50).

$$Z_{c12} = \frac{1}{2} (Z_{c1} + Z_{c2}) \quad (50)$$

where Z_{c1} = compressibility factor of component 1 at the critical point and

Z_{c2} = compressibility factor of component 2 at the critical point.

For normal fluids, the values according to Pitzer are as follows:

$$Z_{c_i} = 0.291 - 0.08 \omega_i \quad (51)$$

A proposed mixing rule for the acentric factor is as follows:

$$\omega_{12} = \frac{1}{2} (\omega_1 + \omega_2) \quad (52)$$

These mixing rules have been proposed simply because they appear to work

in certain cases, however, rules for these and other variables may be formulated by using fundamental molecular properties and statistical mechanics.

Statistical mechanics has been used to derive expressions relating second virial coefficients to the potential energy between the two molecules involved. It is known that the following relation holds (Prausnitz, 1969, p. 97):

$$B = 2 \pi N_A \int_0^{\infty} (1 - e^{-\mathcal{U}(r)/kT}) r^2 dr \quad (53)$$

where B = the second virial coefficient,

N_A = Avagadro's number,

$\mathcal{U}(r)$ = potential energy function,

r = distance between molecular centers, and

k = Boltzmann's constant.

The value of B calculated from the previous equation will apply only to the interaction between the two molecules under consideration. In a binary mixture where three types of two-molecule interactions occur, the values due to each type of interaction must be combined to get an overall value of B . As was shown before, the applicable combining rule is:

$$B_{\text{mixture}} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_j^2 B_{jj} \quad (54)$$

In order to arrive at a value of B_{ii} , B_{jj} , or B_{ij} , the integral of Equation (45) must be evaluated and therefore the potential function, $\mathcal{U}(r)$, must be known. It is generally accepted that the potential energy is the sum of repulsive energy and attractive energy. It is also accepted that

these energies are related to molecular distances by an inverse power law. Therefore the following equation has been proposed (Prausnitz, 1969, p. 65):

$$\mathcal{J}_{\text{total}} = \frac{A}{r^n} - \frac{B}{r^m}, \quad (55)$$

where A, B, N, and m are positive constants with $n > m$.

Lennard-Jones suggested that $n = 12$ and $m = 6$. After appropriate rearrangement and substitution of the definition of ϵ , the following expression results:

$$\mathcal{J} = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (56)$$

where σ = intermolecular distance when $\mathcal{J} = 0$, and

ϵ = the negative of the minimum potential energy.

The previous equation is thus known as the Lennard-Jones potential.

London proposed the following equation for the attractive potential:

$$\phi_{12} = -\frac{3}{2} \frac{I_1 I_2}{(I_1 + I_2)} \frac{\alpha_1 \alpha_2}{r_{12}^6}, \quad (57)$$

where I = the ionization potential, and

α = the polarizability.

If the mixing rule of,

$$\sigma_{12} = \frac{\sigma_1 \sigma_2}{2}, \quad (58)$$

is used, the following expression results:

$$\epsilon_{12} = \left\{ \frac{2(I_1 I_2)^{1/2}}{I_1 + I_2} \right\} \left\{ 2^6 \frac{\sigma_1^3 \sigma_2^3}{(\sigma_1 + \sigma_2)^6} \right\} (\epsilon_1 \epsilon_2)^{1/2}. \quad (59)$$

The previous equation was proposed by Hudson and McCoubrey (1960, p. 762).

Equation (59) can be further extended to critical temperatures by the

following equation:

$$T_{c12} = \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2} \right\} \left\{ 2^6 \frac{\sigma_1^3 \sigma_2^3}{(\sigma_1 + \sigma_2)^6} \right\} (T_{c1} T_{c2})^{\frac{1}{2}} \quad (60)$$

If instead of Equation (50), the equation,

$$\sigma_{12} = (\sigma_1 \sigma_2)^{\frac{1}{2}}, \quad (61)$$

were used, the following equation would result:

$$T_{c12} = \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{(I_1 + I_2)} \right\} (T_{c1} T_{c2})^{\frac{1}{2}}. \quad (62)$$

It has been suggested by Prausnitz that the deviation from the true geometric mean mixing rule can be accounted for by the term k_{12} in the equation,

$$T_{c12} = (T_{c1} T_{c2})^{\frac{1}{2}} (1 - k_{12}). \quad (63)$$

This term ideally represents a constant independent of temperature, composition, and density. Using the form of Equation (63) it is convenient to compare different mixing rules by comparing the respective values of k_{12} . For instance, using Equation (60),

$$k_{12} = 1 - \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 + I_2} \right\} \left\{ 2^6 \frac{\sigma_1^3 \sigma_2^3}{(\sigma_1 + \sigma_2)^6} \right\}. \quad (64)$$

If Equation (62) is used,

$$k_{12} = 1 - \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{(I_1 + I_2)} \right\}. \quad (65)$$

Two other proposed mixing rules are compared in the "Analysis of Data" section and shall be discussed here briefly. Sikora (1970, p.1480)

considered both attractive and repulsive energies in developing the following equation:

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{\frac{1}{2}} g(I) f(v) \quad (66)$$

$$\text{where } g(I) = \frac{4I}{(1+I)^2}, \quad I \equiv \frac{I_2}{I_1},$$

$$\text{and } f(v) = \frac{2^{13} v^{\frac{1}{2}}}{(1+v^{1/13})^{13}}, \quad v \equiv \frac{\epsilon_{22} \sigma_2^{12}}{\epsilon_{11} \sigma_1^{12}}$$

Therefore,

$$k_{12} = 1 - \left\{ g(I) f(v) \right\}, \quad (67)$$

for the Sikora model.

An empirical equation proposed by Hiza and Duncan (1970, p. 736) is,

$$k_{12} = 0.17 (I_1 - I_2)^{\frac{1}{2}} \ln \left(\frac{I_1}{I_2} \right). \quad (68)$$

This equation was determined solely by empirical calculations using light hydrocarbons, hydrogen, helium, and neon.

Reviewing, we can see that we have finally arrived at our final goal of relating phase equilibrium to fundamental molecular quantities. If we know the values of ionization potential, polarizability, and the other necessary molecular quantities of the molecules in the system, they may be substituted into the appropriate mixing rules which in turn may be used to evaluate the potential function and thus the value of B_{12} . In addition, if the mixing rules determined from molecular considerations are in fact accurate, they may be applied to critical properties and the

value of B_{12} found from generalized correlations based on the Theory of Corresponding States. These values of B_{12} , along with B_{11} and B_{22} values, can then be used in equations such as Equation (39) to calculate phase equilibrium behavior.

The system chosen for the present investigation involves a large ($\sigma = 7.42 \text{ \AA}$) quasi-spherical molecule, neopentane, and a small ($\sigma = 3.5 \text{ \AA}$) spherical molecule, argon, (Tee and others, 1966). The results of the investigation should provide insight into the relative importance of molecular size by demonstrating the predictive capabilities of the various mixing rules for this particular system.

PROCESS FLOW

It is convenient to visualize the entire experimental apparatus as being four separate systems working together. We shall identify these systems as the refrigeration system, the equilibrium system, the instrumentation system, and the analysis system.

The Refrigeration System

Liquid nitrogen was acquired from the United States Welding Co., in vacuum-jacketed dewars containing 160 liters of liquid. On the dewar was a pressure relief valve set at 25 psig. This feature made it possible to control the degree of cooling simply by controlling the flow rate with a 1/16-inch-port valve. Were it not for the relief valve, our flow rate, and therefore our cooling rate, would be dependent not only on valve position, but on a changing upstream pressure as well. To eliminate cold spots in the upper level of the bath, the 1/4-inch copper line from the liquid nitrogen supply entered from the top of the equilibrium dewar, ran directly to the bottom of the constant-temperature bath, and then spiraled upward in a helical coil before exiting to the atmosphere through a throttle valve. There was approximately 20 feet of 1/4-inch copper tubing used for cooling within the bath.

The constant-temperature bath was contained in a stainless steel vacuum dewar 9 3/8 inches in diameter and 24 inches deep with a 27 liter capacity. The bath fluid was a 50 volume percent mixture of carbon tetrachloride and chloroform. Thermal gradients were minimized through the use of a variable speed stirrer with dual three-bladed impellers.

Obviously, the bath would eventually reach the temperature of the liquid nitrogen were it not for the effect of some heat input which compensated for the heat removal. This balancing was accomplished through the use of a 125-watt heater controlled by a Bayley proportional controller. Once a set point was established for the controller, it would control the temperature of the bath by compensating for the difference between the bath temperature and the set point by either adding heat through the electrical heater or by allowing the liquid nitrogen to cool the bath. It is here that operator experience and technique became factors, as the cooling rate of the liquid nitrogen had to be manually set with the outlet throttle valve so as to be within the controlling range of the temperature controller. An additional 125-watt heater with variac control was also available to expedite the process of changing the system to a higher temperature.

The Equilibrium System

The argon (99.998 mol percent min.) from the storage cylinder first passed through a pressure reducing valve which lowered the pressure to a value slightly higher than the pressure in the equilibrium cell. The argon then passed through a vernier throttle valve which was used to control the inlet flow rate. It then exchanged heat with the exiting argon-neopentane vapor in a 1/8-inch counter-current heat exchanger 8 feet long, passed through the constant-temperature bath in a 9 1/2-foot coil and entered the bottom of the equilibrium cell. The gas passed over the trays of solid neopentane (99.0 mol percent min.) in the cell, picking up an equilibrium amount of neopentane in the process, and finally exited

FIGURE 1

Schematic of Equilibrium and Refrigeration Systems

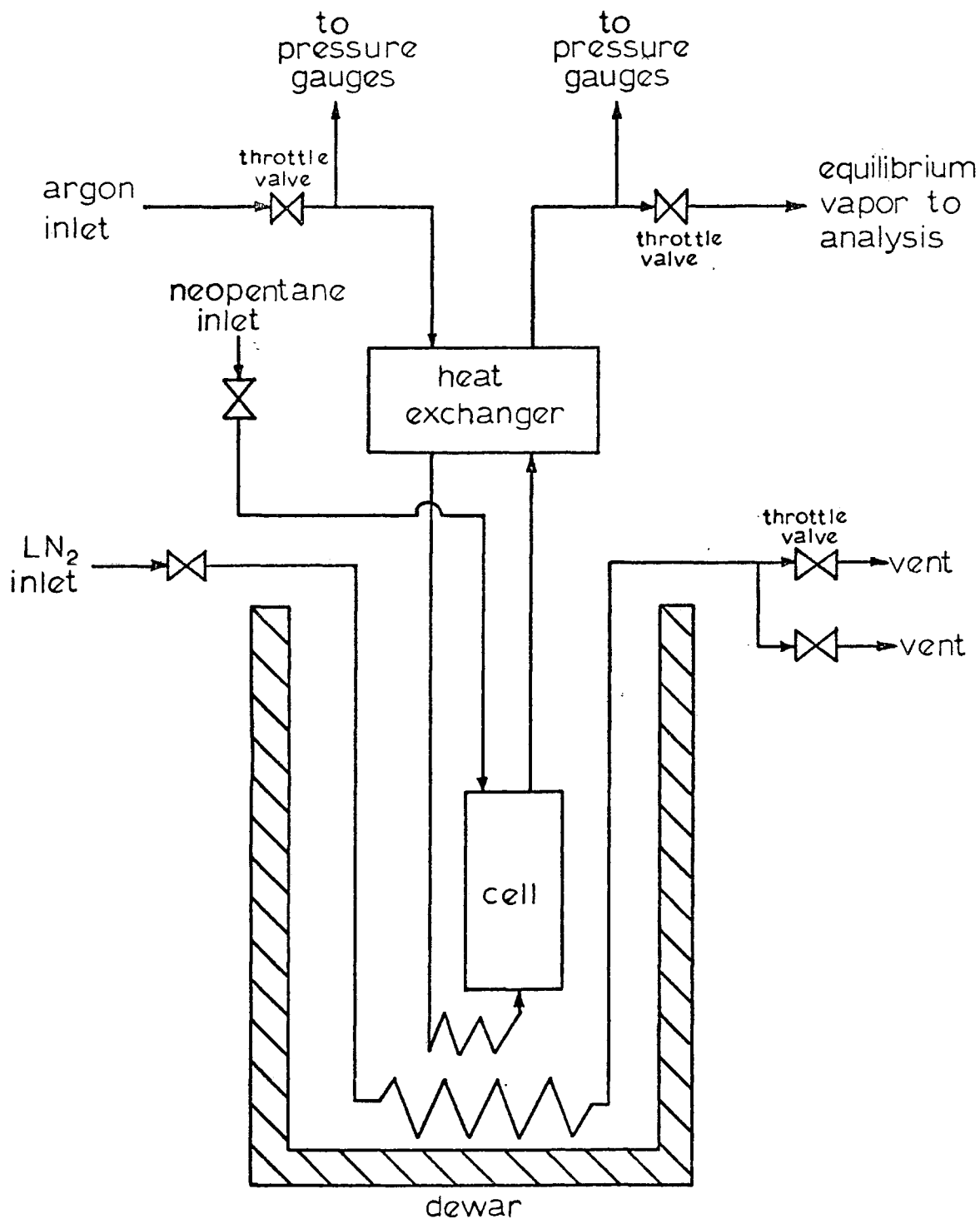


FIGURE 2

Plan View of Equilibrium Dewar
(Dustin, 1970, p. 13)

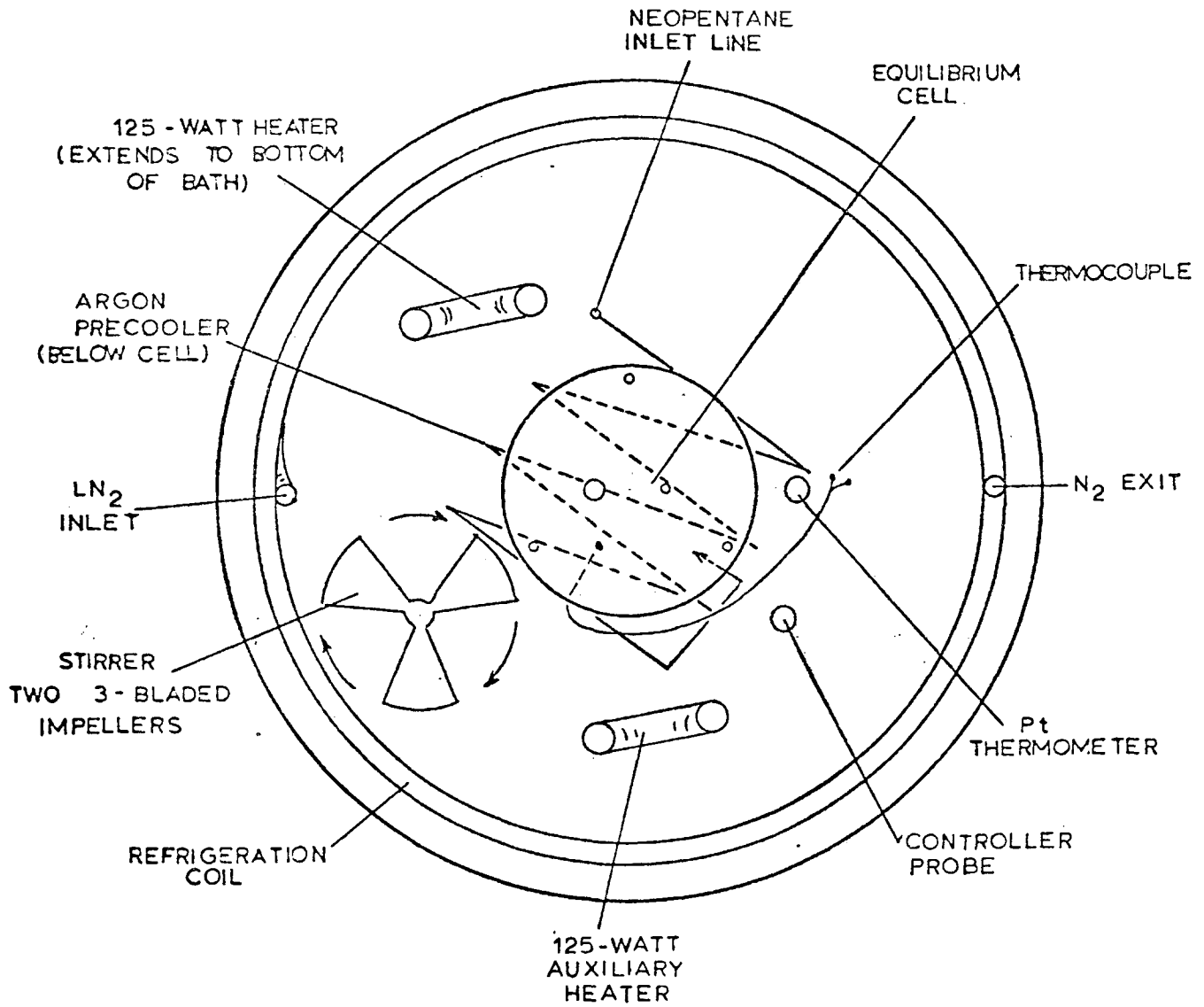
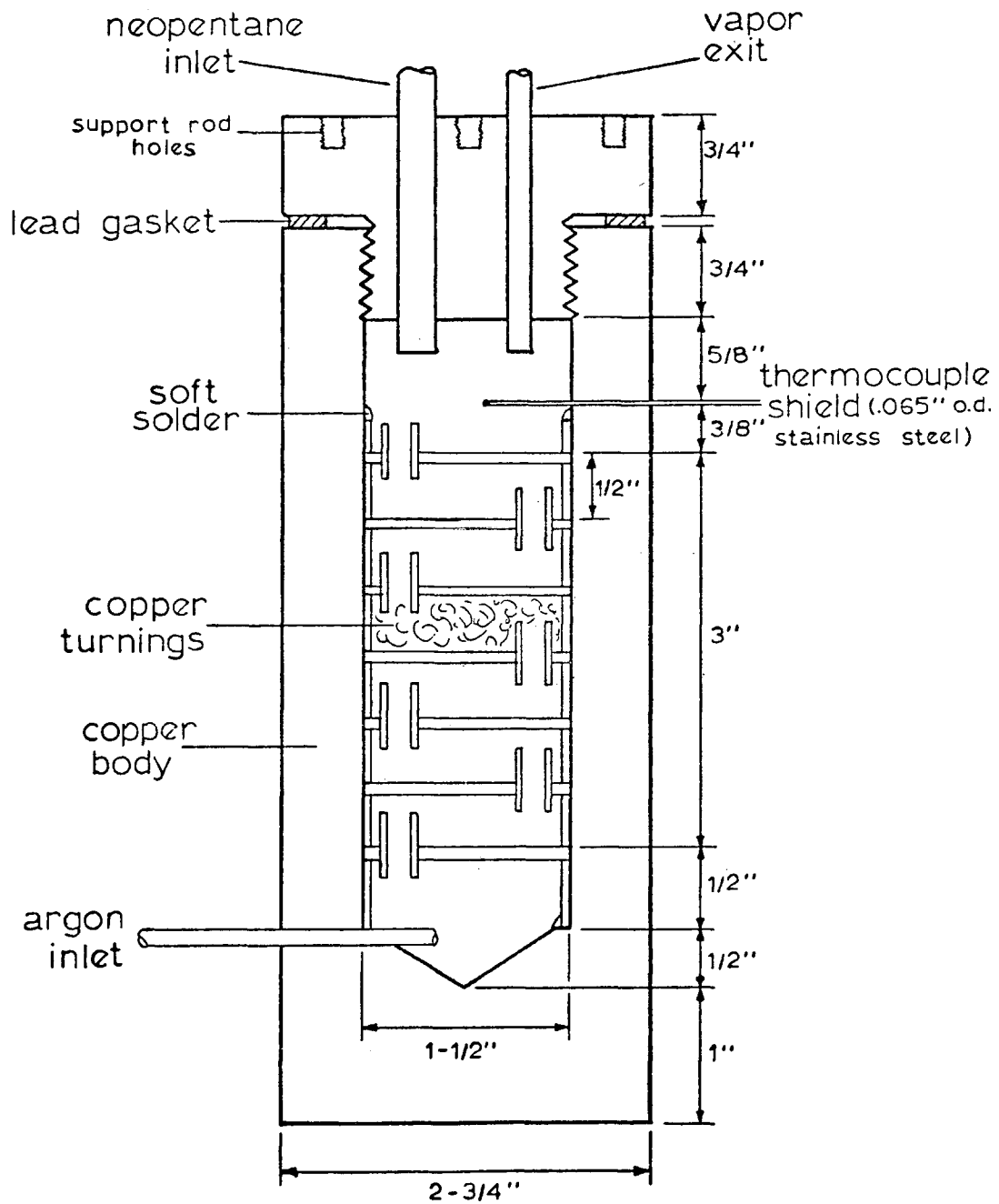


FIGURE 3

Detail of Equilibrium Cell
(Dustin, 1970, p. 9)



through the top of the cell. It then exchanged heat energy with the incoming argon and went through another throttle valve to the analysis system.

The flow rate of gas was monitored in the analysis system but was controlled by the exit throttle valve in the equilibrium system. At a given pressure and given valve setting, flow rate remained constant, but the outflow had to be matched by an equal inflow through the vernier throttle valve in order to keep the pressure in the cell constant. Here again operator technique and experience played important roles, for it was only by occasionally opening or closing the vernier that the pressure could be kept constant. The standard flow rate used during the experimental runs was 28.4 cc/minute, however, occasional checks were made at 14.2 cc/minute. If the system was at equilibrium, the data taken at both flow rates was identical. In all cases, the flow rate of 28.4 cc/minute allowed the system to reach equilibrium. Both of these rates are approximate.

The Instrumentation System

The system may be further subdivided into temperature measurement, pressure measurement, and gas analysis.

Temperature Measurement: Since the equilibrium cell was an enclosed unit and had to withstand pressures in excess of 80 atmospheres, it was not feasible to put a thermometer directly into the cell. Instead, a Leeds and Northrup platinum resistance thermometer was placed in the constant-temperature bath immediately outside the cell. The thermometer leads were attached to a Mueller bridge which in turn was connected to a null detector. When a 1-ma. current was passed through the thermometer,

the resistance of the platinum coil at the end of the thermometer could be measured. This resistance was a direct function of the temperature of the thermometer coil and therefore the temperature of the bath. This resistance was measured by balancing the Mueller bridge with an equal resistance and reading the values of this second resistance. When the two resistances were equal there was no deflection on the null detector. The resistances read on the Mueller bridge were then converted to temperatures by using the calibration table accompanying the thermometer.

Since the equilibrium temperature was inside the cell and the temperature being measured was outside the cell, the question naturally arose "How did you know both temperatures were the same?" This difficulty was alleviated by putting a thermocouple junction inside the cell with the reference junction in the liquid bath adjacent to the platinum resistance thermometer, and measuring the net emf generated. If no emf was generated, as indicated by a zero deflection on a potentiometer, the temperatures were the same.

Pressure Measurement: Pressures were measured using a 0-100 psig Heise gauge, a 0-100 psig Seegers gauge, and a 0-100 atmosphere Heise gauge. All were bourdon-tube type gauges. The valving was such that pressure on the downstream side or the upstream side of the cell could be monitored. This arrangement proved invaluable when trying to locate obstructions in the system.

A low-pressure vent valve was used to vent pressure from the low-pressure gauges when they were not in use and also as a manual safety relief when necessary. The safety relief valves on the 100 psig and

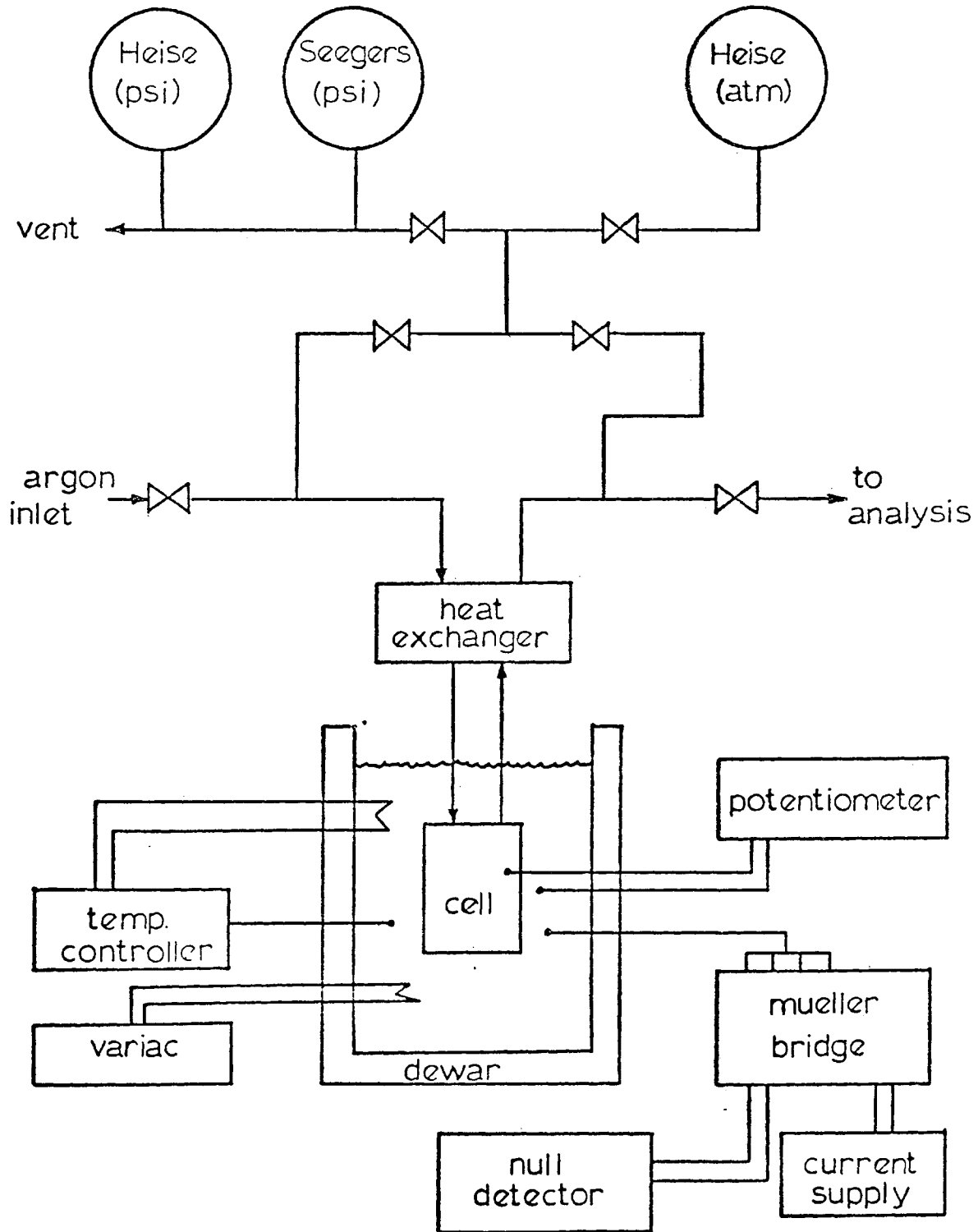
100 atmosphere lines were used to eliminate the possibility of inadvertently overpressurizing the gauges.

Gas Analysis: Analysis of the equilibrium gas was carried out using a Beckman GC 72-5 gas chromatograph with liquid partition columns and a thermal conductivity detector. With the chromatograph variables used, the recorder peaks for both argon and neopentane were very sharp. Therefore, peak heights were used as the units of measure rather than peak areas. In order to relate the peak heights back to a percentage of neopentane, it was necessary to calibrate the gas chromatograph with a standard argon-neopentane mixture. This mixture, obtained from Matheson Gas Products, contained 0.81 mole percent neopentane in argon. While keeping the sample loop size constant, the calibration gas was injected at pressures covering the entire range of the manometer (-725 to +725 mm). The absolute pressure under which the gas was injected multiplied by 0.0081 was therefore the partial pressure of neopentane. The corresponding peak heights and chromatograph attenuations were then read and noted. After referring all peak heights back to a base attenuation, peak heights were plotted versus partial pressures. This curve was then the final calibration curve to be used in determining unknown compositions.

In order to determine the composition of a given sample from the equilibrium system, the sample loop was pressurized with sample gas to a known pressure, injected, and the peak height measured. After making appropriate attenuation corrections to the base attenuation, the peak height was converted to a partial pressure by using the calibration curve. A given partial pressure divided by the total pressure in the

FIGURE 4

Schematic of Instrumentation System



loop as read on the manometer was then the mole fraction of neopentane in the sample.

The Analysis System

After passing through the exit throttle valve in the equilibrium system, the argon-neopentane mixture entered the analysis system through the sample gas valve. The gas was then either vented through a rotameter, vented through a bypass, or channeled into the chromatograph sample loop to be analyzed. The bypass vent was used to purge the system quickly or when the flow rate was higher than the capacity of the rotameter. The metered vent was used during normal operation to maintain the desired flow rate.

Before any sample gas was allowed to enter the chromatograph sample loop, the sampling section of the system was evacuated thoroughly with a vacuum pump. The vacuum pump was then isolated by means of a valve and the sample gas was channeled into the loop by the appropriate use of valves. The gas was allowed to enter until the sampling section, and therefore the sample loop, was at the desired pressure. The gas from the equilibrium system was then allowed to pass through the rotameter and the sample loop full of sample gas was injected. After the peak height was read and attenuation duly noted, the procedure was repeated for the next sample.

Valving was designed to enable the operator to change from sample gas to calibration gas quickly. This was essential because after each set of data points was taken, a "sensitivity check" was made to eliminate the effect of any changes in gas chromatograph sensitivity and/or baro-

metric pressure. These checks consisted of injecting calibration gas at a constant pressure and comparing the peak height produced with a peak height similarly produced on the day the calibration curve was made. Another benefit of running these checks was that it enabled the operator to determine whether the analysis system was at fault if unlikely results were being obtained.

FIGURE 5
Schematic of Analysis System

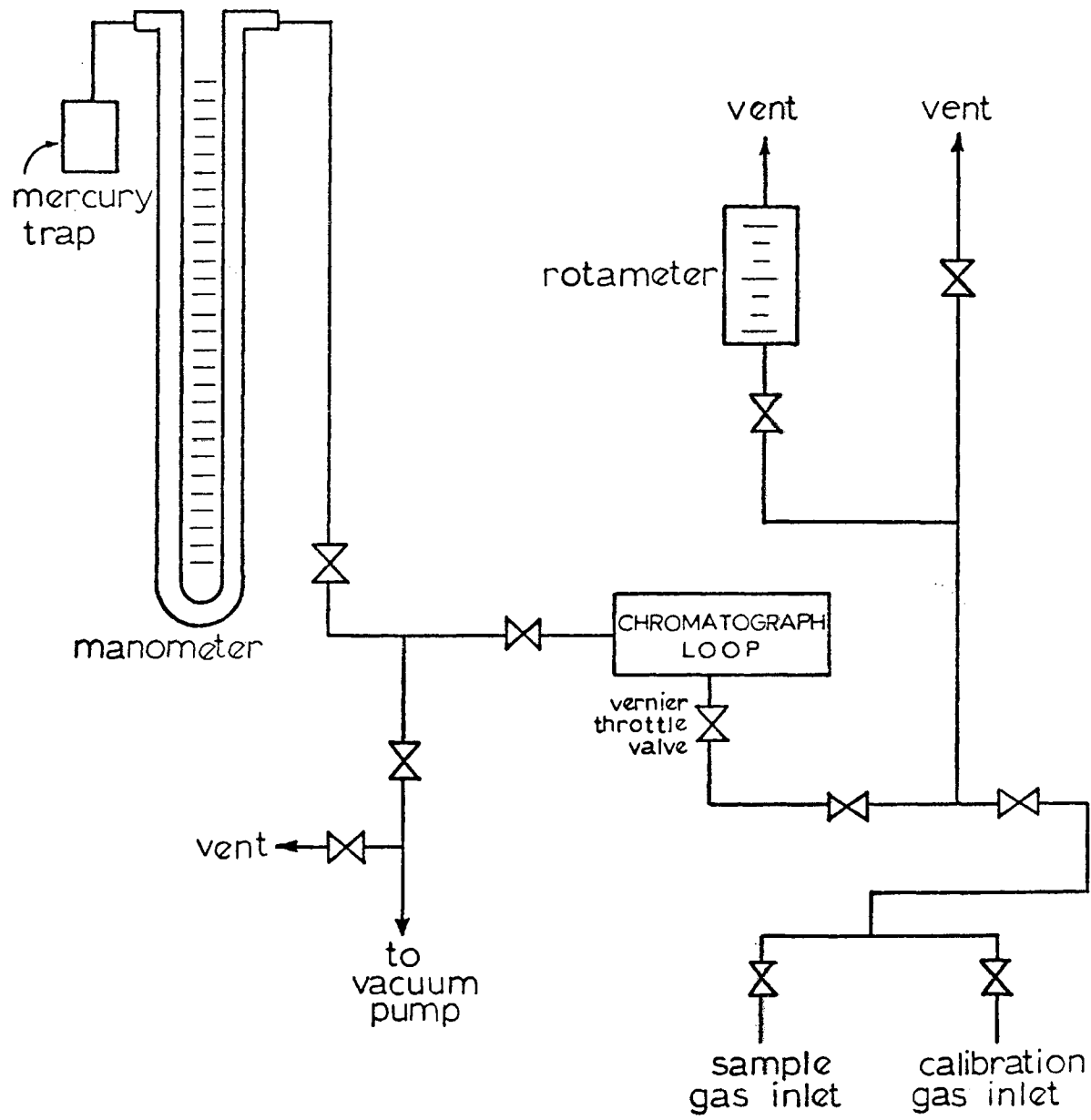


FIGURE 6

Sketch of Equilibrium System

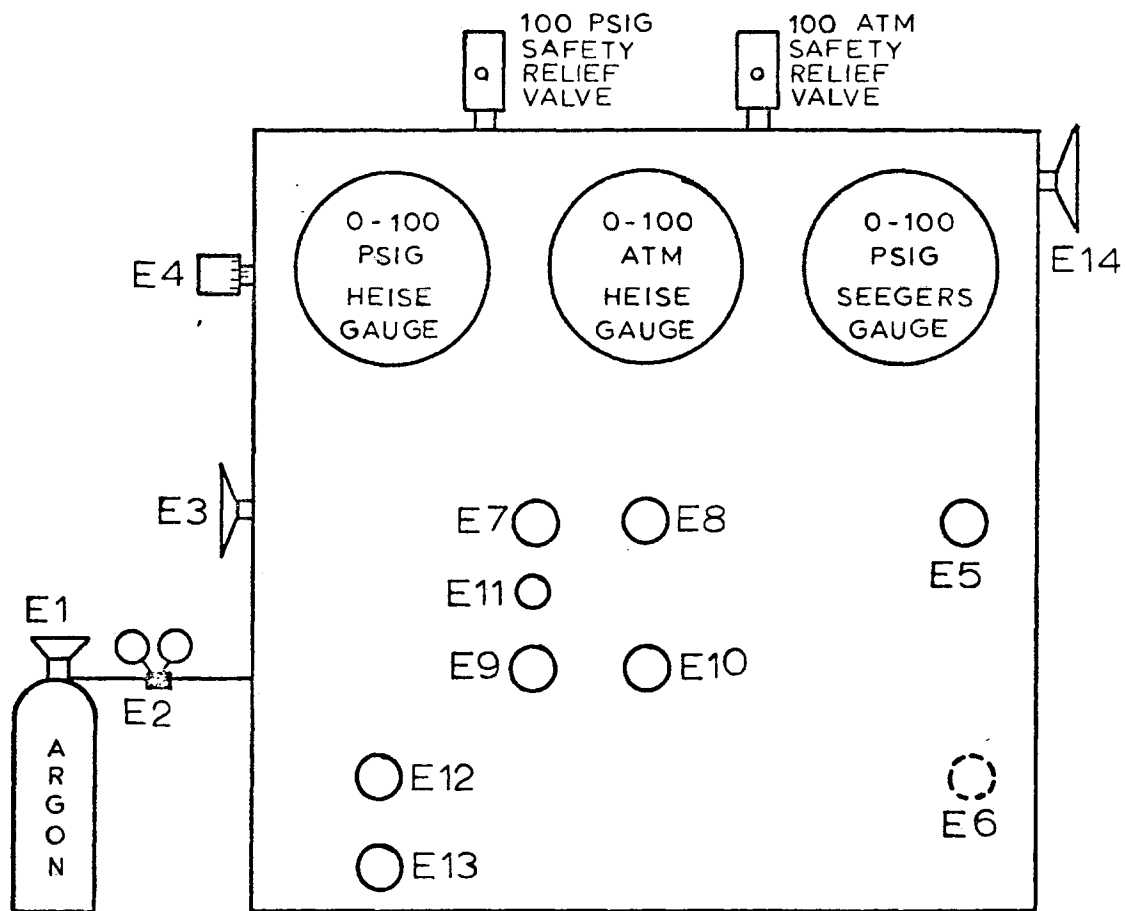
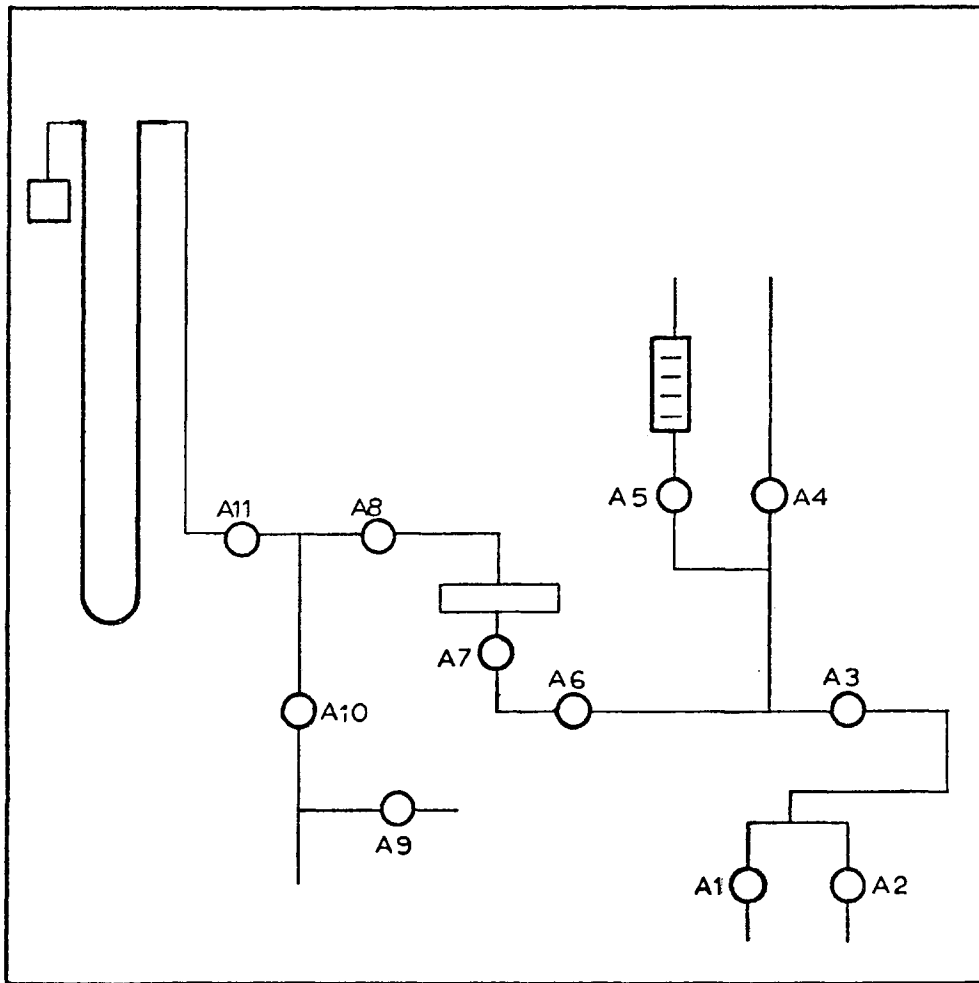


FIGURE 7

Sketch of Analysis System



OPERATING PROCEDURESEquipment Warmup

- 1) Turn on chromatograph "Main Power" switch.
- 2) Set chromatograph variables.
 - a) current @ 75 ma.
 - b) TCD power "off".
 - c) other variables as per Appendix K.
- 3) Set helium variables.
 - a) Open gas cylinder valve.
 - b) Set PRV at 80 psig.
 - c) Set flow rate to 30 cc/min.
 - d) Open toggle switches on chromatograph.
- 4) Allow helium to flow for 15 minutes.
- 5) Turn recorder to "on" position.
- 6) Set pen control on "standby".
- 7) Set attenuation to "infinity".
- 8) Set pen control on "record".
- 9) Set recorder zero with "zero" knob on recorder.
- 10) Set chromatograph "zero" knob five turns from either stop.
- 11) Set attenuation to "1".
- 12) Turn on power supply to TCD.
- 13) Allow one minute for warmup.
- 14) Obtain upscale reading with "polarity" switch.

- 15) Bring on scale with attenuation switch.
- 16) Adjust to approximately zero with "balance" control.
This was done to insure that no serious imbalance due to filament damage, air leak into carrier gas, etc., had occurred.
- 17) Increase current to desired value.
- 18) Adjust baseline with "zero" control on chromatograph.
- 19) Turn on temperature controller.
- 20) Turn on thermometer current supply.
- 21) Turn on null detector.
- 22) Balance the Mueller bridge.

Sensitize Gas Chromatograph

- 1) Set valves in the following positions:
 - a) closed: A1, A2, A4, A5, A7, A10,
 - b) open: A9, A8, A11, A6, A3,
 - c) sample injection valve in "fill" position.
- 2) Plug in analysis vacuum pump.
- 3) Close A9.
- 4) Open A10.
- 5) Evacuate manometer.
- 6) Open A7.
- 7) Evacuate.
- 8) Open calibration gas cylinder valve.
- 9) Set PRV on 16 psig.
- 10) Close A7.
- 11) Open A2.

- 12) Close A10.
- 13) Open A7.
- 14) Allow mercury level to fall until right leg is opposite "5".
This procedure purges the analysis system with calibration gas.
- 15) Close A7.
- 16) Open A10.
- 17) Evacuate.
- 18) Repeat steps 12 to 17 three times.
- 19) Close A10.
- 20) Open A7 until right leg of manometer is opposite "5".
- 21) Close A7.
- 22) Change sample injection valve to "inject" position.
- 23) Wait for recorder response.
- 24) Adjust attenuation if necessary to maximize response within chart scale.
- 25) Change sample injection valve to "fill" position.
- 26) Open A10.
- 27) Evacuate.
- 28) Repeat steps 19 to 27 until neopentane peaks are reproducible.
- 29) Relieve pressure on PRV diaphragm.
- 30) Open A4 until PRV gauge reads "0".
- 31) Close A4.
- 32) Close A2.

Equilibrium System Preparation

- 1) Set valves in the following positions:
 - a) closed: E1, E2, E3, E4, E5, E6, E11, E14,
 - b). Open: E9, E10, E7, E8, E12, E13.
- 2) Turn on equilibrium system vacuum pump.
- 3) Open E6.
- 4) Open E5 slowly until gauges read "0".
- 5) Close E8.
- 6) Close E8.
- 7) Open E5 slowly.
- 8) Evacuate completely.
- 9) Close E5.
- 10) Open E1.
- 11) Tighten E2 until PRV gauge reads approximately 200 psig.
- 12) Open E3.
- 13) Open E8 very slowly until gauge drops slowly.
- 14) Open E4 until movement of gauge needle stops.
- 15) Open E8 fully.
- 16) Open E4 further to bring gauge needle to 10 atm.
- 17) Close E4.
- 18) Open E5 until gauge needle drops to "0".
- 19) Close E8.
- 20) Open E5 fully.
- 21) Evacuate.
- 22) Repeat steps 13 to 21 three times.

Gas from the equilibrium system will now be tested to check for traces

of neopentane.

- 23) Close E5.
- 24) Open A1.
- 25) Open A4.
- 26) Allow vacuum pump to draw air.
- 27) Turn off vacuum pump.
- 28) Close E6.
- 29) Close A4.
- 30) Close A1.
- 31) Open A10.
- 32) Open A7.

This evacuates air from the analysis system, to eliminate any possible damage to the detector filaments. Air should never be allowed to pass through an operating detector.

- 33) Close E9.
- 34) Open E8 very slowly until gauge needle drops slowly.
- 35) Open E4 until movement of gauge needle stops.
- 36) Open E8 fully.
- 37) Open E4 further to bring gauge needle to 5 atm.
- 38) Close E4.
- 39) Open A1.
- 40) Evacuate sample gas line.
- 41) Close A10.
- 42) Slowly open E5 until manometer legs are equal.
- 43) Close E5.
- 44) Close A7.

- 45) Open A5.
- 46) Wait until rotameter float settles.
- 47) Slowly open E5 until rotameter shows flow.
- 48) Allow to flow for approximately two minutes.
- 49) Close A5.
- 50) Open A7 slightly until right leg of manometer is opposite "50".
- 51) Close A7.
- 52) Set attenuation to "2".
- 53) Set baseline with "zero" on chromatograph.
- 54) Open A5.
- 55) Inject sample.
- 56) Wait for recorder response.
- 57) Change sample injection valve to "fill" position.
- 58) Repeat steps 49 through 57 to be sure no large neopentane peaks appear.

When pressure drops below 3 atm., open E4 slowly to increase pressure to 5 atm.

Cooldown Procedure

- 1) Carefully raise dewar with winch. (Be sure lid is seated properly).
- 2) Lock winch.
- 3) Slide clamps under support and tighten.
- 4) Open liquid outlet valve on liquid nitrogen storage dewar.
- 5) Start stirrer (CCW @ 3).
- 6) Calculate "N" position reading at 258.5°K.
- 7) Monitor temperature continuously.

- 8) When temperature reaches 260°K , set E12 eight turns from fully closed.
- 9) Monitor temperature continuously.
- 10) Set Mueller bridge resistance to value corresponding to 258.5°K .
- 11) As null detector needle approaches "0", adjust "temperature range" and "temp adjust" knobs on controller until controller meter registers approximately "40".
- 12) Wait until temperature remains fairly constant.
- 13a) If temperature is too high, reduce controller settings slightly.
- 13b) If temperature is too low, increase controller settings slightly.
- 14) Repeat steps 12 through 13 until temperature is near or equal to 258.5°K .
- 15a) If controller controls at a value greater than "40", close E12 slightly.
- 15b) If controller controls at a value less than "10", open E12 slightly.

Neopentane Injection

- 1) Fill a small beaker with water.
- 2) Put the analysis vent line exit into the water.
- 3) Close A5.
- 4) Open A4.
- 5) Close E4, if open.
- 6) Open E7 slowly.
- 7) Open E5 fully.
- 8) Wait until bubbling ceases.
- 9) Close E5.
- 10) Close A4.
- 11) Set all gauges to "0".
- 12) Close E9.
- 13) Close E10.

- 14) Close small valve on neopentane line.
- 15) Open main valve on neopentane bottle.
- 16) Disconnect black plastic fill line from E14.
- 17) Turn on scale light of thermocouple potentiometer.
- 18) Slowly open the small valve on the neopentane line until neopentane flows out of the black plastic line.
- 19) Purge fitting on E14 with neopentane.
- 20) Connect black plastic line to E14.
- 21) Close small valve on neopentane line.
- 22) Weigh neopentane bottle.
- 23) Slowly open E14.
- 24) Depress "high" sensitivity button on thermocouple potentiometer.
- 25) Slowly open small valve on neopentane line until deflection occurs on thermocouple potentiometer scale.
- 26) Maintain a deflection of "5" units to the right on the thermocouple potentiometer scale with the small valve.

The reason for injecting the neopentane at such a slow rate is to avoid the possibility of getting pure neopentane gas in the heat exchanger. By adding neopentane slowly it has an opportunity to liquify by the time it reaches the top tray of the cell. If pure neopentane gas should enter the heat exchanger, it will condense upon pressurizing the system, thus leading to erroneous results.

- 27a) If the deflection is less than "5", open the small valve slightly.
- 27b) If the deflection is greater than "5", close the small valve slightly.
- 28) After 20 grams of neopentane have been injected (by difference weighings) close E14.
- 29) Close the small valve on the neopentane line.

- 30) Close the main valve on the neopentane bottle.
- 31) Disconnect the black plastic line from E14.
- 32) Wait until there is no deflection on the thermocouple potentiometer scale nor on the null detector.
- 33) Turn off scale light of thermocouple potentiometer.

Cool Down to the Desired Temperature

- 1) Open E9 and E10 simultaneously.
- 2) Open E4 slowly until pressure is approximately 40 psig.
- 3) Close E4.
- 4) Close E9.
- 5) Open A5 fully.
- 6) Open E5 until flow is detected.
- 7) Maintain pressure at 40 psig with E4.
- 8) Turn "temperature range" and "temp adjust" knobs to "0".
- 9) Open E13.
- 10) As temperature reaches a value 1°K above the desired temperature (approximately the desired resistance plus 0.1000 ohm) close E13.
- 11) Set Mueller bridge resistance to the value corresponding to the desired temperature.
- 12) Monitor the decreasing temperature on the null detector.
- 13) As the null detector needle approaches "0", increase the controller settings until the controller meter registers "40".
- 14) Wait until the temperature remains fairly constant.
- 15a) If temperature is too high, decrease the controller settings slightly.
- 15b) If temperature is too low, increase the controller settings slightly.
- 16) Wait until the temperature remains fairly constant.

- 17) Repeat steps 14 through 15 until temperature is that desired.
- 18) Record "N" and "R" readings on Mueller bridge when balanced.
- 19a) If controller meter reading is less than "10", open E12 slightly.
- 19b) If controller meter reading is greater than "40", close E12 slightly.
- 20) Wait until temperature is constant.
- 21) Pressure control during cooldown is discussed in Appendix M.

Pressurizing to Desired Pressure and Controlling

- 1) Close E5.
- 2) Close A5.
- 3) Open E10.

E10 is opened to allow the incoming argon to bypass the cell in order to equalize pressure on both sides of the cell. Were it not for this, the higher pressure on the upstream side may force some solid (or liquid) neopentane into the heat exchanger, thus causing erroneous readings.

- 4) Slowly open E4 to increase pressure in the system.
- 5) Keep the pressure on the PRV slightly above the pressure recorded on the system gauges in order to maintain a positive driving force.
- 6) Increase pressure to the desired value.
- 7) Close E4.
- 8) Close E9.
- 9) Wait for temperature to equilibrate.

The sample line will now be evacuated in order to minimize the length of time it will require for new equilibrium gas to reach the analysis system.

- 10) Close A7.

- 11) Open A10.
- 12) Evacuate manometer.
- 13) Open A7.
- 14) Evacuate sample line.
- 15) Close A10.
- 16) Open E5 until manometer legs are equal.
- 17) Close E5.
- 18) Close A7.
- 19) Open A5.
- 20) Wait for rotameter float to settle.
- 21) Open E5 slowly until desired flow is detected.
- 22) Open E4 slowly to maintain desired pressure.

Sampling Equilibrium Gas

- 1) Open A10.
- 2) Evacuate manometer.
- 3) Close A10.
- 4) Close A5.
- 5) Open A7.
- 6) Allow pressure to increase until right leg of manometer is opposite desired scale reading.
- 7) Close A7.
- 8) Open A5.
- 9) Inject sample.
- 10) Wait for recorder response.
- 11) Change sample injection valve to "fill" position.
- 12) Repeat steps 1 through 11 until neopentane peaks are reproducible.
- 13) Record the difference between the heights of the manometer legs.

- 14) Record the flow rate of sample gas.
- 15) Record chromatograph attenuation.
- 16) Record barometric pressure.
- 17) Record peak heights.

A "sensitivity check" will now be taken using calibration gas.

- 18) Close E4.
- 19) Close E5.
- 20) Close A5.
- 21) Close A1.
- 22) Open A10.
- 23) Evacuate manometer.
- 24) Open A7.
- 25) Evacuate analysis line.
- 26) Increase PRV setting on calibration gas bottle to 16 psig.
- 27) Close A7.
- 28) Close A10.
- 29) Open A2.
- 30) Open A7 until right leg of manometer is at "5".
- 31) Close A7.
- 32) Open A10.
- 33) Evacuate manometer.
- 34) Close A10.
- 35) Repeat steps 30 through 34 three times.
- 36) Open A7 until right leg of manometer is opposite "5".
- 37) Close A7.
- 38) Inject sample.

- 39) Wait for recorder response.
- 40) Change sample injection valve to "fill" position.
- 41) Open A10.
- 42) Evacuate manometer.
- 43) Close A10.
- 44) Repeat steps 36 through 43 until neopentane peak height is reproducible.
- 45) Record peak heights as "machine sensitivity".
- 46) Relieve pressure on PRV diaphragm.
- 47) Open A5.
- 48) Vent calibration gas until PRV reads "0".
- 49) Close A5.
- 50) Close A2.
- 51) Open A10.
- 52) Evacuate manometer.
- 53) Open A7.
- 54) Open A1.
- 55) Evacuate sample line.
- 56) Close A10.

Changing to a Higher Pressure

- 1) Open E9.
- 2) Open E4 slowly to increase pressure.
- 3) Keep PRV set slightly above system pressure.
- 4) If system pressure is greater than 90 psig, close E7, and monitor pressure on atmosphere gauge.
- 5) Open E4 until desired pressure is reached.

- 6) Close E4.
- 7) Close E9.
- 8) Open E5 slowly until manometer legs are equal.
- 9) Close E5.
- 10) Close A7.
- 11) Open A5.
- 12) Wait for rotameter float to settle.
- 13) Open E5 until desired flow rate is detected.
- 14) Open E4 to maintain desired pressure.

Change to a Lower Pressure

- 1) Open E9.
- 2) Reduce PRV gauge pressure with E2.
- 3) Open E14 slowly to vent gas until pressure is at desired value.
- 4) Close E14.
- 5) Close E9.
- 6) Open E5 slightly until manometer legs are equal.
- 7) Close E5.
- 8) Close A7.
- 9) Open A5.
- 10) Wait until rotameter float settles.
- 11) Open E5 slowly until desired flow is detected.
- 12) Open E4 to maintain desired system pressure.

Shut Down Procedure

- 1) Close valve on liquid nitrogen supply dewar.
- 2) Turn off stirrer.
- 3) Turn TCD current supply "off".

- 4) Turn TCD current supply to 75 ma.
- 5) Turn off recorder power.
- 6) Turn off temperature controller.
- 7) Turn off thermometer power supply.
- 8) Turn off null detector.
- 9) Close E1.
- 10) Relieve pressure on E2 to bleed off line between E2 and E4.
- 11) Open E5 slowly until right leg of manometer is opposite "5".
- 12) Close E5.
- 13) Close A7.
- 14) Close A1.
- 15) Open A9.
- 16) Unplug analysis system vacuum pump.
- 17) Open E14.
- 18) Bleed pressure to 2-4 psig.
- 19) Close E14.
- 20) Close E3.
- 21) Release clamps under dewar support.
- 22) Lower dewar carefully with winch.
- 23) Support lid to eliminate strain on thermometer, leads, etc.
- 24) Scrape off frozen bath fluid from liquid nitrogen coils.
- 25) Cover dewar.
- 26) Decrease helium flow rate to 10 cc/min.
- 27) If equipment will not be operated for some time (one week or more) the main power to the chromatograph may be turned off, but helium flow should always be maintained at 10 cc/min.

Balancing the Mueller Bridge

This procedure should be followed prior to every experimental run.

Adjusting the Bridge Ratio:

- 1) Insert plug firmly in "RATIO" position.
- 2) Place commutator midway between "N" and "R".
- 3) Set plug switch, X1, and X.1 switches on "0"
- 4) Balance by adjusting the lower three dials until the null detector exhibits a minimum deflection when the "0" button is depressed.
- 5) Set X1 and X.1 dials to "R".
- 6) Depress the "0" button.
- 7a) If null detector deflects the same as before, the bridge is in proper adjustment.
- 7b) If null detector deflections differ, adjust the "ADJ RATIO" dial to bring the deflection to a value that is the mean of the previous deflections.
- 8) Place X1 and X.1 dials in "0" position.
- 9) Repeat steps 4 through 8 until the deflection is the same for the "0" and "R" positions of the X1 and X.1 dials.

Adjusting the Bridge Zero:

- 1) Insert plug in position marked "ZERO".
- 2) Set all switches at "0" (this includes the plug switch).
- 3) Place commutator in "N" position.
- 4) Depress the "0" button.
- 5) Balance to zero deflection using "ADJ ZERO" dial.
- 6) Change commutator to "R" position.
- 7) Check the deflection.
- 8a) If the deflection is zero, the bridge zero is correct.
- 8b) If the deflection is not zero, the bridge ratio is not correct and must be rechecked.

Measuring the Bath Temperature

- 1) Be sure thermometer leads are correctly attached.
- 2) Balance the Mueller Bridge.
- 3) Put plug switch in "Measure".
- 4) Set all rheostat dials at "0"
- 5) Set commutator in "N" position.
- 6) Depress "10000" button.
- 7) Increase bridge resistance until minimum deflection is noted on null detector.
- 8) Depress "0" button.
- 9) Adjust bridge resistance until null detector deflection is zero.
- 10) Change commutator to "R" position.
- 11) Depress the "0" button.
- 12) Adjust bridge resistance until null detector deflection is zero.
- 13) Calculate the average of the two resistance.
- 14) Divide this resistance by the thermometer resistance at 0°C.
- 15) Use this ratio to find the temperature by linear interpolation between values on the calibration table.

OPERATIONAL CALCULATIONS

The purpose of this section is to illustrate and explain the various calculations which were made before, during, and after the raw data were obtained. Included are descriptions of the major difficulties encountered throughout the course of the experimental work. Should future investigators experience similar problems, perhaps the solutions and ideas presented here will be of assistance to them in their work.

Construction of a Calibration Curve

Sample gas from the equilibrium system contained varying amounts of neopentane. When this gas was injected into the gas chromatograph a peak was produced on the recorder and the height of this peak then had to be related to a known quantity of neopentane. Therefore, in order to calibrate the gas chromatograph, different amounts of neopentane had to be injected and the resulting peak heights noted. It was decided that the most convenient method by which to accomplish this was to purchase a cylinder of a known argon-neopentane composition and inject a constant volume of gas into the gas chromatograph at various pressures. The standard concentration was first assumed to be 0.96 mole percent neopentane in argon, as stated by the supplier. The pressure under which it was injected was monitored with the manometer in the analysis system. Since the manometer measured only the pressure relative to the prevailing atmospheric pressure, in order to determine the absolute pressure, the manometer reading was added to the barometric pressure.

The barometric pressure was measured on a standard barometer located in the laboratory.

Using the equation,

$$pp_A = y_A P_t , \quad (69)$$

where pp_A = the partial pressure of component A,

y_A = the mole fraction of component A in the system, and

P_t = the total pressure of the system,

it followed that the absolute pressure times 0.0096 would be the partial pressure of neopentane. Each partial pressure would produce a corresponding peak height on the recorder. After applying the appropriate attenuation correction, these related values could then be plotted to give a calibration curve.

Sample Calculation:

Calibration gas injected at manometer pressure = -375 mm Hg.

Barometric pressure as read on barometer = 618.2 mm Hg.

Absolute injecting pressure = -375 mm + 618.2 mm = 243.2 mm Hg.

Partial pressure neopentane = (0.0096)(243.2 mm) = 2.335 mm Hg.

Chromatograph attenuation = 2.

Base attenuation used for calibration curve = 4.

Attenuation correction factor = 1/2.

Peak height read on recorder = 5.00 units.

Corrected peak height = 1/2 X 5.00 units = 2.50 units.

Value plotted on abscissa = 2.335 mm Hg.

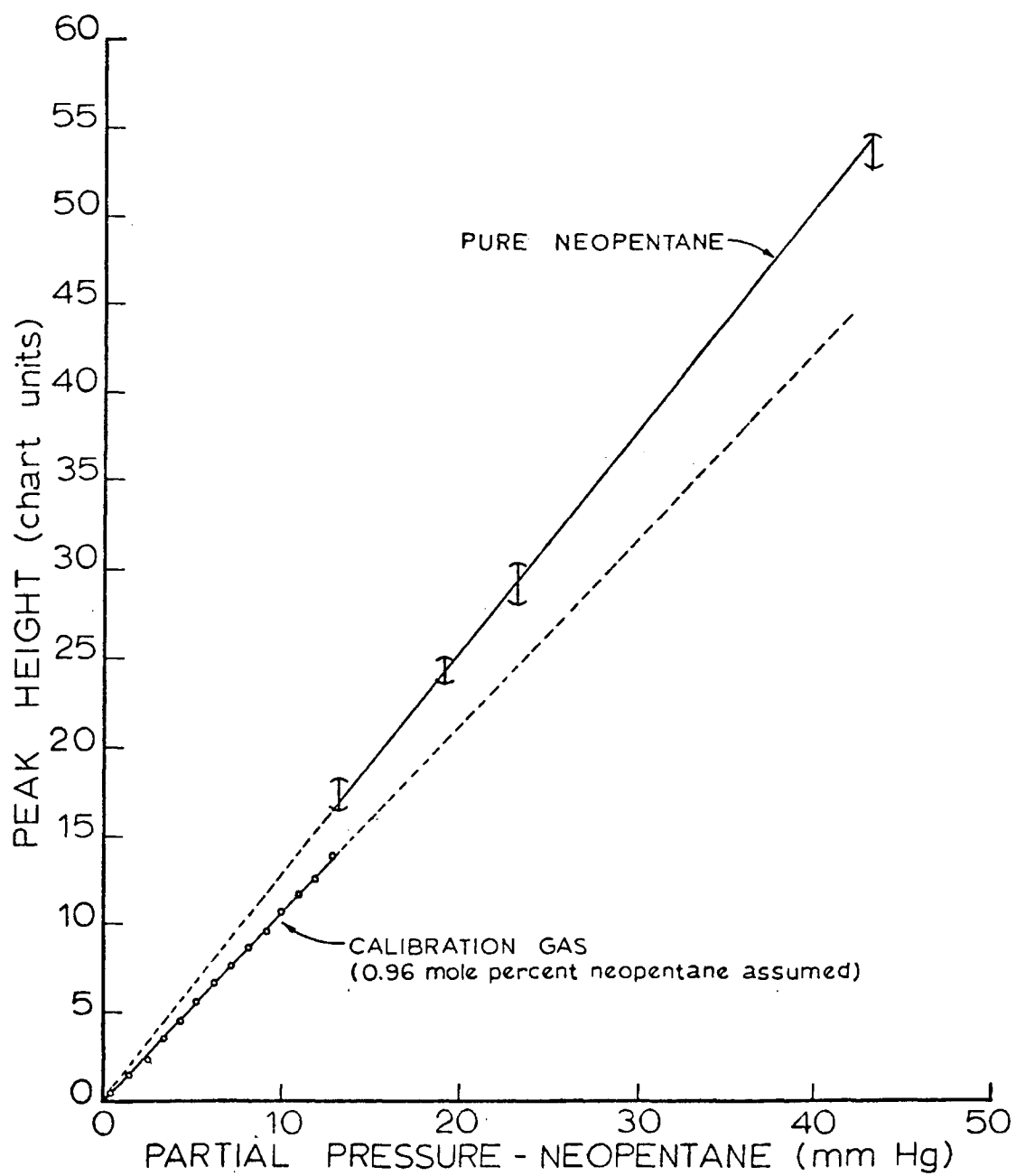
Value plotted on ordinate = 2.50 units.

When the first calibration curve was made, the gas chromatograph used was a Hewlett-Packard Model 5750 with flame ionization detectors. The gas injection valve was designed with a sliding, stainless steel piston within a stainless steel barrel. Seals between the chambers were Viton O-rings. The initial results indicated that there was something wrong with the analysis system since non-reproducible results were being obtained. The difficulty was eventually traced to the gas injection valve where neopentane was being absorbed in the lubricant and was eventually being adsorbed (or possibly absorbed) by the O-rings, thus weakening them substantially. Buna rubber and silicon rubber O-rings were tried, but the lubrication problem remained. Teflon O-rings would have solved the problem but they were not suitable to the design of the piston. The problem was finally solved by purchasing an entirely new Teflon-packed valve. With this valve and the Hewlett-Packard chromatograph, a useable calibration curve was obtained.

When funds became available, a new Beckman GC 72-5 gas chromatograph was purchased for the project. The valve in this system was a Teflon-packed sliding disc valve manufactured by Carle Valves, Inc. No absorption or leakage problems were noted with this valve.

A new calibration curve was produced using the same calculational procedures as previously described. It was then felt that the calibration gas composition should be checked using pure neopentane as a standard. To do this pure neopentane was injected over the entire manometer pressure range and the data plotted on the same graph as the calibration gas. The two curves should have overlapped, or at least been continuous, but they were not. The pure neopentane curve was extrapolated to the origin and

FIGURE 8
Preliminary Calibration Curves



the extrapolated curve was used for all further calculations. By ratioing the slopes of the two lines, the new curve was found to correspond to a gas composition of 0.805 mole percent neopentane.

The calibration gas composition was checked at a later date using chromatographic techniques. Pure neopentane was injected at a known pressure and peak height and attenuation were noted. Calibration gas was then injected and the appropriate readings were taken. By referring both measurements to a common attenuation, it was determined that the calibration gas was actually 0.81 mole percent neopentane. Since all data had been taken using the graphically determined 0.805 mole percent figure, the partial pressure was multiplied by a factor of 0.81/0.805 to arrive at the correct value of partial pressure.

Checking the Calibration Curve

At various times, the calibration curve was checked to be sure that no chromatograph variables had drastically changed, thus affecting the curve. The procedure was essentially the same as that used before, except that allowances had to be made for a different barometric pressure and a different gas chromatograph sensitivity. In order to make these corrections an arbitrary pressure was chosen which could be easily reproduced on the manometer. It was decided to choose a right leg of "5", which corresponded to a manometer pressure of 725 mm Hg. above atmospheric pressure. With different barometric pressures this would correspond to different absolute pressures, so all values of peak height obtained were multiplied by ,

$$725 + \text{b.p.} / 725 + 618.2, \quad (70)$$

where b.p. = the prevailing barometric pressure, and

618.2 = the barometric pressure on the day the calibration curve was made.

The sensitivity of the gas chromatograph also varied significantly with time. These changes were corrected for by multiplying all peak heights by a factor,

$$6.85 / m.s. , \quad (71)$$

where 6.85 = the peak height recorded on the day the calibration curve was made when the right leg was "5", and

m.s. = the peak height read on the day of the check when the right leg was at "5".

Sample Calculation:

Barometric pressure = 617.3 mm Hg.

Peak height when right leg was at "5" = 6.56 units.

Attenuation = 8.

Manometer pressure during injection = +425 mm Hg.

Peak height = 5.11 units.

$(5.11 \text{ units})(725 + 617.3 / 1343.2)(6.85 / 6.56) = 5.33 \text{ units.}$

Attenuation factor = 2.

Final corrected peak height = 10.66 units.

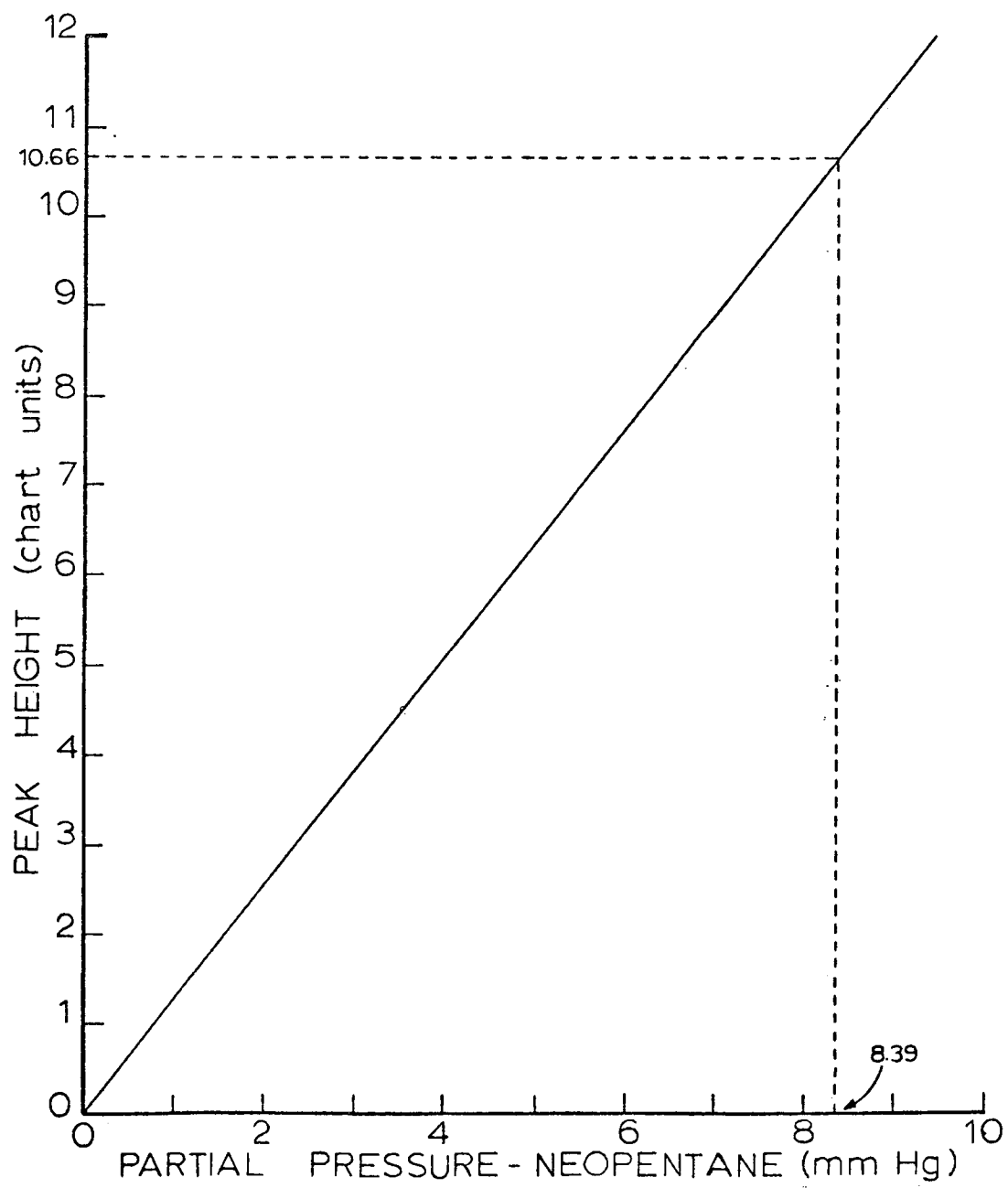
Partial pressure = $(617.3 \text{ mm} + 425 \text{ mm})(0.00805) = 8.39 \text{ mm Hg.}$

Value plotted on abscissa = 8.39 mm Hg.

Value plotted on ordinate = 10.66 units.

This does correspond to the calibration curve, drawn by extrapolating the pure neopentane curve, as shown in Figure 9.

FIGURE 9
Final Calibration Curve



Temperature Measurement

The temperature of the bath was measured using a Leeds and Northrup platinum resistance thermometer. To make a measurement a 1 ma. current was applied to the thermometer and the resistance of the platinum coil balanced with a resistance on a Mueller bridge. The bridge resistance could then be read off the resistance dials. There were two positions in which measurements could be made, normal and reverse. By averaging these two, the resistance of the thermometer leads was eliminated, thus giving the resistance of the platinum coil alone. This average value was then divided by the value of resistance at 0°C. as given by the calibration table accompanying the thermometer. Using this ratio the temperature was determined by interpolation from the values in the calibration table.

Sample Calculation:

Resistance measured on N position = 21.1233 ohms.

Resistance measured on R position = 21.0569 ohms.

Average resistance = 21.0901 ohms.

Resistance at 0°C = 25.5071 ohms.

Ratio of resistance at temperature to resistance at 0°C = 0.826833

From calibration table,

<u>RATIO</u>	<u>°K</u>
.822807	229
.826849	230

Interpolating between 229 °K and 230 °K, we find that 21.0901 ohms corresponds to 229.996 °K.

The first thermometer used in the equipment was a Leeds and Northrup Model No. 8163-C, Serial No. 1547841 calibrated by the National Bureau of Standards on IPTS-68. Soon after data were being obtained, this thermometer was inadvertently broken, and another one, Model No. 8164, Serial No. 1793436, had to be used in place of the first one. Unfortunately the second thermometer had not been calibrated. However, the project was continued using the uncalibrated thermometer while the first one was being repaired and recalibrated by Leeds and Northrup using IPTS-68.

While taking data the exact temperature did not need to be known very accurately as it was only necessary to be able to reproduce the temperature, regardless of what it was. However, in order to have some approximation of the true temperature the calibration table for the broken thermometer was used with the new thermometer. It was later found that the true temperature was about 0.5°K lower than the "measured" temperature.

By the time the raw data had been taken, the broken thermometer had been repaired and recalibrated. Both thermometers were then placed in the bath and the resistances of both were read at various controlled temperatures. From this data a graph of $(T_{\text{uncalibrated}} - T_{\text{calibrated}})$ versus $(T_{\text{uncalibrated}})$ was made. By looking up the temperature that had been read from the uncalibrated thermometer using the old calibration table, the correction factor necessary to convert to the true temperature could be determined. Applying this correction to the uncalibrated thermometer reading, the true temperature was calculated.

Sample Calculation:

Resistance on "N" position = 19.0551 ohms.

Resistance on "R" position = 18.9893 ohms.

Average resistance = 19.0225 ohms.

Resistance at 0 C = 25.5071 ohms.

Ratio of resistances = 19.0225 ohms / 25.5071 ohms = .745773

From calibration table:

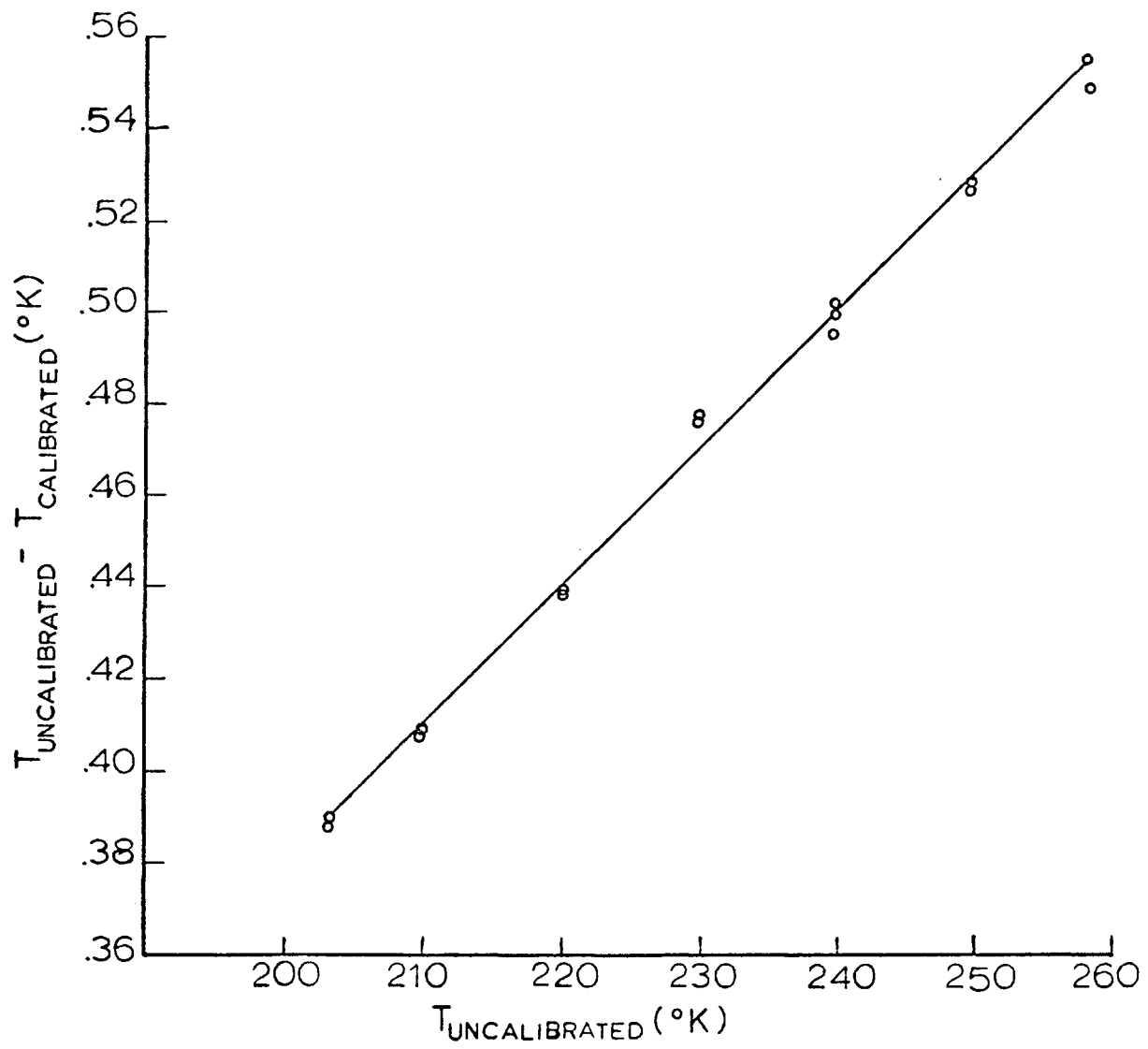
RATIO	$^{\circ}\text{K}$
.745765	210
.749833	211

By interpolating between these temperatures, the temperature was found to be 210.002 $^{\circ}\text{K}$.

Correction factor from Temperature Correction Curve = .408 $^{\circ}\text{K}$.

The temperature = 210.002 $^{\circ}\text{K}$ - .408 $^{\circ}\text{K}$ = 209.594 $^{\circ}\text{K}$.

FIGURE 10
Thermometer Correction Curve



Pressure Measurement

Pressures within the cell were measured using a 0-100 psig Heise gauge, a 0-100 psig Seegers gauge, and a 0-100 atmosphere Heise gauge. Neither 0-100 psig gauge was designed for vacuum applications so it was necessary to "zero" them relative to atmospheric pressure. The 0-100 atmosphere Heise gauge was designed to measure absolute atmospheres directly, however, to set the gauge to "0", it would be necessary to draw a very high vacuum on the gauge and a vacuum pump capable of doing this was not immediately available. Therefore, all gauges were set to zero at atmospheric pressure and the barometric pressure was later added to the readings in order to obtain the absolute pressures. An added advantage to this method was that the investigator could easily check for any drastic inaccuracies by simply comparing the psig and atmosphere gauges.

In order to initially set the gauges to zero, the system was slightly pressurized and then vented through a bubbling device until all activity ceased. The pressure on the gauges was then exactly the same as atmospheric pressure.

All system pressures were reported in atmospheres and the conversion factors used were as follows:

$$760 \text{ mm Hg.} = 1 \text{ atmosphere,} \quad (72)$$

and

$$14.69 \text{ psi} = 1 \text{ atmosphere.} \quad (73)$$

Sample Calculation:

Pressure read on gauges = 73.5 psig.

Gauge pressure in atmospheres = $73.5 / 14.69 = 5.003$ atmospheres.

Barometric pressure = 622.5 mm Hg. = 0.819 atmospheres.

Absolute pressure = $5.003 \text{ atm.} + 0.819 \text{ atm.} = 5.822$ atmospheres.

Taking Experimental Data

In order to convert the raw data into useable information, a series of calculations were performed. These calculations were made in the following order:

1) Calculate System Pressure.

The system pressure, as read on the equilibrium pressure gauges, was added to the prevailing barometric pressure. This total pressure was the absolute system pressure and was recorded in atmospheres.

2) Record Chromatograph Attenuation.

This attenuation corresponded to the setting on the chromatograph at the time the sample gas was being injected.

3) Record Manometer Pressure.

This pressure corresponded to the difference in height between the two legs of the manometer during injection. It was therefore the gauge pressure under which the sample gas was injected. The value was recorded in mm Hg.

4) Calculate the Absolute Injection Pressure.

This pressure was the sum of the gauge pressure under which the gas was injected and the prevailing barometric pressure. This pressure was expressed in mm Hg.

5) Record Peak Height.

This value was the average height of the peaks obtained on the recorder following the injection of the sample gas. It was expressed in chart paper scale units.

6) Record Machine Sensitivity.

This value was the peak height measured at attenuation "8" when calibration gas was injected at a manometer pressure of 725 mm Hg.

This information was obtained from a "sensitivity check" run immediately after the sample gas data were taken. This value could then be used as a basis on which to relate the present data back to the calibration curve by eliminating the effects of a different barometric pressure and machine sensitivity.

7) Record the Barometric Pressure.

This pressure, in mm Hg., was read from a barometer located in the laboratory.

8) Calculate a Sensitivity Correction.

If the sensitivity of the chromatograph was greater on the day the data were taken than on the day the calibration curve was run, all values will be correspondingly higher. Thus to offset this effect, all values must be multiplied by the factor of,

$$\text{calibration sensitivity} / \text{"machine sensitivity"} \quad (74)$$

In our case the "calibration sensitivity" was 6.85 chart units.

9) Calculate the Barometric Pressure Correction.

The sensitivity correction forces the new data point to lie on a line horizontal with the old data point run at the same manometer reading. Since they may not have been made at the exact same absolute pressure it is necessary to shift the new point along this horizontal line by using a barometric pressure correction. Each peak height was multiplied by the ratio,

$$\frac{725 \text{ mm Hg} + \text{barometric pressure on day of experiment}}{725 \text{ mm Hg} + \text{barometric pressure on day calibration curve was made.}}$$

10) Multiply Sensitivity Correction by the Barometric Pressure Correction.

11) Multiply the Peak Height (#5) by the Correction Factors (#10).

This provides a raw peak height which is now on the same basis as the calibration curve.

12) Calculate Attenuation Correction.

The attenuation factors, as previously determined, relate the peak height read on one attenuation to what the same conditions would have produced at the attenuation used to make the calibration curve. This was necessary because even though a peak height of 15 (say) could be graphed and used on the calibration curve, such a height could not be directly measured on the 10-unit chart paper.

13) Multiply the Corrected Peak Height (#11) by the Attenuation Factor (#12).

14) Determine the Partial Pressure of Neopentane in the Sample.

Using the peak height found by multiplication in step #13, the calibration curve was used to determine the corresponding partial pressure.

15) Determine the Corrected Partial Pressure.

Since the calibration curve was drawn for 0.805 mole percent neopentane and the correct composition was 0.81 mole percent neopentane, the value of #14 must be multiplied by the ratio,

$$0.81 / 0.805 . \quad (76)$$

16) Calculate the Vapor Composition.

The composition was found by dividing the partial pressure of neopentane (#15) by the total pressure in the injection system (#4).

17) Calculate the Enhancement Factor.

Calculation of the enhancement factor provided a quick check on the quality of the data. Small irregularities in the data were quickly noted by plotting enhancement factor versus total system pressure. If the system were ideal, the partial pressure exerted by the solid phase component would be the same as its vapor pressure at that temperature, but since the system is not ideal, the deviation from ideality can be measured by,

$$yP / p^0 \quad (77)$$

where y = mole percent neopentane in the vapor,

P = the total system pressure, and

p^0 = the vapor pressure of neopentane at the given temperature.

All of the above calculations were made as the data were being taken to provide a constant check on the operation of the system. If any irregularities in either the composition calculation or enhancement factor were noted, the system could be checked out and the data point repeated before either the temperature or pressure was changed.

Sample Calculation:

1) System Pressure.

Barometric pressure = 621.3 mm Hg = 0.818 atmosphere.

Gauge Pressure = 40 psig = 2.723 atmosphere.

Total Pressure = 3.541 atmosphere.

2) Attenuation = 2.

3) Manometer Pressure = +25 mm Hg (right leg at 60).

4) Absolute Pressure of Injection = 621.3 + 25 = 646.3 mm Hg.

5) Peak Height.

Peak Heights Recorded: 4.06,
4.06,
4.07,
4.08,
4.05.

Average Peak Height = 4.06 units.

6) Machine Sensitivity = 6.80 units.

7) Barometric Pressure = 621.3 mm Hg.

8) Sensitivity Correction = 6.85 / 6.80 = 1.0074

9) Barometric Pressure Correction = 621.3 + 725/1343.2 = 1.0023.

10) Total Correction = (1.0023)(1.0074) = 1.0097.

11) Corrected Peak Height = (1.0097)(4.06) = 4.10 units.

12) Attenuation Correction = 0.5 (base attenuation = 4).

13) Final Peak Height = 2.05 units.

14) Partial Pressure as determined from the Calibration curve = 1.63 mm Hg.

15) Corrected Partial Pressure = (1.63)(.81) / .805 = 1.64 mm Hg.

16) Vapor Composition = 1.64 / 646.3 = 0.00254 mole fraction neopentane.

17) Enhancement Factor = (.00254)(3.541) / (.006292) = 1.4277.

ANALYSIS OF DATA

As data were taken during an experimental run, vapor compositions and enhancement factors were immediately calculated and plotted as in Figure 19 through Figure 21 in the "Results" section of this report. This was done to insure that the equipment was working properly and reasonable values were being obtained. In this way, poor data points could be quickly detected and rechecked. The data points were then cross-plotted as shown in Figure 11 through Figure 13 to provide additional checks for possible erroneous data points. Numerous data points were reproduced on different days (see Appendix E) to establish the fact that the data are in fact accurate.

After the experimental runs were made and the data were accepted on the basis of the above analysis, values of B_{12} were calculated from the equation,

$$B_{12} = \frac{1}{2Py_2^2} \left\{ B_{11}P_1^0 + v_1^C (P - P_1^0) - P [B_{11} + y_2^2 (-B_{11} - B_{22})] \right\} \quad (78)$$

$$- \frac{RT}{2Py_2^2} \ln \frac{y_1 P}{P_1^0} .$$

This was done quickly on a PDP-10 computer by using Program I as shown in Appendix I. Ideally, the calculated values of B_{12} should be independent of pressure and thus all values calculated for one isotherm should have been constant. However, in some cases the values at different pressures varied significantly from one another and therefore an analysis

FIGURE 11

Cross Plot of Composition versus Temperature

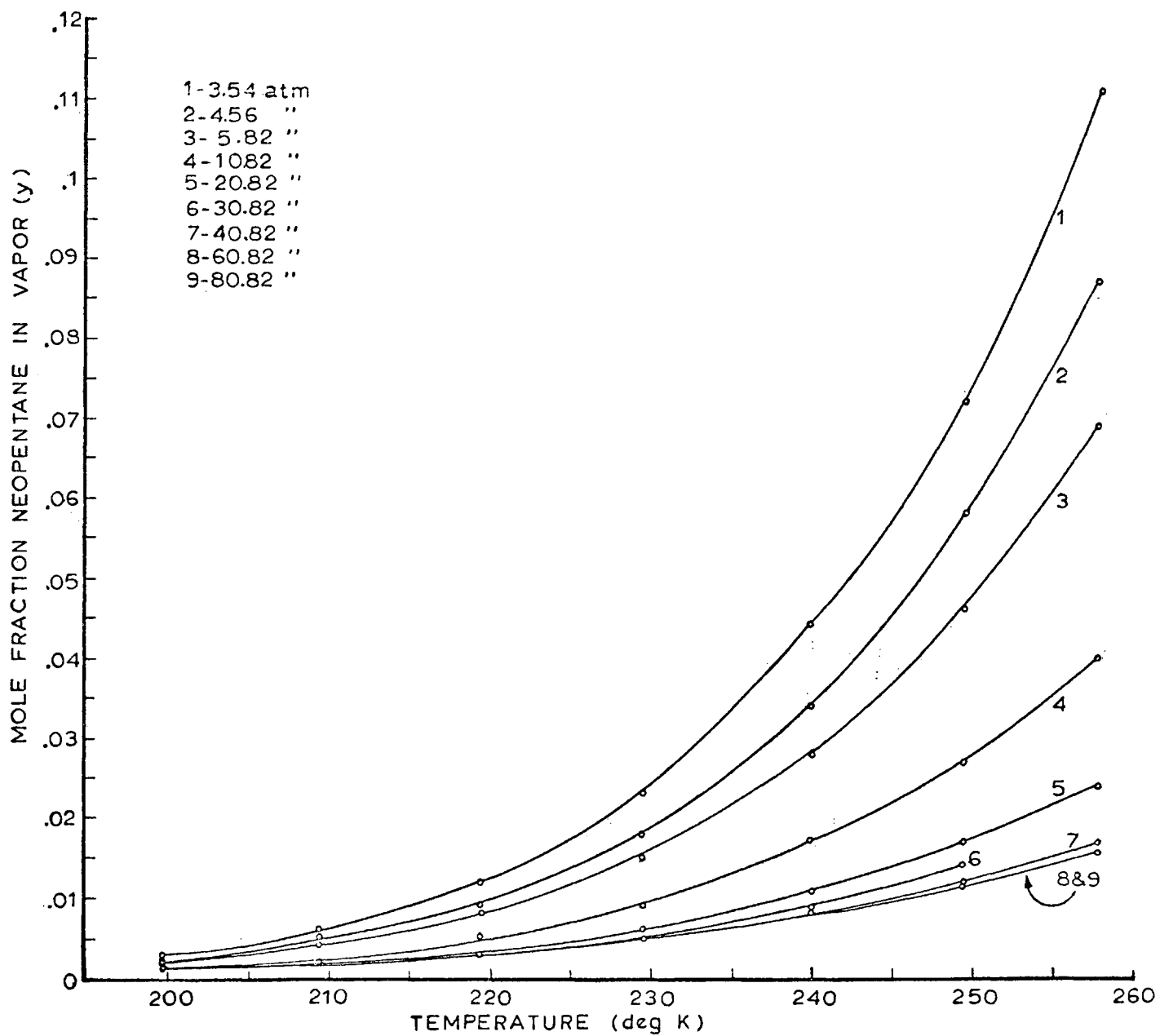


FIGURE 12
Semi-log Cross Plot of Enhancement Factor
versus Temperature Inverse

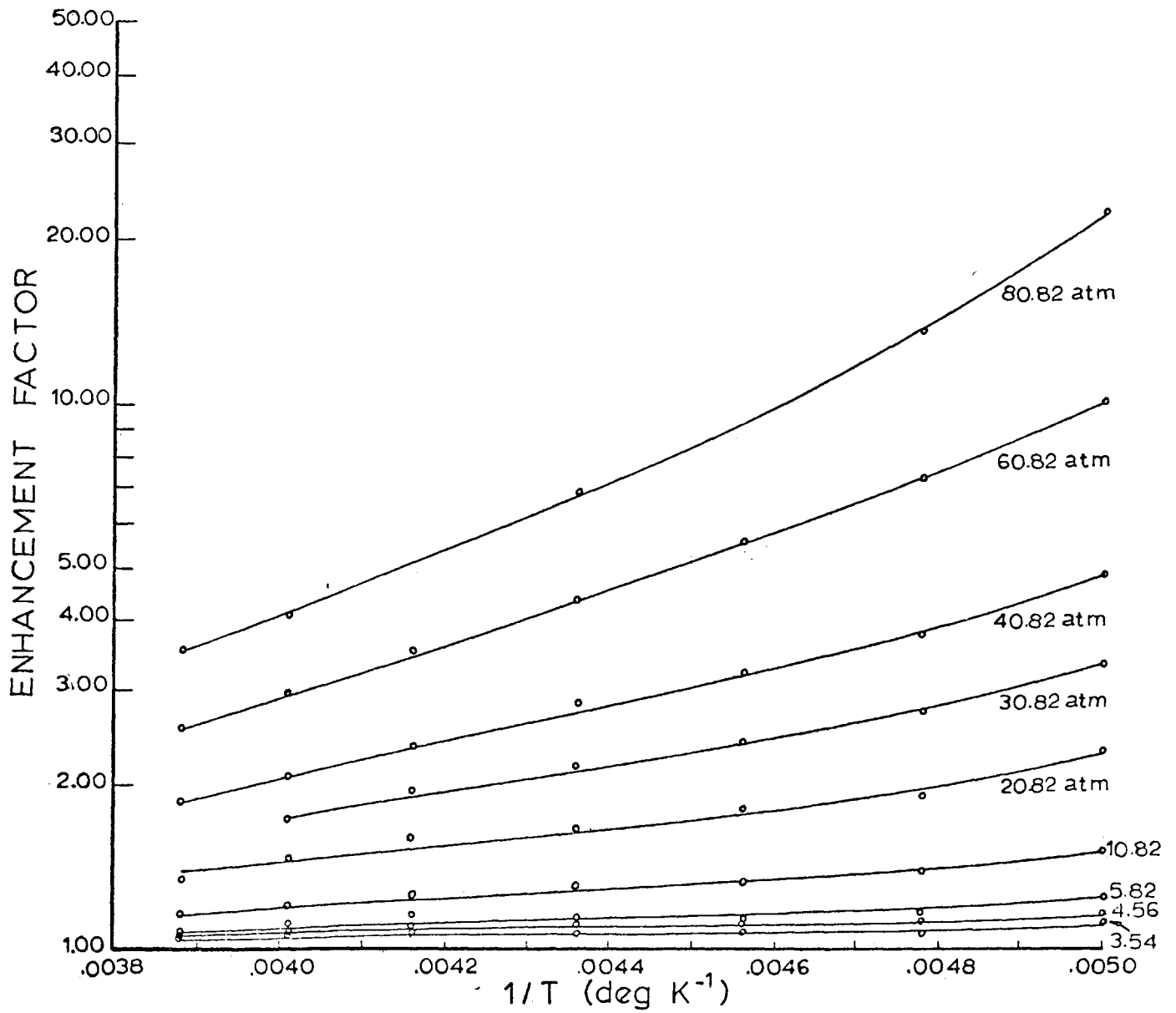
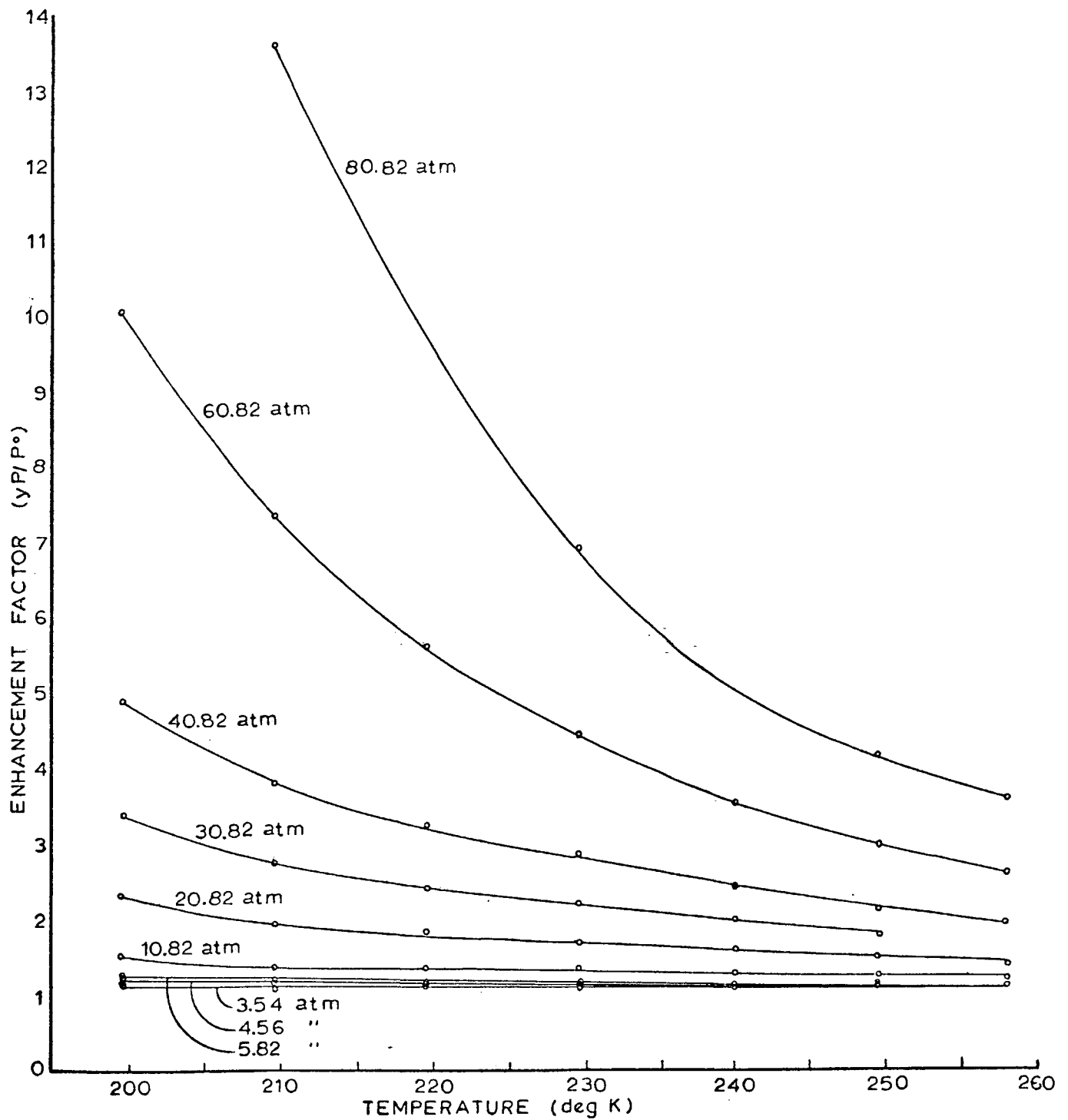


FIGURE 13

Cross Plot of Enhancement Factor versus Temperature



was carried out to determine if the error inherent in the experimental procedure could account for the deviations. It was determined that the following errors may have been present in the various readings:

- 1) manometer ± 0.5 mm Hg,
- 2) atmosphere gauge. ± 0.05 atmosphere,
- 3) psig gauges ± 0.2 psig,
- 4) peak height ± 0.01 unit, and
- 5) partial pressure. ± 0.01 mm Hg.

If, for any data point, errors of the maximum magnitude were made in all readings, it was determined that an error of 1.3% would result in the value of y , the mole fraction neopentane in the vapor. In addition to y -values, the other variables in Equation (78) were also changed by small amounts to determine their effect on values of B_{12} as calculated by using Program I. The results of this analysis for one isotherm are shown in Table 3. As can be seen, the quantity which most greatly affects the B_{12} values when varied within experimental bounds is the y -value. It therefore was apparent that of all the variables that could have caused the B_{12} values to vary from a constant, the y -value was the most significant.

Following this reasoning, Program I was designed so as to increment values of y in Equation (78) and to calculate the corresponding B_{12} values. The y -values ranged from -1.5% to +1.5% of the original value in increments of 0.2%. The B_{12} values obtained for each isotherm over this range were then analyzed to determine the values of y which produced the most constant values of B_{12} . Since these y -values were within the experimental error of the apparatus, this new set of pressures, y -values, enhancement

factors, and B_{12} values were taken as the best available data within the accuracy of the experimental apparatus.

The new values of B_{12} were then analyzed to determine a representative value. In some cases one or more data points were considerably larger or smaller than the others and therefore tended to skew the average unnecessarily. Therefore, a 90% confidence level was chosen and a confidence interval calculated for the data. All B_{12} values falling outside this confidence interval were rejected and not included in the averaging procedure. The remaining values were averaged and the standard deviation calculated. The results are shown in Table 4. Also shown are the results of the averaging procedure when applied to all of the original data.

The accepted values of B_{12} were then used to obtain the experimental points on Figure 14. When compared to the generalized correlation of McGlashan, Potter, and Wormold, the value of k_{12} for each data point was determined. These values are shown in Table 5. Also calculated were the values of $T_{c_{12}}$ which would have been necessary to fit the experimental data exactly to the generalized correlation.

The values of temperature, pressure, and y-value were recorded to more decimal places than significant figure calculations justify in order to minimize roundoff errors.

TABLE 1

Sensitivity Analysis Variables

<u>Variable</u>	<u>Base Value</u>	<u>Magnitude of Change</u>	<u>Value used Appropriate Calculation</u>
Temperature (T)	249.453 ⁰ K	+0.01 ⁰ K	249.463 ⁰ K
Vapor Pressure (P ₀)	0.24097 atm.	+0.00004 atm.	0.24101 atm
System Pressure (P)	-	+0.1 atm, or +0.1 psig	-
Vapor Composition (y)	-	+1.3%	
Second Virial Coefficient of Neopentane (B ₁₁)	-1415.52 cc/gmole	-30 cc/gmole	-1445.52 cc/gmole
Second Virial Coefficient of Argon (B ₂₂)	-28.20 cc/gmole	-1.0 cc/gmole	-29.20 cc/gmole
Specific Volume (v)	100.0 cc/gmole	+10 cc/gmole	110.0 cc/gmole

TABLE 2

Sensitivity Analysis Base Values

<u>System Pressure (atm)</u>	<u>Mole Fraction Neopentane in Vapor (y-value)</u>	<u>Enhancement Factor</u>	<u>B₁₂ (cc/gmole)</u>
3.539	0.07222	1.0607	-99.46
4.560	0.05771	1.0921	-136.24
5.815	0.04587	1.1070	-120.51
10.815	0.02718	1.2199	-137.77
20.815	0.01718	1.4839	-147.36
30.815	0.01370	1.7522	-140.49
40.815	0.01235	2.0925	-139.43
60.815	0.01177	2.9705	-136.63
80.815	0.01227	4.1160	-131.14

TABLE 3
Results of Sensitivity Analysis
B₁₂ Values after changing respective variable (ccgmole)

System Pressure (atm)	Original Data	T and p ₀	P	y	B ₁₁	B ₂₂	v
3.539	-99.46	-98.85	-105.59	-141.40	-98.22	-99.26	-94.05
4.560	-136.24	-135.80	-139.76	-168.02	-135.24	-136.74	-130.91
5.815	-120.51	-120.00	-122.50	-144.60	-119.72	-121.01	-115.25
10.815	-137.77	-137.61	-144.84	-150.22	-137.27	-138.27	-132.60
20.815	-147.36	-147.34	-148.81	-153.72	-147.01	-147.86	-142.25
30.815	-140.49	-140.40	-140.90	-144.64	-140.19	-140.99	-135.39
40.815	-139.43	-139.31	-139.49	-142.47	-139.14	-139.93	-134.33
60.815	-136.63	-136.61	-136.60	-138.68	-136.33	-137.13	-131.53
80.815	-131.14	-131.09	-131.04	-132.59	-130.81	-131.64	-126.03

TABLE 4
Calculated B_{12} Values

Temperature $^{\circ}\text{K}$	Average B_{12} (all data) (cc/gmole)	Standard Deviation	Average B_{12} (90% confidence)	Standard Deviation
257.906	-109.44	8.69	-110.74	5.26
249.453	-145.56	9.49	-142.72	3.74
240.153	-170.45	10.73	-171.56	3.89
229.528	-195.68	14.53	-201.26	4.87
219.562	-227.19	9.04	-224.24	2.44
209.594	-238.07	21.57	-241.45	9.64
199.618	-287.33	12.04	-289.48	4.26

FIGURE 14

Experimental Data versus Generalized Correlation

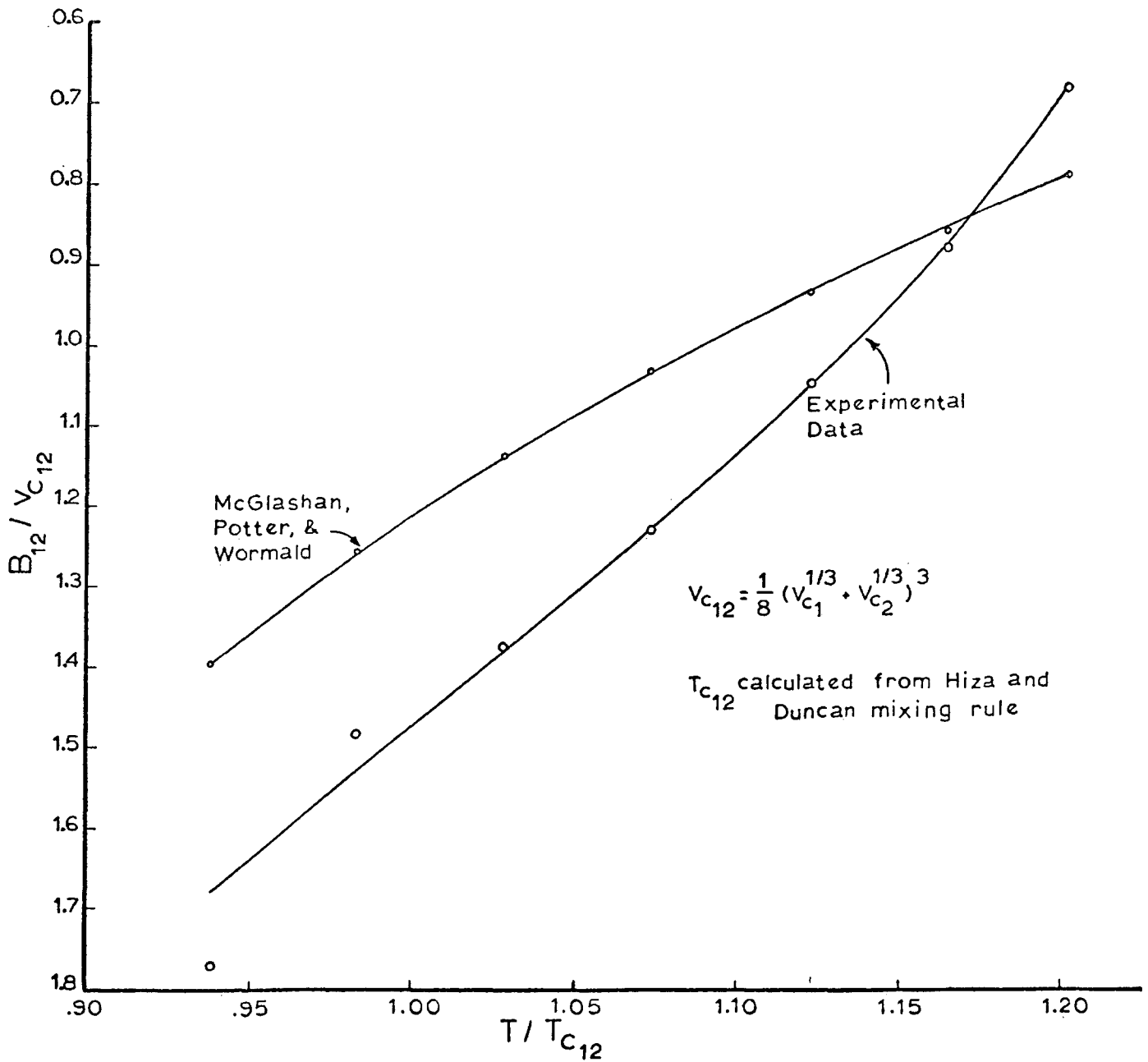


TABLE 5Calculated k_{12} values

Temperature ($^{\circ}$ K)	k_{12}	T_{c12} ($^{\circ}$ K)
257.906	0.227	197.66
249.453	0.165	213.68
240.153	0.125	223.75
229.528	0.099	230.38
219.562	0.094	231.88
209.594	0.104	229.22
199.618	0.070	237.84

$$\bar{k}_{12} = 0.126$$

TABLE 6

Comparison of k_{12} values by Mixing Rules

<u>Rule</u>	<u>k_{12}</u>
1) Hudson & McCoubrey	
$k_{12} = 1 - \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{(I_1 + I_2)} \right\} \left\{ 2^6 \frac{\sigma_1^3 \sigma_2^3}{(\sigma_1 + \sigma_2)^6} \right\}$	0.353
2) Equation (65)	
$k_{12} = 1 - \left\{ \frac{2(I_1 I_2)^{\frac{1}{2}}}{(I_1 + I_2)} \right\}$	0.0213
3) Sikora	
$k_{12} = 1 - \left\{ g(I) f(v) \right\}$	0.60
4) Hiza & Duncan	
$k_{12} = 0.17(I_1 - I_2)^{\frac{1}{2}} \ln \left(\frac{I_1}{I_2} \right)$	0.164

where:

I (volts)	<u>Argon</u> 15.755	<u>Neopentane</u> 10.35
ϵ ($^{\circ}$ K)	118.13	233.66
σ (\AA)	3.499	7.420

The second method used to determine the representative value of B_{12} was the method proposed by Canfield and Chiu. By using Program II and the best values of pressure, y , and enhancement factor, as determined by the previous procedures, the corresponding values of "ERT" were calculated. The results are shown in Table 7. Using 20 atmospheres as the lowest pressure, the values were plotted versus pressure, the data were to fit with the best straight line, and the line was extrapolated to the vapor pressure of neopentane (essentially zero on the curves). Using the expression,

$$ERT_i = B_{11} - 2B_{12} \quad , \quad (79)$$

where ERT_i = value of ERT at the intercept,

B_{11} = the second virial coefficient of argon, and

B_{12} = the interaction virial coefficient,

the value of B_{12} was determined. The results of the analysis are shown in Table 8. Table 8 also shows the values obtained using an estimated curve, not necessarily a straight line. The straight line approximation will probably not yield the most accurate value of ERT_i as it is unlikely that the function is linear, however the approximation is used in order to provide data for the statistical analysis.

A drawback to the method of Canfield and Chiu is the argument that the higher pressure points determine the slope of the "best fit" line and therefore the intercept, and it is precisely these points which are the most subject to error due to the possible effect of the third virial coefficient, which in this case was ignored. In order to determine whether

the pressures used in this experiment were in fact great enough to cause such difficulties, the following analysis was made.

Under the assumptions of ideality the following expression holds:

$$Z = \frac{Pv}{RT} = 1 \quad (80)$$

where Z = the compressibility factor,

P = the system pressure,

v = the molar volume,

R = the appropriate gas constant, and

T = the absolute temperature.

Deviations from ideality in a pure component system are accounted for by the virial coefficients in the following expression:

$$Z = 1 + \frac{B_{11}}{v} + \frac{C_{11}}{v^2} + \dots \quad (81)$$

Since the mole fraction of neopentane in the vapor phase is so small at high pressures, we may assume the vapor to be essentially pure argon.

If this assumption holds and the virial equation is truncated after the second term, the following expression applies:

$$Z = 1 + \frac{B_{11}P}{RT} \quad (82)$$

At four different temperatures, the compressibility factor was calculated from literature values (Gosman and others, 1969) of P , v , R , and T for pure argon using Equation (80). Then by using the value of B_{11} accepted for the experimental calculations, the compressibility factor was also calculated using Equation (82). If any large deviations occurred between the two z -values for one temperature, the third and higher coefficients would have been important. However, as can be seen by the results

in Table 9, no significant deviations are apparent. Thus the procedure of truncating the virial equation after the second term was considered acceptable.

TABLE 7

Data for "ERT" plots (Figures 12,13,14, and 15)

Temperature (°K)	Sys. Pressure (atm.)	Original Data "ERT"	Best Data 'ERT'
199.618	3.540	439.08	475.63
	4.562	474.48	504.99
	5.819	522.25	534.84
	10.819	532.75	538.77
	20.819	554.56	555.88
	30.819	542.44	544.17
	40.820	532.25	533.06
	60.820	515.83	517.67
	80.821	523.42	524.70
209.594	3.535	266.95	328.64
	4.556	360.75	410.31
	5.812	384.10	421.05
	10.812	424.67	444.14
	20.813	441.97	454.43
	30.813	457.11	464.79
	40.813	457.06	463.33
	60.813	455.42	458.38
	80.813	444.11	447.01
219.562	3.537	346.22	404.04
	4.558	412.63	455.82
	5.813	372.36	407.97
	10.813	376.74	403.57
	20.813	406.26	415.18
	30.813	405.61	411.21
	40.814	408.94	413.48
	60.814	400.17	403.62
	229.528	3.533	228.29
4.556		317.76	363.20
5.811		336.28	374.20
10.811		358.53	377.77
20.811		359.71	369.54
30.811		368.22	374.42
40.813		368.42	373.07
60.814		345.97	349.36
80.816		333.08	335.82
240.153	3.534	287.22	313.71
	4.555	240.15	263.56
	5.810	283.99	302.10

Table 7 (cont'd.)

<u>Temperature</u> (°K)	<u>Sys. Pressure</u> (atm)	<u>Original Data</u> "ERT"	<u>Best Data</u> 'ERT'
240.153	10.811	298.12	307.15
	20.811	332.63	336.19
	30.811	323.47	324.87
	40.811	301.71	302.46
	60.811	289.68	288.92
249.453	3.539	166.10	242.89
	4.560	240.00	298.85
	5.815	213.45	254.26
	10.815	247.65	268.79
	20.815	266.69	277.44
	30.815	252.89	259.90
	40.815	250.73	255.86
	60.815	245.12	248.57
	80.815	235.37	236.59
257.906	3.541	115.23	212.88
	4.562	118.29	167.39
	5.817	125.27	176.25
	10.817	161.33	187.24
	20.817	174.72	187.55
	40.809	205.40	212.16
	60.814	200.67	204.85
	80.814	202.58	205.62

FIGURE 15

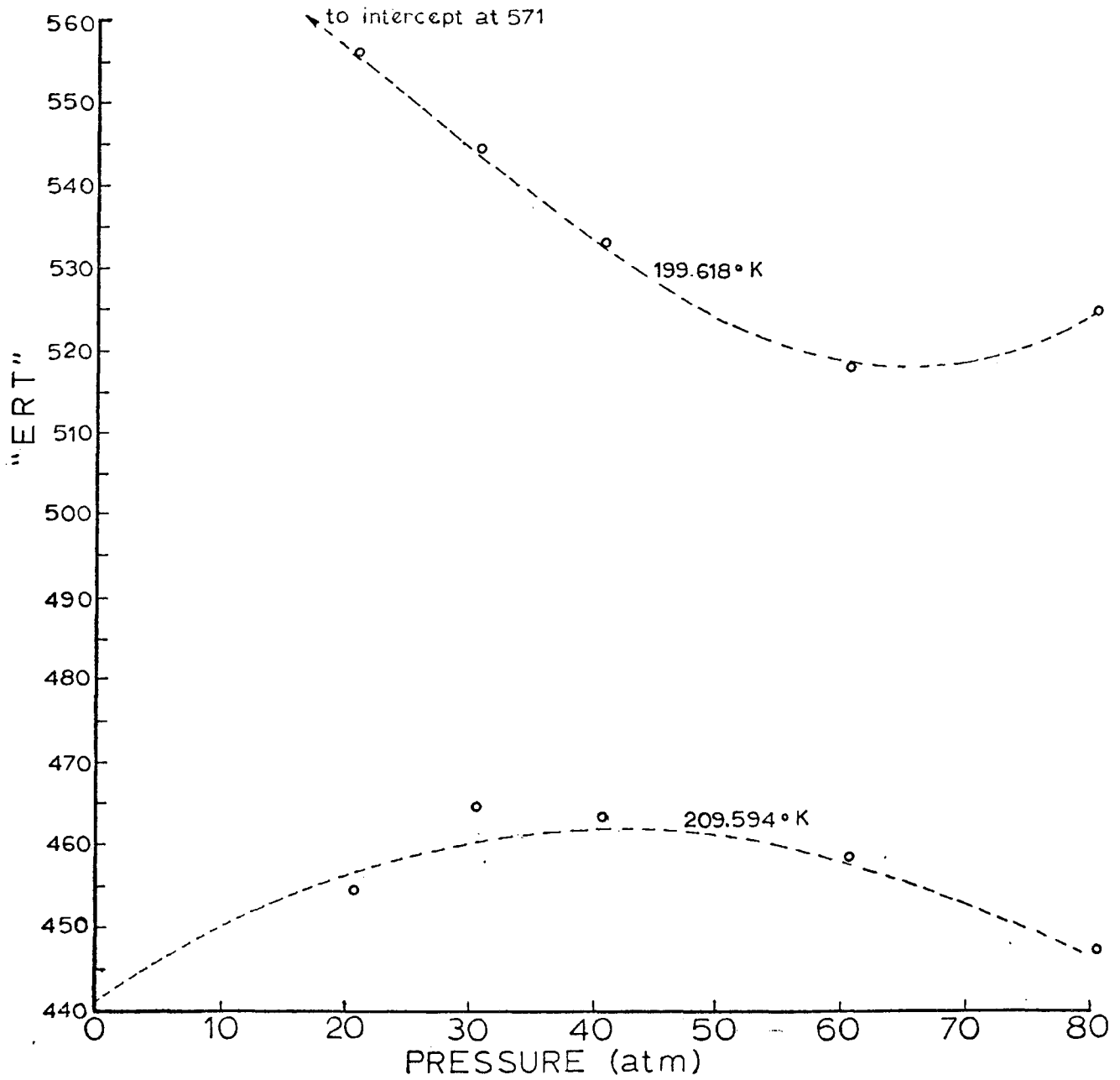


FIGURE 16

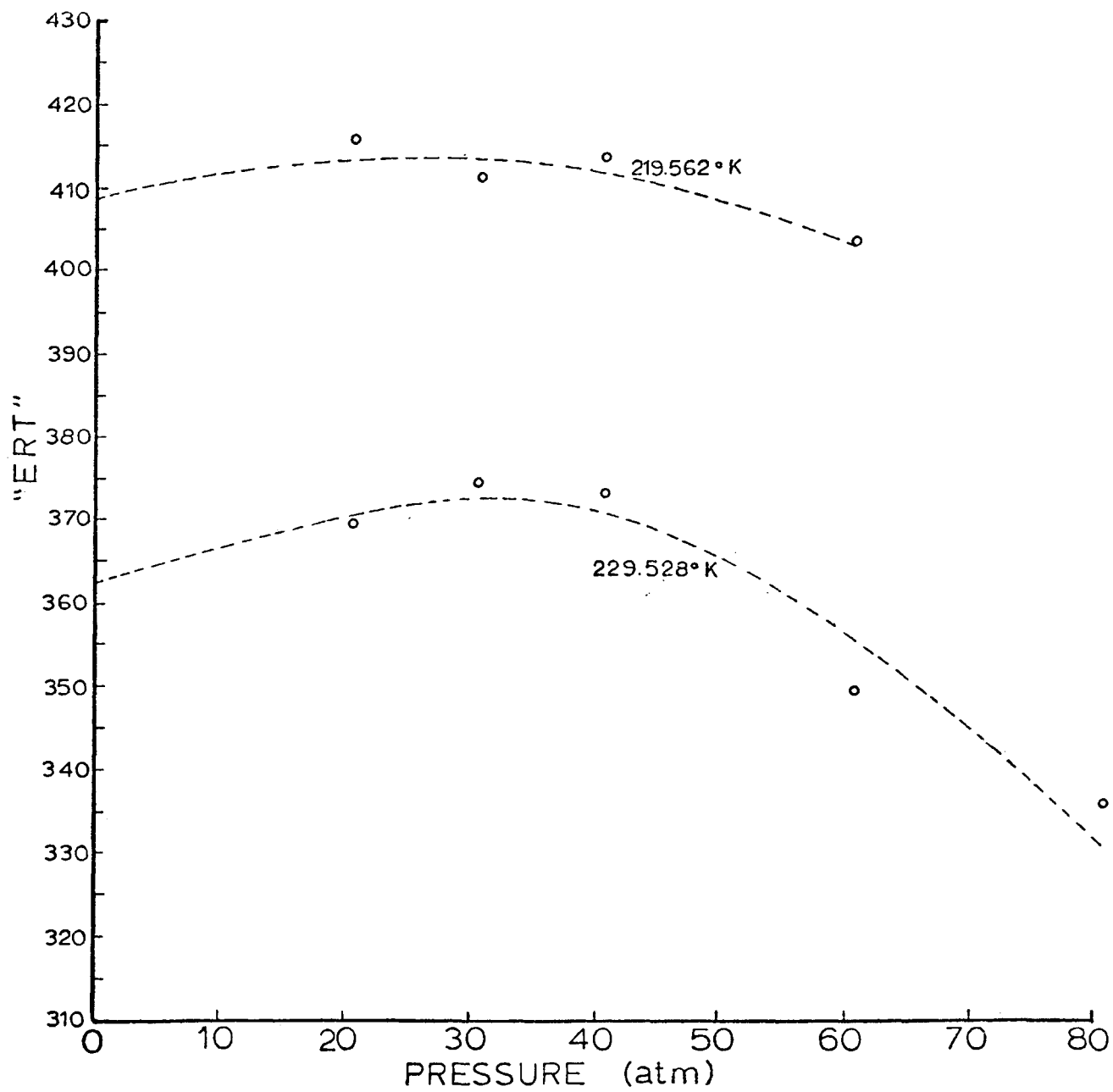


FIGURE 17

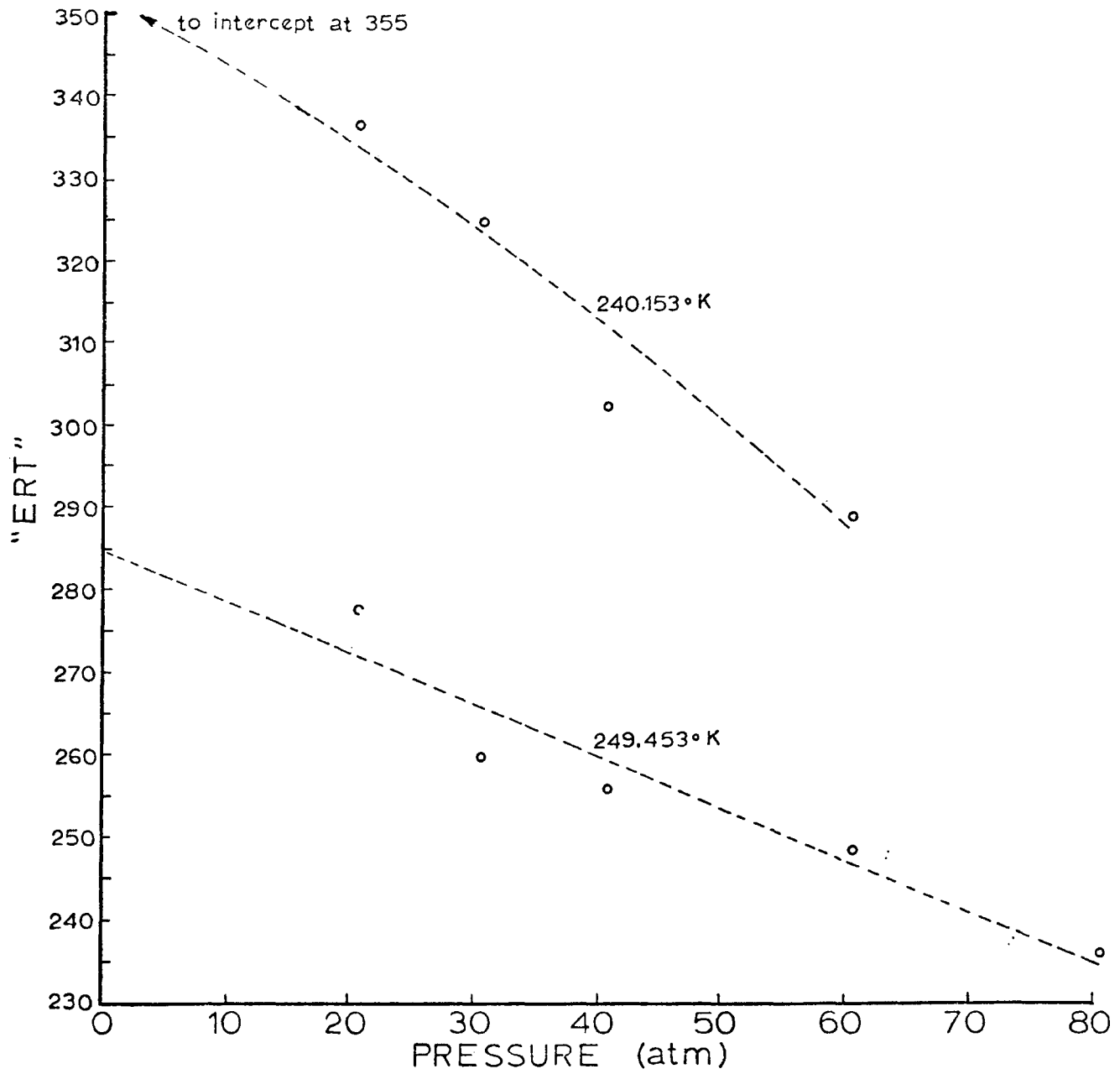


FIGURE 18

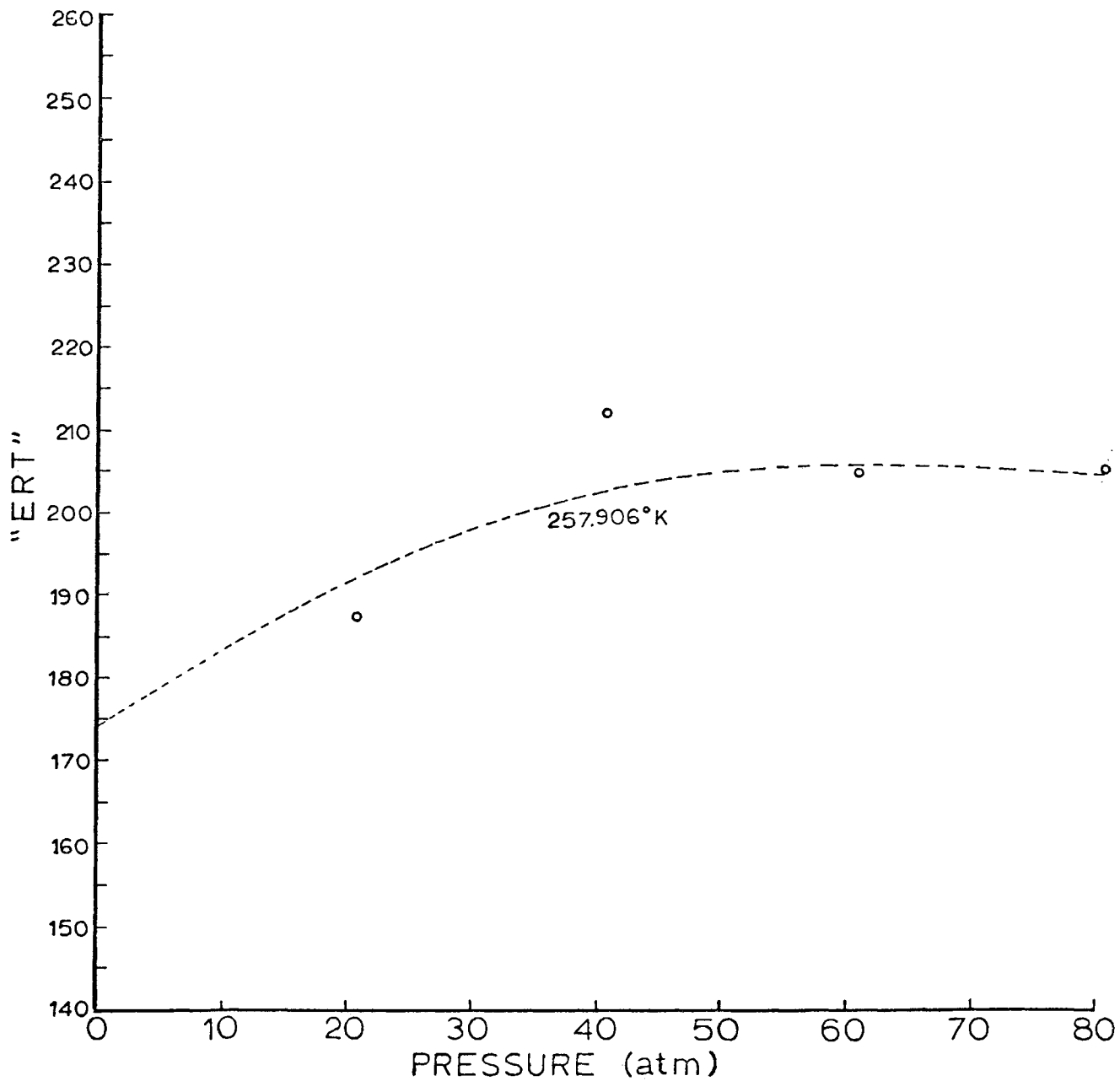


TABLE 8

Results of Canfield and Chiu Analysis

Temperature (°K)	ERT _i by straight line approximation	B ₁₂ (cc/gmole)	ERT _i by rough curve approximation	B ₁₂ (cc/gmole)
199.618	560.76 ± 66.64	-304±33.32	571.0	-310.06
209.594	465.03 ± 50.07	-254±25.04	441.5	-242.61
219.562	414.36 ± 22.98	-227.19±11.49	409.5	-224.76
229.528	391.32 ± 54.70	-213.29±27.35	364.0	-199.63
240.153	358.62 ± 47.00	-194.97±23.50	355.0	-193.16
249.453	283.61 ± 39.06	-155.91±19.54	284.0	-156.10
257.906	190.62 ± 76.33	-108.03±38.17	174.0	-99.72

TABLE 9

Compressibility Factor Comparisons

<u>Approximate Temperature (°K)</u>	<u>Z Equation (82)</u>	<u>Z Equation (80)</u>	<u>% Difference</u>
258	0.9029	0.9169	1.55
249	0.8887	0.9030	1.61
210	0.7946	0.8033	1.09
200	0.7576	0.7593	0.22

RESULTS

This section contains the pertinent information derived from the experimental data. Table 10 lists the enhancement factors and mole fractions of neopentane in the vapor for all temperatures and pressures investigated. Figure 19 shows how the vapor composition changes with respect to pressure for all seven isotherms studied. Figure 20 shows how enhancement factor varies with respect to pressure over the entire pressure range studied, whereas Figure 21 shows only the data points at the lower pressures, where the points become quite close together on Figure 20. Table 11 summarizes the B_{12} and k_{12} values determined by the Canfield and Chiu method.

TABLE 10

Composition and Enhancement Factor Data

Temperature (°K)	System Pressure (atm)	Mole Fraction Neopentane in Vapor Phase	Enhancement Factor
199.618	3.540	.00254	1.1249
	4.562	.00206	1.1750
	5.819	.00171	1.2491
	10.819	.00112	1.5218
	20.819	.00088	2.3062
	30.819	.00087	3.3696
	40.820	.00095	4.8795
	60.820	.00132	10.0527
	80.821	.00225	22.7758
209.594	3.535	.00557	1.0807
	4.556	.00453	1.1323
	5.812	.00370	1.1805
	10.812	.00235	1.3951
	20.813	.00170	1.9371
	30.813	.00162	2.7363
	40.813	.00170	3.7991
	60.813	.00219	7.3228
	80.813	.00307	13.5942
219.562	3.537	.01173	1.0951
	4.558	.00949	1.1422
	5.813	.00762	1.1689
	10.813	.00469	1.3377
	20.813	.00329	1.8089
	30.813	.00295	2.4029
	40.814	.00299	3.2235
	60.814	.00349	5.5976
229.528	3.533	.02252	1.0694
	4.556	.01816	1.1122
	5.811	.01474	1.1505
	10.811	.0092	1.6809
	30.811	.00528	2.1877
	40.811	.00515	2.8264
	60.816	.00539	4.4036
	80.816	.00635	6.8865
240.153	3.534	.04361	1.0799
	4.555	.03421	1.0910
	5.810	.02777	1.1295

Table 10 (cont'd)

Temperature °K	System Pressure (atm)	Mole Fraction Neopentane in Vapor Phase	Enhancement Factor
240.153	10.811	.01622	1.2580
	20.811	.01102	1.6053
	30.811	.00920	1.9849
	40.811	.00830	2.3705
	60.810	.00824	3.5080
249.453	3.539	.07222	1.0598
	4.560	.05771	1.0910
	5.815	.04587	1.1070
	10.815	.02718	1.2199
	20.815	.01718	1.4839
	30.815	.01370	1.7522
	40.815	.01235	2.0925
	60.815	.01177	2.9705
	80.815	.01227	4.1160
257.906	3.541	.11084	1.0540
	4.562	.08670	1.0665
	5.817	.06931	1.0835
	10.817	.04015	1.1670
	20.817	.02408	1.3471
	40.809	.01724	1.8891
	60.814	.01562	2.5522
	80.814	.01634	3.5477

FIGURE 19

Semi-log Plot of Composition versus Pressure

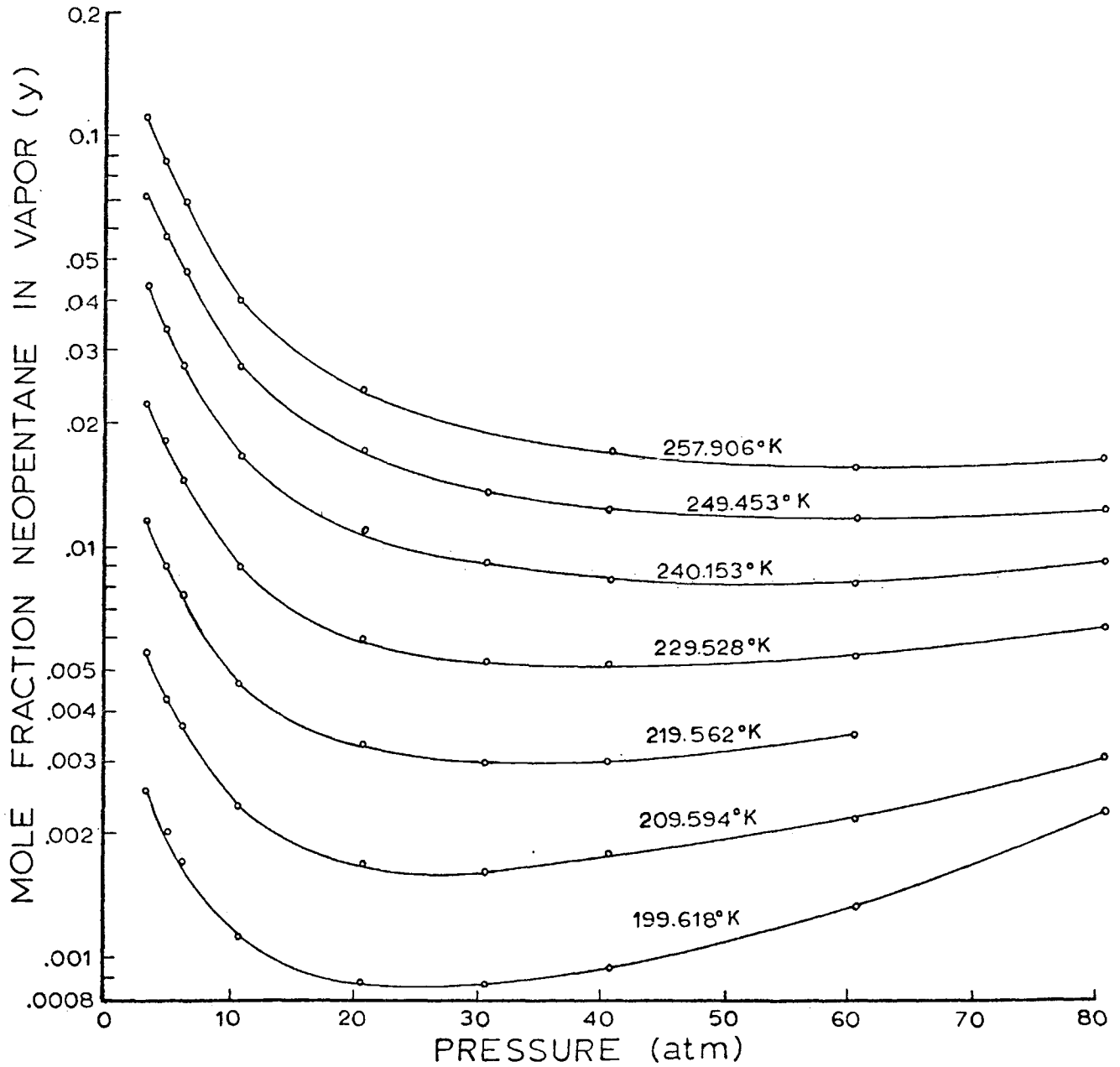


FIGURE 20

Enhancement Factor versus Pressure
(0-80 atmosphere)

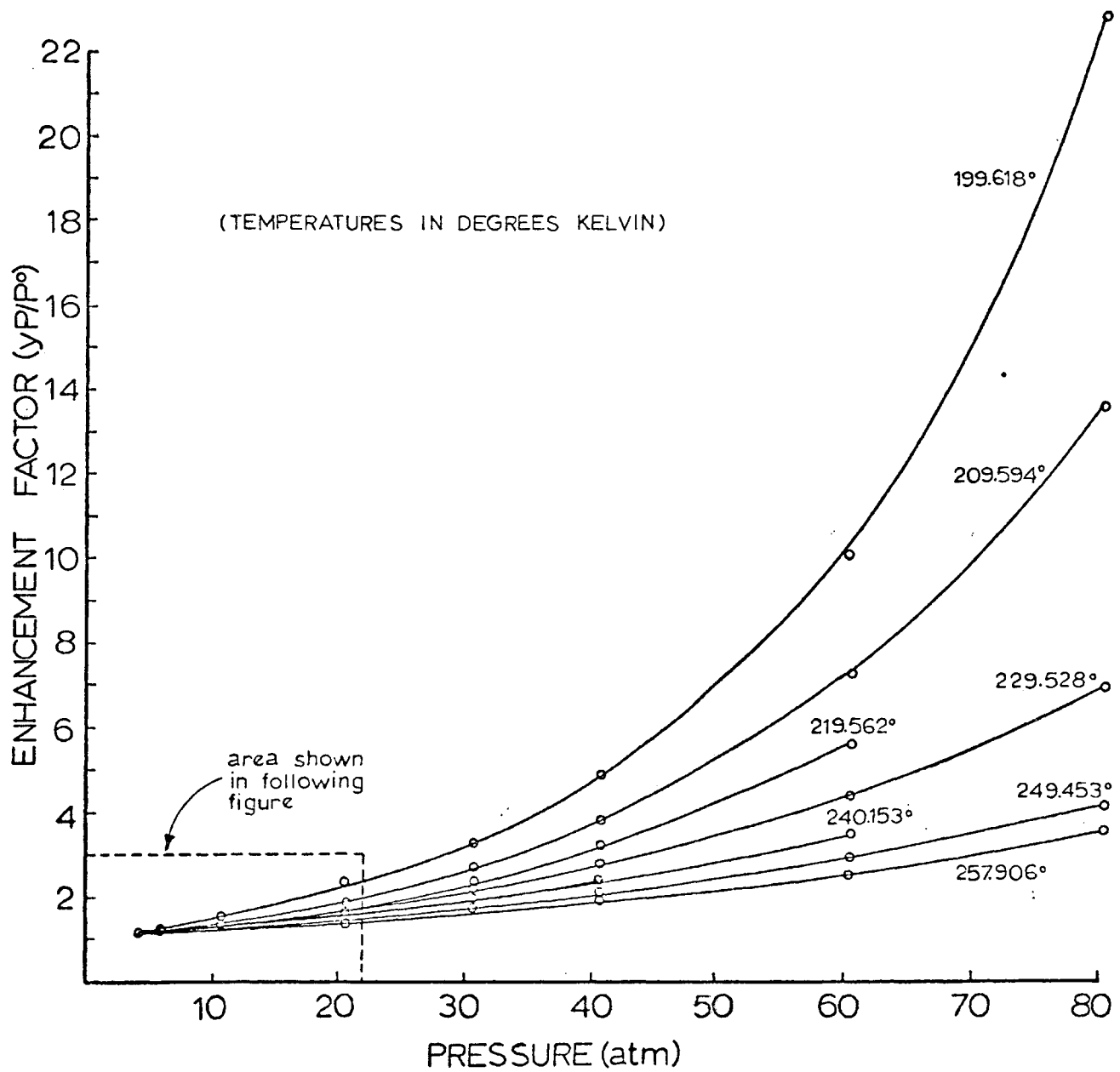


FIGURE 21

Enhancement Factor versus Pressure
(0-20 atmosphere)

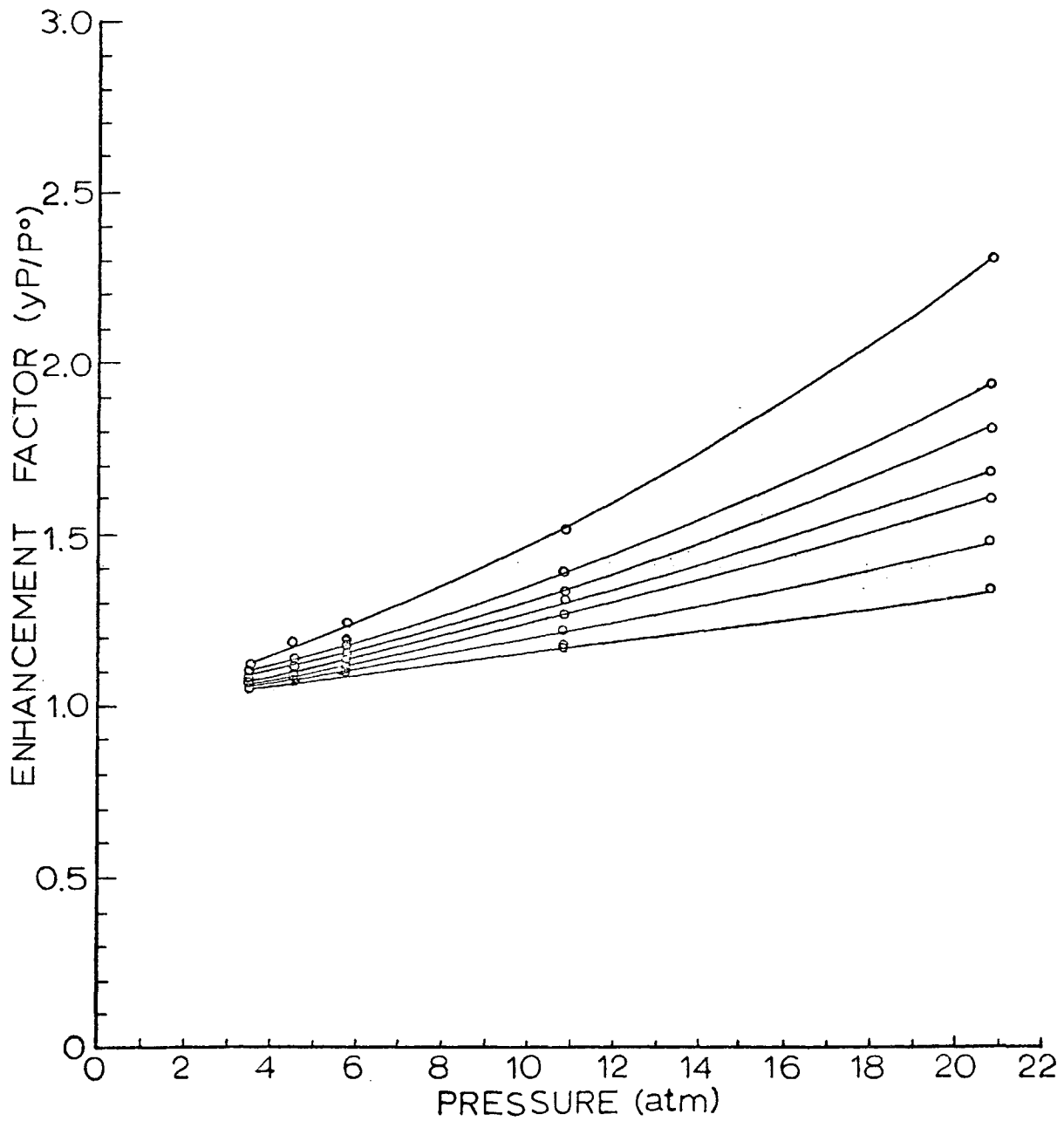


TABLE 11

Experimental B_{12} and k_{12} Values

Temperature	From Equation (40) Calculations			From Canfield and Chiu Method using linear approximation		
	B_{12}	$\frac{+}{-}$	k_{12}	B_{12}	$\frac{+}{-}$	k_{12}
257.906	-110.74	5.26	0.227	-108.03	38.17	0.235
249.453	-142.72	3.74	0.165	-155.91	19.54	0.131
240.153	-171.56	3.89	0.125	-194.97	23.50	0.072
229.528	-201.26	4.87	0.099	-213.29	27.35	0.075
219.562	-224.24	2.44	0.094	-227.19	11.49	0.088
209.594	-241.45	9.64	0.104	-254.37	25.04	0.082
199.618	-289.48	4.26	0.0702	-304.95	33.32	0.047

CONCLUSIONS

The material presented in this report represents the results of years of work by several investigators designing and constructing the experimental apparatus. Therefore one of the most important conclusions which may be drawn from the results of the study is that the equipment is in fact capable of making the measurement for which it was designed. However, the purpose of the project was not merely to construct a good piece of equipment, but rather to produce worthwhile data. From the results of this original data for the argon-neopentane system, the following conclusions may be drawn:

- 1) the vapor composition of the argon-neopentane system varies with pressure and temperature as shown in Figure 19,
- 2) the data is consistent, as shown by the various cross-plots, reproduced points, and Figures 20 and 21 which show the enhancement factor approaching 1.0 as the system pressure approaches zero,
- 3) the experimental data does not fit exactly either generalized correlation studied, thus indicating that much work has yet to be done on such correlations, and
- 4) no mixing rule exactly predicts the experimental results, however all rules attempting to account for molecular size were less successful than the empirical rule proposed by Duncan and Hiza, thus providing evidence that mixing rules involving molecular size grossly overcorrect for the size effect.

RECOMMENDATIONS

The following are recommendations to improve the operation of the present apparatus and therefore improve the experimental results:

- 1) replace the exit and inlet throttle valves with vernier throttle valves not loaded with spring releases,
- 2) install a positive shut-off valve between the equilibrium system and the analysis system,
- 3) install a vent line for the equilibrium vacuum pump,
- 4) replace the present connections between the analysis system and the analysis vacuum pump,
- 5) replace the present analysis vacuum pump with one capable of drawing extremely high vacuums, thus enabling the analysis manometer to be used as an accurate barometer, and
- 6) install an inclined manometer to minimize reading error.

The following are recommendations for additions to the present apparatus to allow more flexibility in the systems studied:

- 1) install a recirculation pump to eliminate the continuous loss of solid-phase component through the vapor, and
- 2) install a capillary in the cell to remove liquid samples, thus allowing liquid-vapor systems to be studied.

APPENDIX ACalibration Curve DataTABLE 12

I. Calibration Gas Samples (assuming 0.96 mole percent neopentane):

Data of 4/21/72

B.P. = 618.2

M.S. = 6.85

Absolute Injection Pressure (mm Hg.)	Attenuation	Peak Height (units)	Corrected Peak Height (units)	Partial Pressure Neopentane (mm Hg)
43.2	1	1.82	0.46	0.4147
143.2	2	2.95	1.48	1.375
243.2	2	5.00	2.50	2.335
343.2	4	3.51	3.51	3.295
443.2	4	4.53	4.53	4.255
543.2	4	5.57	5.57	5.215
643.2	4	6.58	6.58	6.175
743.2	4	7.58	7.58	7.135
843.2	4	8.60	8.60	8.095
943.2	8	4.80	9.60	9.055
1043.2	8	5.31	10.62	10.015
1143.2	8	5.81	11.62	10.975
1243.2	8	6.32	12.64	11.935
1343.2	8	6.85	13.70	12.895

II. Pure Neopentane Samples:

Absolute Injection Pressure (mm Hg.)	Attenuation	Peak Height (Units)	Corrected Peak Height (Units)	Partial Pressure Neopentane (mm Hg)
13.2	16	4.12-4.55	18.20-16.48	13.2
19.2	16	5.88-6.26	25.04-23.54	19.2
23.2	16	7.00-7.55	30.20-28.00	23.2
43.2	32	6.60-6.82	54.56-52.80	43.2
84.2	64	6.36	101.76	84.2
143.2	128	5.43	173.76	143.2
243.2	256	4.51	288.64	243.2
443.2	512	3.96	506.88	443.2
643.2	512	5.45	697.60	643.2
1043.2	1024	4.01	1026.56	1043.2

APPENDIX BCalibration Curve Check DataTABLE 13

Data of 5/4/72

Barometric Pressure = 617.3 mm Hg. Machine Sensitivity = 6.56 units

<u>Injection Pressure (abs)</u>	<u>Attenuation</u>	<u>Peak Height</u>	<u>Corrected P.H.</u>	<u>P. P. Neopentane</u>
1342.3 mm Hg.	8	6.56	13.70	12.89 mm Hg.
1042.3	8	5.11	10.66	10.06
842.3	4	8.28	8.64	8.09
443.3	4	4.35	4.55	4.26
243.3	4	2.39	2.49	2.34

Data of 5/10/72

Barometric Pressure = 615.5 mm Hg. Machine Sensitivity = 7.32 units

<u>Injection Pressure (abs)</u>	<u>Attenuation</u>	<u>Peak Height</u>	<u>Corrected P.H.</u>	<u>P. P. Neopentane</u>
1340.5	8	7.32	13.68	12.87
1040.5	8	5.68	10.60	9.99
441.5	4	4.80	4.48	4.24

APPENDIX CChromatographic Analysis of Calibration Gas

(I) Calibration Gas to be Analyzed:

Barometric pressure = 620.7 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 8.
 Peak Height = 6.906 units

Sensitivity Check for Calibration Gas:

Barometric pressure = 620.7 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 16.
 Peak height = 3.456 units.

Pure Neopentane (base of calculations):

Barometric pressure = 620.3 mm Hg.
 Injection pressure = -514 mm Hg.
 Attenuation = 64.
 Peak Height = 8.258 units.

Sensitivity Check for Pure Neopentane:

Barometric pressure = 620.4 ~ 620.3 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 16.
 Peak height = 3.412 units.

Attenuation correction factor = 8.048.

Pure neopentane peak @ attenuation = 8.....66.460 units.
 Calibration gas peak @ attenuation = 8..... 6.906 units.

Barometric pressure correction = $620.7 + 725/620.3 + 725$.

Machine sensitivity correction = $3.412/3.456$.

Total correction factor = 0.987562.

Corrected Calibration Gas Peak Height = 6.820 units.

Mole fraction neopentane in sample = $(106.3/1345.7)(6.820/66.460)=0.00811$.

Appendix C (cont'd).

(II) Calibration Gas to be Analyzed:

Barometric pressure = 620.4 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 8.
 Peak height = 7.104 units.

Sensitivity Check for Calibration Gas:

Barometric pressure = 620.4 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 8.
 Peak height = 7.104 units.

Pure Neopentane (base of calculations):

Barometric pressure = 619.2 mm Hg.
 Injection pressure = -514 mm Hg.
 Attenuation = 64.
 Peak height = 8.555 units.

Sensitivity Check for Pure Neopentane:

Barometric pressure = 619.1 ~ 619.2 mm Hg.
 Injection pressure = +725 mm Hg.
 Attenuation = 8.
 Peak height = 7.110 units.

Attenuation correction factor = 8.048.

Pure neopentane peak @ attenuation = 8 68.847 units.
 Calibration gas peak @ attenuation = 8 7.104 units.

Barometric pressure correction = $620.44 + 725/619.2 + 725$.

Machine sensitivity correction = $7.110/7.104$.

Total correction factor = 1.001813.

Corrected Calibration Gas Peak Height = 7.117 units.

Mole fraction neopentane in sample = $(105.2/1345.4)(7.117/68.847) = 0.00808$.

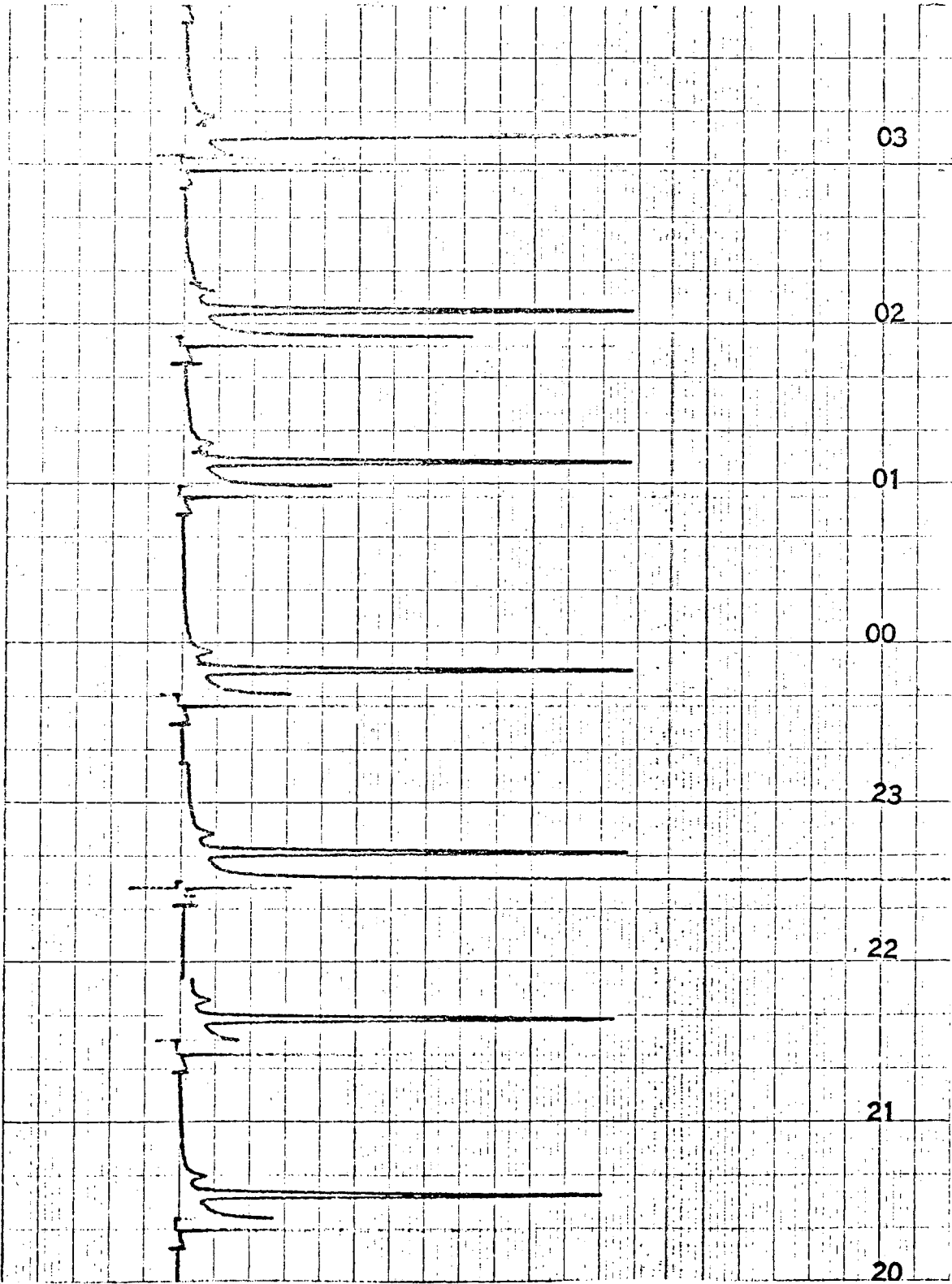
APPENDIX DAnalysis of Recorder Output

As with any chromatographic analysis, the quantity of the measured component can be determined by measuring the areas under the peaks produced on the recorder. However, if the peaks are sharp, as are the neopentane peaks shown in Figure 22, the area is directly related to the height of the peak, which is easily measured. All peaks recorded during the experiments resembled those depicted in Figure 22, having equal base widths, and thus any changes in area were evidenced by varying peak heights.

In order to obtain a value of peak height to be used in the calculations a series of no less than five peaks were obtained and their heights averaged. The five successive peaks were accepted only if they were reproducible within 0.05 chart units and only when random scatter was noted within the range.

FIGURE 22

Typical Recorder Peaks



APPENDIX ERaw Data

The data taken to provide the information necessary to plot one experimental data point consisted of the following:

- 1) reading the system pressure from the appropriate pressure gauges;
- 2) measuring the bath temperature with the platinum resistance thermometer,
- 3) recording the injection pressure as read on the manometer,
- 4) measuring the peak heights produced on the recorder by the injected sample gas,
- 5) measuring the peak heights produced on the recorder by calibration gas injected at 725 mm Hg. above atmospheric pressure,
- 6) reading the barometric pressure on the laboratory barometer and
- 7) recording the chromatograph attenuation.

Using this data and following the steps outlined in "Operational Calculations", the composition of the sample gas was calculated.

TABLE 14

Temp.	Pressure	AII	Inject. Press.	P.H.	M.S.	B.P.	y
257.906	3.540	8	-534	6.00	6.76	621.1	.11114
257.900	3.541	8	-534	5.88	6.61	621.6	.11084
257.906	4.561	8	-514	5.81	6.76	621.1	.08749
257.900	4.562	8	-514	5.70	6.65	621.6	.086699
257.906	5.817	8	-474	6.80	6.76	621.1	.07464
257.900	10.817	8	-374	6.04	6.62	621.6	.04015
257.906	10.817	8	-374	6.27	6.76	621.1	.04091
257.900	20.817	8	-274	5.08	6.62	621.6	.02408
257.914	20.802	8	-274	5.50	7.32	614.7	.02392
257.914	40.809	8	-76	6.12	7.16	615.0	.01724
257.914	60.809	8	-76	5.70	7.16	615.0	.01601
257.901	60.814	8	-76	5.44	6.98	619.0	.01562
257.901	80.814	8	-76	5.69	6.98	619.0	.01634
249.469	3.539	8	-534	4.01	7.01	620.4	.07222
249.469	4.560	8	-514	3.93	7.01	620.4	.05771
249.469	5.816	8	-474	4.30	7.01	620.4	.04583
249.453	5.815	8	-474	4.30	7.04	619.4	.04587
249.453	10.815	8	-374	4.30	7.04	619.4	.02718
249.453	20.815	8	-274	3.77	6.95	619.2	.01718
249.453	30.815	4	-274	6.00	6.95	619.2	.01370
249.453	40.815	4	-174	7.01	6.95	619.2	.01235
249.453	60.815	4	-174	6.68	6.95	619.7	.01177
249.453	80.815	4	-174	6.97	6.95	619.7	.01227
240.153	3.534	8	-474	4.00	7.04	615.7	.04361
240.153	4.555	8	-374	5.40	7.09	616.3	.03421
240.153	5.810	8	-274	6.16	7.04	615.7	.02777
240.153	10.811	8	-274	3.70	7.09	616.3	.01662
240.153	20.811	4	-374	3.43	7.03	616.3	.01102
240.153	30.811	4	-274	4.04	7.03	616.3	.00920
240.153	40.811	4	-174	4.73	7.03	616.3	.00830
240.153	60.810	4	-174	4.69	7.03	615.7	.00824
240.153	80.810	4	-174	5.14	6.90	615.7	.00919
229.528	3.533	8	-374	3.42	6.83	616.0	.02252
229.528	4.556	8	-374	2.80	6.83	616.8	.01816
229.528	5.811	4	-274	6.31	6.83	616.0	.01474
229.528	10.811		-274	3.84	6.80	616.6	.00902
229.547	10.815	4	-274	3.99	7.06	619.2	.00895
229.528	20.811	4	-174	3.30	6.80	616.6	.00601
229.528	30.811	2	-274	4.48	6.80	616.6	.00528
229.528	40.813	2	-274	4.38	6.76	617.5	.00515
229.547	60.814	2	-174	6.11	7.03	618.9	.00539
229.547	80.816	2	-174	7.16	6.97	619.8	.00635

Table 14 (cont'd.)

PT	Temp.	Pressure	ATT	Inject. Press.	P.H.	M.S.	B.P.	y
	219.562	3.537	4	-274	5.21	7.04	618.5	.0113
	219.562	4.558	4	-274	4.21	7.04	618.5	.00949
	219.562	5.813	4	-274	3.40	7.09	618.0	.00762
	219.562	10.813	2	-174	5.42	7.09	618.0	.00471
	219.562	10.813	2	-174	5.40	7.10	617.9	.00469
	219.562	20.813	2	-174	3.71	6.99	617.5	.00329
	219.562	30.813	2	-174	3.32	7.03	617.5	.00295
	219.565	30.822	2	-174	3.38	7.10	624.6	.00293
	219.562	40.814	2	-174	3.33	6.97	618.6	.00299
	219.562	60.814	2	-174	3.94	6.97	618.6	.00349
	209.594	3.535	4	-174	3.15	6.98	617.3	.00557
	209.594	4.556	4	-74	3.14	7.00	617.1	.00453
	209.594	5.812	4	-74	2.58	7.03	617.0	.00370
	209.594	10.812	2	+25	3.90	7.03	617.1	.00235
	209.594	20.813	2	+25	2.80	6.98	617.6	.00170
	209.594	30.813	2	+25	2.62	6.98	617.6	.00162
	209.594	40.813	2	+25	2.74	6.98	617.5	.00170
	209.594	60.813	2	+25	3.54	6.94	617.5	.00219
	209.594	80.813	2	+25	5.03	6.94	617.5	.00307
	199.619	1.162	2	-274	6.36	7.18	623.5	.00698
	199.619	1.497	2	-174	6.24	7.03	620.1	.00549
	199.619	1.501	2	-174	6.40	7.15	623.5	.00549
	199.619	2.857	2	+25	5.00	7.05	619.5	.00303
	199.619	3.538	2	+25	4.18	7.05	619.5	.00253
	199.618	3.540	2	+25	4.06	6.80	621.3	.00254
	199.618	4.562	2	+25	3.30	6.88	621.6	.00206
	199.618	5.819	2	+25	2.73	6.81	622.5	.00171
	199.618	10.819	2	+125	2.07	6.80	622.8	.00112
	199.618	20.819	2	+225	1.79	6.78	622.8	.00088
	199.618	30.819	2	+225	1.77	6.75	622.5	.00087
	199.618	40.820	2	+225	1.95	6.75	623.5	.00095
	199.618	60.820	2	+225	2.75	6.75	623.5	.00132
	199.618	80.821	2	+225	4.74	6.79	623.7	.00225

APPENDIX FTemperature Correction Data

TABLE 15

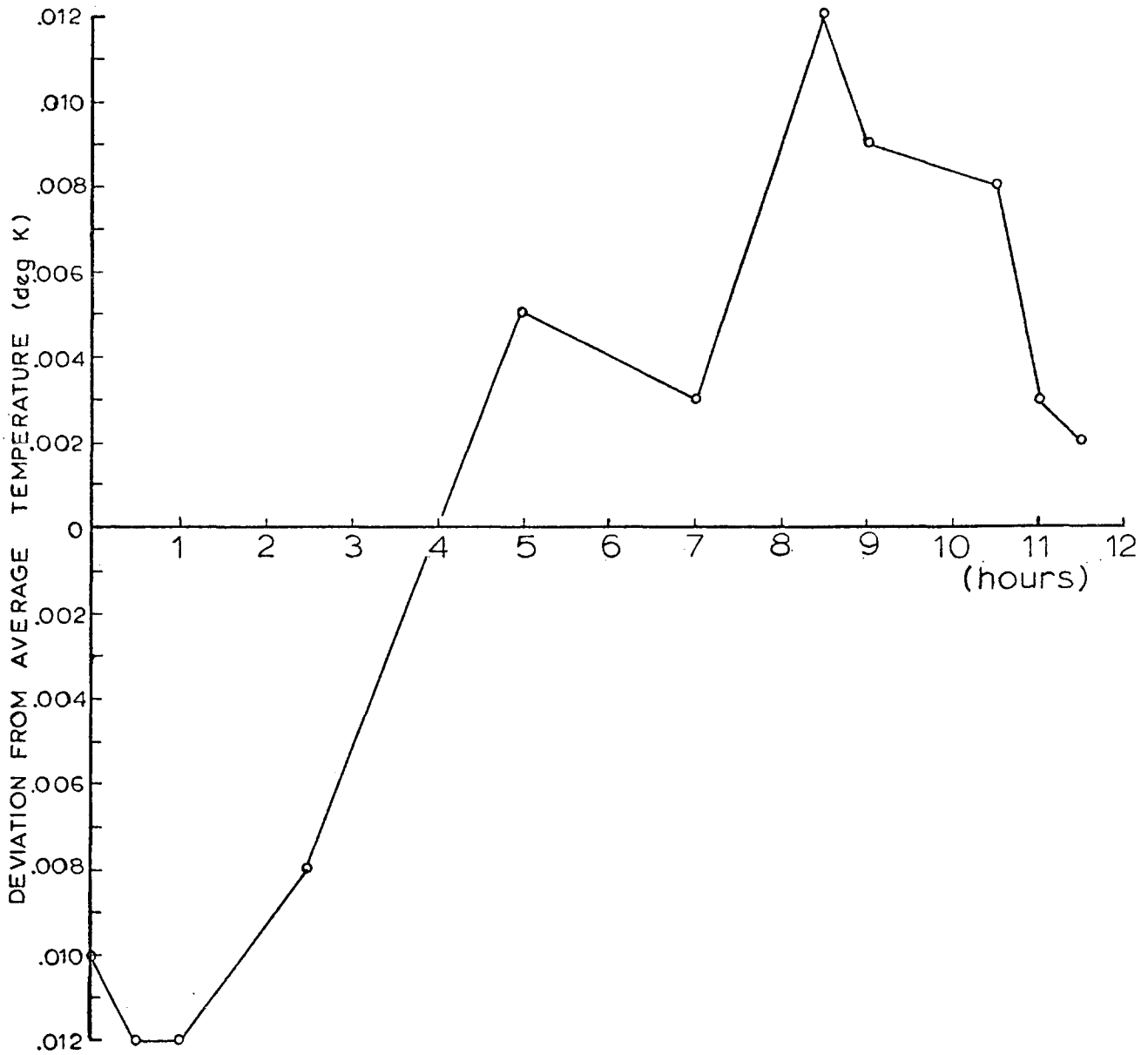
T (uncalibrated) ($^{\circ}\text{K}$)	(T uncalibrated - T calibrated) ($^{\circ}\text{K}$)	Direction of Temperature Change (increase/decrease)
258.397	+0.555	D
258.392	+0.555	D
258.401	+0.549	I
249.973	+0.562	D
249.973	+0.529	D
249.973	+0.523	I
239.978	+0.500	D
239.980	+0.502	D
239.970	+0.495	I
229.993	+0.468	D
229.994	+0.467	D
229.988	+0.466	I
219.999	+0.438	D
219.996	+0.438	D
219.998	+0.440	I
209.991	+0.407	D
209.992	+0.407	D
209.997	+0.409	I
209.990	+0.407	I
199.999	+0.390	-
200.000	+0.388	-

APPENDIX G

Long Term Temperature Stability Data

FIGURE 23

Long Term Temperature Stability
(Duston, 1970, p. 43)



APPENDIX HData Analysis Calculations

Determining representative B_{12} value using 90% confidence interval.

Temperature = 249.453 °K.

<u>Pressure</u> (atm)	<u>B_{12}</u> (cc./gmole)	<u>Values within</u> <u>Confidence Interval</u>
3.539	-135.08	
4.560	-163.09	
5.815	-140.91	X
10.815	-148.33	X
20.815	-152.75	
30.815	-144.00	X
40.815	-141.99	X
60.815	-138.36	X

\bar{B}_{12} (all data) = -145.56 cc/gmole.

Degrees of freedom = 7.

Standard deviation = 9.49.

$B_{\text{neopentane}}$ = -1415.52 cc/gmole.

P_1^0 = partial pressure = 0.23701 atmosphere.

$t_{\alpha/2} = 1.895$ ($\alpha = 0.1$).

90% confidence interval..... -138.10 μ > -150.08

\bar{B}_{12} (90% data) = -142.72 cc/gmole.

Standard deviation = 3.74.

Appendix H (cont'd)

Comparison of compressibility factor values.

$$T = 249.453 \text{ } ^\circ\text{K.}$$

$$P = 80.815 \text{ atmospheres.}$$

$$B = -28.20 \text{ cc/gmole.}$$

$$z = 1 + \frac{(-0.0282)(80.815)}{(0.082057)(249.453)} = 0.8887.$$

$$T = 249^\circ\text{K.}$$

$$P = 80 \text{ atmospheres.}$$

$$\rho = 4.33614$$

$$z = \frac{80.0}{(4.33614)(.082057)(249)} = 0.9030.$$

$$\% \text{ difference} = \frac{0.9030 - 0.8887}{0.8887} \times 100 = 1.61\%$$

APPENDIX IProgram I

```

DIMENSION P(9),Y1(9,16),Y2(9,16),E1(9,16),B12(9,16)
IIN=3
IN=4
IOUT=4
205  FORMAT ('/TYPE IN OUTPUT FILE NAME'/)
      WRITE (4,205)
      READ (4,206) FILE0
206  FORMAT (A5)
      CALL OFILE (IIN,FILE0)
      WRITE (IOUT,5)
5    FORMAT ('/TYPE IN B11,B22,P10,T,VIS. '/)
      READ (IN,10) B11,B22,P10,T,VIS
10   FORMAT (5F)
15   FORMAT ('/ TYPE IN P(I),Y1(I,1),E1(I,1)'/)
      WRITE (IOUT,15)
      DO 20 I=1,9
      J=1
      READ (IN,25) P(I),Y1(I,J),E1(I,J)
25   FORMAT (3F)
20   CONTINUE
      Y0CK=.000
      DO 100 J=1,16
      Y0CK=Y0CK+.002
      WRITE (IIN,50) T
50   FORMAT (/,'/TEMPERATURE',3X,F10.5)
      WRITE (IIN,55)
55   FORMAT (6X,'PRESSURE',3X,'Y1',7X,'E',5X,'B12')
      DO 100 I=1,9
      Y1(I,J+1)=(Y0CK+.983)*(Y1(I,J))
      E1(I,J+1)=(P(I)*Y1(I,J+1))/P10
      Y2(I,J)=1.0-(Y1(I,J))
      A=(1.0)/((2.0*P(I))*(Y2(I,J)**2.0))
      R=82.057
      B=A*R*T*(-1.0)*(ALOG(E1(I,J)))
      C=B11*P10
      D=VIS*(P(I)-P10)
      E=P(I)*B11*((Y2(I,J)**2.0)-1.0)
      F=P(I)*B22*(Y2(I,J)**2.0)
      W=A*C
      X=A*D
      Y=A*E
      Z=A*F
      B12(I,J)=(A*(C+D+E+F))+B
      WRITE (IIN,75) P(I),Y1(I,J),E1(I,J),B12(I,J)
      WRITE (IIN,76) B,W,X,Y,Z
76   FORMAT (/,5F10.2)
75   FORMAT (3X,F10.4,2X,F6.5,F8.4,F8.2)
100  CONTINUE
      STOP
      END

```

APPENDIX JProgram II

```

DIMENSION P(9),Y1(9),Y2(9),E2(9),ERT(9),ERTF(9)
IN=4
IOUT=4
60  FORMAT ('/TYPE IN N,K,IP. '/')
    WRITE (IOUT,60)
    READ (IN,65) N,K,IP
65  FORMAT (3I)
    WRITE (IOUT,5)
5   FORMAT ('/TYPE IN T, V2C, P2C, B22, VC, TC, D. '/')
    READ (IN,10) T,V2C,P2C,B22,VC,TC,D
10  FORMAT (7F)
15  FORMAT ('/TYPE IN P(I),Y2(I),E2(I)')
    WRITE (IOUT,15)
    DO 20 I=1,9
    READ (IN,25) P(I),Y2(I),E2(I)
25  FORMAT (3F)
20  CONTINUE
    WRITE (IOUT,50) T
50  FORMAT ('/TEMPERATURE',3X,F10.5)
    WRITE (IOUT,55)
55  FORMAT (6X,'PRESSURE',10X,'ERT')
    DO 100 I=1,9
    Y1(I)=1.0-Y2(I)
    R=82.057
    TR=T/TC
    A=(.232*(TR**-0.25))+(0.468*(TR**-5.0))
    B=(1.0-(EXP(1.0-(1.89*(TR**2.0))))))
    C=(D*(EXP(-2.49+(2.3*TR)-(2.7*(TR**2.0))))))
    C222=((A*B)+C)*(VC**2.0)
    X=(1.0/((Y1(I)**2.0)*P(I)))
    Y=R*T*(ALOG(E2(I)))-V2C*(P(I)-P2C)
    S=(1.-(Y1(I)**2.0))*(B22*P(I))-(B22*P2C)
    W=S+Y
    Z=((B22**2.0)-C222)*(P2C**2.0)/(2.0*R*T)
    ERT(I)=X*(W+Z)
    ERTF(I)=ERT(I)*P(I)
    WRITE (IOUT,75) P(I),ERT(I),C222
75  FORMAT (3X,F10.4,5X,F10.2,6X,F12.3)
100 CONTINUE
    CALL FIT(P,ERTF,N,K,B,IP,(7))
    STOP
    END

```

APPENDIX KChromatograph Variables

Column Temperature.....100^oC.
Detector Temperature.....160^oC. (setting = 175)
Line Temperature.....125 C. (setting = 44)
Valve Temperature.....103^oC. (setting = 51)
Inlet Setting.....10
Helium Flow Rate.....30 cc/minute
Helium Pressure.....80 psig.
Current.....250 ma.
Recorder Selector.....DET 1
Left Head Pressure.....7 psig.
Right Head Pressure.....11 psig.
Chart Speed.....0.2 inch/minute
Recorder Range.....1 mv.

APPENDIX LAttenuation Correction FactorsTABLE 16

Attenuation Correction Factor Data

<u>Manometer Pressure (mm Hg.)</u>	<u>Attenuation</u>	<u>Peak Height (units)</u>
-474	2	3.50
-474	1	7.00
-274	2	8.33
-274	4	4.16
-75	4	6.59
-75	8	3.30
+725	32	1.77
+725	16	3.54
+725	8	7.10

FIGURE 24

Attenuation Factors

To convert a reading made at an attenuation in the attenuation column to a reading at an attenuation in the attenuation row, multiply the reading by the value in the table at the intersection of the row and column.

Row Column	1	2	4	8	16	32
1	1.0	0.50	0.250	0.063	--	--
2	2.00	1.0	0.499	0.250	0.062	--
4	4.004	2.002	1.0	0.501	0.249	0.062
8	16.008	3.998	1.997	1.0	0.498	0.249
16	--	16.024	4.008	2.007	1.0	0.499
32	--	--	16.112	4.020	2.003	1.0

APPENDIX M

Trouble Shooting

Many problems were encountered during the course of the experimental work. Often the difficulties were solved only to reappear later. The experience acquired by repeatedly solving these problems proved invaluable for the smooth operation of the equipment. The contents of this section should provide future investigators with some insight into the possible solutions of various difficulties, should the situations arise.

System Leaks

- 1) Frequently used valves (e.g. A10) should be checked periodically for leaks around the valve stems.
- 2) The glass-plastic coupling on the right leg of the manometer tube is prone to occasional leakage.
- 3) High pressure valves on the equilibrium panel board are apt to rotate slightly within the panel and thus fatigue the copper tubing adjacent to the valve. The only solution is to replace the faulty tubing.

Vibrations During Operation

- 1) Most common cause of vibration is the formation of ice in and around the hole in the dewar lid reserved for the stirrer shaft. This ice can usually be melted or chipped away.
- 2) After prolonged operation the bath fluid accumulates in solid form around the liquid nitrogen coil and eventually touches the stirrer impellers. This can usually be remedied by adjusting the dewar with various tensions on the three support rods.

Chromatograph Difficulties - refer to the manual accompanying the gas chromatograph.

No Neopentane Peaks from Sample Gas

1) This problem will arise if both E9 and E10 are open. The entering argon then bypasses the cell. The solution is obviously to close one of the valves.

2) Neopentane may have been exhausted in the cell. However, this situation can usually be noted by a continually decreasing peak height rather than an immediate lack of peaks.

Low Liquid Nitrogen Pressure

1) If the dewar was recently filled, the heat leak may not have been sufficient to increase the internal pressure to 25 psig. maximum.

2) The safety relief valve on the liquid nitrogen dewar may have been inadvertently set at a pressure below 25 psig.

3) If the level indicator on the liquid nitrogen dewar is low, the dewar may in fact be empty, as the level indicators are occasionally in error.

Blocks of Solid Neopentane in the System

By necessity, the path the argon takes in passing through the equilibrium cell is fairly tortuous. Therefore, it is quite possible that the path may become blocked by solid neopentane. Detecting these obstructions and removing them will become easier as the operator gains experience, however, the following procedure will provide a starting point from which the new operator may begin. By regulating pressures on either side of the obstruction, the operator must be able to detect any obstruction and then remove it by forcing it out of the vapor path without allowing any solid neopentane to enter the external heat exchanger. If any neopentane does

get into the heat exchanger, it will usually require several hours to vaporize the solid and flush out all traces.

Detecting an Obstruction During Cooldown:

- 1) Maintain low flow rate through the cell.
- 2) Maintain pressure with E4.
- 3) Close E9.
- 4) Open E10.
- 5) If pressure drops, open E4 slightly.
- 6) If pressure continues to decrease, close E4.
- 7) Close E10.
- 8) Open E9.
- 9) Increase upstream pressure by opening E4 until pressure is about one atmosphere above the desired pressure.
- 10) Close E4.
- 11) Close E9.
- 12) Open E10.
- 13) If this pressure is significantly lower than the upstream pressure, there is a block.

Determining the Location of the Obstruction:

- 1) Close E9.
- 2) Open E10.
- 3) Open E14 slightly.
- 4a) If gas escapes quickly and then stops, there is a block on the top tray of the cell.
- 4b) If pressure drops quickly, there is a block on an intermediate tray in the cell.
- 4c) If gas escapes quickly but pressure remains constant, there is a block in the outlet line between the cell and the heat exchanger.

Removing the Obstruction:

- A) Block on the Top Tray.
 - 1) Open E9.
 - 2) Open E10.
 - 3) Pressurize system to approximately 70 psig.
 - 4) Close E10.
 - 5) Open E11 and vent gas until pressure on upstream side is 5 psig.
 - 6) The higher pressure on the downstream side should force the solid block into the cell.
- B) Block on an Intermediate Tray.
 - 1) Close E10.
 - 2) Open E9.
 - 3) Increase pressure quickly to 60 psig by using E4.
 - 4) Close E9.
 - 5) Open E10.
 - 6a) If pressure is the same, the block has been removed.

- 6b) If pressure is considerably lower, the block is still present.
 - 7) Open E11 until pressure on downstream side is 20 psig.
 - 8) Close E10.
 - 9) Open E9.
 - 10a) If pressure is the same, the block has been removed.
 - 10b) If the pressure is higher but decreasing, the block has been weakened.
 - 10c) If the pressure remains high, follow procedure for removing a block from the top tray.
- C) Block between the Cell and Heat Exchanger:
- 1) Follow procedure for removing block from the top tray.
 - 2) If step 1 is not successful it may be necessary to warm the cell until the neopentane liquifies.

APPENDIX N

Pressure Gauge Corrections

FIGURE 25

Heise Gauge H35532 Calibration Curve
(Duston, 1970, p.65)

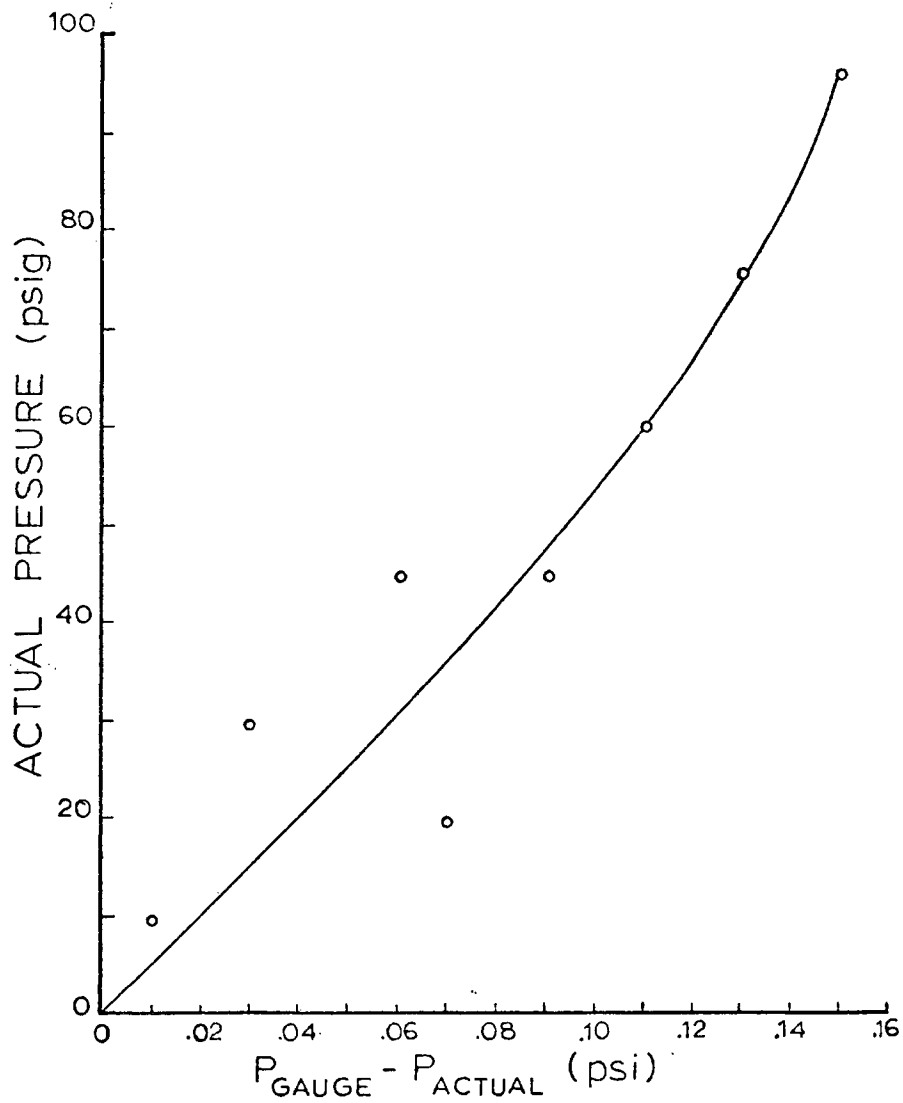


TABLE 17

Heise Gauge C58810 Calibration Data

<u>Actual Pressure (atm)</u>	<u>Gauge Error (atm)</u>
2.039	+0.05
3.059	+0.04
4.079	+0.03
5.166	+0.02
6.526	+0.02
5.166	+0.03
4.079	+0.03
3.059	+0.04
1.359	+0.03
0.689	+0.03
9.925	-0.02
14.004	0.00
20.802	+0.05
27.601	+0.09
33.719	+0.03
20.802	0.00
9.925	-0.04
41.197	+0.05
47.996	+0.09
54.794	+0.01
61.593	+0.06

Table 17 (cont'd)

<u>Actual Pressure (atm)</u>	<u>Gauge Error (atm)</u>
68.392	0.00
75.191	0.00
81.989	-0.09
88.879	0.00
95.587	+0.01
98.987	+0.01
81.989	-0.09
61.593	+0.01
41.197	-0.05

APPENDIX OEquipmentI. Gas Chromatograph

Manufacturer: Beckman Instruments, Inc.
Model No.: GC 72-5
Instrument No.: CSM 35152
Columns: 40 DC 200/500 SERF556
Detector: Thermal Conductivity (solid state power supply)
Carrier Gas: Helium
Other Features: Heated Injection Valve
Emergency High-Temperature Shut-Off Switch
Injection Valve: Carle mini-volume valve, Series 5500
(utilizes shear sealing principle)

II. Recorder

Manufacturer: Beckman Instruments, Inc.
Model No.: 1005
Style: 10-inch Linear
Instrument No.: CSM 35151
Features: Pen damping system to minimize overshoot
Pen drive clutch in case pen is driven off scale
1, 10, 100 mv ranges

III. Platinum Resistance Thermometers

- A. Manufacturer: Leeds and Northrup
Model No.: 8164
Serial No.: 1793436
Sheath: Helium-filled Platinum
Range: -261°C to $+250^{\circ}\text{C}$
Size: Approximately 2.5 in long, 3/8 in diameter.
Function: Used to measure bath temperature during final runs.
- B. Manufacturer: Leeds and Northrup
Model No.: 8163-C
Serial No.: 1547841
Sheath: Air-filled Pyrex
Range: -183°C to $+650^{\circ}\text{C}$
Size: 3/8 in diameter, 18 in long.
Function: Used by D. D. Duston to measure vapor pressure of CO_2 .
Inadvertently broken prior to argon-neopentane experiments, repaired, recalibrated, and used as standard to calibrate #1793436

IV. Temperature Controller

Manufacturer: Bayley Instrument Co.
Model No.: 121
Mode: Proportional
Rating: -200°C to +100°C
Bandwidth Range: 0.01°C to 2.0°C
Accuracy: 0.001°C
Sensing Probe: Platinum resistance in hermitically sealed stainless steel sheath.
Heater: 125-watt tubular heater

V. Mueller Bridge

Manufacturer: Rubicon Instruments, Inc.
Serial No.: 115682
Instrument No.: CSM 35841
Resistance Range: 0 ohms to 141.110 ohms
Limit of Error: 0.0005 ohm or 0.02% of setting (whichever is larger)

VI. Null Detector

Manufacturer: Minneapolis-Honeywell Regulator Co.
Model No.: 104W1-G
Serial No.: 59002369002
Scale: Logarithmic
Features: Adjustable sensitivity

VII. Pressure Gauges

- A. Manufacturer: Heise
Serial No.: H35532
Type: Bourdon tube
Range: 0-100 psi
Scale Divisions: 0.1 psi
Max NBS deviation: 0.15 psi
"Zero" Pressure: atmospheric
Features: temperature compensated from -25°F to +125°F.
- B. Manufacturer: Seegers
Model No.: SS 2170-100
Serial No.: S1730
Type: Bourdon tube
Range: 0-100 psi
Scale Divisions: 0.1 psi
Max NBS deviation: 0.06 psi
"Zero" Pressure: Atmospheric

- C. Manufacturer: Heise
Serial No.: C58310
Type: Bourdon tube
Range: 0-100 atmosphere
Scale Divisions: 0.1 atm
Max NBS deviation: 0.09 atm
"Zero" Pressure: atmospheric
Features: May be zeroed at zero pressure

VIII. Stirrer System

- A. Controller
Manufacturer: Cole-Parmer
Model No.: 4555-3
Features: Solid State
Adjustable Speed Control
Directional Switch
- B. Motor
Manufacturer: Cole-Parmer
Model No.: 45556
Serial No.: 1563
Features: Variable Speed
CW or CCW Operation
- C. Stirrer
Manufacturer: CSM Instrument Shop
Material: Stainless Steel
Features: Two Impeller Blades

IX. Constant Temperature Bath

- Manufacturer: Sulfrian Cryogenics, Inc.
- Material: Stainless Steel
- Insulation: Vacuum
- Size: 9 3/8 in diameter
24 in deep
capacity = 27 liters
- Bath Fluid: 50 volume percent carbon tetrachloride
50 volume percent chloroform
- Features: Fluid is non-flammable
Fluid has freezing point of -81.4°C
Fluid is liquid at room temperature and atmospheric pressure.
Fluid viscosity not prohibitive at low temperatures

APPENDIX PEquipment Suppliers

1. Swagelok fittings and Whitey Valves

Denver Valve and Fitting Co.
980 Simms
Denver, Colorado
Phone 238-1319

2. Hoke valves and Wallace & Tiernan rotameters

Ross Equipment
2149 South Clermont
Denver, Colorado
Phone 759-4215

3. Liquid nitrogen, compressed gas (Ar, N₂, H₂)

United States Welding Co.
600 South Santa Fe Drive
Littleton, Colorado
Phone 777-6671

4. O-rings

Rocket Seal Co.
2805 South Raritan
Denver, Colorado
Phone 789-1858

5. Gas Chromatograph and Recorder

Beckman Instruments, Inc.
2500 Harbor Blvd.
Fullerton, California 92634

Local Distributor

Beckman Instruments, Inc.
2527 Havanna
Denver, Colorado
Phone 344-8220

6. Sample valve

Carle Instruments, Inc.
1411 East Ash Ave.
Fullerton, California 92631

Local Distributor

Beckman Instruments, Inc.
2527 Havana
Denver, Colorado
Phone 344-8220

7. Tubular Heaters

Van Waters and Rogers, Inc.
4300 Holly Street
Denver, Colorado
Phone 388-5651

8. Pressure Gauge

Heise Bourdon Tube Co., Inc.
Newton, Connecticut 06470
Phone 203-426-4406

9. Temperature Controller

Bayley Instrument Co.
Box 538
Danville, California
Phone 837-4649

10. Copper Tubing

McCombs Supply Co.
215 Wazee Market
Denver, Colorado
Phone 244-6674

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