SOLVENTS SCREENING FOR HYDROCARBONS SEPARATION OF CLOSE MOLAR VOLUMES

BY

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ABSTRACT

The approximate physical model for solute-solvent interactions presented by J. M. Prausnitz and R. Anderson[1] is briefly discussed. Applicability of Weimer, Prausnitz[3] and Helpinstill, Van Winkle[7] models is investigated using experimental values of activity coefficients for C5 hydrocarbons in 13 solvents including one nonpolar and 12 polar solvents. Independent correlations, based on our experimental values at 45°C for normal and isopentane have been developed. Although the required thermodynamic properties are obtained through a comparative analysis of all the available and estimated methods, dependable values of activity coefficients for Isopentane and 1-Pentene could not be obtained through the experiments. Developing separate correlations for normal and isoparaffins, therefore, could not be made possible.

It is concluded that, in spite of the close molar volumes, the main contributions to the selectivity functions result from physical effects, especially from dispersion forces. Selectivities have been better correlated using our model (after adjusting the values of solutes solubility parameters) than predicted by other models[3,7]. Effects of chemical forces could not be precisely stated.

APPROVAL OF THESIS

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CHAPTER 1

INTRODUCTION

Separation of close boiling components or azeotropic mixtures in chemical industries is often accomplished by using extractive distillation. This requires use of a polar solvent having much higher selectivity for one type of hydrocarbon than for the other. Selectivity is the ability of a solvent to increase or decrease the volatility of one type of molecule relative to the other. Defining the relative volatility of component i with respect to j,

$$\alpha_{ij} = \frac{\gamma_i p_i^o}{\gamma_j p_j^o} \quad \text{---(A)}$$

where p_i and p_j are the vapor pressures of i and j components, respectively.

and $S_{ij} = \frac{\gamma_i}{\gamma_j}$ ---(B) is the selectivity of i with respect to j in the presence of the solvent.

Criterion of a better separation is thus, the value of relative volatility, its value being away from unity.

Measurement of the activity coefficients and thus the selectivity can be done experimentally using various available methods for every system in consideration. However, for estimation and screening purposes, thermodynamic models based on the present knowledge of solute-solvent interations including an allowance for any unknown interactions empirically, have been developed[1, 2, 3, 7]. The original

Scatchard-Hildebrand[2] (S-H) relation for excess Gibbs free energy of mixing is $\Delta G^E = \phi_1 \phi_2 (x_1 v_1 + x_2 v_2)(C_{11} + C_{22} - C_{12})$ ---(1)

where C_{11} and C_{22} are pure component cohesive energies defined

as $C_{ii} = \frac{\Delta U_i}{v_i} = \frac{\text{molar energy of vaporization}}{\text{molar volume}}$ (cal/cc)

$= \lambda_i^2$, λ_i is the solubility parameter

and C_{12} as $C_{ij} = (C_{ii} C_{jj})^{1/2}$

ϕ_1, ϕ_2 are the volume fractions defined as $\phi_i = \frac{x_i v_i}{\sum_{i=1}^{n} x_i v_i}$ --(2)

x - molefraction, v - molar volume (cc/gmol)

Weimer and Prausnitz[3] (W-P) extended the original S-H[2] model to include the effects of a polar solvent, and obtained

$$\Delta G^E = \phi_1 \phi_2 (x_1 v_1 + x_2 v_2)\left[(\lambda_1 - \lambda_2)^2 + \tau_1^2 - 2\psi_{12}\right] \quad ---(3)$$

where, τ_1 , is the polar solubility parameter of the solvent and ψ_{12} is the term added to include induction effects between the polar and nonpolar molecules.

Correcting for change of volume upon mixing by adding Flory-Huggins entropy term, W-P model obtained infinite dilution coefficient as,

$$RT \ln \gamma_2^{\infty} = v_2 \left[(\lambda_1 - \lambda_2)^2 + \tau_1^2 - 2\psi_{12}\right] + RT\left[\ln \frac{v_2}{v_1} + 1 - \frac{v_2}{v_1}\right] ---(4)$$

Helpinstill and Van Winkle[7] (H-V) extended the W-P model to take into effects of slightly polar solutes. Corresponding H-V model equation to obtain infinite dilution coefficient is,

$$RT \ln \gamma_2^{\infty} = v_2 \left[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}\right] + RT\left[\ln \frac{v_2}{v_1} + 1 - \frac{v_2}{v_1}\right] ---(5)$$

To evaluate the induction energy term ψ_{12}, in terms of known physical properties, eq. 4 and 5 are rearranged as,

$$RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] = V_2\left[\tau_1^2 - 2\psi_{12}\right] \text{W-P EQ.} \quad \text{---(6)}$$

$$= V_2\left[(\tau_1-\tau_2)^2 - 2\psi_{12}\right] \text{H-V EQ.} \quad \text{---(6A)}$$

By plotting the parameters as $X = RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right]$ and $Y = V_2\tau_1^2$ for W-P[3] model OR $Y = V_2(\tau_1-\tau_2)^2$ for H-V model; a linear relationship was obtained in both the researches. However, values of the slopes of these Y vs X lines varied depending upon the class of hydrocarbon solutes considered. This corresponds to yield an empirical equation to determine induction energy term ψ_{12} as,

$$\psi_{12} = k\tau_1^2 \quad \text{---(7)}$$

$$= k(\tau_1-\tau_2)^2 \quad \text{---(7A)}$$

Substituting eq. 7 and 7A in eq. 6 and 6A respectively,

$$RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] = (1-2k)V_2\tau_1^2 \quad \text{---(8)}$$

$$= (1-2k)V_2(\tau_1-\tau_2)^2 \quad \text{---(8A)}$$

'k' can be, therefore, calculated from slope of Y-X line as,

$$k = \frac{1 - (\text{Slope of Y-Xplot})}{2} \quad \text{---(9)}$$

W-P[3] correlation for the term ψ_{12} has been developed for systems of saturated n-paraffinic solutes in the polar solvents, while

H-V[7] have correlated term for saturated n-paraffinic, unsaturated and aromatic hydrocarbons. The average error (%) in determining '$\ln \gamma_2^{\infty}$' through these models have been reported as within 10% for W-P[3] and 6% for H-V[7] model.

It may be noticed here that the induction energy term as calculated through eq. 7 or 7A contains all energies between 1 and 2, but does not include any specific forces leading to formation of any complex molecules in the solution.[1] These forces are generally described as chemical forces and are results of acid-base interactions following the Lewis definitions.[12]

Selectivity of a pair of solutes in a solvent can be obtained using above models by taking the ratio of infinite dilution coefficients as determined through the correlations.

It is the purpose of this work to:

(1) examine the feasibility of developing two separate correlations for normal and isoparaffins in various solvents.

(2) examine the contributions to the selectivity of a pair of paraffins solutes of close molar volumes in several solvents.

(3) evaluate the general applicability of the W-P[3] and H-V[7] models in determining the activity coefficients and selectivities.

(4) observe contributions of chemical effects, if any.

(5) establish more reliable approach in the screening of potential solvents for hydrocarbon solutes.

For this purpose, infinite dilution activity coefficients values of n-C5 and iso--C5 (differences in molar volumes less than 1%) have been determined using gas-liquid chromatography. Literature values are also utilized.

CHAPTER 2

THEORY AND BACKGROUND

I Infinite Dilution Activity Coefficients through Gas Liquid Chromatography (GLC)

The theoretical and experimental aspects of determining infinite dilution activity coefficients through GLC have been extensively discussed in the literature[6, 38, 42]. The solvent is employed as the partitioning liquid in a chromatographic column, and a small amount of the solute is injected in the column. Then, according to Porter, et. al.

$$\gamma_2^{\infty} = \frac{M_s R T}{H_i^o P_i^o} \qquad \text{---(10)}$$

For infinite dilution conditions, Kwantes and Rijnders have suggested that the amount of solvent on the solid support must be at least 15wt%, and Porter, et. al. have suggested that amount of solute charged should be as small as possible. The partition coefficient H_i^o can be calculated as[37]

$$H_i^o = \frac{V_g^o - V_{air}}{V_{solvent}}$$

where, V_g^o is the corrected retention volume. ---(11)

Martire and Pollara[4] obtained following expression for determining the activity coefficients with certain assumptions.

$$\gamma_i^{\infty} = \frac{1.704 \times 10^4}{M\ P_i^o V_g^o} \qquad \text{---(12)}$$

where, $V_g^0 = \frac{DV}{ZS} \cdot \frac{273}{T_f} \cdot \frac{p_o - p_w}{p_o} \cdot \frac{3}{2} \left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right]$ ---(13)

The assumptions are:

i) The partition coefficient, H_i^0 is a constant

ii) The solute component is at infinite dilution in liquid phase.

iii) Column behaves as a hypotehtical one with no pressure drop across it.

iv) Equilibrium exists at all points in the column

v) There is no absorption of solute upon solid support

vi) The liquid phase behaves as the bulk partitioning liquid

vii) None of the solute-solute, solute-carrier gas or carrier gas-carrier gas interactions takes place in the vapor phase.

The justifications of these various assumptions are discussed by Martire and Pollara[38]. The agreement of the GLC values with similar static data constitutes the major justification of various assumptions[5, 11].

II The Physical Model to determine activity coefficient and Selectivity

In its general form, Scatchard-Hildebrand equation for G^E, the excess Gibbs energy of mixing, is given as:

$$\Delta G^E = \phi_1 \phi_2 (x_1 V_1 + x_2 V_2)(C_{11} + C_{22} + C_{12}) \quad \text{---(1)}$$

If both the species are nonpolar, the various ('C" terms) energy density terms are defined as,

$C_{11} = \frac{\Delta U_1}{V_1} = \lambda_1^2$, being the solubility parameter of component 1

$C_{22} = \frac{\Delta U_2}{V_2} = \lambda_2^2$, being the solubility parameter of component 2

$C_{12} = (\lambda_1^2 \cdot \lambda_2^2)^{1/2} = \lambda_1 \cdot \lambda_2$

Substituting these energy density terms in the eq. 1, Scatchard-Hildebrand (S-H) equation becomes,

$$\Delta G^E = \phi_1 \phi_2 (x_1 V_1 + x_2 V_2)(\lambda_1 - \lambda_2)^2 \qquad \text{---(14)}$$

Considering one of the species (solvent) being polar, Weimer and Prausnitz extended S-H model by defining the polar component (polar component-1) 'C' term as,

$$C_{11} = \frac{\Delta U_1 (\text{TOTAL})}{V_1} = \underset{\substack{\text{NONPOLAR}\\ \text{PART}}}{\frac{\Delta U_1}{V_1}} + \underset{\substack{\text{POLAR}\\ \text{PART}}}{\frac{\Delta U_1}{V_1}} = \lambda_1^2 + \tau_1^2 \qquad \text{---(15)}$$

where τ_1 is the polar solubility parameter.

To correct for the original assumption of no volume change upon mixing, a term corresponding to the Flory[39]-Huggins[40] energy of mixing was added. To include induction effects due to polar-nonpolar interations, term ψ_{12} was also added. Resulting W-P equation expressing the excess energy is,

$$\Delta G^E = \phi_1 \phi_2 [x_1 V_1 + x_2 V_2][(\lambda_1 - \lambda_2)^2 + \tau_1^2 - 2\psi_{12}] + RT\left[x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2}\right] \qquad (16)$$

Extending the W-P equation to include effects due to another polar component, Helpinstill and Van Winkle[7] (H-V) defined the C_{22} term as,

$$C_{22} = \frac{\Delta U_2}{V_2} = \frac{\Delta U_2\left(\text{NON POLAR}\right)}{V_2} + \frac{\Delta U_2(\text{POLAR})}{V_2} = \lambda_2^2 + \tau_2^2 \quad \text{---(17)}$$

where τ_2 is the polar solubility parameter of the solute component 2.

The expression for excess Gibbs Energy, including the Flory-Huggins entropy term and the induction term ψ_{12}, then becomes:

$$\Delta G^E = \phi_1 \phi_2 [x_1 V_1 + x_2 V_2][(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}] + RT\left[x_1 \ln\frac{\phi_1}{x_1} + x_2 \ln\frac{\phi_2}{x_2}\right] \quad \text{---(18)}$$

Differentiating this eq. 18 with respect to x_2, and taking the limits as x_2 approaches zero, Helpinstill and Van Winkle[7] related the activity coefficient at infinite dilution conditions as:

$$RT \ln \gamma_2^{\infty} = V_2\left[(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}\right] + RT\left[\ln\frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] \quad \text{---(5)}$$

It can be noticed here that, eq. 18, 5 are general equations relating activity coefficient at infinite dilution with various physical parameters for the interaction between polar-polar species, from which eq. 4, 14, 16 for nonpolar-nonpolar, or polar-nonpolar interactions can be derived.

Evaluation of all the necessary terms in eq. 5, except the induction energy term ψ_{12} is discussed in the following chapters. The induction energy term ψ_{12}, in terms of physical properties, is empirically correlated. Rearranging the general eq. 5 as:

$$RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1}+1-\frac{V_2}{V_1}\right] = V_2\left[(\tau_1-\tau_2)^2 - 2\psi_{12}\right] \quad \text{---(6A)}$$

For systems with $\tau_2 = 0.0$ (nonpolar solutes in polar solvents) using activity coefficients values of Pierotti and Gerster et. al. W-P[3] observed a linear relationship by plotting

$$Y = RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1}+1-\frac{V_2}{V_1}\right] \quad \text{vs} \quad X = V_2\left[\tau_1-\tau_2\right]^2$$

Similarly, H-V obtained a linear relationship for systems containing saturated, unsaturated and aromatic (polar solutes, $\tau_2 > 0.0$) solutes in polar solvents by plotting,

$$Y = RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1}+1-\frac{V_2}{V_1}\right] \quad \text{vs} \quad X = V_2\left[\tau_1-\tau_2\right]^2$$

A linear relationship between these two parameters shows that induction energy term ψ_{12} is proportional to $(\tau_1-\tau_2)^2$, which means

$$\psi_{12} = k\,\tau_1^2 \quad \text{---(7)} \quad \text{or} \quad \psi_{12} = k(\tau_1-\tau_2)^2 \quad \text{---(7A)}$$

Substituting these values in eq. 6 and 6A, respectively,

$$RT\ln\gamma_2^{\infty} - V_2(\lambda_1-\lambda_2)^2 - RT\left[\ln\frac{V_2}{V_1}+1-\frac{V_2}{V_1}\right] = (1-2k)V_2\tau_1^2 \quad \text{---(8)}$$

$$= (1-2k)V_2(\tau_1-\tau_2)^2 \quad \text{---(8A)}$$

'k' can be evaluated as:

$$k = \frac{1 - \text{Slope of X vs Y plot}}{2} \quad \text{---(9)}$$

Table No. 32 gives the reported correlations for induction energy term ψ_{12} for different class of hydrocarbon solutes in polar solvents.

In their lists of solutes W-P[3] and H-V[7] do not indicate including branched chain saturated hydrocarbons. When comparing the induction energy forces resulted due to interaction of a straight chain hydrocarbon solute in the polar solvent, with those due to interaction of a branched chain hydrocarbon, some difference in their values is expected because of different structural arrangement. However, this is subject to investigation.

Prausnitz and Anderson[1] expressed selectivity in terms of the physical model and analysed the contributing factors to the selectivity in the following manner.

For the system of components 1 (polar) and 2, 3 (nonpolar); activity coefficients as predicted through the physical models following above eq. 5, are:

$$R\,T\,\ln\gamma_2^{\infty} = V_2\tau_1^2 + [V_2(\lambda_1-\lambda_2)^2] - 2V_2\psi_{12} + RT\left[\ln\frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] \quad \text{---(19)}$$

$$R\,T\,\ln\gamma_3^{\infty} = V_3\tau_1^2 + [V_3(\lambda_1-\lambda_3)^2] - 2V_3\psi_{13} + RT\left[\ln\frac{V_3}{V_1} + 1 - \frac{V_3}{V_1}\right] \quad \text{---(20)}$$

Subtracting eq. 20 from eq. 19

$$\begin{aligned} R\,T\,\ln S_{23} = R\,T\,\ln\frac{\gamma_2^{\infty}}{\gamma_3^{\infty}} &= [(V_2-V_3)\tau_1^2] + [V_2(\lambda_1-\lambda_2)^2 - V_3(\lambda_1-\lambda_3)^2] \\ &+ [2V_3\psi_{13} - 2V_2\psi_{12}] \\ &+ \left[RT\left(\ln\frac{V_2}{V_3} - \frac{V_2-V_3}{V_1}\right)\right] \quad \text{---(21)} \end{aligned}$$

The four bracketed terms in eq. 21 are, respectively, Polar, Dispersion, Induction and Flory-Huggin's entropy terms contributing to the selectivity S_{23}. Using notations,

$$R\,T \ln S_{23} = P + D + I + F\,; \quad \text{where } P = (V_2 - V_3)\tau_1^2$$

$$D = V_2(\lambda_1 - \lambda_2)^2 - V_3(\lambda_1 - \lambda_3)^2$$

$$I = 2V_3\psi_{13} - 2V_2\psi_{12}$$

$$\text{and} \quad F = RT\left[\ln\frac{V_2}{V_3} - \frac{V_2 - V_3}{V_1}\right]$$

---(22)

Prausnitz and Anderson[1], in view of the eq. 22 suggested following conclusions in regards to contributions to the selectivities.

i) In absence of chemical effects, inductive term does not make a major contribution to the selectivity.

ii) Polar effect is proportional to the difference in molar sizes of the two hydrocarbons to be separated.

iii) In case of solute components of close or identical size polar term vanishes; and the dispersion term cannot account for significant selectivity; and for such cases selectivity can be based on the chemical forces which will selectively increase the induction energy between the solvent and one of the hydrocarbons.

From above discussion, it can be seen that selectivity can be determined from solution theory concept of physical effects. A rigorous treatment to determine selectivity from eq. 19 and 20 or from eq. 22 is given in later chapters.

It is interesting to note here that in the case of separation of hydrocarbons having small but significant differences (as in C_4-C_5 class) in their molar volumes some selectivity can be still achieved on the basis of size difference and difference in nonpolar solubility parameters of the solutes. Spelyng and Tassios[33] in their work using n-octane and isooctane (close % molar volumes) as solutes in different solvents have concluded that main contributions to the selectivity result from physical effects, especially from dispersion forces. They found no significant contributions to the selectivity from chemical effects.

III Chemical Effects

The chemical viewpoint of solution considers that nonideality in solution results from association and solvation of molecules resulting sometimes into formation of complexes. The inductive energy term Ψ does not include any specific forces leading to the formation of complex. Accordingly, a complex is result of an acid-base interaction following Lewis definitions that a base (solute) is an electron donor) having low ionization potential and an acid (electron acceptor) having large electron affinity. Ionization potentials have been known for many organic compounds. However electron affinity has only been indirectly indicated through Sigma or Lewis Scales expressing Lewis acidities.

Presence of chemical effects and their contributions to the activity coefficient and selectivity functions in solute-solvent interactions has been studied by Prausnitz and Harris[12]. They have established a relative approximate scale of Lewis acidities for typical organic compounds, which can be of direct use for estimation of solvent selectivities in extractive separations.

However, Spelyng and Tassios[33] have attempted to explain the differences between observed and calculated values of selectivities through chemical effects by plotting the quantity $Q = R\ T\ (\ln S_{OBS} - \ln\ S_{CALC})$ against relative Lewis acidity (K_x) of the solvents, and concluded that there is no interdependency and chemical effects do not contribute significantly to the selectivity even in case of close molar volumes.

CHAPTER 3

EQUIPMENT AND PROCEDURES

A Varian-Autoprep model A700 Gas Chromatograph equipped with a 4.5 feet (1/8 in. OD) Stainless Steel column was used in this study. The column was packed with high performance Glass beads as inert solid supports of recommended maximum liquid loading of 5%. The inert gas employed was high purity He with its flow rate ranging from 20 to 60 cc/min as the case may be. He flow rate for a particular run was measured within 1% with the help of a soap-film flowmeter attached at the chromatograph outlet.

Each solvent was injected into the column after complete removal of the previous solvent by increasing and maintaining the column at temperature 20 to 30 degrees higher than the boiling point of the solvent for a minimum of six hours. Solvent placement into the column was made possible by maintaining the injector, and the detector cells at temperature higher than the boiling point of the solvent while maintaining column temperature at room conditions. After each injection of solvent, sufficient time was allowed to have complete and uniform distribution of solvent in the column. Most of the solvents used have a negligible vapor pressure at the operating temperature, however loss of solvent per unit time was computed for every solvent so that accurate amount of solvent present at any time can be precisely used in the calculations. This was done by measuring the weight of the column before,&after the injection of the solvent and at intermediate periods as well as at the end of the run . Temperature of the chromatographic block was maintained at 45°C within 1% accuracy with the help of temperature controller.

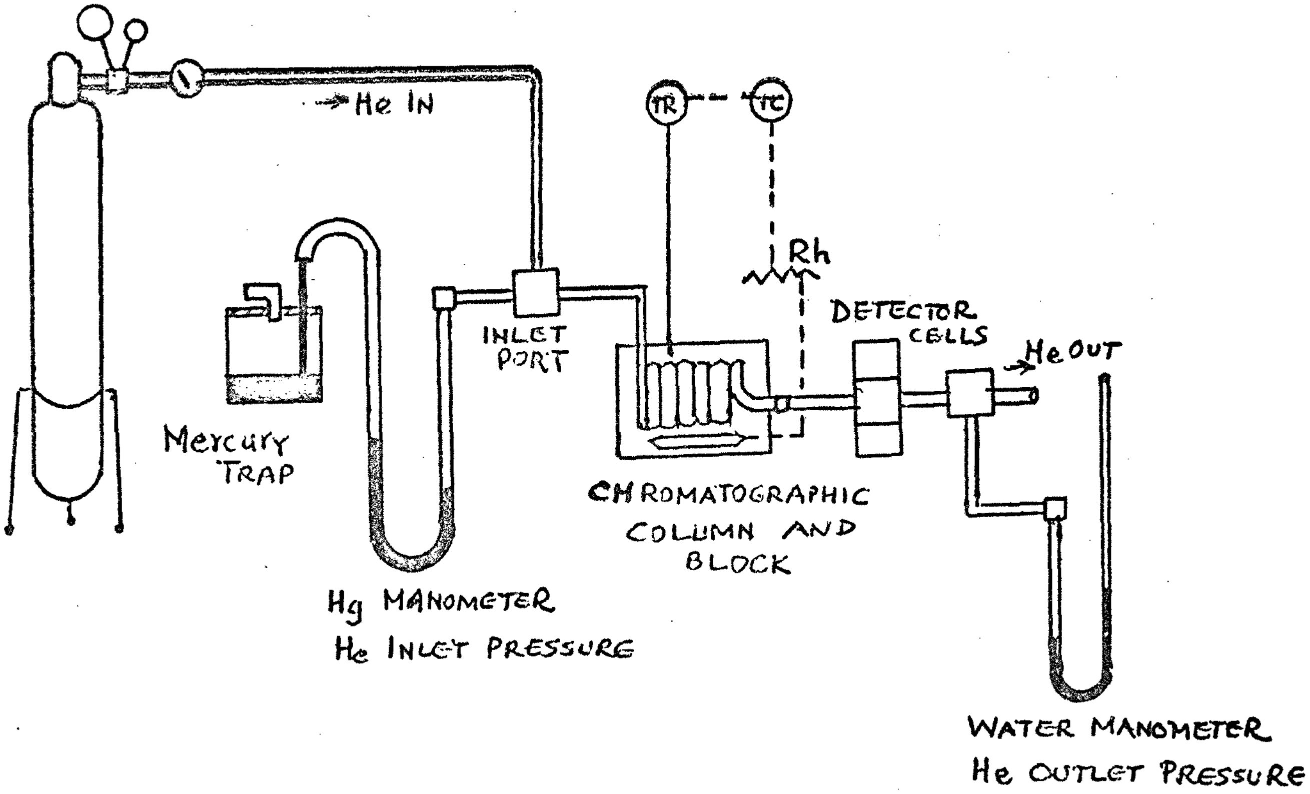

FIGURE No. 1 : EXPERIMENTAL SET-UP AND ARRANGEMENT

CHAPTER 4

SELECTION OF SYSTEMS

In order to develop two separate correlations for predicting activity coefficients and selectivity terms for normal and isoparaffins, n-Pentane and Isopentane were considered as solutes in various polar solvents. Selection of these solutes and the solvents was based on the availability of useful information of solubility parameters and activity coefficients in some cases. The difference in their molar sizes is only 0.7%. Lower hydrocarbons could not be attempted because of their high vapor pressures at the temperatures considered. 1-Pentene was also employed in each run to obtain its activity coefficient values.

To minimize the loss of weight per time of active operation of the column, solvents should have very low vapor pressure at the temperature of the experiment. For this reason solvents selected have a reasonably high boiling point. Selection of solvents was also based on their polar solubility parameters in the range of 0 to 10. Most of the solvents are included in the work of Gerster, et. al.[11] so that the results of this study can be compared with those of a static measurements. To consider the chemical effects on selectivity, five of the solvents were selected on the basis of their stand on the Lewis acidity constants scale[12].

The hydrocarbons used were of 99.0 mole percent minimum purity, and obtained from Eastman Kodak Company. The solvents were obtained from Eastman Kodak Company, K and K Chemicals and Fisher Scientific Co.

Table No. 1 lists all the solvents with their formula and B. Pt.

CHAPTER 5

EVALUATION OF REQUIRED PARAMETERS

Specific Volume, v cc/gmol

Specific volumes of Hydrocarbons at different temperatures are readily available in literature[8, 16]. Specific volumes or density data for solvents selected, however, are scattered and limited and are not sufficient to exactly predict the volumes at 45°C. Reid and Sherwood and Hougen, Watson and Ragatz presents correlation of obtaining liquid densities for molar volumes on the basis of critical properties and reduced densities. Accordingly, the reduced density is a function of reduced temperature, pressure and compressibility factor. If the critical constants P_c, V_c, T_c and Z_c of a compound are determined and density (gms/cc) at any temperature (say T_1) is known, then reduced density of the liquid at temperature T_1 or reduced temperature $T_{r1} = T_1/T_c$ and reduced pressure $p_{r1} = p_1/p_c$ is obtained using the given tables. This value is to be corrected for the value of Z_c other than 0.27 as,

$$\rho'_{r_1} = \rho_{r_1} + D\,(Z_c - 0.27),$$ where D is a correction factor to be read from the tables.

---(23)

Similarly, reduced density at other temperature T_2 is obtained.

Then, density at temperature T_2 is given as:

$$\rho_2 = \frac{\rho_1 \rho_{r_2}'}{\rho_{r_1}'} \qquad \text{--- (24)}$$

and specific volume as: $V_2 = \frac{\rho_{r_1}' M}{\rho_1 \rho_{r_2}'}$ cc/gmol

Determination of specific volumes using above estimation requires knowledge of critical properties and density at one temperature. Unfortunately however, critical constants of only some of the solvents have been reported in available literature sources. An estimation procedure for determination of critical constants of organic compounds specially recommended for the purpose is the Lyderson's method[14] and has been extensively used in this work.

Nonpolar Solubility Parameter

For a nonpolar molecule according to the Scatchard and Hildebrand theory,

$$\lambda_2 = \frac{\Delta U_2}{V_2} = \frac{\text{Energy of vaporization (cal/gmole)}}{\text{Specific volume (cc/gmol)}}$$

$$= \frac{\Delta H_2 - RT}{V_2} \qquad \text{---(25)}$$

Heat of vaporization of hydrocarbons at different temperatures can be obtained through Clausius-Clapeyron equation using Vapor

Pressure data. Thus at temperature T,

$$\Delta H_2 = \frac{1}{P} \left| \frac{dP}{dT} \right|_T RT^2 \qquad \text{---(26)}$$

Nonpolar solubility parameters λ_1 for n-Pentane and Isopentane following the above calculations at 45°C are 6.94 and 7.29 $(\text{cal/cc})^{1/2}$ respectively.

<u>Solubility parameters of Polar solvent, λ_1 and τ_1</u>

As discussed earlier, the energy of vaporization of a polar molecule consists of two parts, i) Nonpolar and ii) Polar.

$$\frac{\Delta U_1}{V_1} (\text{TOTAL}) = \frac{\Delta U_1}{V_1} (\text{NONPOLAR}) + \frac{\Delta U_1}{V_1} (\text{POLAR}) \qquad \text{---(27)}$$

$$= \lambda_1^2 + \tau_1^2 \qquad \text{---(28)}$$

$\frac{\Delta U_1}{V_1}(\text{TOTAL})$: The total energy change of vaporization (left side of the eq. 27 can be determined in one of the following ways.

A. If reliable vapor pressure data of the solvent over a suitable range are available, dP/dT slope at the required temperature (45°C in our case) is obtained to evaluate Heat of Vaporization H of the solvent at the temperature using Clausius-

Claperyron equation. Knowing the heat of vaporization ΔH can be calculated through the equation

$$\frac{\Delta U}{V} = \frac{\Delta H - RT}{V} \qquad \text{---(29)}$$

if Antoines constants B and C of the vapor pressure equation for the Solvent are known, $\Delta U/v$ can be obtained also through the eq. 33 on page No. 25.

B. If vapor pressure data are not available in the range require or are scattered or cannot be precisely used without involving a serious error, an estimation method to determine heat of vaporization at 45°C can be used. Reid and Sherwood presents two of the modifications to the reduced Kirchoff's equation to determine the heat of vaporization at the boiling point of the solvent. Using Klein-Fishtine modification we have,

$$\Delta H_b = \left[\frac{2\cdot303\, R T_b T_c K_v \log_{10} p_c}{T_b - T_c} \right] \left(1 - \frac{1}{p_c T_{br}^3} \right)^{1/2} \qquad \text{---(30)}$$

Where $K_v = 1\cdot045$ for our Solvents since $T_b > 300^\circ K$

From this, at any temperature T (T_r), using Watson correlation

$$\Delta H = \Delta H_b \left[\frac{1 - T_r}{1 - T_{rb}} \right]^{0\cdot38} \qquad \text{---(31)}$$

Substituting eq. 31 in eq. 30, and simplifying

$$\Delta H = \frac{4.781984\ T_b T_c \log_{10} P_c}{T_c - T_b} \left(1 - \frac{T_c^3}{P_c T_b^3}\right)^{1/2} \times \left(\frac{T_c - T}{T_c - T_b}\right)^{0.38} \qquad \text{---(32)}$$

$\left.\frac{\Delta U}{V}\right|_{TOTAL}$ can be then evaluated using equations 29 and 32. It may be noted here that again critical constants are required to use this correlation.

In the case of solvents of known or limited vapor pressure data the values of ΔH calculated using method B have been compared with those obtained using methodA and are found to be in close agreement as shown in Appendix No. II.

$\left.\frac{\Delta U}{V}\right|_{\text{NONPOLAR PART}}$: FOR POLAR SPECIES The dispersion of nonpolar contribution to the energy of vaporization of a polar species is evaluated using the homomorph concept. In the definition proposed by Bondi and Simkin[7], the homomorph of a compound is the equistructural hydrocarbon at the same reduced temperature. More recently, Anderson[8] suggested that the homomorph should have the same molar volume as the solvent. Since experimental data indicate that the properties of a series of similar liquids such as Aliphatics, vary in a smooth predictable manner, it has been possible to construct "homomorph plots" from which the dispersion energy density at any desired temperature can be read. Weimer and

Prausnitz[3] and Helpinstill and Van Winkle[7] in their work have produced homomorph plots for n-Paraffins, Cycloparaffins and Aromatic hydrocarbons. By simple thermodynamics it has been shown that

$$\Delta U = \frac{2.303\,R T^2 B}{(t + c)^2} - RT \qquad \text{---(33)}$$

where B and C are the constants of Antonie's equation,

$$\log_{10} p = A - \frac{B}{t + C}$$

W-P[3] used properties of nonpolar hydrocarbons to construct these plots with the ordinates $\frac{\Delta U_1}{V_1} = \lambda_1^2$ and the abscissa of 'v', the specific volume. Using the plots, square root of the ordinate value corresponding to the specific volume of the equivalent homomorph hydrocarbon compound of the solvent gives the value of

$\left(\frac{\Delta U_1}{V_1}\right)$ /polar part :

This term and the polar solubility parameter τ_1 are determined by the difference, from the equation:

$$\tau_1 = \left[\frac{\Delta U_1}{V_1}_{\text{TOTAL}} - \lambda_1^2\right]^{1/2} \qquad \text{---(34)}$$

Typical calculations for the determination of these parameters as well as the specific volume and the critical constants are presented in Appendix I.

Since accurate information of critical properties and vapor-pressure data is not available for some of the solvents used in the experiments, values of λ_1 and τ_1 are obtained using two separate procedures. Primarily, values of λ_1 and τ_1 in Set I (procedure 1) are calculated using estimated values of heat of vaporization through eq. 32., while for those in Set II (procedure 2) heat of vaporization is calculated using reliable vapor pressure data. The two procedures are as follows:

Procedure 1 (SET I)

Critical properties P_c, T_c, V_c, Z_c are estimated using Lyderson's techniques. Specific volume 'v' is calculated using these properties. Nonpolar solubility parameter is obtained using homomorph plots. Total heat of vaporization is obtained using eq. 32 (Method B). Polar solubility parameter τ_1 is then obtained through eq. 34.

Procedure 2 (SET II)

Critical properties are obtained from literature sources. In cases when they are not available, Lyderson's estimation techniques are used. Specific volume and nonpolar solubility parameter are calculated using these critical properties and homomorph plots. The heat of vaporization is calculated using vapor-pressure data in the suitable range or using Antoine's vapor-pressure equation constants (MethodA). Polar solubility parameter τ_1 is then calculated through equations 29 and 34.

Appendix II presents the values of ΔH, λ_1 and τ_1 following the various properties and the procedure used for calculation. Table No. 2 summerizes these values of parameters.

CHAPTER 6

EXPERIMENTAL RESULTS

Table No. 3 presents all the measurements involved in the experiments in the determination of the activity coefficients and the obtained activity coefficient values. Since more than one measurement was involved, the mean values are also included. These mean values are summarized in the Table No. 4 against the values available in the literature. A typical experimental log-sheet for the solvent Dimethyl Acetamide is shown in the Appendix III. Corresponding chromatograms are presented in the Appendix IV.

From Table No. 4, we can see that our values of activity coefficients for n-Pentane are in a close agreement with those obtained in the literature[11, 43]. For 1-Pentene, however, our values are as off as 40% in case of Furfural. Activity coefficients for Iso-pentane in these solvents could not be obtained from any literature sources to our knowledge. For comparison purpose; Martes and Colburn[44] values for C_4 hydrocarbons in Furfural are given in Table No. 4.

CHAPTER 7

CORRELATION OF INFINITE DILUTION ACTIVITY COEFFICENTS

a) The Equation:

The extended H-W[7] model equation for the induction energy term ψ_{12} for a general system (of any polar-non-polar components) is:

$$\psi_{12} = k(\tau_1 - \tau_2)^2 \qquad \text{---(7A)}$$

Corresponding equation for activity coefficient at infinite dilution is,

$$RT \ln \gamma_2^{\infty} - v_2(\lambda_1 - \lambda_2)^2 - RT\left[\ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] = V_2\left[(\tau_1 - \tau_2)^2 - 2\psi_{12}\right]$$
$$= (1-2k)V_2(\tau_1 - \tau_2)^2 \qquad \text{---(8A)}$$

Defining the two parameters 'X' and 'Y' as,

$$Y = RT \ln \gamma_2^{\infty} - V_2(\lambda_1 - \lambda_2)^2 - RT\left[\ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right] \qquad \text{---(35)}$$

$$X = V_2(\tau_1 - \tau_2)^2 \qquad \text{---(36)}$$

Or for nonpolar paraffinic solutes, since $\tau_2 = 0.0$

$$X = V_2 \tau_1^2 \qquad \text{---(37)}$$

Equation 8A shows that a plot of 'Y' vs 'X' should yield a straight line.

b) Non Zero Intercept:

Equation 8A suggests that a plot of Y vs X should yield a straight line passing through origin. However, as a first attempt to correlate the data, an intercept was allowed in the regression analysis. Fig. 2 through 5 present such plots for the solutes n-Pentane and Isopentane for the two sets (Set I and II) of solvent parameters λ_1 and τ_1 Fig. 6 and 7 present such plots for 1-Pentene, a polar solute. Linear regression analysis for the points (X, Y) is shown in the Appendix VI.

Linear regression analysis, allowing for an intercept, for our data yielded the following.

$$Y = (\text{slope})\, X + \text{intercept}; \qquad k = \frac{1 - \text{Slope}}{2} \qquad \text{---(8B)}$$

			k
For n-Pentane: (component 2)	Using Set I data for λ_1 & τ_1	$Y = 0.165\,X + 98.5$	0.417 (k_2)
	Using Set II data for λ_1 & τ_1	$Y = 0.176\,X + 146.4$	0.412 (k_2)
For Isopentane, (component 3)	Using Set I data for λ_1 & τ_1	$Y = 0.167\,X + 226.1$	0.416 (k_3)
	Using Set II data for λ_1 & τ_1	$Y = 0.178\,X + 248.3$	0.411 (k_3)
For 1-Pentene (component 4)	Using Set I data for λ_1 & τ_1	$Y = 0.183X - 200$	0.408 (k_4)
	Using Set II data for λ_1 & τ_1	$Y = 0.193\,X - 130$	0.403 (k_4)

From these equations calculated values of activity coefficients (GAMAC) γ^{∞} were determined.

Percentage Difference (PD) in calculating these coefficients through correlations is calculated as:

$$(PD) = \frac{\log \gamma_{EXPT} - \log \gamma_{CAL}}{\log \gamma_{EXPT}} \times 100 \qquad \text{---(38)}$$

Percentage Difference PD is calculated as

$$[PD] = \frac{\gamma_{EXPT} - \gamma_{CAL}}{\gamma_{EXPT}} \times 100 \qquad \text{---(38A)}$$

Average Absolute Deviation (AAD) is then, calculated as:

$$AAD = \frac{\sum |PD|}{\text{No. of solvents}} \qquad \text{---(39)}$$

Results of these correlations are presented in Table No. 5 through 8. As it can be seen from the tables No. 5 and 6, for n-Pentane, using Set I (estimated) values of λ_1 and η_1, Average Absolute Deviation (AAD) in determining γ_2^{∞} is 8.7%, with maximum of 17% for 2-5 Hexanedione. However, using Set II (ΔH from vapor-pressure) values for these parameters, AAD is 16.0% with a maximum of 54% for Trimethyl Phosphate.

Similarly, for Isopentane (from Tables No. 7 and 8), using Set I values, AAD in determining γ_3^{∞} is 8% with a maximum of 13% in case of Acetophenone, while using Set II values, AAD is 14.4% with a maximum of 48% for Trimethyl Phosphate.

Since the purpose of this research is mainly to investigate correlations for straight and branch chained saturated nonpolar hydrocarbon solutes, 1-pentene being polar and unsaturated is,not considered any further.

Only one nonpolar solvent, Dodecane, is included in the regression analysis of our data. Other hydrocarbon solvents, n-Tetracosane, n-Pentatriacontane, n-Eicosane and Squalane are not included since their 'Y' values are not close to the origin,being away from the origin in the range of 600 to -600 cal/gmol. These points are, however, shown on the plots.

c) <u>Forcing the intercept to be zero:</u>

In this case, the regression analysis of the Yvs X data was forced to yield a straight line passing through zero as suggested by eq. 8A. Following expressions were obtained for

$$Y = (\text{slope})\, X \qquad \text{---(8C)}$$

		k
<u>Set I points:</u>		
n-Pentane:	$Y = 0.182X$	0.409 (k_2)
Isopentane:	$Y \div 0.205\ X$	0.398 (k_3)
1-Pentene:	$Y = 0.136\ X$	0.432 (k_4)
<u>Set II points</u>		
n-Pentane:	$Y = 0.197\ X$	0.401 (k_2)
Isopentane:	$Y = 0.215\ X$	0.393 (k_3)
1-Pentene:	$Y = 0.145\ X$	0.428 (k_4)

Activity coefficients from the correlations (GAMAC1) are calculated using above equations. Percentage Differences (PD) and Average Absolute Deviation (AAD) are calculated as in (b). Above lines are shown on the plots - fig. 2 through 7. Results of these correlations are presented in Tables No. 9 through 12.

As it can be seen from Table No. 9 and 10, for n-Pentane using Set I points, AAD in determining γ_2^∞ is 7.8% with a maximum of 18.3% in case of 2-5 Hexanedione, using Set II points, AAD is 14.3% with a maximum of 57% in case of Trimethyl Phosphate. Similarly, from Tables No. 11 and 12 for Isopentane, using Set I datapoints, AAD in determining γ_3^∞ is 8.5% with a maximum of 29% in case of Acetophenone, and using Set II points, AAD is 13.5% with a maximum of 54% for Trimethyl Phosphate.

As it can be seen from part (b) and (c), the value of k_2 and k_3 in eq. 7A, from our correlation of the data, is in the neighborhood of 9.4 for the n-C_5 and iso-C_5 hydrocarbons.

d) Adjusting the nonpolar solute parameter λ_2 values:

Hildebrand[31] has stated that by adjusting the paraffin solute solubility parameters, activity coefficients through the solution theory concept can be better correlated. Kyle and Leng[32] in screening the solvents for extractive distillation purpose, observed that adjusting the conventional paraffin solute solubility parameter (obtained from energy of vaporization) agreement between experimental and calculated values of $\gamma_2^\infty/\gamma_3^\infty$ was improved.

In attempting to correlate our data better, solute solubility parameters obtained from energy of vaporization, were adjusted.

It is observed from tables 13 through 16A that by lowering the values of n-C_5 and i-C_5 solubility parameters the value of intercept of the regressed line can be markedly brought near to origin, but the values of Average Absolute Deviation and the Maximum % error are not reduced. Increased disagreement is observed in some cases. Increasing these solubility parameters make the values of intercept larger, which is against the theoretical prediction.

For Set I points, following equations are obtained, after adjusting the value of solute solubility parameter,

	Lowering λ_2 by	
For n-Pentane:	0.2	(b) $Y = 0.163 X + 25.9$; $k_2 = 0.418$
		(c) $Y = 0.167 X$; $k_2 = 0.416$
	and λ_3 by	
For Isopentane:	0.6	(b) $Y = 0.159 X + 28.9$; $k_3 = 0.420$
		(c) $Y = 0.164 X$; $k_3 = 0.418$

Subtracting 0.2 from n-Pentane solubility parameter as obtained from energy of vaporization, results with and without intercept for Set I points are given in Tables no. 13 and 13A. Subtracting 0.6 from the Isopentane solubility parameter, results are given in Tables No. 14 and 14A. Fig. 8 for n-Pentane and Fig. 9 for Isopentane plots the corresponding X vs Y points.

As it can be seen from the Tables No. 13 and 13A, the AAD of determining γ_2^∞ is 9.3% with a maximum of 19% error in case of 2-5 Hexanedione. Also, for Isopentane, from Tables No. 14 and 14A, AAD is about 9.4% with a maximum of 18T error in case of 2-5 Hexanedione. The value of the intercept, however, is reduced from 98.5 to 25.9 in case of n-Pentane and 226.1 to 28.9 in case of Isopentane.

Following equations are obtained, for Set II points, on adjusting the solute solubility parameters.

	Lowering λ_2 by		k =(1-slope)/2
For n-Pentane:	0.5	(b) Y = 0.167 X -17	0.416 (k_2)
		(c) Y = 0.164 X	0.418 (k_2)
	and λ_3 by		
For Isopentane	0.9	(b) Y = 0.162 X - 15.2	0.419 (k_3)
		(c) Y = -.160 X	0.420 (k_3)

Subtracting 0.5 from n-Pentane solubility parameter as obtained from energy of vaporization, results fro Set II points are given in Tables No. 15 and 15A. Subtracting 0.9 from the Isopentane solubility parameter, results are given in Tables No. 16 and 16A. Figure 10 for n-Pentane and Fig. 11 for Isopentane plots the corresponding X vs Y points.

As it can be seen from the Tables No. 15 and 15A, the AAD of determining γ_2^∞ is 18.3% with a maximum of 60% error in case of Trimethyl Phosphate. Also, for Isopentane, from Tables No. 16 and 16A, AAD in determining γ_3^∞ is about 18% with a maximum of 60% error in case of Trimethyl Phosphate. The value of the intercept, however, in case of n-Pentane is reduced from 146.4 to -17 by subtracting 0.5 from λ_2, while for Isopentane it is reduced from 248.3 to -15.2 by subtracting 0.9 from the λ_3 values obtained from energy of vaporization.

This shows that, in determining activity coefficients from our correlation for C_5 hydrocarbons, adjusting the values of solute solubility parameter arbitrarily does not improve to yield better correlation, except for the fact that it helps reducing the intercept of the regressed lines.

CHAPTER 8

CORRELATION OF INFINITE DILUTION SELECTIVITIES

a1) The Equation:

Rearranging eq. 22, the expression for selectivity in a system containing a polar solvent and nonpolar solute, we have:

$$R\,T\,\ln S_{23} - P - D - F = I \text{ (Induction Energy term)}$$

$$= 2\,v_2\,\psi_{12} - 2\,v_3\,\psi_{13} \qquad \text{---(22)}$$

(substituting for ψ_{12} and ψ_{13})

$$= 2\,v_2 k_2 \tau_1^2 - 2 v_3 k_3 \tau_1^2 \qquad \text{---(40)}$$

We have shown earlier that constants k_2 and k_3 for n-C_5 and iso-C5 are nearly equal, and therefore writing $k_2 = k_3 = k$ in eq. 40,

$$R\,T\,\ln S_{23} - P - D - F = 2k\,\tau_1^2 (V_2 - V_3) \qquad \text{---(41)}$$

Defining two related parameters X' and Y' as,

$$X' = (V_2 - V_3) \cdot \tau_1^2 \qquad \text{---(42)}$$

and

$$Y' = R\,T\,\ln S_{23} - P - D - F \qquad \text{---(43)}$$

Equations 41 through 43 show that a plot of X' vs Y' should be a straight line with a slope of '2K' and passing through origin.

b1) Non Zero Intercept:

Eq. 41 suggests that a plot of X' vs Y' should yield a straight line passing through origin. However, as a first attempt to correlate selectivities, an intercept was allowed in the regression analysis.

Fig. 12 and 13 present such plots for the n-C_5 and iso-C_5 solutes using both the sets (Set I and II) of solvent solubility parameters λ_1 and τ_1.

Linear regression analysis of the X', Y' points, allowing for an intercept, for Set I yielded following equation.

$$Y' = -\ 0.630\ X' - 127.6 \qquad ---(44)$$

Calculated values of selectivities through this equation and the % Error (PD) in determining them are tabulated in Table No. 17. PD is defined as,

$$PD = \%\ \text{Difference} = \frac{(S_{expt} - S_{cal}) \times 100}{S_{expt}}$$

$$\text{Average Absolute Deviation} = AAD = \frac{\Sigma |PD|}{\text{no. of solvents}}$$

From Table No. 17, it can be seen that AAD in determining selectivity through equation above, is 8%, with the maximum of 14.7% error.

Similar analysis for Set II points gave,

$$Y' = -0.498\ X' - 101.8 \qquad ---(45)$$

with an AAD of 9.3% and a maximum of 20.4% error in determining selectivity. Results using this equation are presented in Table No. 18.

c1) <u>Forcing the intercept to be zero:</u>

In this case, as suggested by the equation No. 41, the regressed line was forced to pass through origin. Following equation was obtained for Set I points:

$$Y' = 2.565 X' \qquad ---(46)$$

with an AAD of 10.7% and a maximum of 33% error in determining selectivities through this equation. Results using this equation are presented in Table No. 19.

Similar equation for Set II is, $Y' = 1.724 X'$ ---(47) with an AAD of 10.9% and a maximum of 34.7% error in determining the selectivity through this equation. Corresponding results are presented in Table No. 20.

Fig. 12 and 13 also show above lines for Set I and II respectively.

d1) Adjusting the nonpolar solutes parameters: (λ_2 and λ_3)

As it can be seen from Tables No. 17 through 20, large amount of % differences (PD) are observed in determining selectivities through the correlations for some of the solvents. Following the earlier discussion (in part 'd'), paraffin solute parameters are adjusted in order to better correlate the selectivities. These adjustments are done in the following two ways.

d11) Adjusting both the solutes parameters (λ_2 and λ_3):

Since we already have adjusted the individual solute parameters in attempt to better correlate the activity coefficients for each set

(I and II), these values (adjusted in part 'd') are attempted. Following equations are obtained.

For Set I points:

Subtracting from $(\lambda)_{E.V.}$			Adjusted Values
0.2	n-C_5,	$\lambda_2 = 6.94$	6.74
0.6	iso-C_5,	$\lambda_3 = 7.29$	6.69

(b) allowing for an intercept: $Y' = -1.382\,X' - 2.92$ ---(48)

(c) zero intercept : $Y' = -1.37\,X'$ ---(49)

The AAD of determining selectivities through these equations, as shown in Tables 21 and 21A is less than 2% with a maximum of 4.2% in case of n-Methyl Pyrrolidone. Fig. 14 plots above equations on X'-Y' coordinates.

Similarly, for Set II points:

Subtracting from		$(\lambda)_{E.V.}$	Adjusted values
0.5	n-C_5,	$\lambda_2 = 6.94$	6.44
0.9	iso-C_5,	$\lambda_3 = 7.29$	6.39

the equations obtained are:

b) allowing for an intercept: $Y' = -1.580\,X' - 1.77$

c) zero intercept $Y' = -1.56\,X'$

The AAD of determining selectivities through these equations, as shown in Tables 22 and 22A is less than 2.4%, with a maximum of 6%

error in the case of Trimethyl Phosphate. Fig. 15 plots above lines on X'-Y' co-ordinates.

Results above show that remarkable correlation of selectivities through solution theory is achieved by adjusting the values of paraffin solubility parameters as obtained from energy of vaporization (E.V.).

d12) <u>Adjusting one of the solute's solubility parameter</u>:

As we may see, the successful correlation of selectivities in part (d11) is attributed mainly to the adjusted values of solute solubility parameters, as suggested by Hildebrand[31] and Kyle and Leng.[32] Logically then, is to attempt this adjustment only to one of the hydrocarbons instead of both.

Subtracting 0.4 (0.6 - 0.2 = 0.9 - 0.5) from the Isopentane Solubility parameter yielded following results.

With $\underline{\lambda_2 = 6.94}$; and $\delta_3 = 7.29 - 0.4$

$\underline{= 6.89}$

<u>For Set I</u>:

(b) allowing for an intercept : $Y' = -1.380\,X' - 5.84$ ---(52)

(c) zero intercept : $Y' = -1.234\,X'$ ---(53)

Fig. 16 presents above equations on X' vs Y' co-ordinates.

The AAD of determining selectivities through above equations, as seen in Tables 23 and 23A is within 2% with a maximum of 4.3% error in case of n-Methyl Pyrrolidone.

Similar results for Set II:

(b) allowing for an intercept : $Y' = -1.571\,X' - 8.93$ ---(54)

(c) zero intercept : $Y' = -1.376\,X'$ ---(55)

Fig. 17 presents above two equations on X' vs Y' co-ordinates.

The AAD of determining selectivities through above equations, as seen in Tables 24 and 24A is within 2.5% with a maximum of 6.0% error in the case of Trimethyl Phosphate.

Above results show that changing only one of the paraffin solutes parameters is really a necessary adjustment, in our systems, to be able to improve the correlation of selectivities. This, however, may or may not be true in other systems.

CHAPTER 9

DISCUSSION

Reliability of our results:

As we can see in Table No. 4, our values of activity coefficients of n-Pentane are well comparable with those obtained by Gerster, et. al.[11] However, when comparing similar values for 1-Pentene, our values are different and deviate as large as 40% in determining actual values in case of Furfural. Considering the worst case of Furfural, from Table No. 4, we notice that,

For C_5 hydrocarbons, $S_{24} = 13.10/7.49 = 1.75$, @ 45°C Ref. 11

$S_{24} = 12.8/7.12 = 1.80$, @ 45°C Ref. 43

$S_{24} = 13.27/4.52 = 2.93$, @ 45°C, this work

For C_4 hydrocarbons $S_{24} = 11.0/6.5 = 1.68$, 50°C, Ref. 44

Isopentane activity coefficients in the solvents are not available in the literature, to our knowledge. However, Mertes and Colburn[44] have reported, for n-Butane and Isobutane in Furfural,

$S_{23} = 11.0/12.5 = 0.88$, @ 50°C Ref. 44

$S_{23} = 13.27/13/57 = 0.98$ @ 45°C, this work

It appears therefore, that in light of the fact that our values of 1-Pentene being significantly different in some cases, our values of activity coefficients for Isopentane could be in a possible error. Nevertheless, experiments were carefully performed and a great amount of reproducibility (See Table No. 3) was also observed, above deviations could be due to relatively impure samples or some unknown experimental errors.

Following discussions are, however, based on the assumption of validity of our experimental results.

A Development of two separate correlations for the Induction Energy Term, ψ

As we can see from Fig. 2 through 5, the values of slopes of regressed X - Y line, relating the physical properties with infinite dilution coefficients of saturated hydrocarbons, ranges from 0.164 to 0.215. The value of slope in each case, physically, depends upon various factors such as; type of hydrocarbon, i.e. straight chained or branched chain; source of solvent properties used in developing the correlation, i.e. using estimation techniques or from vapor pressure data; and the experimental error in determination of activity coefficients at infinite dilution conditions. As a result, it is difficult to observe, in our work, the nature of the X - Y line plots and thus to develop two separate equations of induction energy term ψ. for two types of saturated hydrocarbons, straight chained and branch chained paraffins.

B Correlation of infinite dilution activity coefficients:

From Tables No. 5 through 16A and 33, we can see that infinite dilution coefficient can only be estimated using the different models, since the percentage errors in some cases are more than 100%. Adjustments in the values of solutes solubility parameters are based on certain guidelines as follows.

For the regression with ZERO intercept, we could not find any favorable adjustment to the solute's solubility parameter that will reduce the magnitude of average absolute deviation for all of the solvents in consideration. It may be noted here that, by increasing the n-C_5 or iso-C_5 solubility parameters, scattering of the points is increased and any improvement in % error for some of the solvents is more than offset by obtaining very large % errors in others. Also, for the regression ALLOWING for an intercept, increasing these parameters bring about a further shift of the line away from the origin. The adjustments which are made, are in fact, those necessary to reduce deviations in determining the selectivities. As can be seen in Table 33, these adjustments bring about excellent correlation of selectivities, but slightly increase the Average Absolute Deviation in determining the activity coefficients.

C Correlation of Selectivities:

From Tables No. 17 through 24A and No. 33, we can see that selectivities can also be only estimated using these correlations. We have noticed that adjusting the values of paraffin's solubility parameters brought about excellent improvement in correlating the selectivities.

D Comparison of this work with W-P[3] and H-V[7] studies:

Table no. 33 summarizes all the necessary informations for this comparison. For the 13 solvents used in developing our correlations, we notice that, for C_5 hydrocarbons:

1. in determining values of Activity coefficients, ($\ln \gamma$):
   Our results without adjusting parameters yielded minimum error (14%) as compared to those obtained using W-P[3] or H-V[7] models (18%).
2. in determining Selectivities (S_{23}):
   Our results, AFTER adjusting the values of solutes' solubility parameters, yielded minimum error (2.4%) as compared to those using W-P[3] (7.4%) and H-V[7] (6.7%). WITHOUT adjusting for the parameters, our results yielded 10.8% error.

For Solvents No. 20, 21 and 22, NOT included in the development of our correlation, W-P[3] correlations gave the most reliable values, following the H-V[7] correlations, and our correlations

WITHOUT adjustment of parameters. Correlations using previous adjustments (for solvents No. 1 - 13), yielded the worst results, showing that the magnitude of adjustments of these parameters depends on various factors, not so well known.

For C_8 hydrocarbons, NOT included in the study, in two of the solvents used in the experiments, no favorable conclusion can be drawn in determining activity coefficients, since all the correlations give values of very large % error. Selectivities obtained through the correlations are also widely different and no favorable conclusion can be drawn except for the fact that values using previous adjustments are closest to the experimental values of selectivities.

D Recommended Procedure:

For a given pair of solutes, a list of potential solvents is established based on literature information.

A) If the difference in molar volumes of the hydrocarbon solutes to be separated is high, more than 5%, consider solvents of high polar cohesive energy.

B) If molar volumes are close, difference less than 5%, following procedure may be adopted.

i) Consult the references 11, 24, 45. In view of the large amount of experimental data covered in these sources, information on some of the systems under consideration might be included.

ii) If any of the hydrocarbons belong to the three groups (saturated, unsaturated, or aromatic),

  a) For a precise information of activity coefficients and selectivities, obtain correlations using experimental values of activity coefficients.

  b) In absence of experimental data, some reliable values of activity coefficients from literature sources may be used to develop necessary correlations.

  In developing these correlations from limited informations (a or b), adjust the values of solutes' solubility parameters to obtain the values of slopes (of X-Y or X'-Y' lines) as reported by W-P^3 for proper case. Use these values of parameters to estimate activity coefficients and selectivities for systems with other solvents.

  c) In absence of experimental or any reliable values of activity coefficients, use W-P^3 correlations to estimate these values.

iii) This work may be referred in dealing with systems involving separating of normal and isoparaffins from their mixtures using solvents extraction.

iv) This work may also be referred to obtain various necessary properties of some known solvents. These properties are, critical properties, specific volumes and solubility parameters.

E Contributions of Various Terms to the Selectivity Function $R\,T\,\ln S_{23}$:

The selectivity function $R\,T\,\ln S_{23}$, as defined earlier, is

$$R\,T\,\ln S_{23} = P + D + I + F \qquad \text{---(22)}$$

where, P = Polar effects = $(v_2 - v_3)\,\tau_1^2$

D = Dispersion effects = $v_2(\lambda_1 - \lambda_2)^2 - v_3\,(\lambda_1 - \lambda_3)^2$

I = Induction effects = $2\,v_3\psi_{13} - 2\,v_2\psi_{12}$

and, F = Entropy effects = $R\,T\,\left(\ln\frac{v_2}{v_3} - \frac{v_2 - v_3}{v_1}\right)$

Tables No. 25 and 26 tabulate these contributions for the selectivities we have calculated using Set I and Set II properties respectively, without adjusting values of solubility parameters. Tables No. 27 and 28 tabulate similar contributions for Set I and II, after adjusting both the solutes' solubility parameters while Tables No. 29 and 30 list the same after adjusting only one of the solubility parameters, for Set I and II respectively.

It can be seen from Tables No. 25 and 26, that major contributing term to the selectivity is the 'dispersion' term. However, after adjusting the values of solutes' solubility parameters, in order to better correlate the selectivities, dispersion forces no more remain to be controlling ones, as we can see from Tables No. 27 through 30.

F Chemical Effects in the solution

Harris and Prausnitz[12] in their work, have suggested possibility of using a Lewis acidity scale for polar organic compounds to correlate variety of kinetic and thermodynamic physiochemical measurements. Since these effects result from the solvent's ability to accept the electrons, the strength of a complex resulting from an acid-base interaction depends on the ionizational potential of the Lewis base (electron donor) and on the electron affinity of the Lewis acid (electron acceptor).

Since the difference in the ionizational potentials of the two hydrocarbons ( ) is larger than the difference in molar volumes (0.68%), chemical effects were sought for by plotting the quantity $Q = R\,T\,\ln S_{23obs} - R\,T\,\ln S_{23cal}$ against K_x, the relative Lewis acidity of the solvents, where available. Table No. 31 presents values of K_x and Q for various types of selectivities calculated earlier.

Figure 18 through 21 present such plots using various selectivities we have calculated through correlations, earlier. As we can see from these figures, there does not appear to be existing any smooth relationship between 'Q' and 'K_x'.

CONCLUSION

Following conclusions are made from this study.

1. In view of the uncertainty of the data of solvent properties for all of the solvents, and uncertain values of experimental activity coefficients for Isopentane, separate correlations for induction energy term (ψ) for normal and Isoparaffins could not be developed.
2. For C5 hydrocarbons, adjusting the values of solute solubility parameters do not help better correlate the activity coefficients through our correlations.
3. Adjusting the values of solute solubility parameters, however, bring about excellent improvements in correlating selectivities through our correlations.
4. Dispersion forces appear to contribute most to the selectivity functions.
5. Effects of chemical forces cannot be precisely determined.

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NOMENCLATURE

AAD = Average Absolute Deviation

A, B, C = Constants of Antonie's Vapor Pressure equation

c_{ii} = Pure component cohesive energy density

c_{ij} = Cohesive energy density for the interaction between unlike species

D = Dispersion forces contribution to the Selectivity, cal/gmol; Distance between the Chromatographic peaks, inches

I = Induction forces contribution to the Selectivity cal/gmol

F = Flory-Huggins Entropy term contribution to the Selectivity, cal/gmol

H = Heat of vaporization, cal/gmol

H_i = Infinite dilution partition coefficient

G = Free energy, cal/gmol

k = Constant of Proportionality

M_s = Moles of stationary solid phase in the column.

M = Molecular weight of the Solvent

n = Number of components

p = Polar forces contribution to the Selectivity, cal/mol

PD = Percentage difference

P_c = Critical Pressure, atm

p_i = Column Inlet pressure, mm Hg abs

p_o = Column Outlet pressure, mm Hg abs

p_w = Water vapor pressure at temperature T_f, mm Hg abs

p_{io} = Vapor pressure of pure i, mm Hg abs

R = Gas constant, Cal/^oK gmol

S = Selectivity; Solvent amount in the column, gms

T = Temperature, ^oK

T_b = Boiling Point, ^oK

T_c = Critical Temperature, ^oK

T_f = Temperature at the Soap-film end, ^oK

T_r = Reduced temperature, T/T_c

U = Energy of vaporization, cal/gmol

V = Specific volume, cc/gmol

V_c = Critical volume, cc/gmol

V_g = Corrected Retention volume, cc/gmol

V = He gas flow rate, cc/min

X = Mole fraction

X, Y = Parameters as defined by equations 31 and 32

X', Y' = Parameters as defined by equations 42 and 43

Z_c = Critical compressibility factor

Subscripts

1 = Solvent component

2, 3, 4 = Solute components; n-pentane, isopentane, and 1-pentene respectively

E. V. = From energy of vaporization, respectively

c = At critical conditions

r = At reduced conditions

Greek Letters

ϕ_i = Volume fraction, defined as = $\dfrac{v_i x_i}{v_i\ x_i\ v_j\ x_j + v_k x_k}$

$\gamma^0 = \gamma^\infty$ = Activity Coefficient at Infinite dilution

λ = Non Polar solubility parameter, $(cal/cc)^{1/2}$

ψ = Ineraction term, cal/cc

α = Relative volatility

τ = Polar Solubility parameter, $(cal/cc)^{1/2}$

ρ = Density, gms/cc

ρ_r = Reduced density, uncorrected

ρ_r' = Corrected reduced density

Δ = Change, incremental

Others

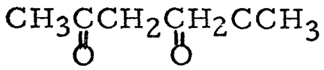
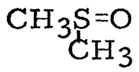
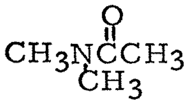
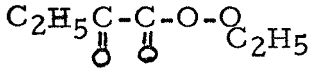
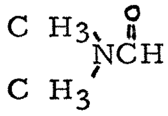
$\left.\dfrac{dP}{dT}\right|_T$ = Slope of the vapor pressure curve at temperature T, mm/°K

PD = Quantities - in ( ) indicate % differences in determining log quantities.

- in [ ] indicate % differences in determining actual quantities.

TABLE #1

List of Solvents and their properties

Solvent Name and Number		Formula	B. Pt.°C
1	- Butyrolactone (BTLA)		204
2	Acetonyl Acetone (HEXD)	 $CH_3\underset{\overset{\|}{O}}{C}CH_2\underset{\overset{\|}{O}}{C}H_2CCH_3$	195
3	Dimethyl Sulfoxide (DMSX)	 $CH_3\underset{CH_3}{S}=O$	189
4.	Trimethyl Phosphate (TMPH)	$C_3H_9O_4P$	197.2
5	Cyclopentanone (CYCP)	$C5H_8O$	130
6	Nitrobenzene (NTBZ)	$C_6H_5NO_2$	210.85
7	Dodecane (DODE)	$C_{12}H_{26}$	216.3
8	N-Methyl Pyrrolidone (NMPL)		202
9	Dimethyl Acetamide (DMAA)	 $CH_3\underset{CH_3}{N}\overset{\overset{O}{\|}}{C}CH_3$	170
10	Acetophenone (ACPH)	$C_6H_5COCH_3$	202
11	Diethyl Oxalate (DEOX)	 $C_2H_5\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-O-O\;C_2H_5$	185.4
12	Dimethyl Formamide (DMFM)	 $\begin{matrix}C\ H_3\\ C\ H_3\end{matrix}\!>\!N\overset{\overset{O}{\|}}{C}H$	149.56
13	Furfural (FURF)		161.7

- See Table No. 3 for References

TABLE #1 (Cont'd)

Following is the list of Solvents for which Activity Coefficients at Infinite dilution are obtained from the reported literature data.

Solvent Name and Number		Formula	B. Pt. °C
14	n-Tetracosane (TRCS)	$CH_3(CH_2)_{22}CH_3$	391.3
15	n-Pentatriacontane (PTCT)	$C_{35}H_{72}$	490
16	n-Eicosane (EICS)	$C_{20}H_{42}$	342.7
17	Squalane (SQAL)	$C_{30}H_{62}$	350

Table No. 2: Values of Specific Volume (v), solubility parameters of solvent (λ_1, τ_1) obtained using different methods

1/2

Solvent No.	Name	Temp °C	Specific Volume v (cc/gmol) from Reduced Density & critical prop.	from Literature *!	Solubility Parameters (cal/cc) Nonpolar Part λ_1 Methods from Homomorph plots Set I	Set II	Polar Part τ_1 Method B Set I	A Set II
1	BTLA	45	78.03	--	9.49	9.49	8.42	8.70
2	HEXD	45	119.88	--	8.08	8.08	6.55	6.53
3	DMSX	45	72.56	--	8.52!	8.52!	--	9.47
4	TMPH	45	117.91	--	7.41!'	7.41!	--	5.82
5	CYCP	45	90.95	--	8.61	8.61	5.49	5.61
6	NTBZ	45	104.69	104.10	9.43	9.43	5.39	5.76
7	DODE	45	232.75	232.8	7.69	7.35+	0.00	0.00
8	NMPL	45	98.2	98.6	9.01	9.01	6.50	7.16
9	DMAA	45	94.8	95.3	8.23	8.09!	6.89	6.75
10	ACPH	45	123.3	119.8	9.20	9.30!	3.57	4.12
11	DEOX	45	139.0	139.3	7.83	7.88!	6.22	6.28
12	DMFM	45	78.8	79.0	8.10!	8.07	7.97	8.10
13	FURF	45	84.8	84.8	8.88	8.81!	7.22	7.34
14	TRCS	93.9	447.5	--	7.19	6.83!	0.00	0.00
15	PTCT	93.9	628.8	--	5.15	6.70!	0.00	0.00
16	EICS	53.2	364.3	--	7.78	7.76!	0.00	0.00
		74.1	370.4	--	7.63	7.50!	0.00	0.00
		93.9	376.1	--	7.50	7.37!	0.00	0.00

17	SQAL	53.2	532.7	--	6.06	7.89!	0.00	0.00
		74.1	541.6	--	5.95	7.75!	0.00	0.00
		93.9	549.8	--	5.84	7.62!	0.00	0.00

*! -- Literature values, for references see Appendix II

† -- From Heat of vaporization value

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of Measurements	γ_2^∞	γ_3^∞	γ_4^∞
1	BTLA	n-C_5	24.9	0.260	1.014	0.685	21.8	770	918.8	19.6	1020	86		21.94		
													5	21.77←Mean		
		i-C_5	24.9	0.225	0.997	0.685	21.8	770	918.8	19.6	1324	86			22.31	
													5	Mean	→ 22.49	
		$=C_5$	24.9	0.695	0.996	0.685	21.8	770	918.8	19.6	1263	86				7.53
													3		Mean→	7.34
2	HEXD	n-C_5	34.2	0.875	1.945	0.685	23.8	760	948.5	22.1	1020	114		8.47		
														8.38←Mean		
		i-C_5	34.2	0.680	1.938	0.685	23.8	760	948.5	22.11	1324	114			8.17	
													4	Mean	→ 8.29	
		$=C_5$	34.2	1.885	1.928	0.685	23.8	760	948.5	22.11	1263	114				3.20
													3		Mean →	3.10

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of Measurements	γ_2^∞	γ_3^∞	γ_4^∞
3	DMSX	nC_5	20.7	0.300	1.997	0.685	23	758	938.3	21.1	1020	78		59.51		
													5	62.77←Mean		
		$i\text{-}C_5$	20.7	0.220	1.909	0.685	23	758	938.3	21.1	1324	78			59.29	
													4	Mean →	59.98	
		$=C_5$	20.69	0.61	1.788	0.685	23	758	938.3	21.1	1263	78				22.21
													2		Mean→	22.43
4	TMPH	$n\text{-}C_5$	27.8[illegible]	0.46	2.669	0.685	26	757	958.0	25.2	1020	140		22.15		
													3	22.17←Mean		
		$i\text{-}C_5$	27.0	0.380	2.661	0.685	26	757	958.1	25.2	1324	140			20.83	
													4	Mean →	20.81	
		$=C_5$	27.0	1.25	2.642	0.685	26	757	958.0	25.2	1263	140				6.49
													3		Mean →	6.53

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg Po	mm Hg Pi	mm Hg Pw	mm Hg Pio	M	No. of measurements	γ_2^∞	γ_3^∞	γ_4^∞
5	CLCP	n-C_5	39.5	1.725	1.676	0.685	25.8	754	961.4	24.9	1020	84		4.33		
													5	4.32←Mean		
		i-C_5	39.5	1.050	1.387	0.685	25.8	754	961.4	24.9	1324	84			4.54	
													5		Mean→4.51	
		$=C_5$	39.5	2.050	1.204	0.685	25.8	754	961.4	24.9	1263	84				2.16
																Mean→2.20
6	NTBZ	n-C_5	24.8	1.680	1.861	0.685	25.8	754	917.8	24.9	1020	84		7.57		
													5	7.50←Mean		
		i-C_5	24.8	1.260	1.853	0.685	25.8	754	917.8	24.9	1324	84			7.82	
													5		Mean → 7.74	
		$=C_5$	24.8	3.545	1.847	0.685	25.8	754	917.8	24.9	1263	84				2.67
													3			Mean→2.88

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of measurements	γ_2^∞	γ_3^∞	γ_4^∞
7	DODE	n-C_5	28.8	3.090	0.5254	0.685	21	743	930.5	18.7	1020	98		0.94		
													4	0.95←Mean		
		i-C_5	28.8	2.195	0.5146	0.685	21	743	930.5	18.7	1324	98			0.97	
													4	Mean→	0.98	
		=C_5	28.8	6.5	0.5082	0.685	21	743	930.5	18.7	1263	98				
													3	Large % error involved		
8	NMPL	n-C_5	44.8	0.535	1.6343	0.685	23.5	758	972.8	21.2	1020	99		9.62		
													5	9.69←Mean		
		i-C_5	44.8	0.445	1.6226	0.685	23.5	758	972.8	21.2	1324	99			9.55	
													5	Mean →	9.59	
		=C_5	44.8	1.255	1.6186	0.685	23.5	758	972.8	21.2	1263	99				3.56
													3		Mean→	3.52

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of measurements	γ_2^∞	γ_3^∞	γ_4^∞
9	DMAA	$n\cdot C_5$	40.0	0.945	1.8374	0.685	21	743	958.2	18.7	1020	87		8.07		
													7	7.83←Mean		
		$i\cdot C_5$	40.0	0.680	1.8209	0.685	21	743	958.2	18.7	1324	87			8.16	
													7	Mean →	8.19	
		$=C_5$	40.0	1.890	1.7982	0.685	21	743	958.2	18.7	1263	87				3.15
													4		Mean→	3.16
10	ACPH	$n\cdot C_5$	28.4	1.475	2.4384	0.685	25	756	944.5	23.8	1020	120		5.05		
													5	5.01←Mean		
		$i\cdot C_5$	29.4	1.005	2.4332	0.685	25	756	944.5	23.8	1324	120			5.39	
													5	Mean →	5.38	
		$=C_5$	29.4	2.830	2.4293	0.685	25	756	944.5	23.8	1263	120				2.85
													3		Mean→	2.88

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min V	in D	gms S	in/min Z	°C TF	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of measurements	γ_2^∞	γ_3^∞	γ_4^∞
11	DEOX	n-C_5	29.7	1.605	2.3848	0.685	24.0	756	936.7	22.4	1020	146		1.922		
			29.7	1.575	2.3834	0.685	24.0	756	936.7	22.4	1020	146		5.013		
			"	1.570	2.3816	"	"	"	"	"	"	"		5.025		
			"	1.510	2.3798	"	"	"	"	"	"	"		5.220		
			"	1.535	2.3786	"	"	"	"	"	"	"		5.133		
												Mean	5	→ 5.060		
		i-C_5	29.8	1.200	2.3753	0.685	24.0	756	936.7	22.4	1324	146			5.052	
			"	1.200	2.3742	0.685	"	"	"	"	"	"			5.050	
			30.4	1.190	2.3730	"	"	"	934.2	"	"	"			4.970	
			"	1.160	2.3718	"	"	"	"	"	"	"			5.094	
			"	1.155	2.3703	"	"	"	"	"	"	"			5.113	
													5	Mean →	5.033	
		=C_5	30.4	2.840	2.3686	0.685	24.0	756	934.2	22.4	1263	146				2.178
			"	2.800	2.3659	0.685	"	"	"	"	"	"				2.207
													2		Mean →	2.186

TABLE NO. 3

EXPERIMENTAL DETERMINATION OF ACTIVITY COEFFICIENTS @ 45°C

Solvent No.	Solvent Name	Solute	cc/min	in	gms	in/min	°C	mm Hg p_o	mm Hg p_i	mm Hg p_w	mm Hg p_{io}	M	No. of measurements	γ_2^∞	γ_3^∞	γ_4^∞
12	DMFM	n-C_5	26.9	0.810	1.8664	0.685	28	758	930.72	28.4	1020	73		12.16		
													7	11.26	Mean	
		i-C_5	29.0	0.600	1.8406	0.685	28	758	930.72	28.4	1324	73			11.54	
													7	Mean	11.53	
		$=C_5$	29.0	1.730	1.8315	0.685	28	758	930.72	28.4	1263	73				5.88
													3		Mean	5.88
13	FURF	n-C_5	30.2	1.065	1.9852	0.685	28	758	932.1	28.4	1020	73		13.32		
													5	13.27	Mean	
		i-C_5	30.2	0.810	1.9636	0.685	28	758	932.1	28.4	1324	73			13.72	
													5	Mean	13.53	
		$=C_5$	30.2	2.535	1.9572	0.685	28	758	932.1	28.4	1263	73				4.63
													3		Mean	4.52

TABLE NO. 4

INFINITE DILUTION ACTIVITY COEFFICIENTS

FOR C_5 HYDROCARBONS, n-PENTANE, ISOPENTANE, 1-PENTENE

All the values at 45°C

Solvent No.	Name	γ_2^∞ This work	γ_2^∞ Literature (Ref)	γ_3^∞ This work	γ_3^∞ Literature (Ref)	γ_4^∞ This work	γ_4^∞ Literatu (Ref)
1	BTLA	21.77	21.14(11)	22.49		7.34	10.75(1
2	HEXD	8.38	8.72(11)	8.29		3.10	5.02(1
3	DMSX	62.77		59.98		22.43	
4	TMPH	22.17		20.81		6.53	
5	CYCP	4.32	4.22(11)	4.51		2.20	2.69(1
6	NTBZ	7.50		7.74		2.88	
7	DODE	0.95		0.98		-	
8	NMPL	9.69	9.00	9.59		3.52	4.90(1
9	DMAA	7.83	7.62(11)	8.19		3.16	4.23(1
10	ACPH	5.01	5.15(11)	5.38		2.88	3.13(1
11	DEOX	5.06	5.56(11)	5.03		2.19	3.40(1
12	DMFM	11.26	11.33(11)	11.53		5.88	6.30(1
13	FURF	13.27	13.10(11)	13.53		4.52	7.49(1
			12.8 (43)				7.12(4
			11.0 (44)*		12.5(44)*		6.55(4

Solvent No.	Name	Temp. °C	n-Pentane	IsoPentane	1-Pentene	Ref.
14	TRCS	93.9	0.74	0.73		41
15	PTCT	93.9	0.62	0.62		41
16	EICS	53.2	53.75	40.79	44.66	4
		74.1	30.68	24.25	26.29	4
		93.9	19.19	15.65	16.65	4
17	SQAL	53.2	48.73	37.51	41.02	4
		74.1	27.49	21.91	23.34	4
		93.9	16.67	13.63	14.49	4

*Values for C_4 Hydrocarbons, n-Butane, Isobutane and 1-Butene

TABLE No. 5

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^∞ FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8B, AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_2^∞ (GAMA)	CALCULATED γ_2^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.2 X	FOR FIG.No.2 Y
1	BTLA	21.77	33.66	-14.2	8525	1234
2	HEXD	8.38	5.79	17.4	5167	1188
3	DMSX	62.77	-	-	-	-
4	TMPH	22.17	-	-	-	-
5	CYCP	4.32	4.94	- 9.1	3630	615
6	NTBZ	7.50	9.39	-11.2	3498	535
7	DODE	0.95	1.09	[11.2]	0	12
8	NMPL	9.69	9.83	- 1.0	5086	932
9	DMAA	7.83	6.94	5.8	5706	1119
10	ACPH	5.01	4.63	4.9	1530	402
11	DEOX	5.06	4.55	6.6	4651	936
12	DMFM	11.26	9.97	5.5	7641	1440
13	FURF	13.27	11.49	5.6	6264	1226
6	NTBZ	7.50	-	-	4332	535*
14	TRCS@93.9°C				0	116*
15	PTCT@93.9°C				0	31*
16	EICS@53.2°C				0	-178*
	@74°C				0	-128*
	@93.9°C				0	-249*
17	SQAL@53°C				0	78*
	@74°C				0	68*
	@93.9°C				0	74*

*Show Points

AAD = 8.7%

MAXIMUM % ERROR = 17.4%

TABLE No.6

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^∞ FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8B, AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_2^∞ (GAMA)	CALCULATED γ_2^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.3 X	Y
1	BTLA	21.77	48.89	-26.3	9099	1234
2	HEXD	8.38	6.74	10.3	5139	1188
3	DMSX	62.77	34.90	14.2	10782	2413
4	TMPH	22.17	4.09	54.6	4080	1932
5	CYCP	4.32	5.82	-20.3	3734	615
6	NTBZ	7.50	12.30	-24.6	3994	535
7	DODE	0.95	1.09	[-14.7]	0	59
8	NMPL	9.69	12.82	-12.3	6175	1055
9	DMAA	7.83	7.23	3.9	5481	1160
10	ACPH	5.01	6.43	-15.5	2046	348
11	DEOX	5.06	5.52	- 5.4	4744	925
12	DMFM	11.26	13.44	- 7.3	7893	1422
13	FURF	13.27	13.90	- 1.8	6487	1257
9	DMAA				6803	1160*
10	ACPH				1830	348*
11	DEOX				4187	870*
12	DMFM				6340	1422*
14	TRCS@93.9°C				0	-10*
15	PTCT@93.9°C				0	70*
16	EICS @53°C				0	-142*
	@74.1°C				0	-146*
	@93.9°C				0	-195*
17	SQAL@53.1°C				0	-223*
	@74.1°C				0	-273*
	@93.9°C				0	-309*

*Show points

AAD = 16%

MAXIMUM % ERROR = 54.6%

TABLE No. 7

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^∞ FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8B, AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT No.	 NAME	EXPERIMENTAL γ_3^∞ (GAMA)	CALCULATED γ_3^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.4 X	 Y
1	BTLA	22.49	31.13	-10.14	8582	1453
2	HEXD	8.29	6.36	12.5	5202	1261
3	DMSX	59.98	-	-	-	-
4	TMPH	20.81	-	-	-	-
5	CYCP	4.51	5.02	- 7.0	3655	769
6	NTBZ	7.74	8.61	- 5.2	3522	747
7	DODE	0.98	1.04	[- 6.2]	0	81
8	NMPL	9.59	9.55	0.2	5122	1083
9	DMAA	8.19	7.49	4.3	5745	1242
10	ACPH	5.38	4.33	12.9	1541	620
11	DEOX	5.03	5.16	- 1.5	4683	992
12	[illegible]FM	11.53	11.03	1.8	7692	1537
13	FURF	13.53	11.40	6.6	6306	1387
6	NTBZ				4361	747*
14	TRCS				0	-225*
15	PTCT				0	69*
16	EICS @53.2°C				0	-225*
	@74.1°C				0	-291*
	@93.9°C				0	-364*
17	SQAL@53°C				0	91*
	@74.1°C				0	72*
	@93.9°C				0	56*

*Show points

AAD = 8 %

MAXIMUM % ERROR = 12.9%

TABLE No. 8

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^∞ FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8B , AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_3^∞ (GAMA)	CALCULATED γ_3^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.5 X	Y
1	BTLA	22.49	44.10	-21.6	9160	1453
2	HEXD	8.29	7.16	6.9	5174	1261
3	DMSX	59.98	35.96	12.5	10854	2504
4	TMPH	20.81	4.72	48.8	4108	1917
5	CYCP	4.51	5.71	-15.6	3760	769
6	NTBZ	7.74	10.91	-16.8	4021	747
7	DODE	0.98	1.20	[21.8]	0	100
8	NMPL	9.59	12.54	-11.9	6217	1185
9	DMAA	8.19	7.67	3.1	5518	1272
10	ACPH	5.38	5.74	- 3.8	2060	575
11	DEOX	5.03	6.01	-10.9	4772	986
12	DMFM	11.53	14.34	- 8.9	7946	1525
13	FURF	13.53	13.46	.23	6530	1414
9	DMAA				6850	1272*
10	ACPH				1842	575*
11	DEOX				4216	948*
12	DMEM				6383	1525*
14	TRCS				0	- 92*
15	PTCT				0	4*
16	EICS @53.2°C				0	-217*
	@74.1°C				0	-229*
	@93.9°C				0	-300*
17	SQAL@53.2°C				0	-317*
	@74.1°C				0	-380*
	@93.9°C				0	-456*

*Show Points

AAD = 14.4%

MAXIMUM % ERROR = 48.8%

TABLE No. 9

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^∞ FOR n-PENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8C , AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_2^∞ (GAMA)	CALCULATED γ_2^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.2 X	Y
1	BTLA	21.77	36.08	-16.4	SEE TABLE NO. 5	
2	HEXD	8.38	5.68	18.3		
3	DMSX	62.77	-	-		
4	TMPH	22.17	-	-		
5	CYCP	4.32	4.65	- 5.0		
6	NTBZ	7.50	8.82	- 8.0		
7	DODE	0.95	0.93	- 2.1		
8	NMPL	9.69	9.62	0.34		
9	DMAA	7.83	6.91	6.9		
10	ACPH	5.01	4.12	12.1		
11	DEOX	5.06	4.40	8.6		
12	DMFM	11.26	10.44	3.1		
13	FURF	13.27	11.60	5.2		

AAD = 7.8%

MAXIMUM % ERROR = 18.3%

TABLE No. 10

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^∞ FOR n-PENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8C , AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_2^∞ (GAMA)	CALCULATED γ_2^∞ (GAMAC)	% DIFF (PD)	FOR FIG.No.3 X	 Y
1	BTLA	21.77	52.96	-28.8	SEE TABLE NO. 6	
2	HEXD	8.38	6.37	12.9		
3	DMSX	62.77	40.05	10.8		
4	TMPH	22.17	3.73	57.2		
5	CYCP	4.32	5.24	-13.2		
6	NTBZ	7.50	11.19	-19.8		
7	DODE	0.95	0.86	- 9.5		
8	NMPL	9.69	12.57	-11.5		
9	DMAA	7.83	6.92	6.0		
10	ACPH	5.01	5.47	- 5.4		
11	DEOX	5.06	5.15	- 1.2		
12	DMFM	11.26	13.97	- 8.9		
13	FURF	13.27	13.77	-1.4		

AAD = 14.3%

MAXIMUM % ERROR = 57.2%

TABLE No. 11

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^{∞} FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8C, AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL γ_3^{∞} (GAMA)	CALCULATED γ_3^{∞} (GAMAC)	% DIFF (PD)	FOR FIG.No. X	Y
1	BTLA	22.49	36.52	-15.6	8582	1453
2	HEXD	8.29	6.09	14.6	5202	1261
3	DMSX	59.98	-	-	-	-
4	TMPH	20.81	-	-	-	-
5	CYCP	4.51	4.37	2.1	3655	769
6	NTBZ	7.74	7.44	1.9	3522	747
7	DODE	0.98	0.87	6.5	0	81
8	NMPL	9.59	9.09	2.4	5122	1083
9	DMAA	8.19	7.40	4.8	5745	1242
10	ACPH	5.38	3.32	28.6	1541	620
11	DEOX	5.03	4.78	3.2	4683	992
12	DMFM	11.53	12.27	2.5	7692	1537
13	FURF	13.53	11.66	5.7	6306	1387

AAD = 8.5%

MAXIMUM % ERROR = 28.6%

TABLE No. 12

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^∞ FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND 8 C, AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF	FOR FIG.No.	
No.	NAME	(GAMA)	(GAMAC)	(PD)	X	Y
1	BTLA	22.49	50.50	-25.9	9160	1453
2	HEXD	8.29	6.52	11.4	5174	1261
3	DMSX	59.98	45.39	6.8	10854	2504
4	TMPH	20.81	4.04	54.0	4108	1917
5	CYCP	4.51	4.79	- 3.9	3760	769
6	NTBZ	7.74	9.29	- 8.9	4021	747
7	DODE	0.98	.85	13.3	0	100
8	NMPL	9.59	12.12	-10.4	6217	1185
9	DMAA	8.19	7.12	6.6	5518	1272
10	ACPH	5.38	4.36	12.5	2060	575
11	DEOX	5.03	5.34	- 3.6	4772	986
12	DMFM	11.53	15.31	-11.6	7946	1525
13	FURF	13.53	13.24	.85	6530	1414

AAD = 13.4%

MAXIMUM % ERROR = 54.0%

TABLE No. 13

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^{∞} FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND Part d, AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS : $\lambda_{2(a)} = \lambda_2 - 0.2$

SOLVENT No.	NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	Y
1	BTLA	21.77	35.49	-15.9	8525	1106
2	HEXD	8.38	5.56	19.4	5166	1128
3	DMSX	62.77	-	-	-	-
4	TMPH	22.17	-	-	-	-
5	CYCP	4.32	4.96	- 9.5	3630	530
6	NTBZ	7.50	10.06	-14.6	3498	411
7	DODE	0.95	1.04	9.0	0	- 29
8	NMPL	9.69	10.14	- 1.9	5087	827
9	DMAA	7.83	6.72	7.4	5706	1052
10	ACPH	5.01	4.91	1.3	1531	288
11	DEOX	5.06	4.29	10.2	4651	888
12	DMFM	11.26	9.47	7.2	7641	1380
13	FURF	13.27	11.66	5.0	6264	1129
6	NTBZ				4332	411*
14	TRCS				0	-193*
15	PTCT				0	76*
16	EICS@53.2°C				0	-281*
	@74.1°C				0	-288*
	@93.9°C				0	-344*
17	SQAL@53.2°C				0	91*
	@74.1°C				0	77*
	@93.9°C				0	77*

*Show Points

AAD = 9.3%

MAXIMUM % ERROR = 19.4%

TABLE No. 13A

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^{∞} FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND "d", AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.2$$

SOLVENT No.	 NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	 Y
1	BTLA	21.77	36.2	-16.5	8525	1106
2	HEXD	8.38	5.53	19.6	5166	1128
3	DMSX	62.77	-	-	-	-
4	TMPH	22.17	-	-	-	-
5	CYCP	4.32	4.89	- 8.4	3630	530
6	NTBZ	7.50	9.89	-13.7	3498	411
7	DODE	0.95	.99	4.3	0	- 29
8	NMPL	9.69	10.1	- 1.7	5087	827
9	DMAA	7.83	6.72	7.5	5706	1052
10	ACPH	5.01	4.76	3.2	1531	288
11	DEOX	5.06	4.26	10.7	4651	888
12	DMFM	11.26	9.58	6.6	7641	1380
13	FURF	13.27	11.69	4.9	6264	1129

AAD = 8.9%
MAXIMUM % ERROR = 19.6%

TABLE No. 14

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^{∞} FOR Isopentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part 4, AND USING SET I PROPERTIES, ALLOWING For an INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.6$

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR FIG. No.	
No.	NAME	(GAMA)	(GAMAC)	(PD)	X	Y
1	BTLA	22.49	36.53	-15.6	8582	1089
2	HEXD	8.29	5.63	18.4	5201	1103
3	DMSX	59.98	-	-	-	-
4	TMPH	20.81	-	-	-	-
5	CYCP	4.51	5.11	- 8.2	3655	533
6	NTBZ	7.74	10.58	-15.3	3522	392
7	DODE	0.98	1.06	7.9	0	- 20
8	NMPL	9.59	10.47	- 3.9	5121	789
9	DMAA	8.19	6.80	8.8	5744	1061
10	ACPH	5.38	5.18	2.3	1541	298
11	DEOX	5.03	4.33	9.3	4683	870
12	DMFM	11.53	9.46	8.2	7692	1380
13	FURF	13.53	11.94	4.8	6306	1112
6	NTBZ				4361	392*
14	TRCS				0	-537*
15	PTCT				0	131*
16	EICS@53.2°C				0	-545*
	@74.1°C				0	-633*
	@93.9°C				0	-733*
17	SQAL@53.2°C				0	61*
	@74.1°C				0	27*
	@93.9°C				0	- 8*

*Show Points

AAD = 9.4%

MAXIMUM % ERROR = 18.4%

TABLE No. 14A

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^∞ FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part 'd', AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.6$

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR FIG. No.	
No.	NAME	(GAMA)	(GAMAC)	(PD)	X	Y
1	BTLA	22.49	37.28	-16.3	8582	1089
2	HEXD	8.29	5.59	-18.6	5209	1103
3	DMSX	59.98	-	-	-	-
4	TMPH	20.81	-	-	-	-
5	CYCP	4.51	5.02	- 7.1	3655	533
6	NTBZ	7.74	10.38	-14.4	3522	392
7	DODE	0.98	1.017	3.2	0	- 20
8	NMPL	9.59	10.41	- 3.6	5121	789
9	DMAA	8.19	6.79	8.9	5744	1061
10	ACPH	5.38	5.01	4.3	1541	298
11	DEOX	5.03	4.29	9.9	4683	870
12	DMFM	11.53	9.58	7.6	7692	1380
13	FURF	13.53	11.97	4.7	6306	1112

AAD = 9%

MAXIMUM % ERROR = 18.6%

TABLE No. 15

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^∞ FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part'd', AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.5$$

SOLVENT No.	 NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	 Y
1	BTLA	21.77	56.47	-31.0	9099	898
2	HEXD	8.38	6.30	13.5	5139	1021
3	DMSX	62.77	32.73	15.7	10782	2192
4	TMPH	22.17	3.42	60.3	4080	1845
5	CYCP	4.32	6.14	-23.9	3735	384
6	NTBZ	7.50	15.12	-34.8	3994	206
7	DODE	0.95	0.95	3.5	0	- 20
8	NMPL	9.69	13.42	-14.3	6175	807
9	DMAA	7.83	6.74	7.3	5481	992
10	ACPH	5.01	7.92	-28.4	2047	35
11	DEOX	5.06	5.00	.76	4744	782
12	DMFM	11.26	12.22	- 3.4	7892	1248
13	FURF	13.27	14.65	- 3.8	6487	1002
9	DMAA				6803	1020*
10	ACPH				1830	155*
11	DEOX				4187	570*
12	DMFM				6340	1380*
14	TRCS				0	- 90*
15	PTCT				0	- 2*
16	EICS@53.2°C				0	-220*
	@74.1°C				0	-246*
	@93.9°C				0	-285*
17	SQAL@53.2°C				0	-270*
	@74.1°C				0	-295*
	@93.9°C				0	-325*

AAD = 18.2%

MAXIMUM % ERROR = 60.3%

*Show Points

TABLE No. 15A

CALCULATED AND EXPERIMENTAL VALUES OF γ_2^{∞} FOR n-Pentane SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part'd', AND USING SET II PROPERTIES, ALLOWING zero INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.5$$

SOLVENT No.	NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	Y
1	BTLA	21.77	55.95	-30.6	9099	898
2	HEXD	8.38	6.34	13.2	5139	1021
3	DMSX	62.77	32.21	16.1	10782	2192
4	TMPH	22.17	3.45	60.1	4080	1845
5	CYCP	4.32	6.21	-24.8	3735	384
6	NTBZ	7.50	15.28	-35.3	3994	206
7	DODE	0.95	0.98	3.0	0	- 20
8	NMPL	9.69	13.45	-14.4	6175	807
9	DMAA	7.83	6.77	7.1	5481	992
10	ACPH	5.01	8.07	-29.6	2047	35
11	DEOX	5.06	5.04	.26	4744	782
12	DMFM	11.26	12.16	- 3.2	7892	1248
13	FURF	13.27	14.66	- 3.8	6847	1002

AAD = 18.3%

MAXIMUM % ERROR = 60.1%

TABLE No. 16

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^{∞} FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part'd', AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{3(a)} = \lambda_3 - 0.9$$

SOLVENT No.	 NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	 Y
1	BTLA	22.49	57.28	-30.1	9161	875
2	HEXD	8.29	6.34	12.7	5175	991
3	DMSX	59.98	32.00	15.3	10855	2137
4	TMPH	20.81	3.41	59.6	4108	1793
5	CYCP	4.51	6.30	-22.2	3760	382
6	NTBZ	7.74	15.83	-34.9	4021	183
7	DODE	0.98+	.98+	1.0	0	- 10
8	NMPL	9.59	13.62	-15.5	6217	769
9	DMAA	8.19	6.76	9.1	5518	1000
10	ACPH	5.38	8.38	-26.3	2060	38
11	DEOX	5.03	5.02	. 27	4772	760
12	DMFM	11.53	12.06	- 1.8	7946	1242
13	FURF	13.53	14.80	- 3.4	6530	984
9	DMAA				6850	1182*
10	ACPH				1842	505*
11	DEOX				4216	900*
12	DMFM				6383	1485*
14	TRCS				0	-125*
15	PTCT				0	- 42*
16	EICS@53.2°C				0	-280*
	@74.1°C				0	-312*
	@93.6°C				0	-348*
17	SQAL@53.2°C				0	-350*
	@74.1°C				0	-400*
	@93.9°C				0	-480*

AAD = 17.8%

*Show points MAXIMUM % ERROR = 59.6%

TABLE No. 16A

CALCULATED AND EXPERIMENTAL VALUES OF γ_3^{∞} FOR ISOPENTANE SOLUTE IN VARIOUS SOLVENTS, BASED ON EQ. 8A AND part'd, AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.9$

SOLVENT No.	 NAME	EXPERIMENTAL (GAMA)	CALCULATED (GAMAC)	% DIFF. (PD)	FOR FIG. No. X	 Y
1	BTLA	22.49	56.82	-29.8	9161	875
2	HEXD	8.29	6.37	12.4	5175	991
3	DMSX	59.98	31.56	15.7	10855	2137
4	TMPH	20.81	3.44	59.3	4108	1793
5	CYCP	4.51	6.37	-22.8	3760	382
6	NTBZ	7.74	15.98	-35.4	4021	183
7	DODE	0.98	1.00	2.0	0	- 10
8	NMPL	9.59	13.64	-15.6	6217	769
9	DMAA	8.19	6.78	8.9	5518	1000
10	ACPH	5.38	8.52	-27.3	2060	38
11	DEOX	5.03	5.05	- .17	4772	760
12	DMFM	11.53	12.01	- 1.7	7946	1242
13	FURF	13.53	14.82	- 3.5	6530	984

AAD = 18%

MAXIMUM % ERROR = 59.3%

TABLE No. 17

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 44 AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR	FIG.No.
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	1.081	-11.7	-58	-161
2	HEXD	1.011	0.910	10.0	-35	- 39
3	DMSX	1.046	-	-	-	-
4	TMPH	1.066	-	-	-	--
5	CYCP	0.958	0.983	-27	-25	-129
6	NTBZ	0.969	1.091	-12.6	-24	-188
7	DODE	0.964	0.879	8.9	0	- 69
8	NMPL	1.010	1.029	- 1.8	-34	-117
9	DMAA	0.956	0.927	3.0	-39	- 84
10	ACPH	0.931	1.068	-14.7	-10	-208
11	DEOX	1.005	0.881	12.3	-31	- 24
12	DMFM	0.977	0.903	7.5	-51	- 45
13	FURF	0.981	1.001	- 2.7	-42	-118
6	NTBZ				-30	-182*
14	TRCS				0	109*
15	PTCT				0	- 38*
16	EICS @53.2°C				0	78*
	@74.1°C				0	92*
	@93.9°C				0	115*
17	SQAL@53.2°C				0	- 12*
	@74.1°C				0	- 3*
	@93.9°C				0	1*

*Show Points

AAD = 8.0%
MAXIMUM % ERROR = 14.7%

TABLE No. 18

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 45 AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR	FIG.No.
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	1.110	-14.6	-62	-157
2	HEXD	1.011	0.941	7.0	-35	- 39
3	DMSX	1.046	0.971	7.2	-73	- 18
4	TMPH	1.066	0.866	18.8	-28	43
5	CYCP	0.958	1.012	- 6.4	-25	-128
6	NTBZ	0.969	1.128	-16.4	-27	-185
7	DODE	0.964	0.875	9.3	0	- 40
8	NMPL	1.010	1.022	- 1.2	-42	- 88
9	DMAA	0.956	0.942	1.5	-37	- 74
10	ACPH	0.931	1.120	-20.4	-14	-212
11	DEOX	1.005	0.918	8.6	-32	- 29
12	DMFM	0.977	0.938	4.1	-53	- 49
13	FURF	0.981	1.031	- 5.2	-44	-112
9	DMAA				-46	- 65*
10	ACPH				-12	-213*
11	DEOX				-28	- 50*
12	DMFM				-43	- 60*
14	TRCS				0	83*
15	PTCT				0	65*
16	EICS@ 53.2°C				0	75*
	@74.1°C				0	83*
	@93.9°C				0	105*
17	SQAL@53.2°C				0	93*
	@74.1°C				0	107*
	@93.9°C				0	127*

AAD = 9.3%

MAXIMUM % ERROR = 20.4%

*Show Points

TABLE No. 19

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 46 AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT No.	NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG.No. X	Y
1	BTLA	0.968	0.988	- 2.1	-58	-161
2	HEXD	1.011	0.933	7.8	-35	- 39
3	DMSX	1.046	-	-	-	-
4	TMPH	1.066	-	-	-	-
5	CYCP	0.958	1.063	-11.0	-25	-129
6	NTBZ	0.969	1.185	-22.3	-24	-188
7	DODE	0.964	1.076	-11.5	0	- 69
8	NMPL	1.010	1.058	- 4.7	-34	-117
9	DMAA	0.956	0.934	2.4	-39	- 84
10	ACPH	0.931	1.240	-33.3	-10	-208
11	DEOX	1.055	0.919	8.5	-31	- 24
12	DMFM	0.977	0.851	12.8	-51	- 45
13	FURF	0.981	0.995	- 1.5	42	-118

AAD = 10.7%
MAXIMUM % ERROR = 33.3%

TABLE No. 20

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 47 AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR FIG.No.	
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	1.05	- 8.4	-62	-157
2	HEXD	1.011	0.978	3.3	-35	- 39
3	DMSX	1.046	0.882	15.7	-73	- 18
4	TMPH	1.066	0.923	13.4	-28	43
5	CYCP	0.958	1.095	-14.3	-25	- 12
6	NTBZ	0.969	1.205	-24.4	-27	-185
7	DODE	0.964	1.028	- 6.6	0	- 40
8	NMPL	1.010	1.037	- 2.6	-42	- 88
9	DMAA	0.956	0.972	- 1.6	-37	- 74
10	ACPH	0.931	1.254	-34.7	-14	-212
11	DEOX	1.005	0.963	4.1	-32	- 29
12	DMFM	0.977	0.913	6.6	-53	- 49
13	FURF	0.981	1.038	- 5.9	-44	-112

AAD = 10.9%
MAXIMUM % ERROR = 34.7%

TABLE No. 21

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 48 AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT, AND ADJUSTING PARAMETERS AS : $\lambda_{2(a)} = \lambda_2 - 0.2$; $\lambda_{3(a)} = \lambda_3 - 0.6$

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR FIG.No.	
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	0.972	-0.4	-57	75
2	HEXD	1.011	0.988	2.3	-35	560
3	DMSX	1.046	-	-	-	--
4	TMPH	1.066	-	-	-	-
5	CYCP	0.958	0.972	-1.5	-25	22
6	NTBZ	0.969	0.951	1.9	-24	42
7	DODE	0.964	0.973	-0.9	0	- 8
8	NMPL	1.010	0.968	4.2	-35	+72
9	DMAA	0.956	0.989	-3.4	-39	29
10	ACPH	0.931	0.948	-1.8	-10	0
11	DEOX	1.055	0.991	1.4	-31	50
12	DMFM	0.977	1.002	-2.6	-52	53
13	FURF	0.981	0.977	.4	-42	58
6	NTBZ				-30	-20*
14	TRCS				0	250*
15	PTCT				0	148*
16	EICS @53.2°C				0	130*
	@74.1°C				0	225*
	@93.9°C				0	290*
17	SQAL@53.2°C				0	45*
	@74.1°C				0	25*
	@93.9°C				0	10*

*Show Points

AAD = 1.9%
MAXIMUM % ERROR = 4.2%

TABLE No. 21A

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 49 ,AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.2$$

$$\lambda_{3(a)} = \lambda_3 - 0.6$$

SOLVENT No. NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG No. X	 Y
1 BTLA	0.968	0.969	-0.2	-57	75
2 HEXD	1.011	0.989	2.2	-35	60
3 DMSX	1.046	-	-	-	-
4 TMPH	1.066	-	-	-	-
5 CYCP	0.958	0.974	-1.7	-25	22
6 NTBZ	0.969	0.952	1.7	-24	42
7 DODE	0.964	0.977	-1.3	0	-8
8 NMPL	1.010	0.968	4.2	-35	72
9 DMAA	0.956	0.989	-3.4	-39	29
10 ACPH	0.931	0.951	-2.2	-10	0
11 DEOX	1.005	0.992	1.3	-31	50
12 DMFM	0.977	1.000	-2.5	-52	53
13 FURF	0.981	0.977	0.4	-42	58

AAD = 1.9%

MAXIMUM % ERROR = 4.2%

TABLE No. 22

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 50 ,AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.5$$
$$\lambda_{3(a)} = \lambda_3 - 0.9$$

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR	FIG No.
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	0.987	-1.9	-61	84
2	HEXD	1.011	0.994	1.7	-35	64
3	DMSX	1.046	1.023	2.2	-73	127
4	TMPH	1.066	1.002	5.9	-28	80
5	CYCP	0.958	0.975	-1.8	-25	27
6	NTBZ	0.969	0.955	1.5	-27	50
7	DODE	0.964	0.975	-1.2	0	- 9
8	NMPL	1.010	0.986	2.5	-42	80
9	DMAA	0.956	0.997	-4.3	-37	30
10	ACPH	0.931	0.946	-1.6	-14	10
11	DEOX	1.055	0.995	0.9	-32	54
12	DMFM	0.977	1.013	-3.6	-53	60
13	FURF	0.981	0.987	-0.7	-44	63
9	DMAA				-46	102*
10	ACPH				-12	2*
11	DEOX				-28	85*
12	DMCM				-43	195*
14	TRCS				0	243*
15	PTCT				0	200*
16	EICS@53.2°C				0	175*
	@74.1°C				0	189*
	@93.9°C				0	245*
17	SQAL@53.2°C				0	210*
	@74.1°C				0	240*
	@93.9°C				0	275*

AAD = 2.3%

MAXIMUM % ERROR = 5.9%

*Show Points

TABLE No. 22A

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 51, AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{2(a)} = \lambda_2 - 0.5$$
$$\lambda_{3(a)} = \lambda_3 - 0.9$$

SOLVENT No.	NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG No. X	Y
1	BTLA	0.968	0.989	-1.8	-61	84
2	HEXD	1.011	0.995	1.6	-35	64
3	DMSX	1.046	1.021	2.4	-73	127
4	TMPH	1.066	1.004	5.8	-28	80
5	CYCP	0.958	0.976	-1.9	-25	27
6	NTBZ	0.969	0.956	1.3	-27	50
7	DODE	0.964	0.978	-1.4	0	- 9
8	NMPL	1.010	0.986	2.4	-42	80
9	DMAA	0.956	0.998	-4.4	-37	30
10	ACPH	0.931	0.948	-1.8	-14	10
11	DEOX	1.055	0.996	0.8	-32	54
12	DMFM	0.977	1.013	-3.6	-53	60
13	FURF	0.981	0.987	-0.7	-44	63

AAD = 2.3%
MAXIMUM % ERROR = 5.8%

TABLE No. 23

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 52, AND USING SET I PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{3(a)} = \lambda_3 - 0.4$$

SOLVENT No.	NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG No. X	Y
1	BTLA	0.968	0.972	-0.4	-58	71
2	HEXD	1.011	0.988	2.3	-35	57
3	DMSX	1.046	-	-	-	-
4	TMPH	1.066	-	-	-	-
5	CYCP	0.958	0.972	-1.5	-25	19
6	NTBZ	0.969	0.951	1.8	-24	39
7	DODE	0.964	0.972	-0.8	0	-11
8	NMPL	1.010	0.968	4.2	-35	69
9	DMAA	0.956	0.988	-3.4	-39	27
10	ACPH	0.931	0.948	-1.9	-10	-4
11	DEOX	1.055	0.990	1.5	-32	47
12	DMFM	0.977	1.002	-2.6	-52	50
13	FURF	0.981	0.977	0.4	-44	55
6	NTBZ				-30	44*
14	TRCS				0	305*
15	PTCT				0	-91*
16	EICS@53.2°C				0	278*
	@74.1°C				0	308*
	@93.9°C				0	348*
17	SQAL@53.2°C				0	-3*
	@74.1°C				0	15*
	@93.9°C				0	32*

*Show Points

AAD = 1.9%

MAXIMUM % ERROR = 4.2%

TABLE No. 23A

CALCULATED AND EXPFRIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ.53 ,AND USING SET I PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{3(a)} = \lambda_3 - 0.4$$

SOLVENT No. NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG No. X	 Y
1 BTLA	0.968	0.968	0.0	-58	71
2 HEXD	1.011	0.989	2.2	-35	57
3 DMSX	1.046	-	-	-	-
4 TMPH	1.066	-	-	-	-
5 CYCP	0.958	0.976	-1.8	-25	19
6 NTBZ	0.969	0.955	1.4	-24	39
7 DODE	0.964	0.981	-1.8	0	-11
8 NMPL	1.010	0.969	4.1	-35	69
9 DMAA	0.956	0.989	-3.4	-39	27
10 ACPH	0.931	0.955	-2.6	-10	-4
11 DEOX	1.055	0.992	1.3	-32	47
12 DMFM	0.977	1.000	-2.3	-52	50
13 FURF	0.981	0.976	0.4	-44	55

AAD = 1.94%

MAXIMUM % ERROR = 4.1%

TABLE No. 24

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ.54 ,AND USING SET II PROPERTIES, ALLOWING FOR AN INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{3(a)} = \lambda_3 - 0.4$$

SOLVENT		EXPERIMENTAL	CALCULATED	% DIFF.	FOR FIG No.	
No.	NAME	(SOBS)	(SCAL)	(PD)	X	Y
1	BTLA	0.968	0.988	-2.1	-62	75
2	HEXD	1.011	0.993	1.8	-35	57
3	DMSX	1.046	1.023	2.3	-73	120
4	TMPH	1.066	1.002	6.1	-27	74
5	CYCP	0.958	0.975	-1.8	-25	19
6	NTBZ	0.969	0.956	1.3	-27	42
7	DODE	0.964	0.975	-1.0	0	-15
8	NMPL	1.010	0.986	2.4	-42	73
9	DMAA	0.956	0.997	-4.3	-37	23
10	ACPH	0.931	9.947	-1.8	-14	2
11	DEOX	1.055	0.994	1.0	-32	48
12	DMFM	0.977	1.013	-3.6	-53	52
13	FURF	0.981	0.988	-0.8	-44	55
9	DMAA				-46	132*
10	ACPH				-12	15*
11	DEOX				-28	150*
12	DMFM				-43	170*
14	TRCS				0	200*
15	PTCT				0	250*
16	EICS@53.2°C				0	275*
	@74.1°C				0	290*
	@93.9°C				0	340*
17	SQAL@53.2°C				0	280*
	@74.1°C				0	320*
	@93.9°C				0	350*

AAD = 2.3%

MAXIMUM % ERROR = 6.1%

*Show Points

TABLE No. 24A

CALCULATED AND EXPERIMENTAL VALUES OF S_{23} FOR C_5 HYDROCARBONS (normal and iso), BASED ON EQ. 55 ,AND USING SET II PROPERTIES, ALLOWING ZERO INTERCEPT, AND WITH THE ADJUSTMENTS OF SOLUBILITY PARAMETERS AS :

$$\lambda_{3(a)} = \lambda_3 - 0.4$$

SOLVENT No. NAME	EXPERIMENTAL (SOBS)	CALCULATED (SCAL)	% DIFF. (PD)	FOR FIG No. X	 Y
1 BTLA	0.968	0.983	-1.5	-62	75
2 HEXD	1.011	0.997	1.4	-35	57
3 DMSX	1.046	1.014	3.1	-73	120
4 TMPH	1.066	1.007	5.5	-27	74
5 CYCP	0.958	0.981	-2.4	-25	19
6 NTBZ	0.969	0.962	0.7	-27	42
7 DODE	0.964	0.988	-2.4	0	-15
8 NMPL	1.010	0.987	2.3	-42	73
9 DMAA	0.956	1.000	-4.6	-37	23
10 ACPH	0.931	0.956	-2.8	-14	2
11 DEOX	1.055	1.000	0.6	-32	48
12 DMFM	0.977	1.010	-3.4	-53	52
13 FURF	0.981	0.988	-0.8	-44	55

AAD = 2.4%

MAXIMUM % ERROR = 5.5%

TABLE No. 25

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET I PROPERTIES

SOLVENT No. NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	Y'	Y'+ P + D + F = RT ln S_{23}
1 BTLA	-53	196	-46	2.4	-161	-20
2 HEXD	-35	81	-28	.04	- 38	8
3 DMSX	--	--	--	--	--	--
4 TMPH	--	--	--	--	--	--
5 CYCP	-25	125	-19	1.4	-129	-28
6 NTBZ	-23	125	-19	0.7	-187	-18
7 DODE	0	48	0	-2.6	-69	-24
8 NMPL	-35	157	-28	1.0	-117	6
9 DMAA	-39	93	-30	1.2	-84	-29
10 ACPH	-11	173	-8	0.04	-208	-46
11 DEOX	-31	60	-25	-0.6	-25	4
12 DMFM	-52	80	-41	2.3	-46	-16
13 FURF	-43	146	-33	1.8	-118	-13

TABLE No. 26

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET II PROPERTIES

SOLVENT No. NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	Y'	Y'+ P + D + F RT ln S_{23}
1 BTLA	-62	196	-49	2.3	-157	-21
2 HEXD	-34	81	-28	0.03	- 39	8
3 DMSX	-73	117	-58	2.8	-18	29
4 TMPH	-28	25	-22	0.10	43	40
5 CYCP	-25	125	-20	1.4	-128	-26
6 NTBZ	-27	191	-22	0.7	-184	-20
7 DODE	0	19	0	-2.1	- 40	-23
8 NMPL	-42	133	-33	1.0	- 88	-48
9 DMAA	-37	82	-30	1.2	- 74	-27
10 ACPH	-14	181	-11	0.03	-212	-45
11 DEOX	-32	64	-26	-0.6	- 29	3
12 DMFM	-53	85	-43	2.3	- 49	-15
13 FURF	-44	141	-35	1.8	-112	-13

TABLE No. 27

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET I PROPERTIES, AND AFTER ADJUSTING THE VALUES OF SOLUTE's SOLUBILITY PARAMETER AS : $\lambda_{2(a)} = \lambda_2 - 0.2$; $\lambda_{3(a)} = \lambda_3 - 0.6$

SOLVENT No. NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	$Y' + P + D + F = R T \ln S_{23}$	
					Y'	
1 BTLA	-57	-39	-46	2.3	75	-19
2 HEXD	-35	-18	-28	0.03	60	7
3 DMSX	--	--	--	--	--	--
4 TMPH	--	--	--	--	--	--
5 CYCP	-25	-26	-20	1.4	22	-27
6 NTBZ	-24	-39	-19	0.6	42	-20
7 DODE	0	-12	0	-2.1	-8	-20
8 NMPI	-34	-32	-27	1.0	72	7
9 DMAA	-39	-20	-31	1.2	29	-30
10 ACPH	-10	-35	- 8	0.03	0	-45
11 DEOX	-32	-14	-25	-0.6	50	4
12 DMFM	-52	-17	-41	2.2	53	-14
13 FURF	-42	-30	-34	1.8	58	-14

$\lambda_{2(a)}$ = Adjusted value

TABLE No. 28

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET II PROPERTIES, AND AFTER ADJUSTING THE VALUES OF SOLUTE's SOLUBILITY PARAMETER AS :

$$\lambda_{2(a)} = \lambda_2 - 0.5 \quad ; \quad \lambda_{3(a)} = \lambda_3 - 0.9$$

SOLVENT No. NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	Y' + P + D + F $Y' = R T \ln S_{23}$	
1 BTLA	-62	-45	-49	2.3	84	-21
2 HEXD	-34	-22	-28	0.03	64	8
3 DMSX	-75	-28	-58	2.8	128	29
4 TMPH	-28	-12	-22	0.10	81	41
5 CYCP	-25	-30	-20	1.4	27	-26
6 NTBZ	-27	-44	-22	0.6	50	-21
7 DODE	0	-12	0	-2.1	0	-21
8 NMPL	-42	-33	-33	1.0	80	6
9 DMAA	-37	-23	-30	1.2	30	-30
10 ACPH	-14	-42	-11	0.03	10	-46
11 DEOX	-32	-19	-26	-0.6	55	4
12 DMFM	-53	-24	-43	2.3	60	-17
13 FURF	-44	-34	-35	1.8	63	-16

$\lambda_{2(a)}$ = Adjusted value

TABLE No. 29

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET I PROPERTIES, AND AFTER ADJUSTING THE VALUES OF SOLUTE's SOLUBILITY PARAMETER AS : $\lambda_{3(a)} = \lambda_3 - 0.4$

SOLVENT No.	NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	Y' = R T ln S_{23}	Y' + P + D + F
1	BTLA	-57	-36	-46	2	71	-22
2	HEXD	-35	-15	-28	0.03	57	7
3	DMSX	--	--	--	--	--	--
4	TMPH	--	--	--	--	--	--
5	CYCP	-25	-23	-20	1.4	19	-39
6	NTBZ	-24	-35	-19	0.7	39	-20
7	DODE	0	-10	0	-2.2	-11	-21
8	NMPL	-34	-29	-28	1.0	69	6
9	DMAA	-39	-17	-31	1.2	27	-29
10	ACPH	-10	-32	- 8	0.03	-4	-46
11	DEOX	-32	-12	-25	-0.6	47	3
12	DMFM	-52	-15	-41	2.3	50	-15
13	FURF	-42	-30	-34	1.8	55	-12

$\lambda_{3(a)}$ = Adjusted value

TABLE No. 30

CONTRIBUTING FORCES TO THE SELECTIVITY FUNCTIONS

FOR C_5 HYDROCARBONS (normal and iso) IN VARIOUS SOLVENTS USING SET II PROPERTIES, AND AFTER ADJUSTING THE VALUES OF SOLUTE's SOLUBILITY PARAMETER AS :

$$\lambda_{3(a)} = \lambda_3 - 0.4$$

SOLVENT No.NAME	POLAR	DISPERSION	INDUCTION	ENTROPY	Y'	Y' + P + D + F = R T ln S_{23}
1 BTLA	-62	-36	-49	2.3	75	-21
2HEXD	-35	-15	-28	0.03	57	7
3 DMSX	-73	-21	-58	2.8	120	29
4 TMPH	-28	- 6	-22	0.1	74	40
5 CYCP	-25	-23	-20	1.4	19	-27
6 NTBZ	-27	-35	-22	0.6	42	-20
7 DODE	0	- 5	0	-2.1	-15	-20
8 NMPL	-42	-25	-34	1.0	73	7
9 DMAA	-37	-15	-30	1.2	23	-29
10 ACPH	-14	-33	-11	0.03	2	-45
11 DEOX	-32	-12	-26	0.6	48	4
12 DMFM	-53	-16	-43	2.3	52	-15
13 FURF	-44	-26	-35	1.8	55	-13

$\lambda_{3(a)}$ = Adjusted value

TABLE NO. 31

$Q = RT(\ln S_{OBS} - \ln S_{CAL})$ vs K_x

Solvent No.	Name	Lewis Relative Acidity Scale K_x (Squalene/ Squalene)	S_{OBS} or S_{EXPT}	$Q(ccAtm/gmol) = RT(\ln S_{OBS} - \ln S_{CAL})$ Using S_{CAL} from					
				Table 19 Set I	Table 21A Set I After Adj BOTH λ	Table 23A Set I After Adj ONE λ	Table 20 Set II	Table 22A Set II Adj Both λ	Table 24A Set II Adj. ONE λ
1	BTLA		0.968	-71.4	-2	-2	-84	-15	-15
2	HEXD		1.011	66	15	15	46	11	11
3	DMSX	1.0	1.046	-	-	-	47	14	14
4	TMPH	1.1	1.066	-	-	-	60	40	40
5	CYCP	0.45	0.958	-15	-8	-8	-46	-8	-8
6	NTBZ	0.55	0.969	-78	12	12	-97	10	10
7	DODE		0.964	59	-2	-2	62	-15	-15
8	NMPL		1.010	- 8	27	27	-9	15	15
9	DMAA		0.956	20	-21	-21	10	-27	-27
10	ACPH		0.931	-91	-15	-15	-116	-15	-15
11	DEOX	0.27	1.055	83	40	40	57	38	38
12	DMFM		0.977	51	-15	-15	-26	-21	-21
13	FURF	0.71	0.981	-15	- 3	- 3	-34	- 2	- 2
				Fig. 18	Fig. 19		Fig. 20	Fig. 21	

TABLE NO. 32

Summary of Various Correlations for Induction Energy Term ψ and their Reported Reliability

Correlations	Average %Error in Calculating ($\ln\gamma^{\infty}$)	Maximum % Error
I For Saturated Hydrocarbons		
W-P Model		
$\psi_{12} = 0.396\ \tau_1{}^2$	10	-
H-W Model		
$\psi_{12} = 0.399(\tau_1 - \tau_2)^2$ with $\tau_2 = 0$	5.8	-
This work^{+}		
(1) $\psi_{12} = 0.402(\tau_1 - \tau_2)^2$ For n-Paraffins, $\tau_2 = 0$	16	57
(2) $\psi_{13} = 0.393(\tau_1 - \tau_3)^2$	14	54
II For Unsaturated Hydrocarbons		
W-P Model: $\psi_{14} = 0.415(\tau_1)^2$	-	-
H-W Model: $\psi_{14} = 0.388(\tau_1 - \tau_4)^2$	8.5	
This work : $\psi_{14} = 0.428(\tau_1 - \tau_4)^2$	-	-

Notes:

+ Using Set II properties and allowing for NO intercepts on X-Y plots
1 Solvent Component
2 n-Paraffins Solute Component
3 Iso-paraffin Solute Component
4 Polar(unsaturated) Solute Component

TABLE NO. 33

Comparison of This Work with W-P[3] and H-V[7]

Solvent No.	Solvent Name	γ_2^∞ @ 45°c (n-C_5)					γ_3^∞ @ 45°c (Iso-C_5)					$S_{23} = \gamma_2^\infty / \gamma_3^\infty$ @ 45°c				
			This Work					This Work					This Work			
		Experimental	With Adj	Without Adj	W-P[3]	H-V[7]	Experimental	With Adj	Without Adj	W-P[3]	H-V[7]	Experimental	With Adj	Without Adj	W-P[3]	H-V[7]
1	BTLA	21.77	55.95	52.96	85.3 (46)	80.7 (45)	22.49	56.82	50.50	86 (50)	82 (48)	.968	.984 [1.65]	1.05 [8.5]	.992 [1]	.984 [0]
2	HEXD	8.38	6.34	6.37	6.2 (14)	6.2 (14)	8.49	6.37	6.52	6.35 (15)	6.35 (15)	1.01	.995 [1.58]	.977 [3.4]	.098 [3]	.098 [3]
3.	DMSX	62.77	32.21	40.05	3.9 (12)	38.5 (12)	59.98	31.56	45.39	41 (12)	41 (12)	1.05	1.02 [2.48]	.882 [15.6]	.94 [10.1]	.94 [10.1]
4	TMPH	22.17	3.45	3.73	4.2 (53)	4.0 (51)	20.81	3.44	4.04	4.3 (54)	4.1 (56)	1.07	1.00 [6.2]	.922 [13.5]	.98 [8]	.98 [8]
5	CYCP	4.32	6.21	5.24	5.6 (18)	5.5 (17)	4.51	6.37	4.79	5.1 (15)	5.1 (16)	.958	.975 [1.78]	1.094 [14.2]	1.10 [14.8]	1.08 [13]
6	NTBZ	7.50	15.28	11.19	12.4 (24)	12.6 (25)	7.74	15.98	9.29	11.1 (23)	11.0 (24)	.969	.956 [1.34]	1.205 [24.4]	1.12 [16]	1.15 [16]
7	DODE	0.95	0.98	0.86	0.92 [3]	0.98 [3]	0.98	1.00	0.85	0.92 [6]	0.92 [6]	.964	.098 [1.66]	1.012 [5.0]	1.00 [3.8]	1.00 [3.8]
8	NMPL	9.69	13.45	12.5	13.3 (14)	13.2 (14)	9.59	13.64	12.1	12.7 (14)	12.7 (14)	1.01	.986 [2.4]	1.037 [2.7]	1.05 [4]	1.04 [3]
9	DMAA	7.83	6.77	6.92	6.86 (20)	6.82 (20)	8.19	6.78	7.1	7.0 (22)	6.95 (22)	.956	1.00 [4.6]	0.972 [1.7]	0.98 [2.5]	0.98 [2.5]

TABLE NO. 33 - cont'd

Solvent No.	Name	γ_2^∞ @ 45°c (n-C$_5$)					γ_3^∞ @ 45°c (Isopentane)					$S_{23}=\gamma_2^\infty/\gamma_3^\infty$ @ 45°c				
		Experimental	This Work With Adj.	This Work Without Adj.	W-P[3]	H-V[7]	Experimental	This Work With Adj.	This Work Without Adj.	W-P[3]	H-V[7]	Experimental	This Work With Adj.	This Work Without Adj.	W-P[3]	H-V[7]
10	ACPH	5.01	8.07	5.47	6.3 (11)	6.2 (11)	5.38	8.52	4.36	5.73 (11)	5.64 (11)	0.931	.947 [1.72]	1.255 [34.8]	1.10 [18.2]	1.10 [18.2]
11	DEOX	5.06	5.04	5.17	5.3 (3)	5.2 (3)	5.03	5.05	5.34	5.55 (4)	5.60 (4)	1.006	1.000 [1]	0.963 [4.2]	0.95 [5.6]	0.94 [6]
12	DMFM	11.26	12.16	13.97	14.2 (9)	14.2 (9)	11.53	12.01	15.31	15.45 (10)	15.40 (10)	0.976	1.010 [3.57]	0.913 [6.5]	0.92 [6]	0.92 [6]
13	FURF	13.27	14.66	13.77	13.9 (3)	13.8 (3)	13.53	14.82	13.24	13.75 (3)	13.65 (3)	0.981	0.988 [1]	1.038 [5.8]	1.01 [3]	1.01 [3]
20$^{\pm}$		15.42[11]	8.00	12.3	14.0	13.0	-	8.51	13.4	13.8	13.8	-	0.94	.92	1.01	.94
21^{+}		26.94[11]	20.00	23.5	25.4	24.6	-	17.9	20.4	21.2	21.2	-	1.12	1.15	1.20	1.16
22^{+}		4.41[11]	3.00	3.3	3.7	3.5	-	3.12	3.06	4.2	4.2	-	0.96	0.98	.89	.84
AAD%		-	18.3	14.3	18	18		18	13.4	18	18		2.4	10.8	7.4	6.7
Max.% Error			60	57	53	51		60	54	54	56		4.6	35	18	18
		(Octane)@90°C*					(Isooctane)@90°C*					Selectivity S_{23} = @90°C				
6	NTBZ	3.95[33]	7.2 (43)	8.5 (55)	8.4 (55)	8.4 (55)	5.95	10.4 (31)	13.1 (45)	12.5 (42)	12.5 (42)	1.06	0.69 35	0.65 39	0.67 37	0.67 37
11	DEOX	4.41[33]	8.2 (42)	6.4 (26)	7.4 (35)	7.4 (35)	3.8[33]	11.2 (82)	11.4 (83)	12.0 (86)	12.0 (86)	1.16	0.72 38	0.56 52	0.62 47	0.62 47

[ ] - %Difference in actual values,
( ) - % Difference in log quantities.,
\+ - Solvents NOT included in developing our correlations.
* - Solutes NOT included in developing our correlations.

GENERAL NOTES FOR FIG. 2 THROUGH 21

Note 1: Subscripts

2 - n-Pentane

3 - isopentane

4 - 1-Pentene

(a) - Adjusted value

Note 2: ■ - Indicate "show" points; not included in the regression analysis of the data

Note 3: Set I and Set II - as described on page 26.

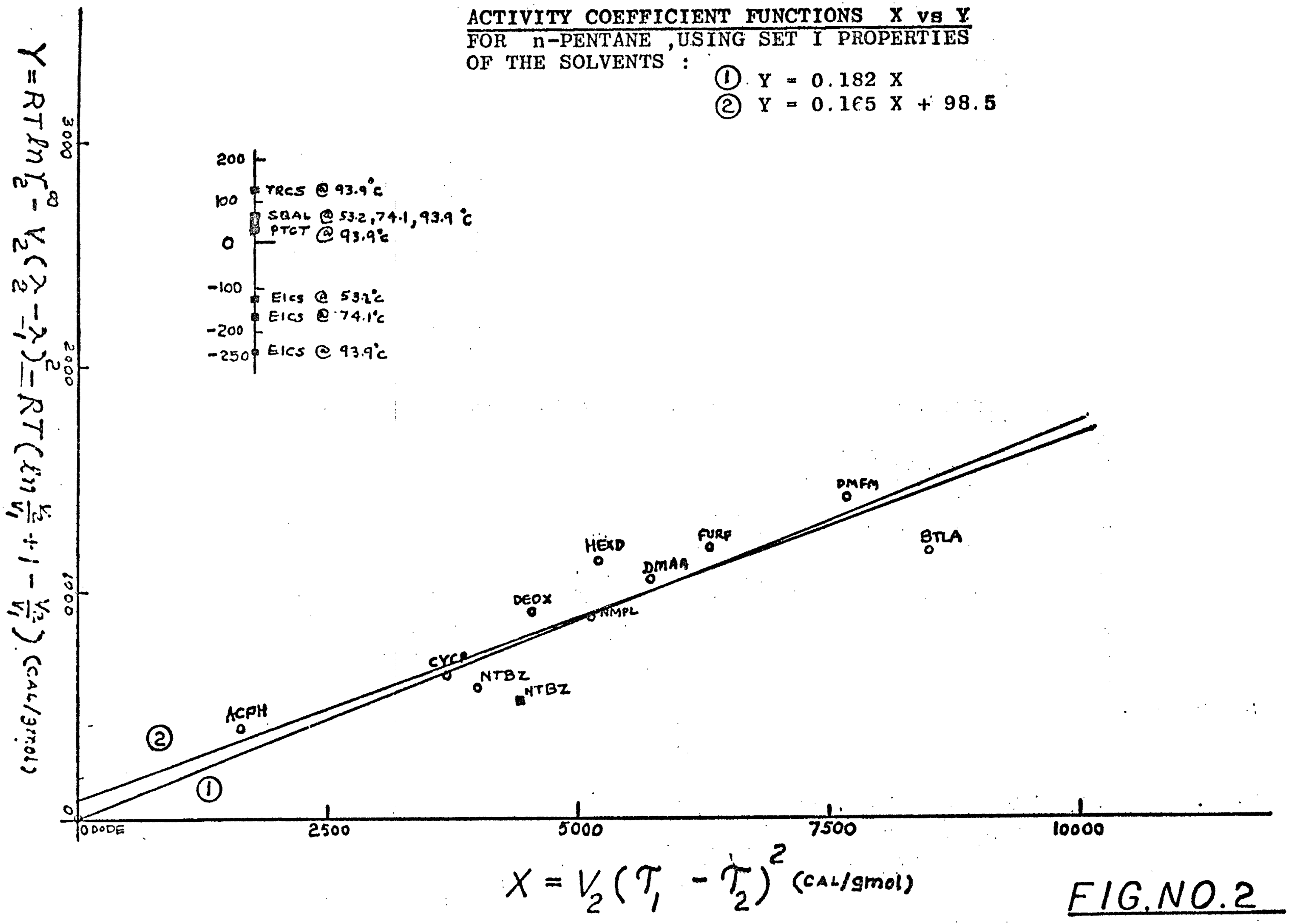
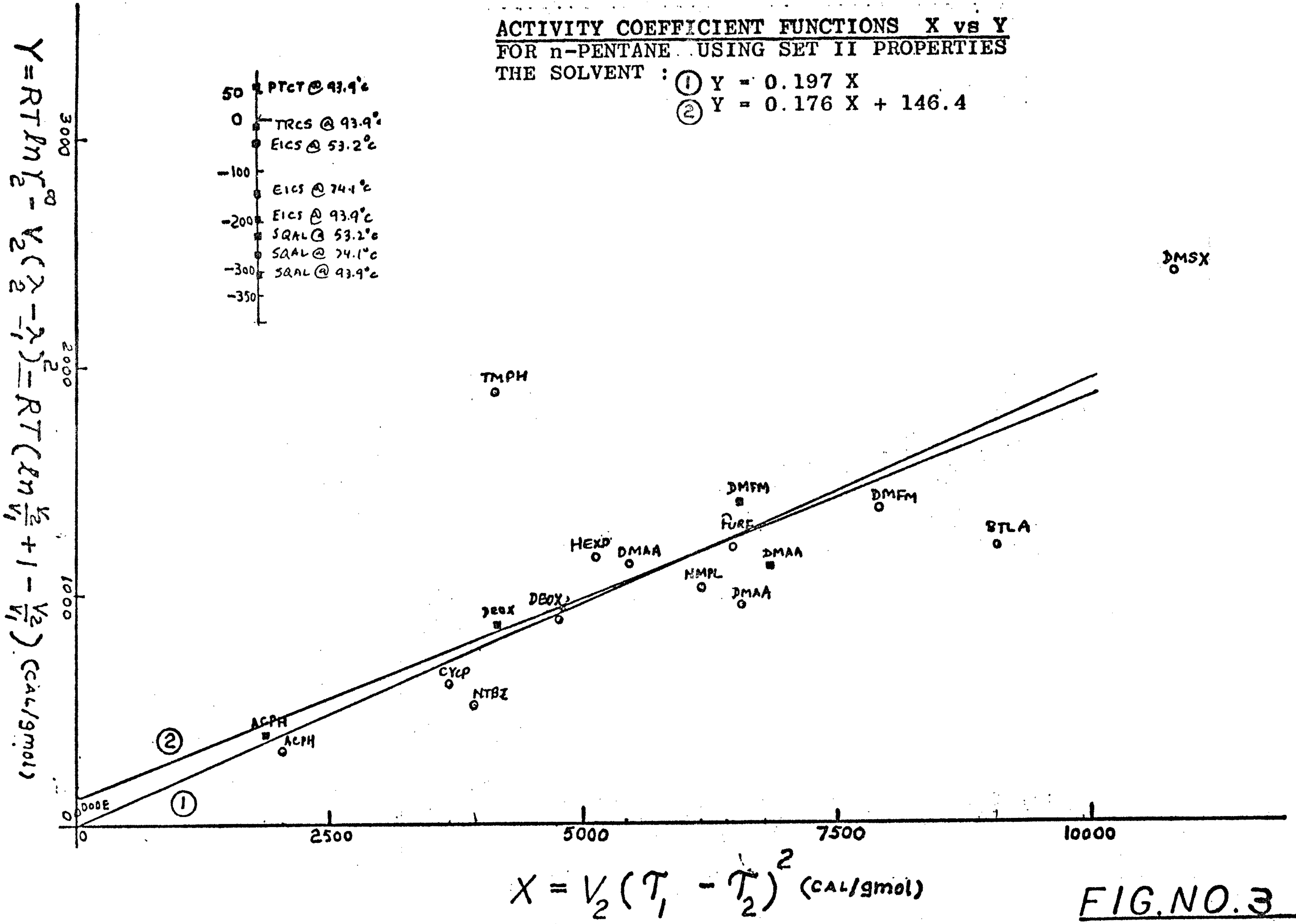
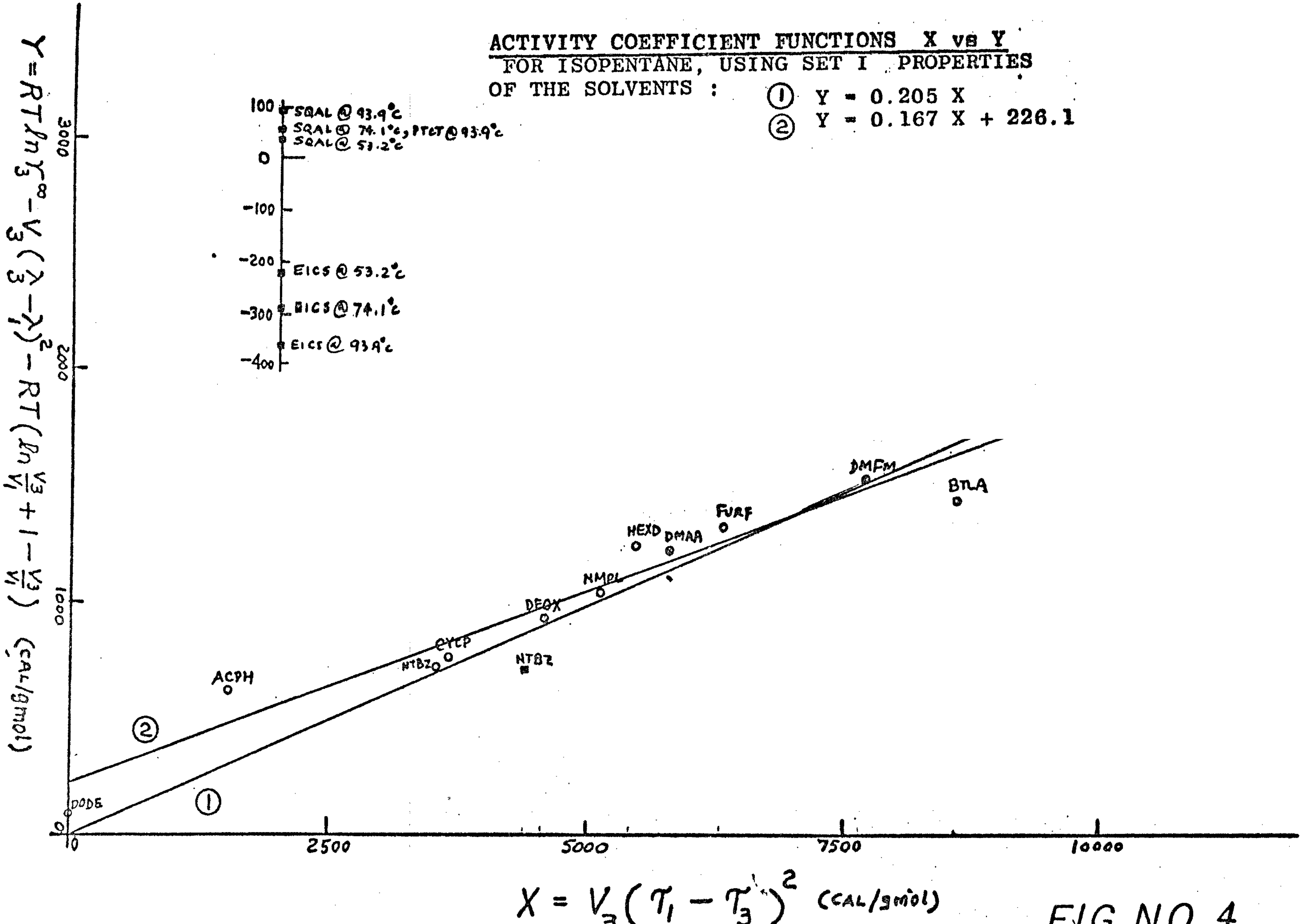

ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR n-PENTANE ,USING SET I PROPERTIES
OF THE SOLVENTS :
① Y = 0.182 X
② Y = 0.165 X + 98.5
$Y = RT \ln \gamma_2^{\infty} - V_2(\lambda_2 - \lambda_1)^2 - RT\left(\ln \frac{V_2}{V_1} + 1 - \frac{V_2}{V_1}\right)$ (CAL/gmol)
3000
2000
1000
0
0 DODE
2500
5000
7500
10000
$X = V_2(\tau_1 - \tau_2)^2$ (CAL/gmol)
200
100
0
-100
-200
-250
TRCS @ 93.9°c
SQAL @ 53.2, 74.1, 93.9 °c
PTCT @ 93.9°c
EICS @ 53.2°c
EICS @ 74.1°c
EICS @ 93.9°c
ACPH
CYCP
NTBZ
NTBZ
DEOX
NMPL
HEXD
DMAA
FURF
DMFM
BTLA
②
①

FIG. NO. 2



ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR n-PENTANE USING SET II PROPERTIES
THE SOLVENT : ① $Y = 0.197\,X$
② $Y = 0.176\,X + 146.4$

FIG.NO.3



ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR ISOPENTANE, USING SET I PROPERTIES
OF THE SOLVENTS :

① $Y = 0.205\,X$
② $Y = 0.167\,X + 226.1$

FIG. NO. 4

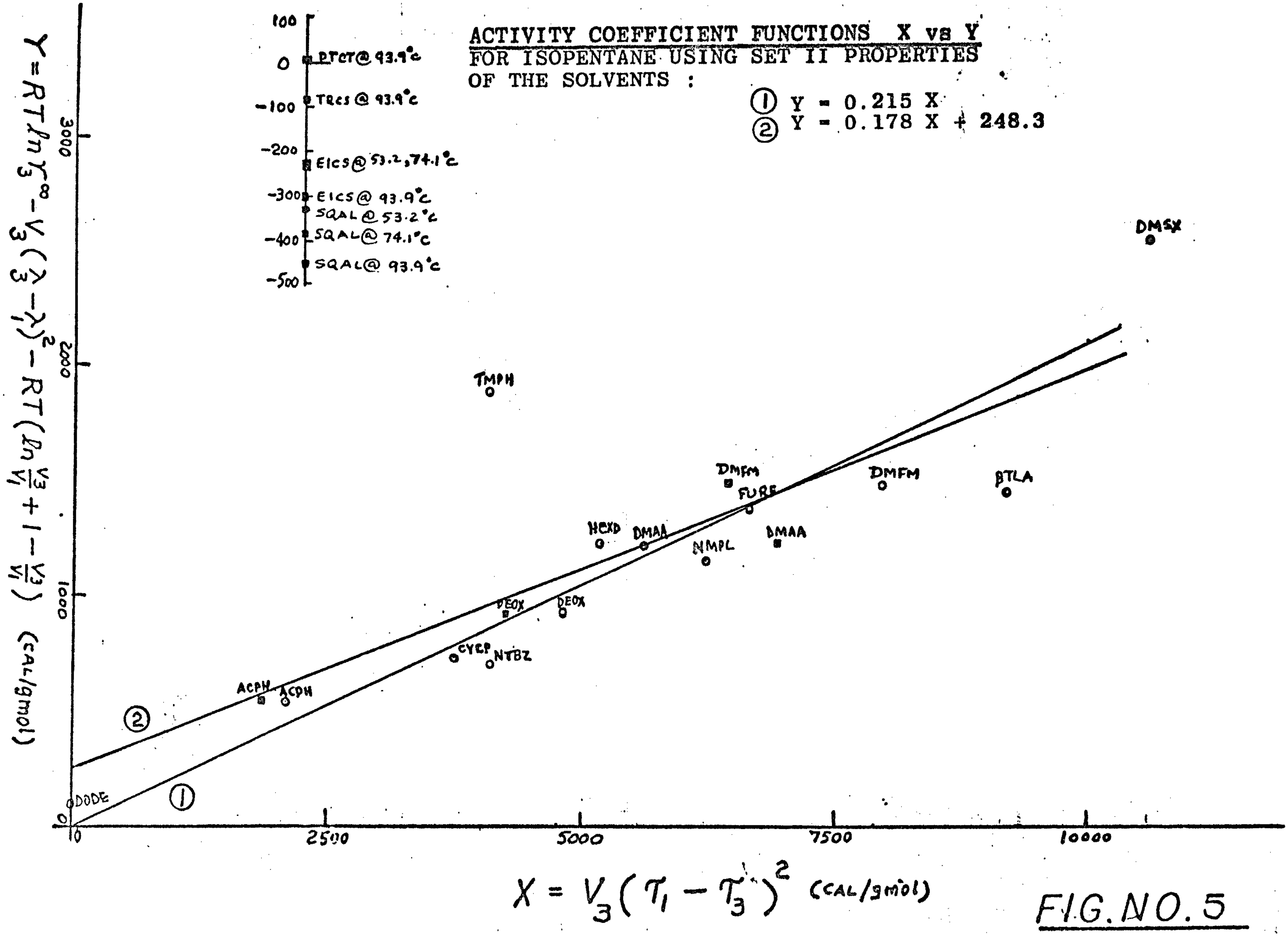
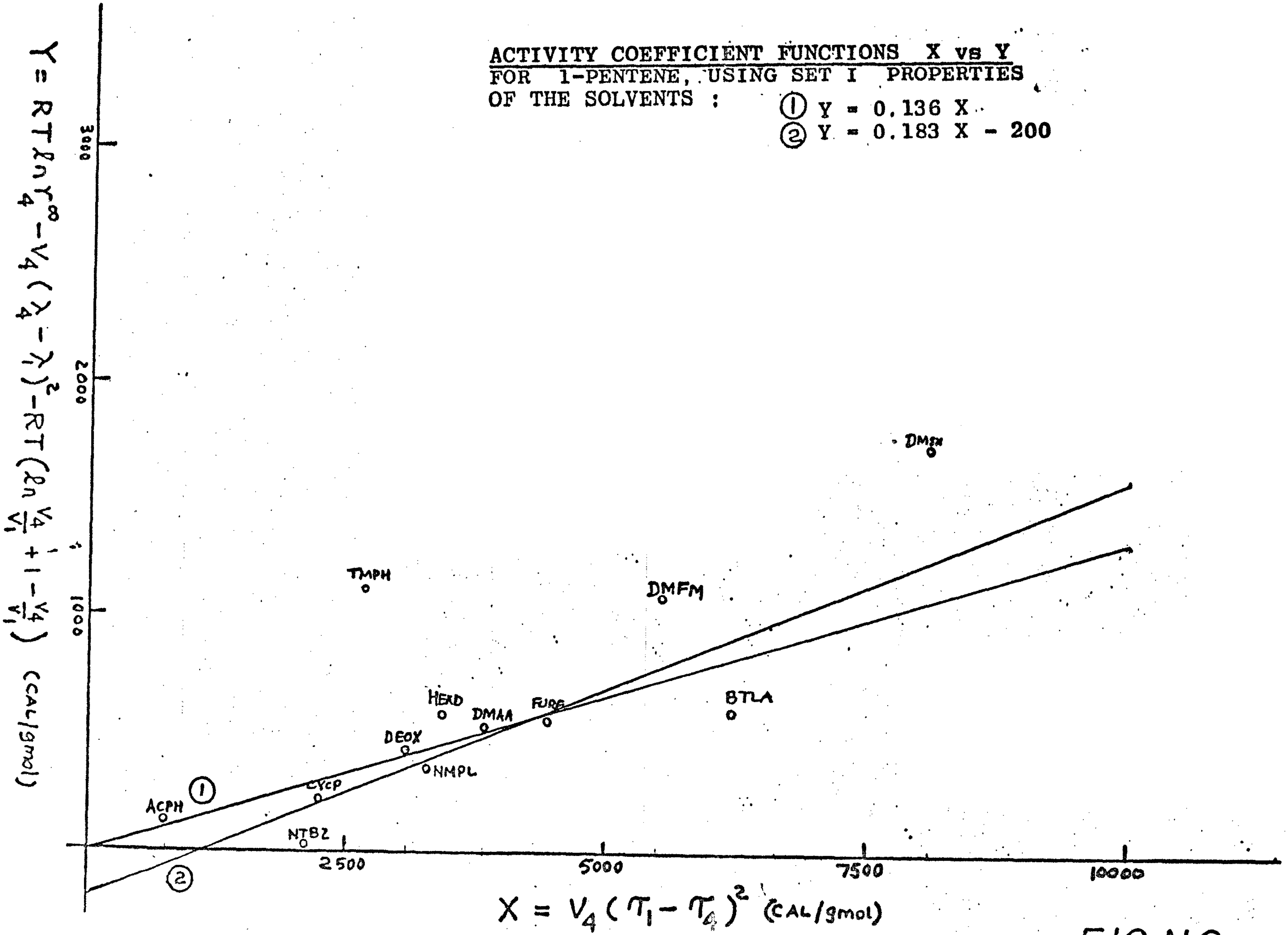
ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR ISOPENTANE USING SET II PROPERTIES
OF THE SOLVENTS :
① Y = 0.215 X
② Y = 0.178 X + 248.3
Y = RT ln γ3∞ − V3 (λ3 − λ1)² − RT (ln V3/V1 + 1 − V3/V1) (CAL/gmol)
X = V3 (τ1 − τ3)² (CAL/gmol)
0
1000
2000
3000
0
2500
5000
7500
10000
100
0
−100
−200
−300
−400
−500
PTCT@ 93.9°c
TRCS @ 93.9°c
EICS@ 53.2, 74.1°c
EICS@ 93.9°c
SQAL@ 53.2°c
SQAL@ 74.1°c
SQAL@ 93.9°c
DMSX
TMPH
DMFM
FURF
DMFM
BTLA
HEXD
DMAA
NMPL
DMAA
DEOX
DEOX
CYCP
NTBZ
ACPH
ACPH
DODE
②
①

FIG. NO. 5

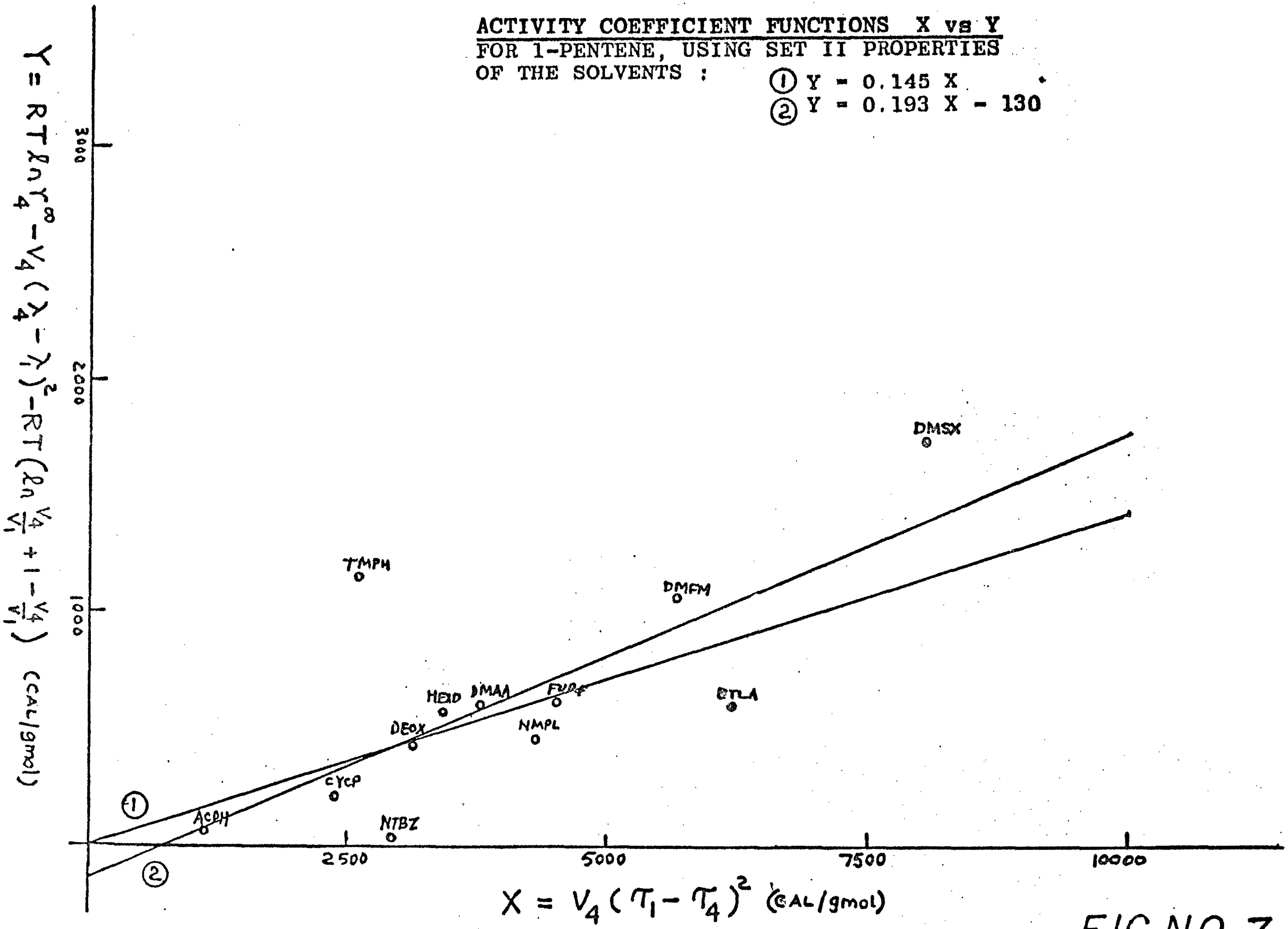


ACTIVITY COEFFICIENT FUNCTIONS X vs Y FOR 1-PENTENE, USING SET I PROPERTIES OF THE SOLVENTS :

① $Y = 0.136\ X$

② $Y = 0.183\ X - 200$

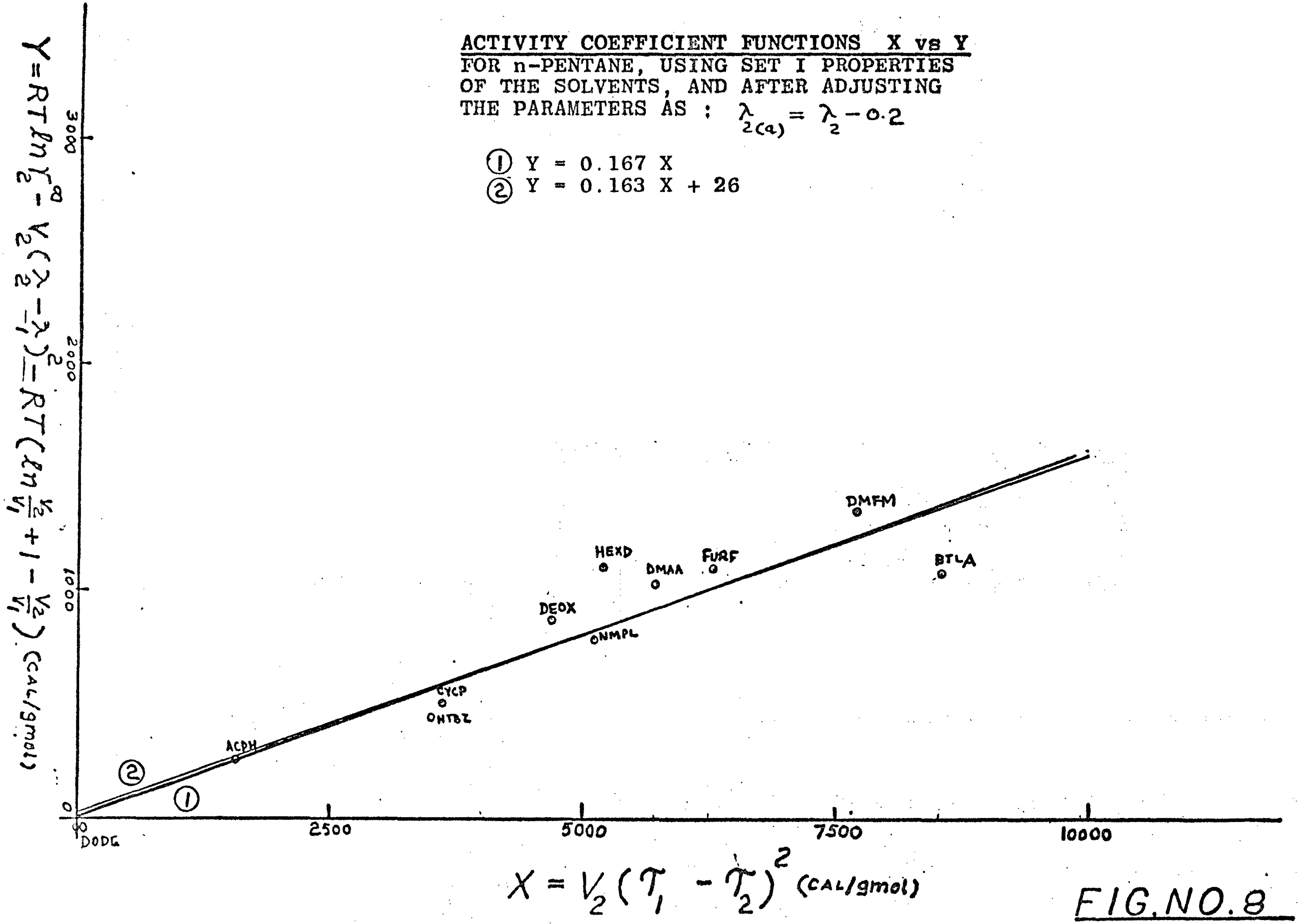
FIG. NO. 6



ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR 1-PENTENE, USING SET II PROPERTIES
OF THE SOLVENTS :

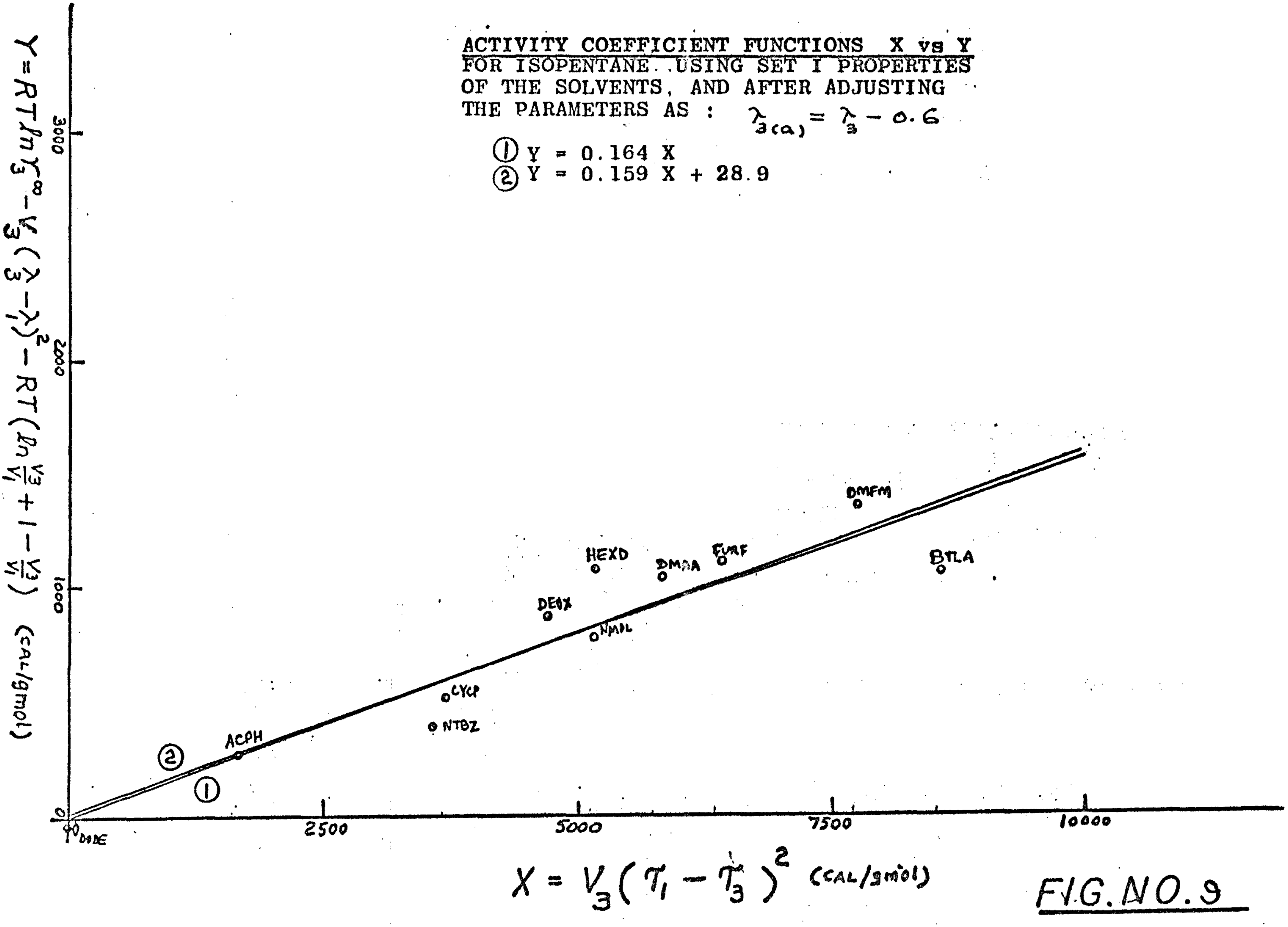
① $Y = 0.145\ X$
② $Y = 0.193\ X - 130$

FIG. NO. 7


ACTIVITY COEFFICIENT FUNCTIONS X vs Y FOR n-PENTANE, USING SET I PROPERTIES OF THE SOLVENTS, AND AFTER ADJUSTING THE PARAMETERS AS : $\lambda_{2(a)} = \lambda_2 - 0.2$

① $Y = 0.167\ X$
② $Y = 0.163\ X + 26$

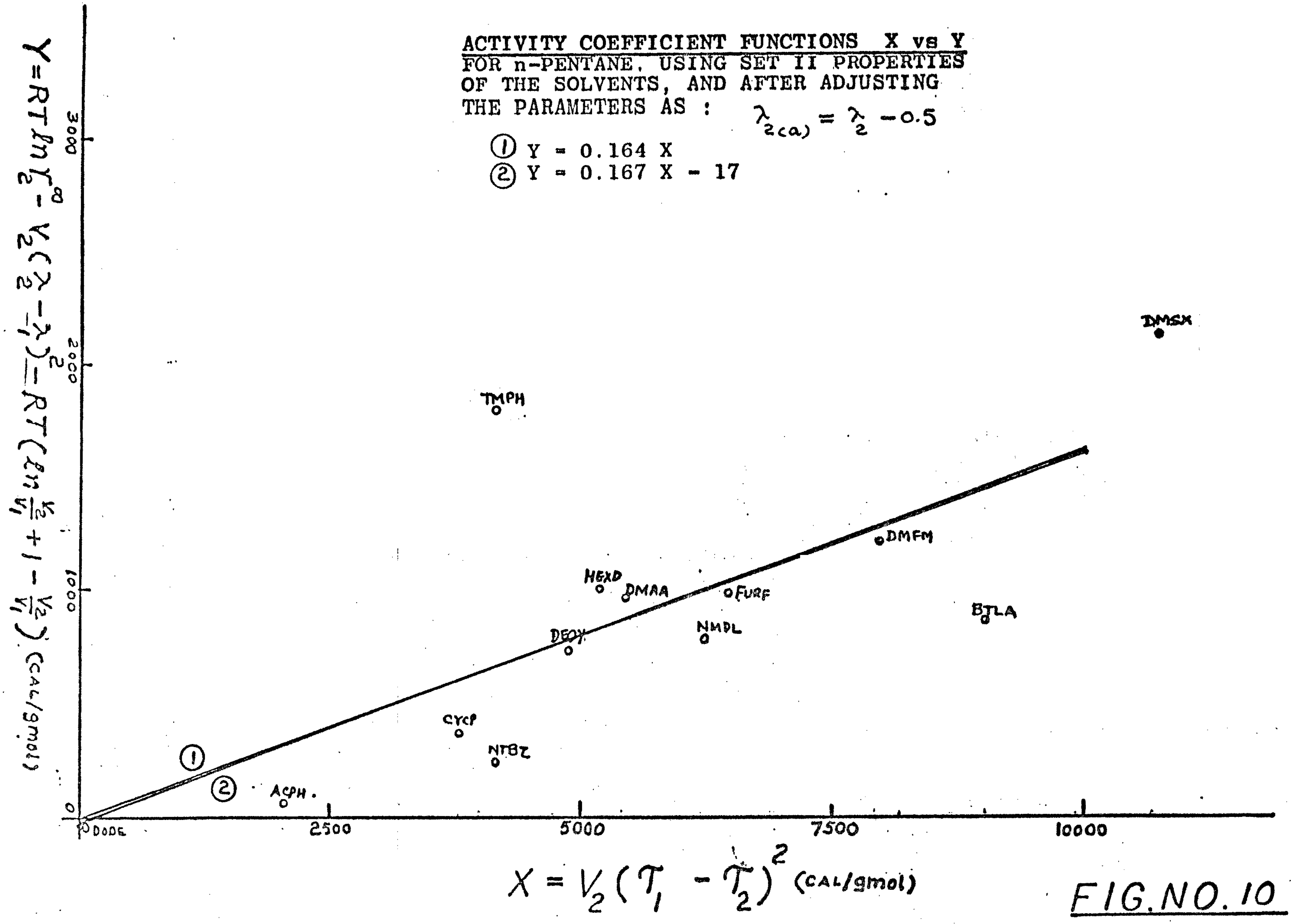
FIG. NO. 8



ACTIVITY COEFFICIENT FUNCTIONS X vs Y FOR ISOPENTANE. USING SET I PROPERTIES OF THE SOLVENTS, AND AFTER ADJUSTING THE PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.6$

① $Y = 0.164\ X$
② $Y = 0.159\ X + 28.9$

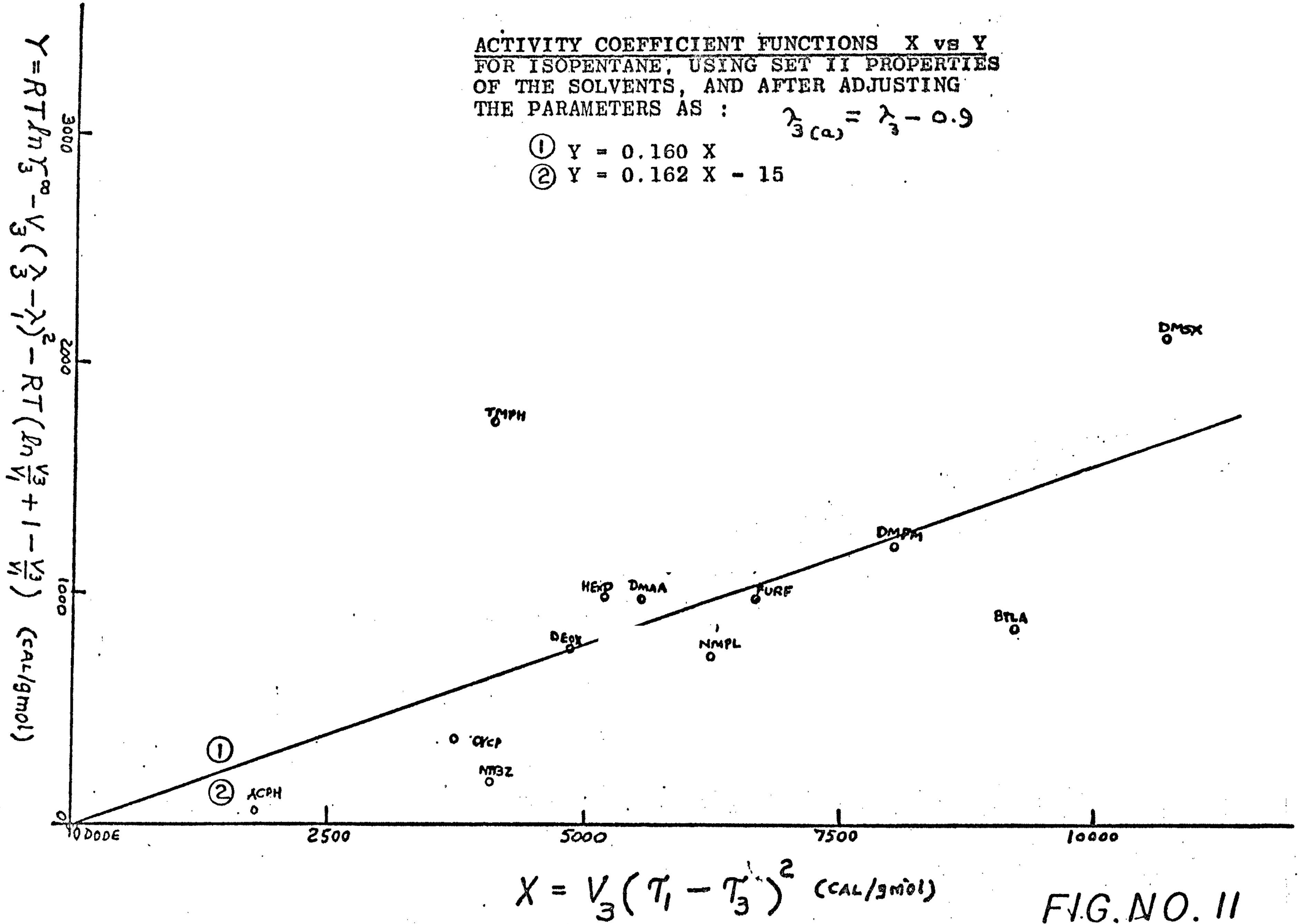
FIG. NO. 9



ACTIVITY COEFFICIENT FUNCTIONS X vs Y
FOR n-PENTANE, USING SET II PROPERTIES
OF THE SOLVENTS, AND AFTER ADJUSTING
THE PARAMETERS AS : $\lambda_{2(a)} = \lambda_2 - 0.5$

① $Y = 0.164 X$
② $Y = 0.167 X - 17$

FIG. NO. 10



ACTIVITY COEFFICIENT FUNCTIONS X vs Y FOR ISOPENTANE, USING SET II PROPERTIES OF THE SOLVENTS, AND AFTER ADJUSTING THE PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.9$

① $Y = 0.160\ X$

② $Y = 0.162\ X - 15$

FIG. NO. 11

SELECTIVITY FUNCTIONS X' vs Y'

USING SET I PROPERTIES

① $Y' = 2.365X'$

② $Y' = -1630X' - 127.6$ — MATHEMATICAL EQUATION ALLOWING FOR AN INTERCEPT

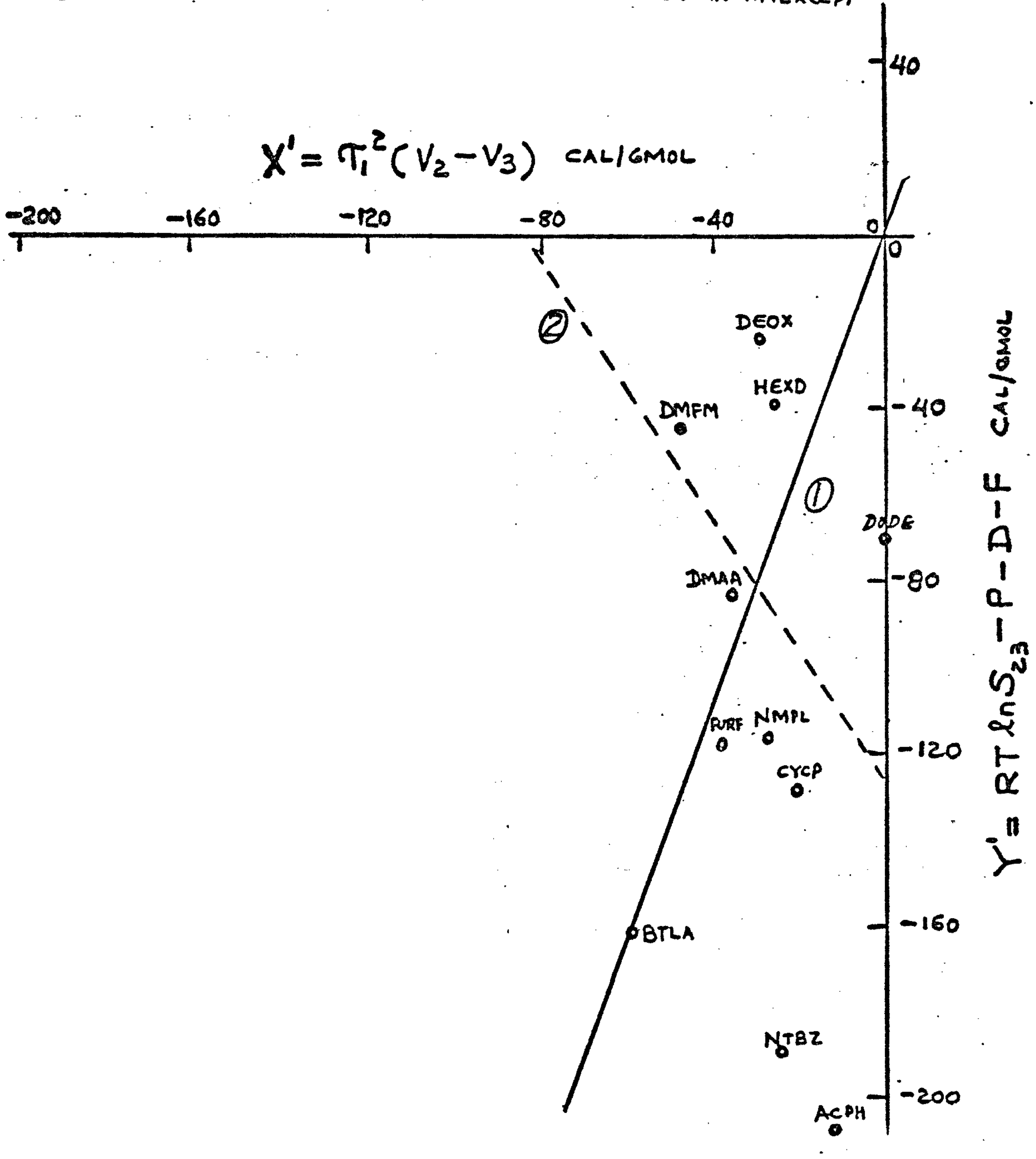


FIG. NO. 12

SELECTIVITY FUNCTIONS X' VS Y'

USING SET II PROPERTIES

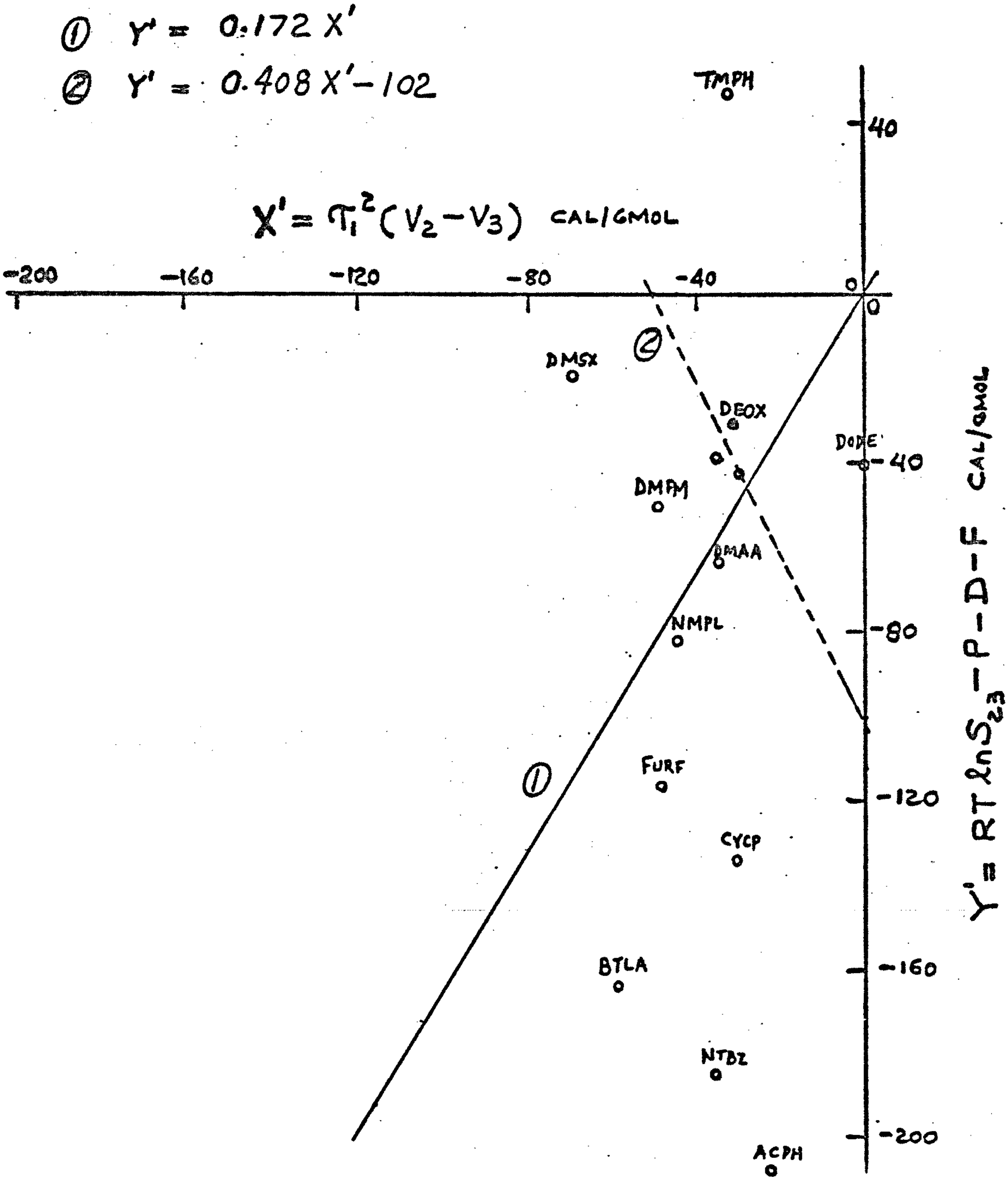


FIG. NO. 13

SELECTIVITY FUNCTIONS X' VS Y'

USING SET I PROPERTIES AND ADJUSTING

PARAMERS AS : $\lambda_{2(a)} = \lambda_2 - 0.2$

$\lambda_{3(a)} = \lambda_3 - 0.6$

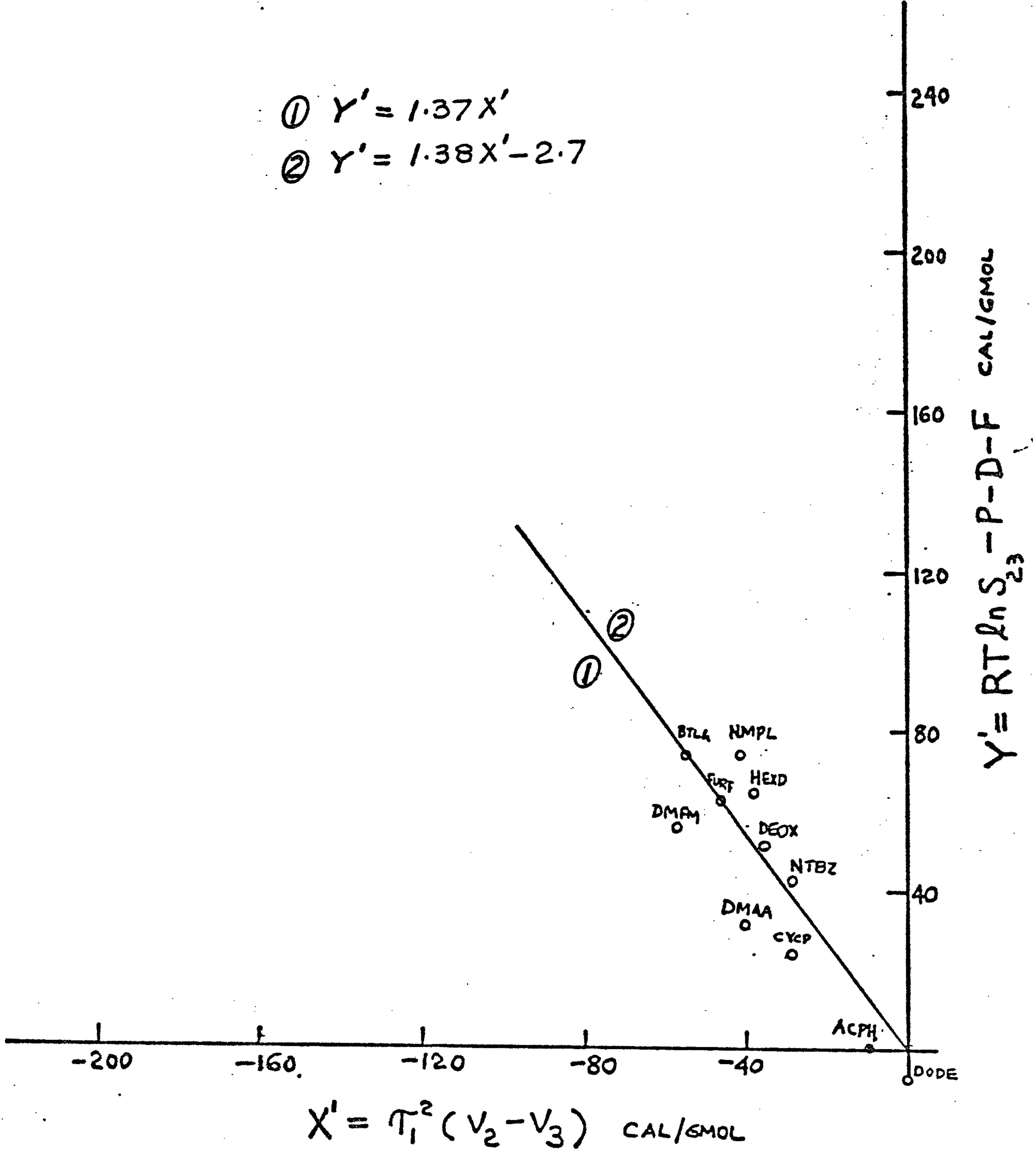


FIG. NO. 14

SELECTIVITY FUNCTIONS X' VS Y' USING SET II PROPERTIES AND ADJUSTING PARAMETERS

AS : $\lambda_{2(a)} = \lambda_2 - 0.5$

$\lambda_{3(a)} = \lambda_3 - 0.9$

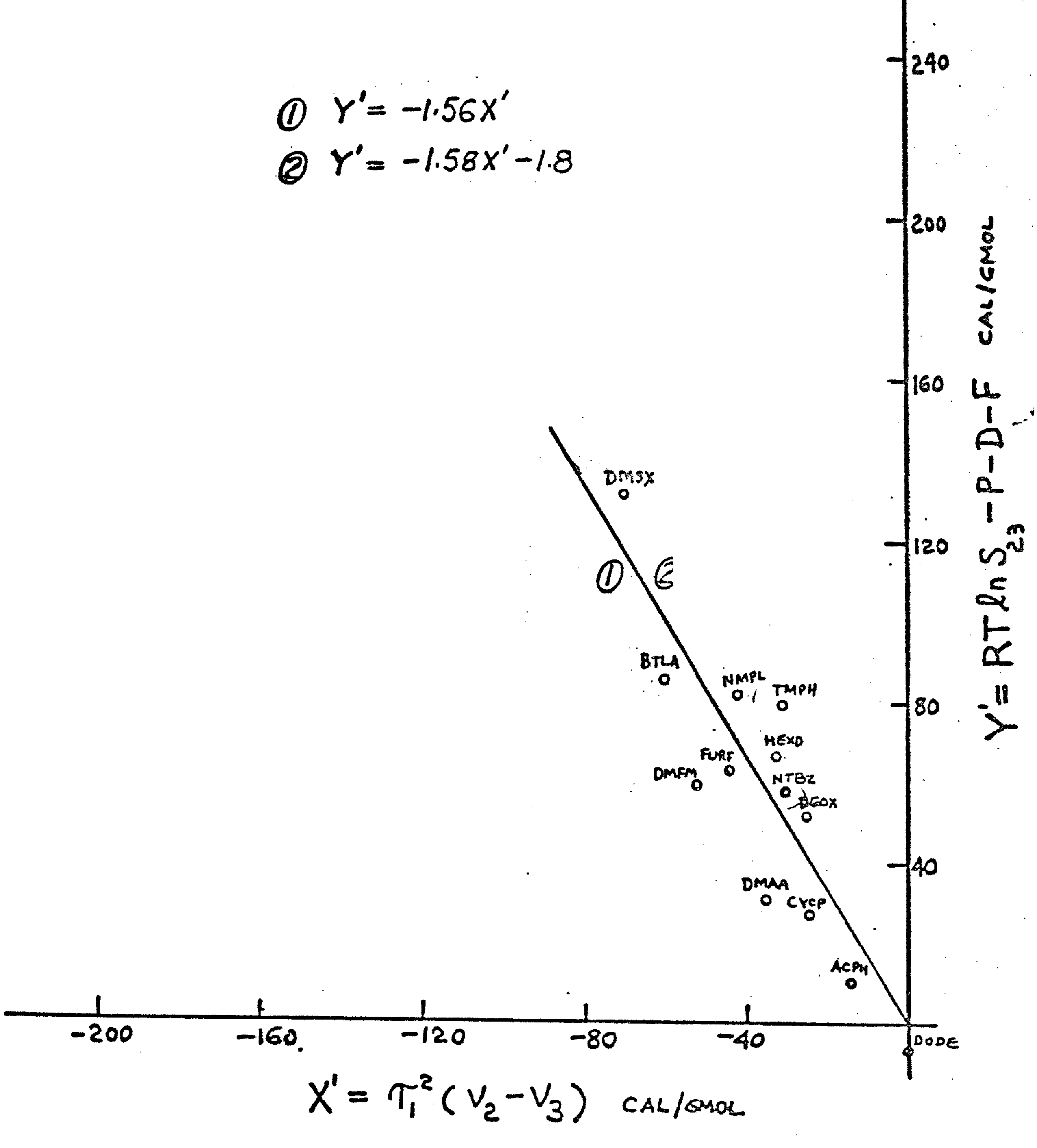


FIG. NO. 15

SELECTIVITY FUNCTIONS X' VS Y' USING SET I PROPERTIES AND ADJUSTING THE PARAMETERS AS : $\lambda_{3(a)} = \lambda_3 - 0.4$

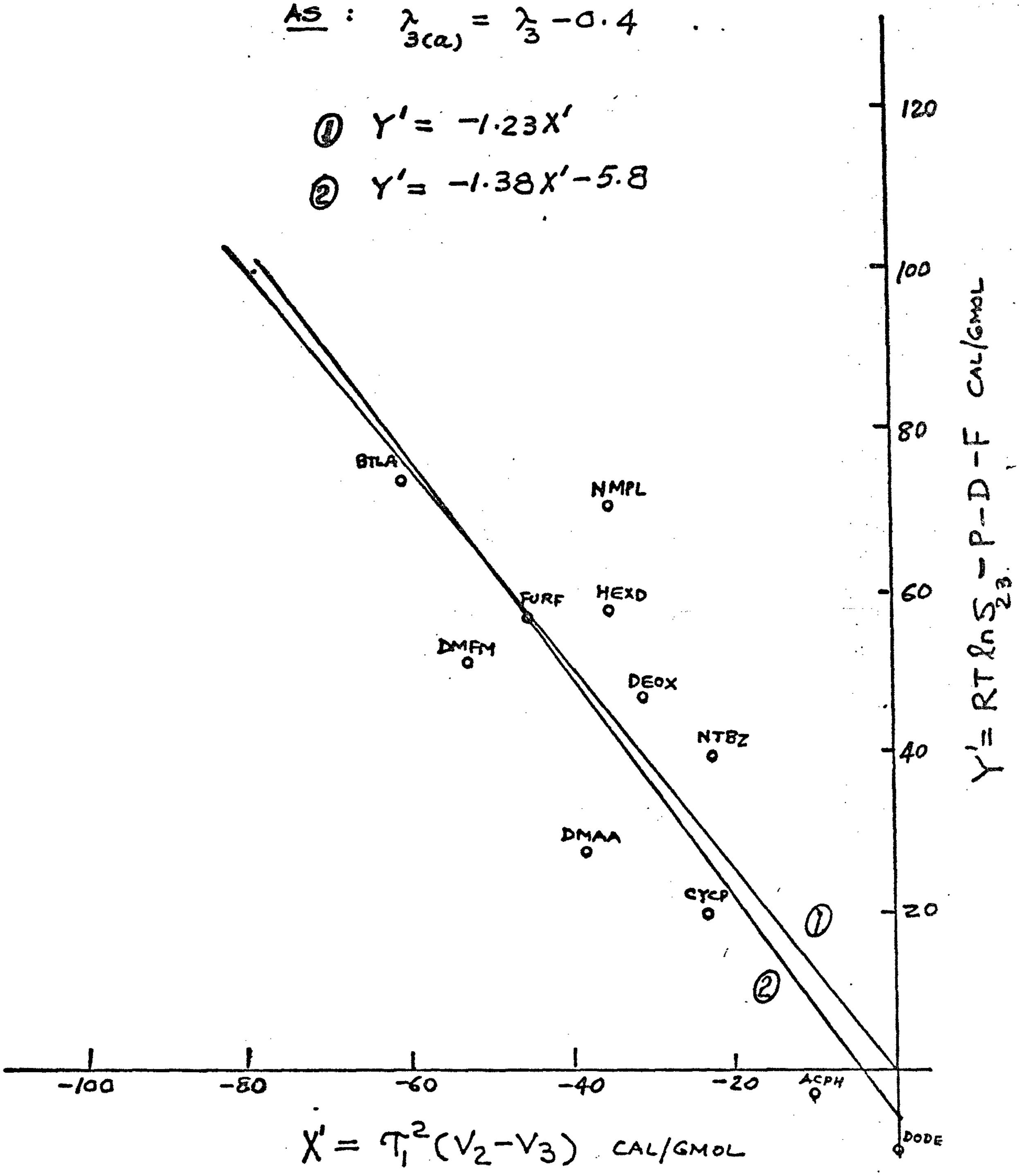


FIG. NO. 16

SELECTIVITY FUNCTIONS X' VS Y'
USING SET II PROPERTIES AND
ADJUSTING THE PARAMETERS
AS : $\lambda_{3(a)} = \lambda_3 - 0.4$

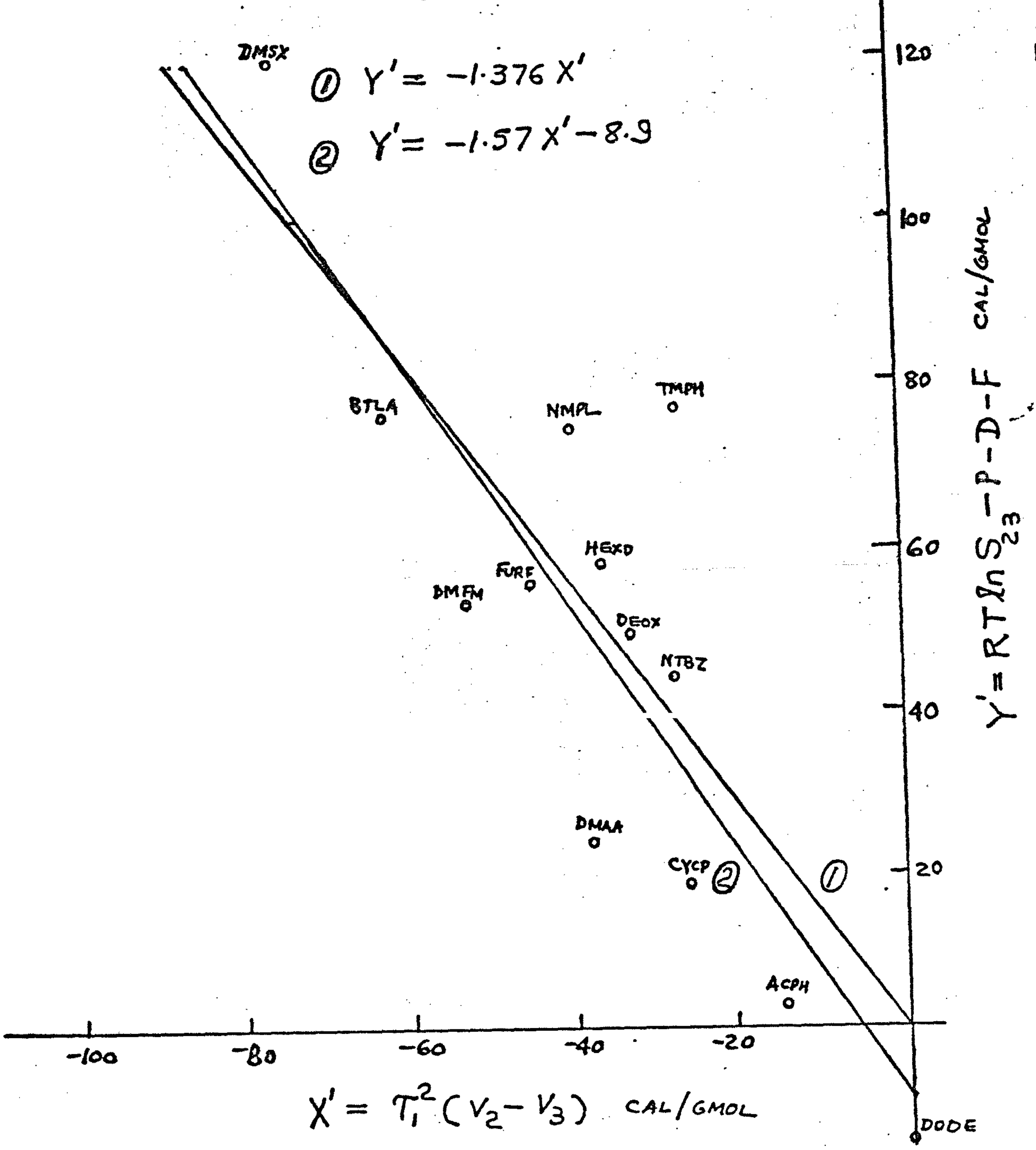


FIG. NO. 17

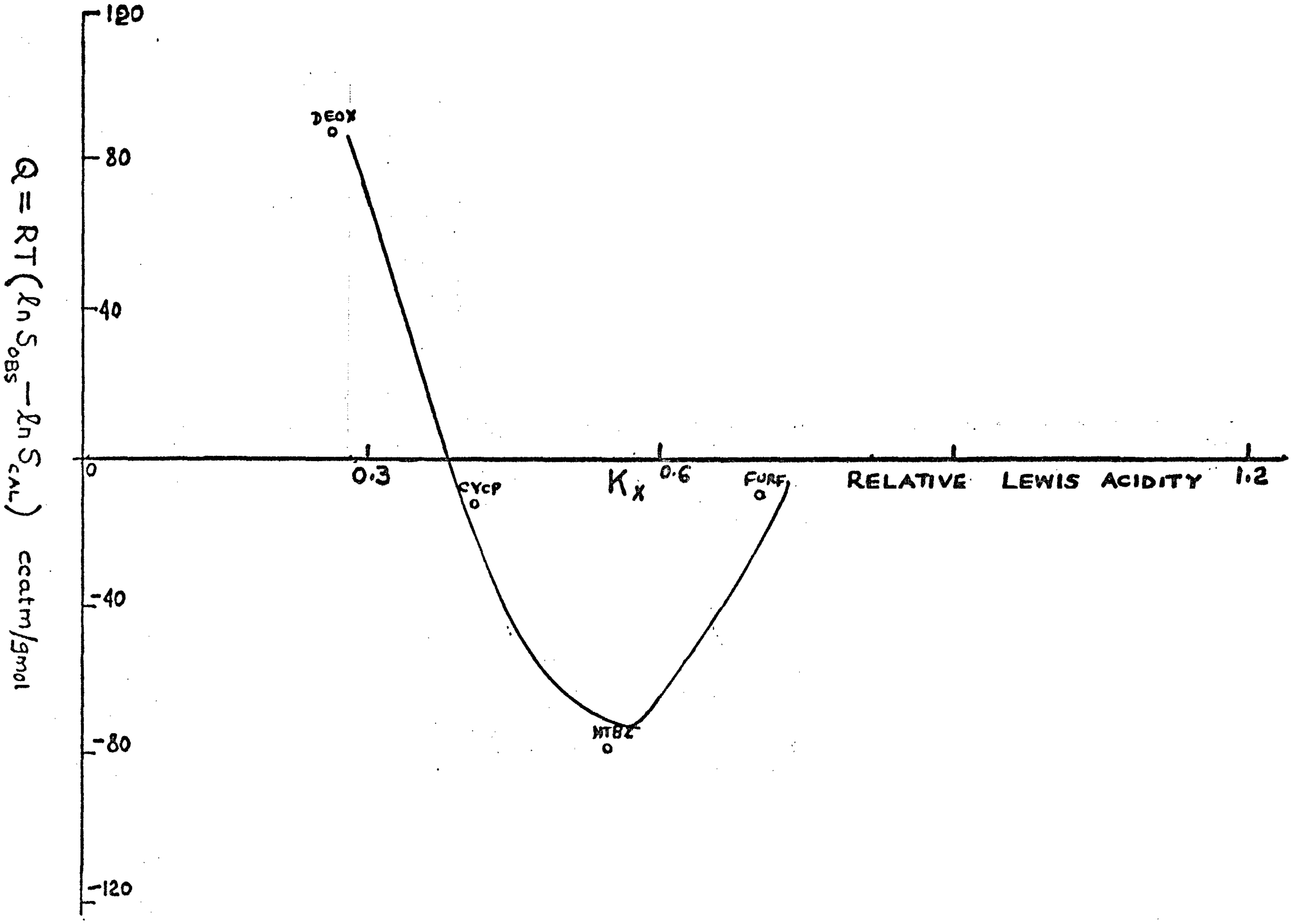
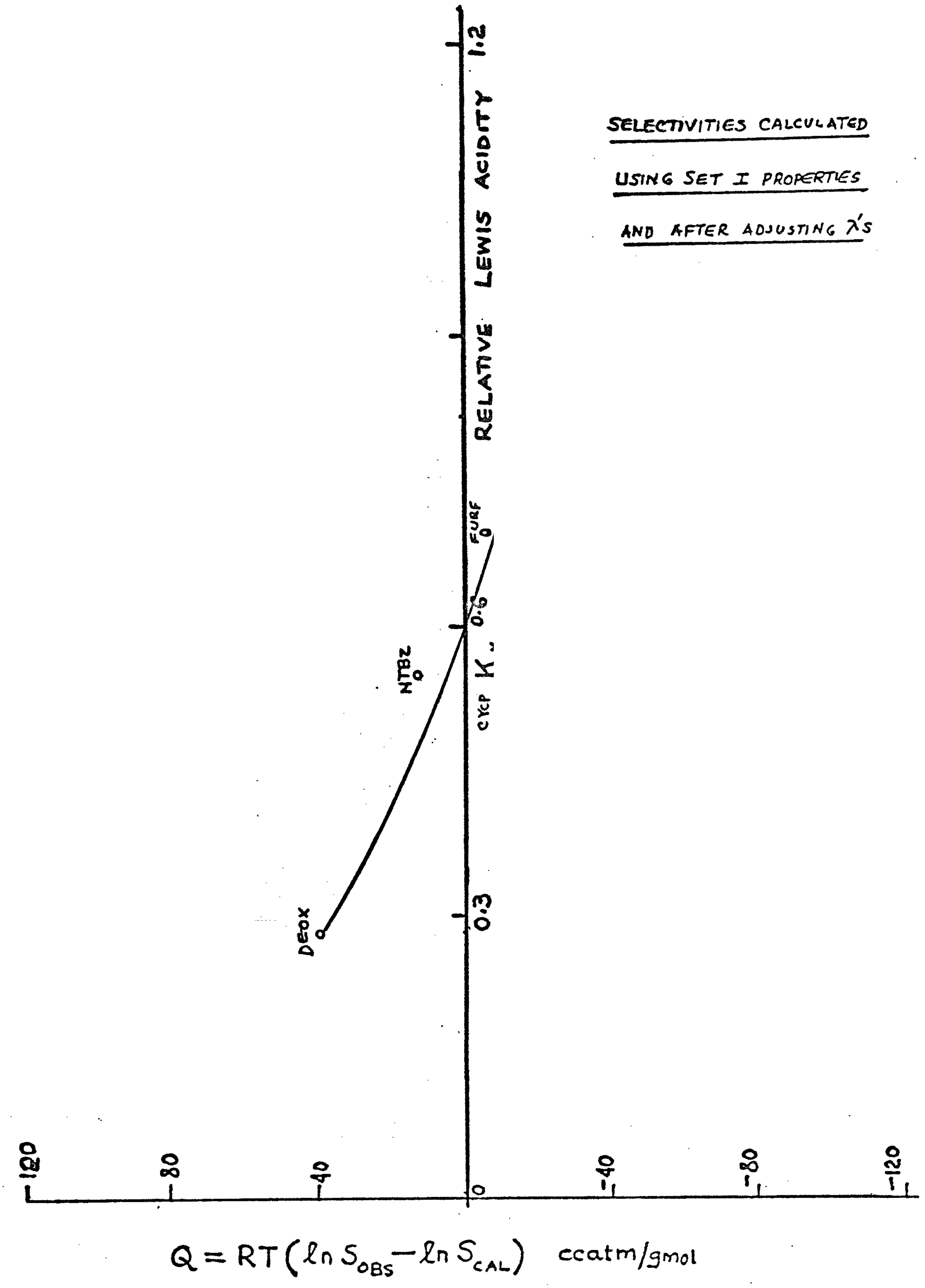

120
80
40
0
-40
-80
-120
Q = RT(ln S_OBS − ln S_CAL) ccatm/gmol
0.3
0.6
1.2
K_X
RELATIVE LEWIS ACIDITY
DEOX
CYCP
NTBZ
FURF

FIG. NO.18

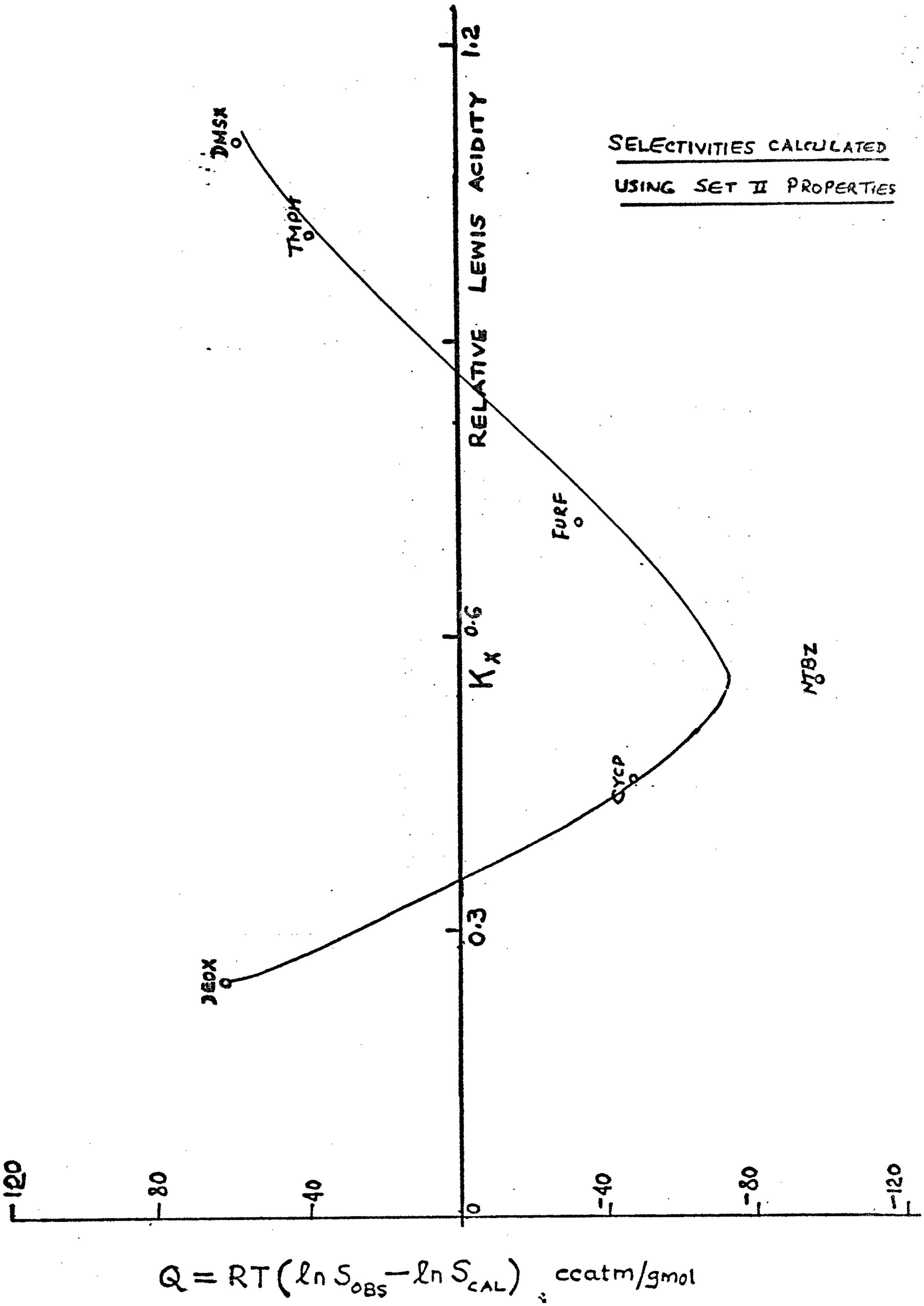


SELECTIVITIES CALCULATED

USING SET I PROPERTIES

AND AFTER ADJUSTING λ'S

FIG. NO. 19



SELECTIVITIES CALCULATED USING SET II PROPERTIES

FIG. NO. 20

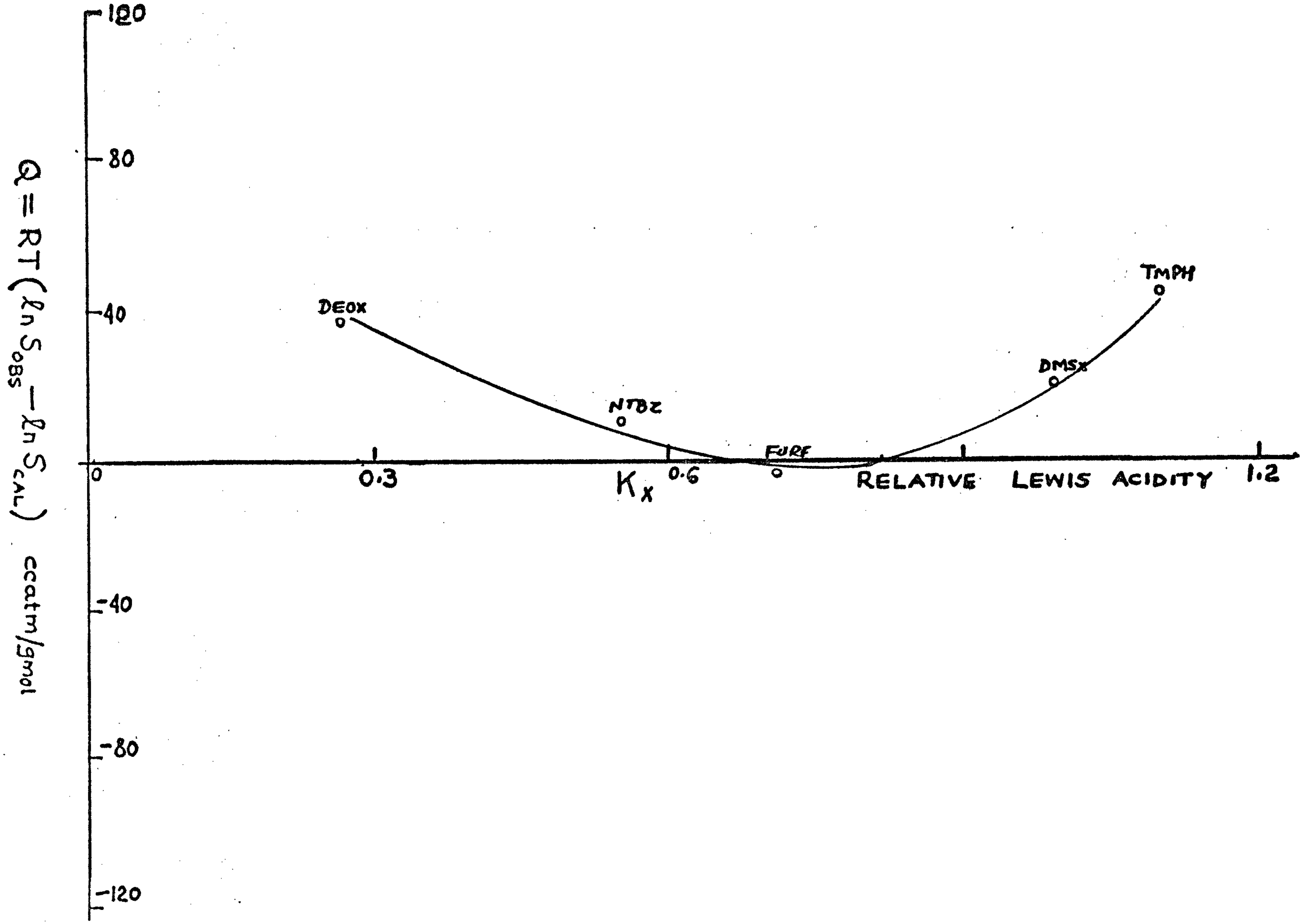

120
80
40
0
-40
-80
-120
Q = RT(ln S_OBS − ln S_CAL) ccatm/gmol
0.3
0.6
1.2
K_X
RELATIVE LEWIS ACIDITY
DEOX
NTBZ
FURF
DMSX
TMPH

FIG. NO.21

APPENDIX I

Determination of Critical Properties, Specific Volume, Polar Solvent Solubility Parameters λ_1 and τ_1 :

Critical Properties

In absence of reliable data Critical Properties are determined through estimation procedures as follows.

Critical Temperature (T_c) is obtained by Lyderson's method[13, 14]

Accordingly, $\theta = 0.567 + \sum\Delta T - (\sum\Delta T)^2$

and $T_c = T_b / \theta$

Critical Pressure (P_c) is obtained by Riedel's method.[14]

$$P_c = M / (\sum\Delta P + 0.34)^2$$

Critical Volume (V_c) is obtained by Lyderson's method.[14]

$$V_c = 40 + \sum\Delta V$$

where $\sum\Delta T$, $\sum\Delta P$, $\sum\Delta V$ are the sum of the contributions made by the individual atoms and their bondings in the compound.

FOR DI ETHYL OXALATE:

Critical Temperature T_c :

$$\sum\Delta T = 2\,(0.020 + 0.020 + 0.040 = 0.021)$$

$$= 0.202$$

$$\theta = 0.567 + 0.202 - (0.202)^2 = 0.7282$$

$$T_c = T_b/\theta = 458.55 / 0.7282 = 629.71\ {}^{o}K$$

Critical Pressure P_c:

$\sum \Delta P = 2\ (0.227 + 0.227 + 0.29 + 0.16)$

$= 1.808$

$P_c = M / (\sum \Delta P + 0.34)^2$

$= 146.123 / (1.808 + 0.34)^2$

$= \underline{31.614 \text{ atm}}$

Critical Volume V_c:

$\sum \Delta V = 4(55) + 2(60) + 2(20)$

$= 380$

$V_c = 40 + 380 = \underline{420 \text{ cc/gmol}}$

Compressibility factor Z_c:

$Z_c = (P_c\ V_c) / R\ T_c$

$= 0.2569$

Specific Volume v cc/gmol at 45°C

Density $\rho_4^{20} = 1.0785$

$Z_c = 0.2569$

At 20°C, $T_{r1} = \frac{293.15}{629.71} = 0.4655$

Using the Table #48 in Chemical Process Principles,[15]

$\rho_{r1} = 3.0016$

and $\rho'_{r1} = 3.1192$ when corrected for $Z_c \neq 0.27$

$$T_{r_2} = 318.15/629.71 = 0.5053$$

At 45°C, ρ_{r2} = 2.9272 using Table 48 in Chemical Process Principles

ρ'_{r2} = 3.0434 when corrected for $Z \neq 0.27$

Specific Volume v_2 at 45°C is then,

$$v_2 = \frac{\rho'_{r1} \cdot M}{\rho'_{r2} \cdot \rho_1}$$

$$= (3.1192 \times 146.13) / (3.0434 \times 1.0785$$

$$= \underline{138.858}$$

Helpinstill and Van Winkle have reported Specific Volume v_2 of Diethyl Oxalate at 45°C as 139.3 cc/gmol.

Comparing with the reported value,

$$\% \text{ Error of Estimation} = \frac{-139.3 = 138.858}{139.3}$$

$$= -0.317\%$$

Specific Volume of 139.3 cc/gmol is used for our purpose.

Solubility Parameters of Polar Solvent, λ_1 and τ_1:

As discussed earlier, (p. 22)

$$\left(\frac{\Delta U_1}{v_1}\right)_t = \left(\frac{\Delta U_1}{v_1}\right)_{np} + \left(\frac{\Delta U_1}{v_1}\right)_p$$

np - nonpolar
p - polar
t - total

$$= \lambda_1^2 + \tau_1^2$$

($\Delta U_1/v_1$) total:

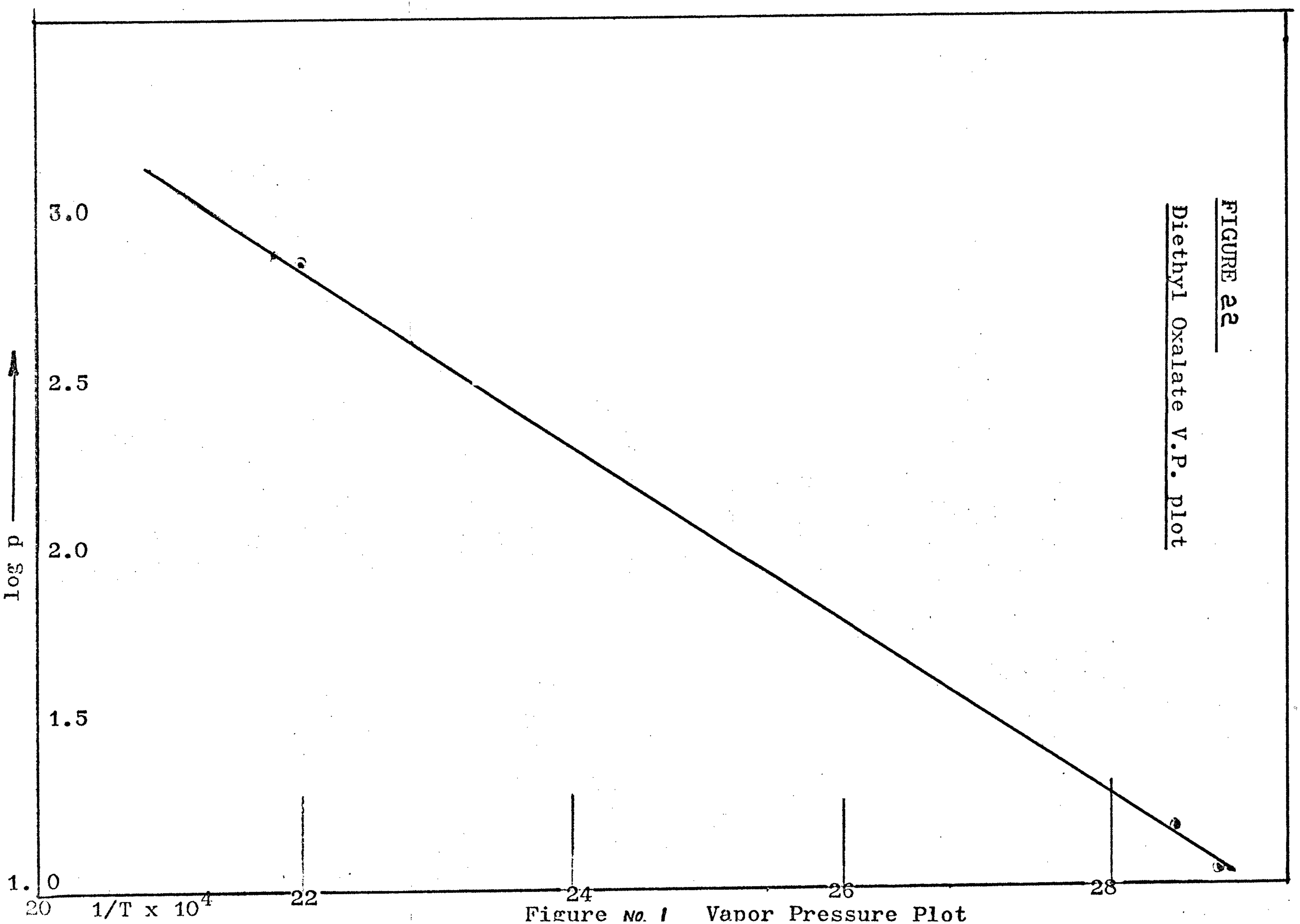


FIGURE 22

Diethyl Oxalate V.P. plot

Figure No. 1 Vapor Pressure Plot

(A) Vapor Pressure Method (p. 22)

Vapor Pressure data for Diethyl Oxalate are given below:

p (mm)	11	15	25	740	760
t (^oK)	74	78	106	181	185
$(1/T) \times 10^4$	28.805	28.48	26.374	22.019	21.807
log(p)	1.0414	1.1761	1.3980	2.8693	2.8808

The consistency of the data is checked by polotting log (p) Vs. 1/T in figure 22, where it is evident that the data are scattered and can be used only with proper interpretation

Considering the first three points (lower side)

$$\text{Slope, } \left(\frac{dp}{dT}\right)_{78^o} = 0.86 \text{ (mm/}^oK)$$

and
$$\Delta H_{78^oC} = \frac{1}{15} (1.987).(351.15)^2.(0.86)$$

$$= 14047.22 \text{ cal/mole}$$

Using Waton's Correlation,

$$\Delta H_{45^oC} = \frac{(629.707 - 318.15)^{0.38}}{(629.707 - 351.15)^{0.38}} \times (14047.22)$$

$$= 14658.27 \text{ cal/mole}$$

$$\frac{\Delta U_1}{v_1} \text{ total} = \frac{\Delta H - R.T.}{v_1}$$

$$= \underline{100.69 \text{ (cal/cc)}}$$ ________ Vap. Pres. data

B) Estimation Method (p. 23)

For Diethyl Oxalate,

T_c = 629.71 °K; P_c = 31.614 atm; V_c = 420 cc/gmol; Z_c = 0.2569

and at 45°C, T = 318.15°K

With all these substituting in equation #C as discussed earlier,

$$\Delta H_{45^\circ C} = \frac{4.781984\, T_b\, T_c \log (P_c)}{T_b - T_c} \left(1 - \frac{T_c^3}{P_c T_b^3}\right)^{1/2} \left(\frac{T_c - T}{T_c - T_b}\right)^{0.38}$$

= 14557.40 cal/mole (Compare with the value of 14658.27 using Vap. Pressure data)

and therefore,

$$\left(\frac{\Delta U_1}{v_1}\right) = \frac{\Delta H - RT}{v_1} = \underline{99.97 \text{ cal/cc}}$$

Nonpolar Contribution λ_1

$$\lambda_1 = \sqrt{\lambda_1^2} = \sqrt{\left(\frac{\Delta U_1}{V_1}\right)_{\text{nonpolar}}}$$

Using the homomorph plot for n-Paraffins, for

$$T_{r2} = \frac{318.15}{629.71} = 0.505$$

and v = 139.3 cc/gmol

$$\lambda_1^2 = \frac{\Delta U_1}{v_1} = 61.3; \qquad \underline{\lambda_1 = 7.289 \quad (\text{cal/cc})^{1/2}}$$

Polar Contribution term τ_1

$$\tau_1 = \sqrt{\left(\left(\frac{\Delta U_1}{V_1}\right)_t - \left(\frac{\Delta U_1}{v_1}\right)_{np}\right)}$$

τ_1 = 100.69 - 61.3 = 6.276 Using V.P. data

= 99.97 - 61.3 = 6.218 Using Estimation methods

Literature Information λ_1, τ_1

	Helpinstill & Van Winkle	Weimer & Prausnitz
λ_1	7.88	8.10
τ_1	6.28	5.90

APPENDIX II

SOLVENT No. NAME	SOURCE for Crit. Prop.	P_c atm	V_c cc/gmol	T_c K	source for V1	V_1 cc/gmol	Source for λ_1 and τ_1	λ_1 $\left(\text{cal/cc}\right)^{\frac{1}{2}}$	ΔH EST (Cal/gmol)	ΔH V.P. (Cal/gmol)	SOURCE for VP data	τ_1 $\left(\text{cal/gmol}\right)^{\frac{1}{2}}$	SET I (cal/gmol$^{\frac{1}{2}}$) λ_1	SET I (cal/gmol$^{\frac{1}{2}}$) τ_1	SET II (cal/gmol$^{\frac{1}{2}}$) λ_1	SET II (cal/gmol$^{\frac{1}{2}}$) τ_1	REMARKS
1 BTLA										13560	17,18	8.70				8.70	
	Lyd	58.6	231.5	739	→	78.03	→	9.49	13188			8.42	9.49	8.42	9.49		
2 HEXD										13580	19,20,21	6.53				6.53	
	Lyd	34.1	380	67	→	119.88	→	8.08	13607			6.55	8.08	6.55	8.08		
3 DMSX										12403	27	9.47				9.47	
	12,25			725	26	72.56	→	8.52					--	--	8.52		
4 TMPH										11117	28	5.82				5.82	
	12			546	19	117.92	→	7.41							7.41		
5 CYCP										9864	22	5.57				5.57	
	Lyd	51.6	268	625	→	90.95	→	8.61	10125			5.49	8.61	5.49	8.61		

SOLVENT No. NAME	SOURCE for Crit. Prop.	P_c atm	V_c cc/gmol	T_c K	source for V1	V_1 cc/gmol	Source for λ and τ_1	λ_1 $\left(\frac{cal}{cc}\right)^{1/2}$	ΔH EST (Cal/gmol)	ΔH V.P.	SOURCE for VP data	τ_1 $\left(\frac{cal}{gmol}\right)^{1/2}$	SET I (cal/gmol$^{1/2}$) λ_1	SET I τ_1	SET II λ_1	SET II τ_1	REMARKS
6 NTBZ										13424	16	5.76				5.76	
	29	43.4	--	718	→	104.2	→	9.43	13708			6.00					
	Lyd	35.1	384	714	→	104.7	→	9.43	12983			5.39	9.43	5.39	9.43		
7 DODE							ΔH_{VP} →	7.35		13191	16	0.0			7.35	0.00	
	8	17.5	700	658													
	Lyd	17.5	700	658	→	232.8	→	7.69	14386			0.0	7.69	0.0			
8 NMPL							7	8.75†				3.73†					
										13705	23	7.16				7.16	
					7	98.6	→	9.01					9.01		9.01		
	Lyd	47.2	255	724	→	98.2			12812			6.50		6.50			
							3	8.09				7.52			8.09	7.52	SHOW
9 DMAA							7	8.07				6.95			8.07		
										11402	29	6.75				6.75	
	29	39.6	--	675.7		95.3	→	8.23					8.23				
	Lyd	39.7	307	663	→	94.8			11580			6.89		6.89			

† APPEARS TO BE MISLEADING DATA

SOLVENT No. NAME	SOURCE for Crit. Prop.	P_c atm	V_c cc/gmol	T_c K	source for V1	V_1 cc/gmol	Source for λ and τ_1	λ_1 $(\text{cal/cc})^{1/2}$	ΔH EST (Cal/gmol)	ΔH V.P. (Cal/gmol)	SOURCE for VP data	τ_1 $(\text{cal/gmol})^{1/2}$	SET I $(\text{cal/gmol})^{1/2}$ λ_1	SET I τ_1	SET II λ_1	SET II τ_1	REMARKS
															9.3	3.90	SHOW
							3,7	9.3				3.90			9.3		
10 ACPH										12924	19	4.12				4.12	
					7	119.8 →		9.20					9.20				
	Lyd	36.6	381	713 →		123.3			12310			3.57		3.57			
							3	8.10				5.90			8.10	5.90	SHOW
11 DEOX							7	7.88				6.28			7.88		
										14658	19	6.28				6.28	
					7	139.3 →		7.83					7.83				
	Lyd	31.6	420	630 →		139.1			14557			6.22		6.22			
							7	8.14				7.26			8.14	7.26	SHOW
12 DMFM							3	8.07				7.91			8.07		
										11870	21	8.10				8.10	
					7	79.0 →		8.10					8.10				
	Lyd	43.7	265	642 →		78.8			11000			7.97		7.97			
							7	8.91				7.27					
13 FURF							3	8.81				7.40			8.81		
										11880	19	7.34				7.34	
					7	84.8 →		8.88					8.88				
	Lyd	48.6	286	657 →		84.8			11730			7.22		7.22			
14 TRCS							ΔH_{vp} →	6.83		21415	19,20	0.0			6.83	0.0	@93.9 C SHOW
	Lyd	10.1	1360	814 →		447.5	→	7.19				0.0	7.19	0.0			
							ΔH_{vp}	6.70		28460	19,20	0.0			6.70	0.0	@93.9 C SHOW
15 PTCT	Lyd	7.2	1965	983 →		629	→	5.15				0.0	5.15	0.0			

APPENDIX II

SOLVENT No. NAME	SOURCE for Crit. Prop.	P_c atm	V_c cc/gmol	T_c K	source for V1	V_1 cc/gmol	Source for λ and τ	λ_1 $(\text{cal/cc})^{\frac{1}{2}}$	ΔH EST (Cal/gmol)	ΔH V.P. (Cal/gmol)	SOURCE for VP data	τ_1 $(\text{cal/gmol})^{\frac{1}{2}}$	SET I $(\text{cal/gmol}^{\frac{1}{2}})$ λ_1	SET I τ_1	SET II λ_1	SET II τ_1	REMARKS SHOW
16 EICS							ΔH_{vp} →	7.76		21945	19,20	0.0			7.76	0.0	@53.2°C
	Lyd	11.9	1140	763	→	364.3	→	7.78				0.0	7.78	0.0			
							ΔH_{vp} →	7.50		21541	19,20	0.0			7.50	0.0	@74.1°C
					→	370.4	→	7.63				0.0	7.63	0.0			
							ΔH_{vp} →	7.37		21157	19,20	0.0			7.37	0.0	@93.9°C
					→	376.1	→	7.50				0.0	7.50	0.0			
							ΔH_{vp} →	7.89		33832	27,28	0.0			7.89	0.0	@ 53.2°C
					→	532.7	→	6.06				0.0	6.06	0.0			
17 SQUAL	Lyd	8.5	1666	765			ΔH_{vp} →	7.75		33300	27,28	0.0			7.75	0.0	@ 74.1°C
					→	541.6	→	5.95				0.0	5.95	0.0			
							ΔH_{vp} →	7.62		32604	27,28	0.0			7.62	0.0	@ 93.9°C
					→	549.8	→	5.84				0.0	5.84	0.0			

APPENDIX II

NOTE : Critical properties from Ref. 8
Vapor pressure data from Ref. 8

SOLUTE		P_c	V_c	T_c	V	FOR SET I AND II $(cal/cc)^{\frac{1}{2}}$		TEMP.
No.	NAME	atm	cc/gmol	K	cc/gmol	λ	τ	°C
2	n-C_5	33.3	304	469.7	120.3	6.94	0.0	45
					121.4	6.87	0.0	53.2
					126.3	6.60	0.0	74.1
					131.3	6.44	0.0	93.9
3	i-C_5	33.4	306	460.4	121.2	7.29	0.0	45
					123.7	7.11	0.0	53.2
					128.8	6.95	0.0	74.1
					134.0	6.83	0.0	93.9
4	=C_5	40.0	305	465	113.0	7.02	1.0*	45

* Ref. No. 3.7

APPENDIX III

Experimental Log Sheet# Date: February 18, 1973

Solvent: Dietyl Oxalate Mol. Wt. 146.15 B.P. 185.4°C

1) Weight of Column + Solvent + Inerts + Wire = x_1 = 145.6061 gms

2) Weight of Column + Inerts + Wire = x_2 = 143.2165 gms

3) Time when He gas flow started through the column: 8:00 A.M.

4)

He gas	cc	20	20	20	20	20	20	20
Flow	sec	40.3	40.2	40.4	39.4	39.5	39.3	39.3
Rate, V	cc/min	29.777			30.457			

5) Hg mamometer Left $\frac{+3.8''}{+3.75''}$ Right $\frac{-3.3''}{-3.25''}$

Water mamometer Left =0.5'' Right -0.5''

6) Weight of column after 10 minutes of He flow at the desired rate = x_3 = 145.6031 gms

7) Soap film temperature T_f = 24°C

8) Column Block Temperature T_{fo} = 45°C

9)

Solute injection	time Hr. Min.	distance D'' between Air and the Solute peaks
n-Pentane	8-16	1.605
	8-21	1.575
	8-27	1.570
	8-33	1.510
	8-37	1.535
Iso Pentane	8-48	1.200
	8-52	1.200
	8-56	1.190
	9-00	1.160
	9-05	1.155
1-Pentene	9-11	2-840
	9-20	2.800

9) Mixtures of Solutes	Time Hr. - Min.	Distance D_1 bet. Air Solute$_1$	Distance D_2 Solute$_1$ Solute$_2$
n-Pentane + 1-Pentene	9-26	1.515	2.810
IsoPentane + 1-Pentene	9-32	1.220	2.855
n-Pentane + IsoPentane	9-40	No separation achieved	

10) Weight of Column + Inerts + Solvent + Wire

at the end of the run, time 9-45, x_4 = 145.5750 gms.

11) Recorder Chart Speed Z = 0.685 in/min

12) Vapor Pressure of Water at the Soap film meter end

temperature T_f = 24°C, p_w = 22.377 mm Hg Abs.

13) Solute Vapor Pressure at the temperature of the experiment

T_{fo}, p_{io} as:

Solute	Temperature °C	Vapor Pressure mm Hg Abs.
n-Pentane	45	1020.00
Iso Pentane	45	1323.86
1-Pentene	45	1262.81

APPENDIX IV

Figure No. 23: Chromatogram of n-Pentane in Diethyl Oxalate

Figure No. 24: Chromatogram of IsoPentane in Diethyl Oxalate

Figure No. 25: Chromatogram of 1-Pentene in Diethyl Oxalate

Figure No. 26: Chromatogram of (n-Pentane + 1-Pentene in Diethyl Oxalate)

Figure No. 27: Chromatogram of (Isopentane + 1-Pentene in Diethyl Oxalate)

Figure No.23

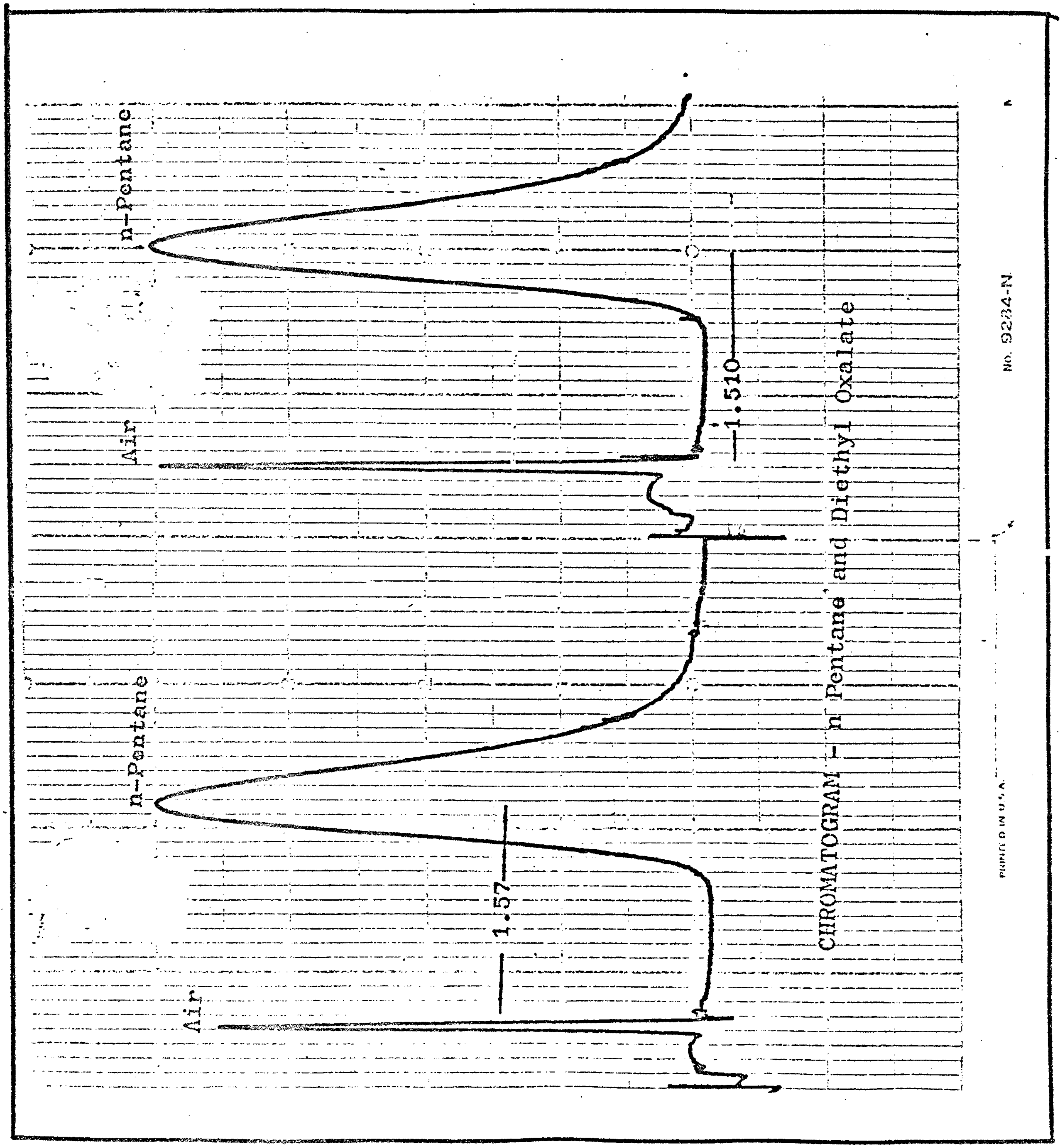
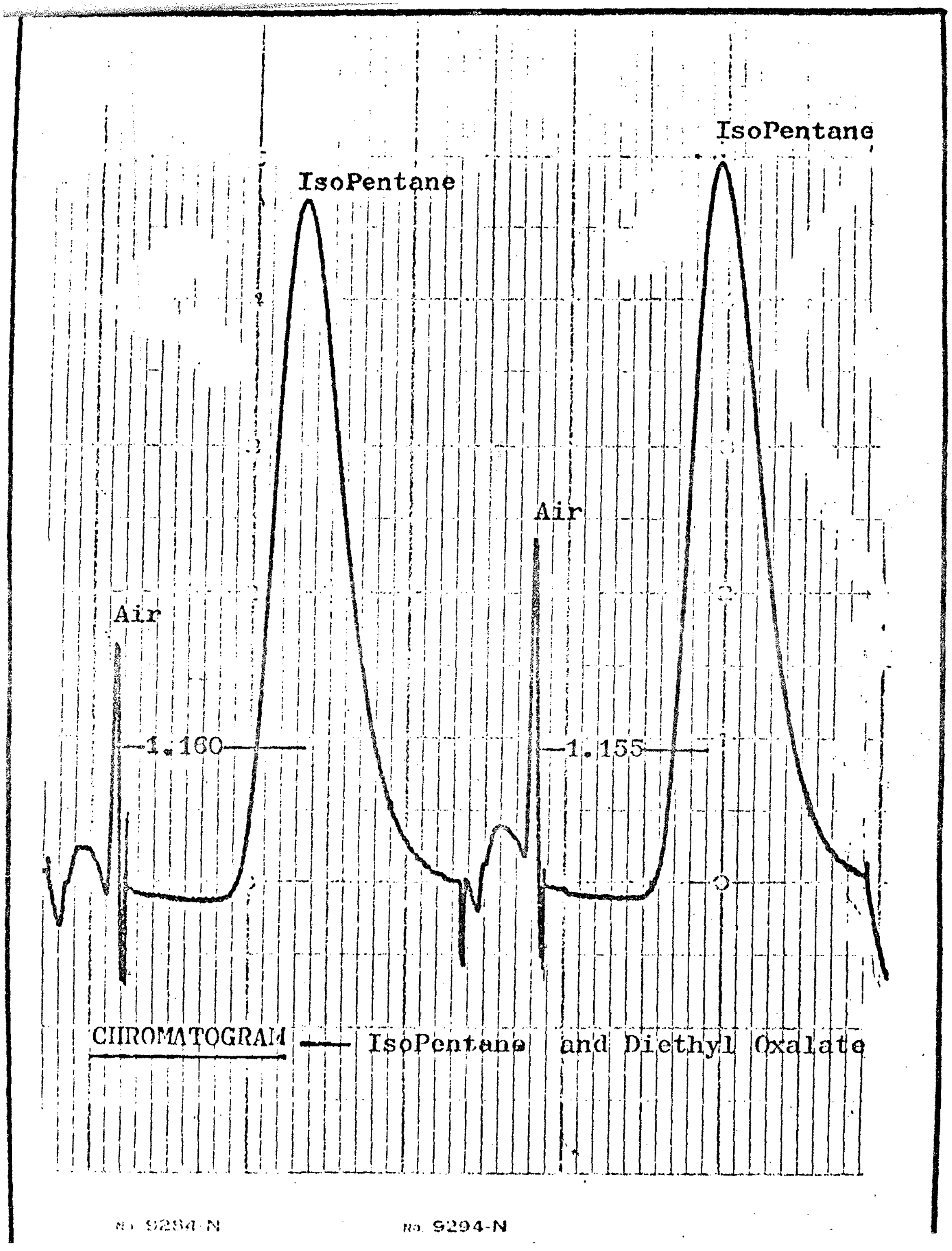
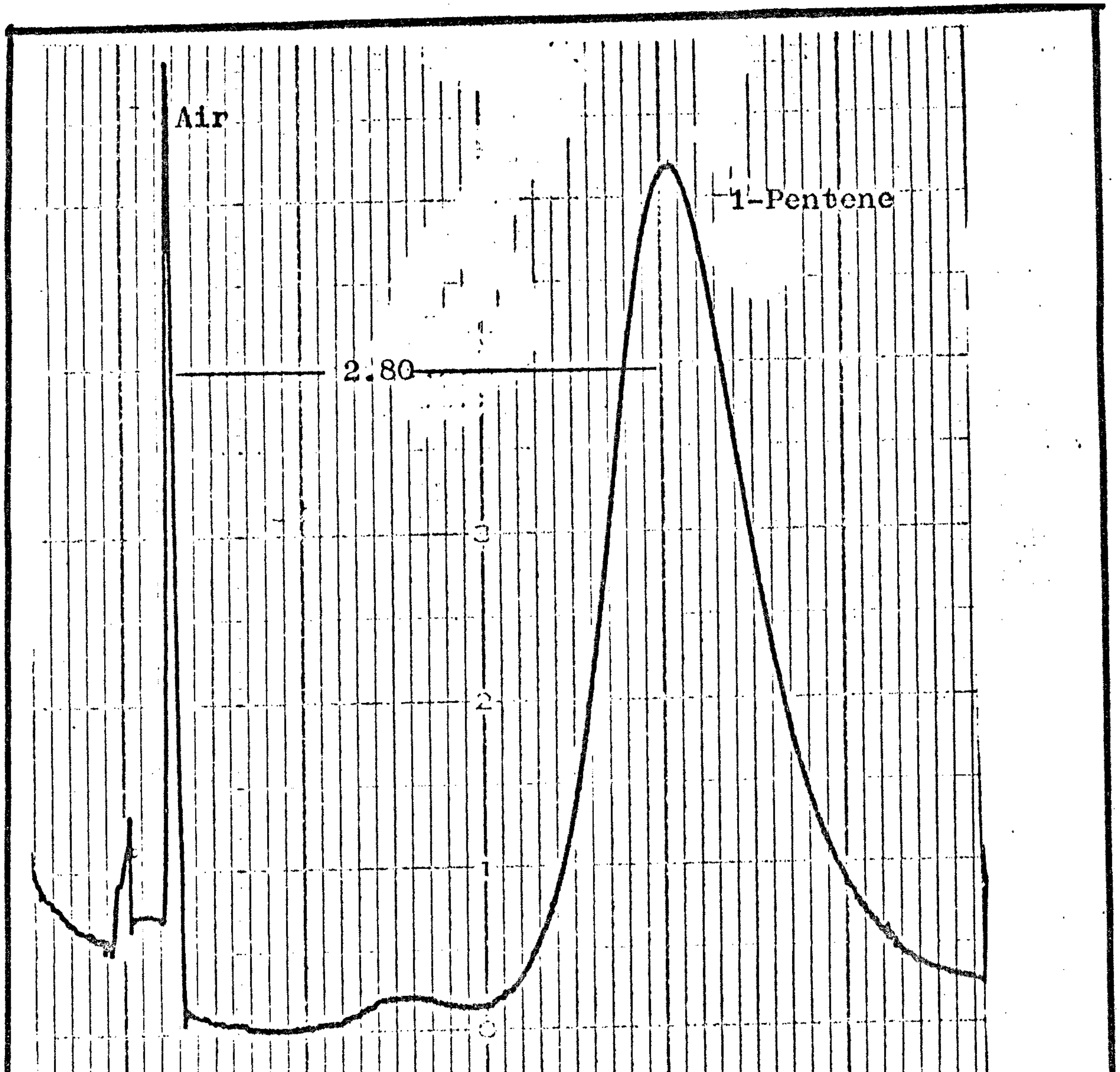

CHROMATOGRAM - n Pentane and Diethyl Oxalate
n-Pentane
Air
1.510
n-Pentane
Air
1.57
No. 9284-N
PRINTED IN U.S.A.

Figure No. 24



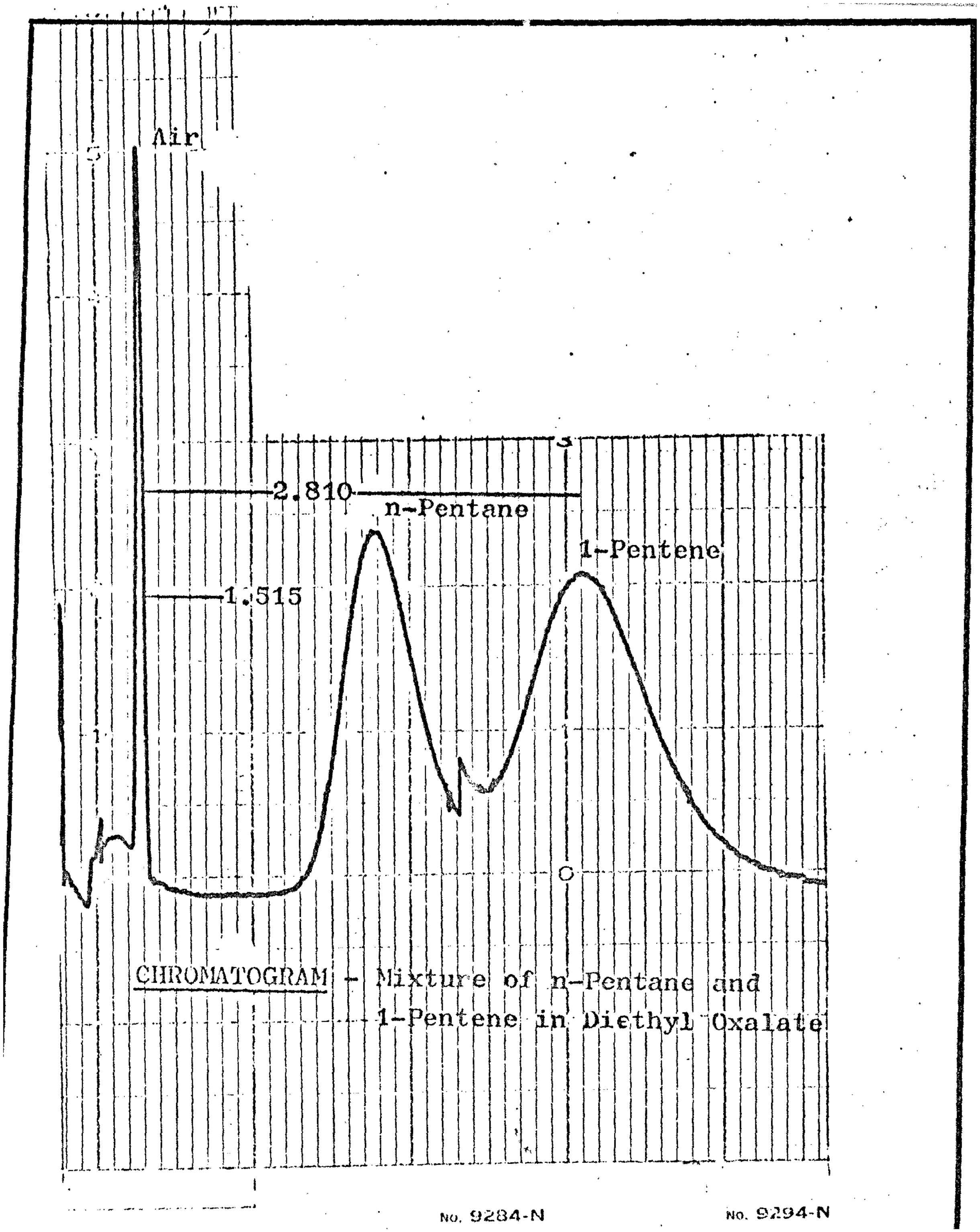
CHROMATOGRAM — IsoPentane and Diethyl Oxalate

Figure No.25



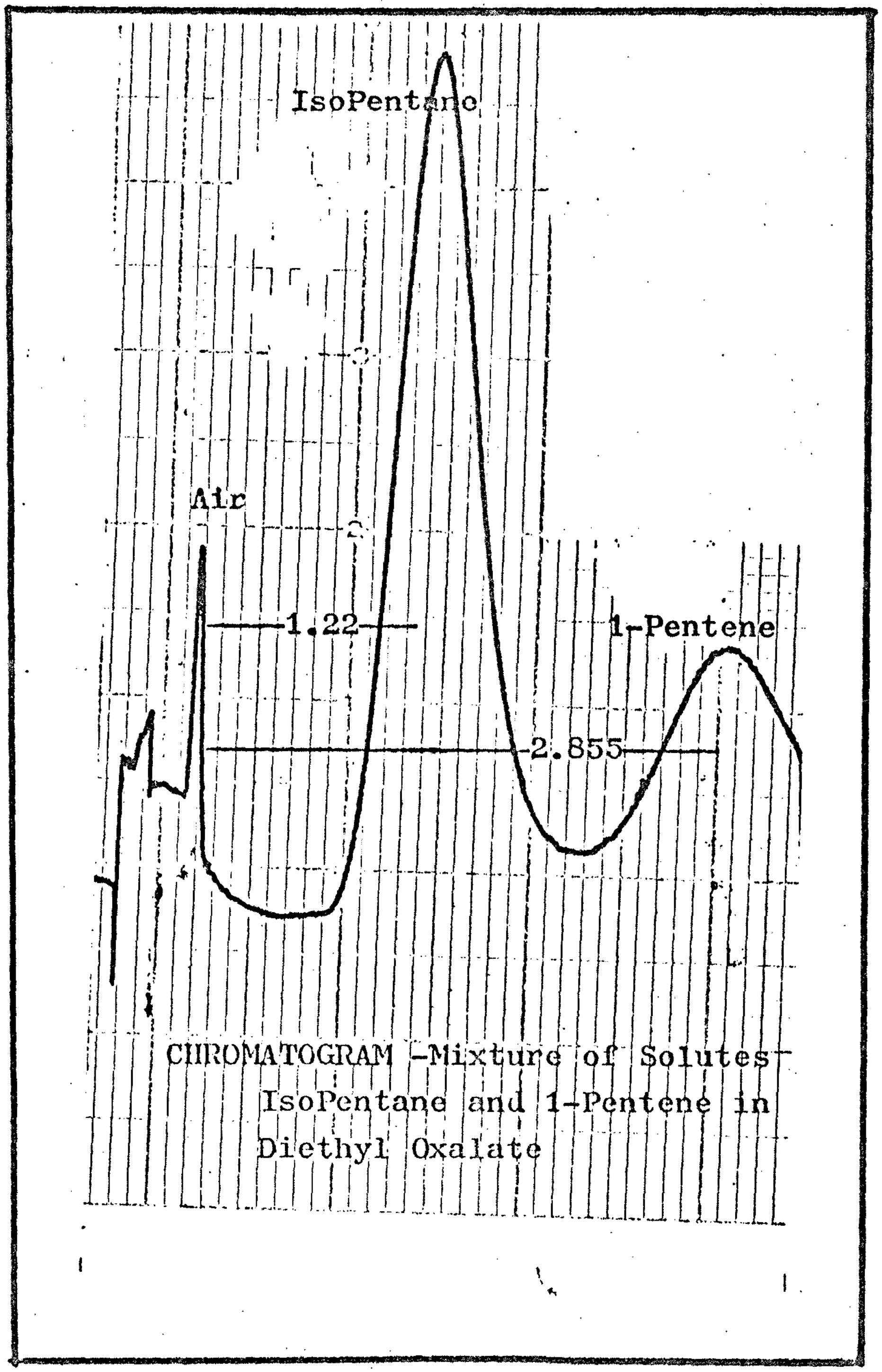
CHROMATOGRAM - 1-Pentene and Diethyl Oxalate

Figure No.26



CHROMATOGRAM - Mixture of n-Pentane and 1-Pentene in Diethyl Oxalate

Figure No.27



CHROMATOGRAM -Mixture of Solutes
IsoPentane and 1-Pentene in
Diethyl Oxalate

APPENDIX V

Calculation of Infinite Dilution Activity Coefficient Through Gas Liquid Chromatography:

Set time $t = 0$ when He gas flow started.

Weight of Solvent + Inerts + Column + Wire $= x_1 = 145.6061$ gms

Weight of Column + Inerts + Wire $= x_2 = 143.2165$ gms

Weight of Solvent at time $t=0$, $S_O = (x_1 - x_2) =$ 2.3986 gms

Weight of Solvent after 10 minutes of He flow

passed + Inerts + Column + Wire $= x_3 = 145.6031$ gms

Weight of Solvent after 10 minutes of flow $= (x_3 - x_2) =$ 2.3866 gms

1) Rate of Loss of Solvent $= \dfrac{(x_1 - x_2) - (x_3 - x_2)}{10} = r_1 =$ 0.0003 gms/min

Weight of Solvent at the end of run $= S_f = x_4 - x_2 = 2.3585$ gms at $t =$ min

2) Rate of Loss of Solvent $= \dfrac{(x_1 - x_2) - (x_4 - x_2)}{t} = r_2 = 0.00029$ gms/min

Average Rate of Solvent $= (r_1 + r_2)/2 = r - 0.2981 \times 10^{-2}$ gms/min

Weight of Solvent in the column at any intermediate time t minutes

after the start $S_t = S_O - t.r$ gms

He-Inlet pressure $p_{in} = 7.1, \ 7.0$ in Hg

$= 936.74, \ 934.2$ mm Hg Abs.

He-Outlet pressure $p_o =$ 1" in water

$=$ 756.00 mm Hg Abs.

With the above Variables known, and the values of He Velocity V, Distance D between the Air and Solute peaks on Chromatogram, Recorder Chart Speed Z, Soap film temperature T_f, Water Vapor - pressure p_w, and the partial pressure of the Solute p_{io} at the temperature T_{fo} (45°C) of the experiment:

Infinite Dilution Coefficient of Solute (2) in Solvent (1) is obtained as,

$$= \frac{(1.704).10^7 . Z . S . T_f . p_o . 2.}{M . p_{io} . D . V. (273).(p_o - p_w). 3} \frac{((p_i/p_o)^3 - 1)}{(p_i/p_o)^2 - 1}$$

Above calculations have been made with the help of a FORTRAN Programming for each of the Solvents selected.

APPENDIX #VI

Following is a mathematical analysis of the observed experimental data points (n points) to be correlated.[30]

Let the data points b (x_k , y_k), where k = 1, 2, ... , n.

Part b: Non zero intercept

Attempting to fit this data to a Straight line - linear regression equation, let the equation of the line fitting the data the best be

$$Y = a + b X \text{------------------------} (1)$$

where a and b represent the intercept and the slope of the line.

Also, let $\phi_k = y_k - a - bx_k$ ------------------------------------ (2)

Applying the Least Square Technique, let

$$\phi = \sum_{k=1}^{k=n} \phi_k = \sum_{k=1}^{k=n} (y_k - a - bx_k)^2 \text{------------------------------} (3)$$

and for the minimum value of ϕ ,

$$\frac{\partial \phi}{\partial a} = 0 \quad \text{and} \quad \frac{\partial \phi}{\partial b} = 0 \text{ --------------------------} (4)$$

Therefore, the two conditions are

$$\left.\begin{array}{l} \displaystyle\sum_{k=1}^{k=n} (y_k - a - bx_k) = 0 \\ \text{and} \\ \displaystyle\sum_{k=1}^{k=n} (y_k - a - bx_k) = 0 \end{array}\right\} \text{-------------------} (5)$$

Rearranging,

$$\left.\begin{aligned} an + b\sum_{k=1}^{k=n} x_k - \sum_{k=1}^{k=n} y_k &= 0 \\ a\sum_{k=1}^{k=n} x_k + b\sum_{k=1}^{k=n} x_k^2 - \sum_{k=1}^{k=n} x_k\ y_k &= 0 \end{aligned}\right) \text{-------------------} \begin{matrix}(6)\\(7)\end{matrix}$$

Dividing by n equation #6 becomes

$$a = b\,\bar{x} - \bar{y} = 0 \quad \text{---}(8)$$

Using definitions, we also have

$$\sum_{k=1}^{k=n} x_k^2 / n = \sigma_x^2 + \bar{x}^2 \quad \text{-----------------------------------} (9)$$

$$\text{and} \quad \sum_{k=1}^{k=n} x_k Y_k / n = \nu_{11} = \mu_{11} + \bar{x} \cdot \bar{y} \text{--------}(10)$$

Substituting these in (7)

$$a\bar{x} = b\,(\sigma_x^2 + \bar{x} . \bar{x}) - (\bar{x} \cdot \bar{y} + \mu_{11}) = 0 \text{ -------------------} (11)$$

Rewriting this as,

$$a\,\bar{x} + b\,\bar{x}^2 - \bar{x}\,\bar{y} + b\,\sigma_x^2 - \mu_{11} = 0 \quad \text{----------------} (12)$$

The first three terms in (12) are equal to zero because of (6)

Therfore,

$$a + b\bar{x} = \bar{y} \qquad \text{------------------------} (13)$$

and

$$b\,\sigma_x^2 = \mu_{11} \qquad \text{------------------------} (14)$$

and

$$b = \frac{\mu_{11}}{\sigma_x^2} \quad \text{and} \quad a = y - \frac{\mu_{11}\,\bar{x}}{\sigma_x^2} \qquad \text{------} (15)$$

The Straight Line Equation is, then

$$Y - \bar{y} = \frac{\mu_{11}}{2} (X - \bar{x}) \qquad \text{--------------------------------} (16)$$

where

$$b = \frac{\mu_{11}}{\sigma_x^2} = \text{Coefficient of Regression}$$

$$\bar{x} = \sum_{k=1}^{k=n} x_k \Big/ n \qquad \bar{y} = \sum_{k=1}^{k=n} y_k \Big/ n$$

and

$$\mu_{11} = \left(\frac{1}{n}\sum_{k=1}^{k=n} x_k y_k\right) - \bar{x}\cdot\bar{y} \qquad \sigma_x^2 = \frac{1}{n}\sum_{k=1}^{k=n} (x_k^2 - \bar{x})^2$$

Above results can be written as,

B = slope of the regressed line $(Y = A + B_x)$

$$= \frac{\text{XYAV} - (\text{XAV})(\text{YAV})}{\text{XXAV} - (\text{XAV})(\text{XAV})} \qquad \text{------------------------------------} (17)$$

and

$$A = (\text{YAV}) - (\text{B})(\text{XAV}) \text{--} (18)$$

<u>Part c: Zero intercept:</u> When the line Y = A + BX is forced to pass through origin, eq. 3 then becomes

$$\phi = \sum_{k=1}^{k=n} \phi_k = \sum_{k=1}^{k=n} (y_k - b_1 x_k)^2 \text{---------------------} (19)$$

For minimum ϕ, $\frac{\partial \phi}{\partial b_1} = 0$ leads to,

$$\sum_{k=1}^{k=n} (y_k - b_1 x_k)\cdot x_k = 0 \qquad \text{---------------------} (20)$$

Rearranging, $b_1 = \sum_{k=1}^{k=n} y_k x_k \Big/ \sum_{k=1}^{k=n} (x_k \cdot x_k) = \frac{\text{SUMYX}}{\text{SUMXX}}$

or

$$B_1 = \frac{SUMXY}{SUMXX} = \frac{XYAV}{XXAV} \text{ ------------------------------------ } (21)$$