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VAPOR-LIQUID EQUILIBRIA OF THE CARBON TETRACHLORIDE, CYCLOHEXANE AND ISOPROPYL ALCOHOL SYSTEM

by

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A thesis submitted to the
Department of Chemical Engineering
of
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I - ABSTRACT

The vapor-liquid equilibrium data of the binary and the ternary systems of carbon tetrachloride, cyclohexane and isopropyl alcohol at a pressure of 760 mm Hg were determined. A Gillespie type still[9] with modification was used. The density and refractive index were used to analyse the vapor and liquid samples. Temperature was measured by means of a copper-constantan thermocouple.

An azeotrope was found for carbon tetrachloride - isopropyl alcohol, cyclohexane - isopropyl alcohol and the ternary system.

The Gibbs-Duhem equation for a binary system at constant pressure was used to check the consistency of the binary data. All three binary systems data were found to be thermodynamically consistent.

The three-constant Redlich-Kister[7] equation for the binary system was found to represent all the three binary systems under investigation and the thirteen-constant, (nine binary constants and the four ternary constants) Redlich-Kister equation was found to represent the ternary system.

II - INTRODUCTION

Since the equilibrium relations of many systems cannot be predicted from theoretical considerations, they can only be determined experimentally.

The experimental determination of vapor-liquid phase equilibrium consists of the determination of the compositions of both the vapor and the liquid phase at equilibrium conditions. These determinations can be carried out either at constant temperature or at constant pressure. For distillation processes, the isobaric data are especially important.

The Gibbs-Duhem equation is the basic principle to test the consistency of the phase equilibrium data. With simplifying assumptions many semi-empirical equations[1-8] have been derived as the special forms of this equation. They are applicable to many systems. The equation proposed by Redlich and Kister[7] appears to be flexible and adequate for representing the vapor-liquid equilibrium data.

The present investigation consists of determining the equilibrium temperature and the composition of the vapor and the liquid phase at atmospheric pressure of the binary and the ternary mixtures of carbon tetrachloride, cyclohexane and isopropyl alcohol. A modified recirculating still of the Gillespie type[9] was used. Temperatures were measured by means of a calibrated thermocouple. The equilibrium compositions

were determined indirectly from refractive indices and densities.

To test the consistency of the experimental data, an integrated form of the Gibbs-Duhem equation was used.[7] It is hoped that the experimental data and the derived thermodynamical properties would not only be useful for these systems in particular, but also able to throw some light on the phase equilibrium problems in general.

III - THEORETICAL CONSIDERATIONS

When two or more components are present in a liquid mixture, the equilibrium vapor composition is in general different from that of the liquid. This fact forms the basis of the physical separation by distillation.

It would be desirable if one could derive theoretically the relationships between compositions of vapor and liquid and pressure or temperature for any liquid. Usually this is not possible for a real system and experimental determinations must be relied on. However, by applying thermodynamic principles, it is often possible to extend the experimental data under certain conditions, such as under constant temperature or pressure, to other conditions accurate enough for most engineering purposes.

When a liquid phase is at equilibrium with a vapor phase, the necessary and sufficient conditions of equilibrium are:

$$P_l = P_v$$

$$T_l = T_v$$

$$(\mu_l)_i = (\mu_v)_i$$

where P_l, P_v are the pressure and T_l, T_v are the temperature of the liquid phase and the vapor phase respectively, and $(\mu_l)_i$, $(\mu_v)_i$ are the chemical potential of component i in the liquid and the vapor phase respectively.

These three potentials form the basis of the thermodynamical analysis. Ibl and Dodge[10] have discussed Gibbs-Duhem equation in detail. Their derivation is presented in the following paragraph.

From Euler's theorem on homogeneous functions, the Gibbs free energy F can be expressed as

$$F = n_1\mu_1 + n_2\mu_2 + \text{---} + n_m\mu_m \qquad (1)$$

where n's are the number of moles of different components which are indicated by the subscripts: 1, 2 ---- m, and μ's are their chemical potentials. This equation may be differentiated at constant temperature and pressure with all components variable to give

$$dF = n_1 d\mu_1 + n_2 d\mu_2 + \mu_1 dn_1 + \mu_2 dn_2 + \text{---} + n_m d\mu_m + \mu_m dn_m \qquad (2)$$

The total differential of $F\ (T, P, n_1, n_2 \text{---} n_m)$ is

$$dF = \left(\frac{\partial F}{\partial P}\right)_{T,n_1,n_2,\text{--}n_m} dP + \left(\frac{\partial F}{\partial T}\right)_{P,n_1,n_2\text{--}n_m} dT + \left(\frac{\partial F}{\partial n_1}\right)_{P,T,n_2\text{--}n_m} dn_1 +$$

$$\left(\frac{\partial F}{\partial n_2}\right)_{P,T,n_1\text{--}n_m} dn_2 + \left(\frac{\partial F}{\partial n_m}\right)_{P,T,n_1,n_2\text{--}n_m} dn_m \qquad (3)$$

$$= VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \text{---} + \mu_m dn_m$$

where V is the total volume and S is the entropy of the liquid. Equating equations (2) and (3), one obtains

$$VdP - SdT = n_1 d\mu_1 + n_2 d\mu_2 + \text{---} + n_m d\mu_m$$

$$= \sum_{i=1}^{i=n} n_i d\mu_i \qquad (4)$$

which is the general form of the Gibbs-Duhem equation.

For a binary mixture, equation (4) is reduced to

$$VdP - SdT = n_1 d\mu_1 + n_2 d\mu_2 \qquad (5)$$

If equation (5) is divided by $n_1 + n_2$, we have

$$\cdots \quad V_m' dP - S' dT = x_1 d\mu_1 + (x_2) d\mu_2, \qquad (6)$$

where x's are the mole fractions of the liquid and V_m' and S' are the volume and entropy of one mole of the liquid phase. The special forms of Gibbs-Duhem equation for binary mixtures are given as follows:

1. At constant temperature

$$V_m' dP = x_1 d\mu_1 + (x_2) d\mu_2 \qquad (7)$$

or

$$V_m' dP = x_1 d\mu + (1-x_1) d\mu_2.$$

At equilibrium, $(\mu_1)_l = (\mu_v)_l$, and if combining equation (7) with

$d\mu = RT\ d \ln f$ at $T =$ constant, where f is the fugacity defined by Lewis and Randall[11] for gases, one obtains

$$\frac{V_m' dP}{RT} = x_1 d \ln f_1 + (1 - x_1) d \ln f_2 \text{ at } T = \text{constant}, \qquad (8)$$

or

$$\frac{d\ln f_1}{d\ln x_1} = \frac{d\ln f_2}{d\ln (1 - x_1)} + \frac{V'_m}{RT} \frac{dP}{dx}, \text{ at } T = \text{constant} \qquad (9)$$

where $\frac{dP}{dx}$ is the slope of the curve of the total pressure vs. the composition of the liquid phase at constant temperature. Usually the term:

$$\frac{V'_m}{RT} \frac{dP}{dx}$$

is negligible. Thus equation (8) becomes

$$\frac{d\ln f_1}{d\ln x_1} = \frac{d\ln f_2}{d\ln (1 - x_1)} \text{ at } T = \text{constant.} \qquad (10)$$

The P-x-y relationship of a binary mixture may be derived as follows:

The total differential of lnf's for the vapor are:

$$d\ln f_1 = \left(\frac{\partial \ln f_1}{\partial T}\right)_{P,y} dT + \left(\frac{\partial \ln f_1}{\partial P}\right)_{T,y} dP + \left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} d\ln y \qquad (11$$

and

$$d\ln f_2 = \left(\frac{\partial \ln f_2}{\partial T}\right)_{P,y} dT + \left(\frac{\partial \ln f_1}{\partial P}\right)_{T,y} dP + \left(\frac{\partial \ln f_2}{\partial \ln (1-y)}\right)_{T,P} d\ln(1-y) \qquad (12)$$

Where y denotes the mole fraction of a component in vapor. Substituting equations (11) and (12) in

$$\frac{V'_m}{RT} dP = x_1 d \ln f_1 + (1 - x_1) d \ln f_2 \qquad (8)$$

one obtains, if y is taken as the mole fraction in vapor of the component, the mole fraction of which in liquid is x_1

$$\frac{V'_m}{RT}\,dP = x\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,y} dT + \left(\frac{\partial \ln f_1}{\partial P}\right)_{T,y} dP + \left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} d\ln y. \quad (13)$$
$$+ (1-x)\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,P} dT + \left(\frac{\partial \ln f_2}{\partial P}\right)_{T,y} dP + \frac{\partial \ln f_2}{\partial \ln(1-y)_{T,y}} d\ln(1-y).$$

If equation (13) is combined with equations (14), (15) and (16)

$$\left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} = \left(\frac{\partial \ln f_2}{\partial \ln(1-y)}\right)_{T,P}, \quad (14)$$

$$\left(\frac{\partial \ln f_1}{\partial P}\right)_{T,y} = \frac{\bar{v}''_1}{RT}, \quad (15)$$

$$\left(\frac{\partial \ln f_2}{\partial P}\right)_{T,y} = \frac{\bar{v}''_2}{RT} \quad (16)$$

where $\bar{v}''_1$ and $\bar{v}''_2$ are the partial molal volume of the component 1 and 2 respectively, one obtains, at T = constant

$$\frac{V'_m}{RT}\,dP = x\left[\frac{\bar{v}''_1}{RT}\,dP + \left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} d\ln y\right] + (1-x)\left[\frac{\bar{v}''_2}{RT}\,dP + \left(\frac{\partial \ln f_2}{\partial \ln(1-y)}\right)_{T,P} d\ln(1-y)\right]. \quad (17)$$

On rearranging, this can be written

$$\frac{dP}{RT}\left[V'_m - x\bar{v}''_1 - (1-x)\,\bar{v}''_2\right] = x\left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} d\ln y + (1-x)\left(\frac{\partial \ln f_2}{\partial \ln(1-y)}\right)_{T,P} d\ln(1-y) \quad (18)$$

or

$$\frac{dP}{RT} = \frac{y-x}{y(1-y)\Delta V}\left[\frac{\partial \ln f_1}{\partial \ln y}\right]_{T,P} dy \quad \text{at } T = \text{constant} \quad (19)$$

where $\Delta V = x\bar{v}_1'' + (1 - x)\,\bar{v}_2'' - V_m'$.

Equation (19) is the exact P-x-y relationship at constant temperature for a binary mixture.

If the vapor phase is an ideal gas and if V_m' is much less than $x\bar{v}_1'' + (1 - x)\,\bar{v}_2'' = \frac{RT}{P}$,

then equation (19) is simplified to

$$\frac{dP}{P} = \frac{y - x}{y(1 - y)}\, dy. \tag{20}$$

2. At constant pressure

The total differentials of lnf are

$$d \ln f_1 = \left(\frac{\partial \ln f_1}{\partial T}\right)_{P,x} dT + \left(\frac{\partial \ln f_1}{\partial x}\right)_{T,P} dx \text{ at } P = \text{constant} \tag{21}$$

and

$$d\ln f_2 = \left(\frac{\partial \ln f_2}{\partial T}\right)_{P,x} dT + \left(\frac{\partial \ln f_2}{\partial (1-x)}\right)_{T,P} d\,(1-x) \text{ at } P = \text{constant} \tag{22}$$

Furthermore,

$$\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,x} = \frac{H_1^o - \bar{H}_1'}{RT^2} \tag{23}$$

$$\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,x} = \frac{H_2^o - H_1'}{RT^2} \tag{24}$$

Where H_1^o and H_2^o are the molal enthapy of the pure component 1 and 2 at the temperature and pressure of the mixture respectively and $\bar{H}_1'$ and $\bar{H}_2'$ are the partial molal enthapy of the components 1 and 2 respectively, hence

$$x \left(\frac{\partial \ln f_1}{\partial T}\right)_{P,x} = x \frac{H_1^o - \bar{H}_1'}{RT^2} \tag{25}$$

and

$$(1 - x)\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,x} = (1 - x)\frac{H_2^o - \bar{H}_2'}{RT^2} \qquad (26)$$

or

$$x\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,x} + (1 - x)\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,x} = \frac{\Delta H}{RT^2} \qquad (27)$$

where $\Delta H = x\bar{H}_1^o + (1-x)\bar{H}_2^o - x\bar{H}_1' - (1-x)\bar{H}_2'$ is heat of mixing

Because of

$$\left(\frac{\partial \ln f_1}{\partial x}\right)_{T,P} = \left(\frac{\partial \ln f_2}{\partial (1-x)}\right)_{T,P},$$

one obtains from equation (21) (22) and (27)

$$\frac{d\ln f_1}{d\ln x} = \frac{d\ln f_2}{d\ln(1-x)} + \frac{\Delta H}{RT^2}\frac{dT}{dx} \quad \text{at } P = \text{constant.} \qquad (28)$$

The exact T-x-y relationship may be derived in the same way as in the case of constant temperature and the equation is

$$\left[\frac{\Delta H}{RT^2} - x\left(\frac{\partial \ln f_1}{\partial T}\right)_{P,y} - (1-x)\left(\frac{\partial \ln f_2}{\partial T}\right)_{P,y}\right] dT = \left(\frac{\ln f_1}{\ln y}\right)_{T,P}\left[\frac{y-x}{y(1-y)}\right] dy \quad \text{at } P = \text{constant.} \qquad (29)$$

If the vapor is a mixture of ideal gases, equation (29) becomes

$$\frac{\Delta H}{RT^2} dT = \frac{x-y}{y(1-y)} dy \quad \text{at } P = \text{constant.} \qquad (30)$$

3. Gibbs-Duhem equation expressed in terms of the activity coefficient.

By definition, the activity coefficient is defined as

$$\gamma_1 = \frac{f_1}{f_1^o} / x_1 \qquad (31)$$

where f_1 and f_1^o are the fugarities of the component 1 in the mixture and of the pure component 1 at the temperature and pressure of the mixture.

The Gibbs-Duhem equation expressed in terms of the activity coefficient therefore are

$$\frac{d\ln\gamma_1}{d\ln x} = \frac{d\ln\gamma_2}{d\ln(1-x)} + [V_m' - xv_1'^o - (1-x)v_2'^o] \frac{1}{RT} \frac{dP}{dx}$$

$$\text{at } T = \text{constant}, \qquad (32)$$

and

$$\frac{d\ln\gamma_1}{d\ln x} = \frac{d\ln\gamma_2}{d\ln(1-x)} + [x\bar{H}_1' + (1-x)\bar{H}_2' - xH'^o_1 - (1-x)H'^o_2]$$

$$[\frac{1}{RT^2} \frac{dT}{dx}] \quad \text{at } P = \text{constant} \qquad (33)$$

where $V_m' - xv_1'^o - (1-x)v'^o_2$ is the volume change accompanying the mixing and $x\bar{H}_1'^o - (1-x)\bar{H}_2' - xH_1'^o - (1-x)H_2'^o$ is the integral heat of mixing.

A summary of the different forms of the Gibbs-Duhem equation is given in Table 1.

4. Integral form of Gibbs-Duhem equation for isobaric condition

For isothermal conditions the Gibbs-Duhem equations 2,4, and 6 in Table 1 should be used. Yet for the accuracy required for engineering purposes, the simplified equations

TABLE 1

Gibbs-Duhem Equation for Binary Mixtures

1.	General Form $VdP - SdT = x d\mu_1 + (1-x)\, d\mu_2$	
2.	$\frac{d \ln f_1}{d \ln x} = \frac{d \ln f_2}{d \ln(1-x)} + \frac{V_m'}{RT} \frac{dP}{dx}$	at T = constant
3.	$\frac{d \ln f_1}{d \ln x} = \frac{d \ln f_2}{d \ln(1-x)}$	at T = constant and V_m' negligible
4.	$\frac{dP}{RT} = \frac{y-x}{y(1-y)(x\bar{v}_1 + (1-x)\,\bar{v}_2 - V_m')} \left(\frac{\partial \ln f_1}{\partial \ln y}\right)_{T,P} dy$	at T = constant
5.	$\frac{dP}{P} = \frac{y-x}{y(1-y)}\, dy$	at T = constant V_m' negligible and vapor is a mixture of ideal gases.
6.	$\frac{d \ln \gamma_1}{d \ln x} = \frac{d \ln \gamma_2}{d \ln(1-x)} + [V_m' - xv_1'^{o} - (1-x)v_2'^{o}] \frac{1}{RT} \frac{dP}{dx}$	at T = constant

7. $\frac{d \ln\gamma_1}{d \ln x} = \frac{d \ln\gamma_2}{d \ln(1-x)}$

At T = constant
V'_m negligible

---

8. $\frac{d \ln f_2}{d \ln x} = \frac{d \ln f_2}{d \ln(1-x)} = \frac{\Delta H}{RT^2} \frac{dT}{dx}$

at P = constant

---

9. $[\frac{\Delta H}{RT^2} - x (\frac{\partial \ln f_1}{\partial T})_{P,y} - (1-x) (\frac{\partial \ln f_2}{\partial T})_{P,(1-x)}] dT$

$= (\frac{\partial \ln f_1}{\partial \ln y})_{T,P} (\frac{x-y}{y(1-y)}) dy$

at P = constant
and the vapor phase is a mixture of ideal gases.

---

10. $\frac{dT}{RT^2} = \frac{x-y}{y(1-y)\Delta H} dy$

at P = constant
and the vapor phase is a mixture of ideal gases.

---

11. $\frac{d \ln\gamma_1}{d \ln x} = \frac{d \ln\gamma_2}{d \ln(1-x)} - \frac{H}{RT^2} \frac{dT}{dx}$ at P = constant

where $H = x\bar{H}'_1 + (1-x)\bar{H}'_2 - xH'^{o}_1 - (1-x)H'^{o}_2$ is the integral heat of mixing.

3, 5, and 7 may be used. On these equations are based most of the semi-empirical forms of the Gibbs-Duhem equation. However, for isobaric conditions, usually equations 8, 9 and 11 should be used.

It is usually required to evaluate a thermodynamic property of one component from the values for the other component or one thermodynamic property from the values for other thermodynamic properties. Thus an integrated form of the Gibbs-Duhem equation is needed. Many integral forms of this equation have been developed.[1-8]

The integral equation for isobaric condition of a binary mixture can be derived as follows:

The excess free energy is defined as

$$\Delta F^E = \Delta F_{mix} - \Delta F^{id}_{mix} \tag{34}$$

where

$$\Delta F_{mix} = n_1(\mu_1 - \mu_1^o) + n_2(\mu_2 - \mu_2^o); \tag{35}$$

and F^{id}_{mix} is the free energy of mixing of an ideal solution. Because of $\mu = RT \ln f = RT \ln f^o \times \gamma$, at T = constant, we have

$$\Delta F_{mix} = \sum_i n_i RT \ln x_i + \sum_i n_i RT \ln \gamma_i \tag{36}$$

and

$$\Delta F^{id}_{mix} = \sum_i n_i RT \ln x_i, \tag{37}$$

because $\gamma = 1$ for ideal solution.

Substituting (36) and (37) in (34), we have

$$\Delta F^E = \sum_i n_i RT \ln \gamma_i . \qquad (38)$$

If a function Q is defined as

$$Q = \frac{\Delta F^E}{\sum_i n_i RT}$$

then (38) becomes

$$Q = \sum_i x_i \ln \gamma_i \qquad (39)$$

For a binary mixture, this reduces to

$$Q = x_1 \ln \gamma_1 + (1-x_1) \ln \gamma_2 \quad \text{at } T = \text{constant and } P = \text{constant} \qquad (40)$$

On differentiating equation (40) with respect to x_1 one obtains

$$\frac{dQ}{dx_1} = x_1 \frac{d \ln \gamma_1}{d x_1} + \ln \gamma_1 + x_2 \frac{d \ln \gamma_2}{d x_1} - \ln \gamma_2 . \qquad (41)$$

If equation (41) is combined with the Gibbs-Duhem equation

$$\frac{x_1 \, d \ln \gamma_1}{d x_1} + \frac{x_2 \, d \ln \gamma_2}{d x_1} = \frac{\Delta H}{RT^2} \, dT, \quad \text{at } P = \text{constant}$$

then we get

$$\frac{dQ}{dx_1} - \ln \frac{\gamma_1}{\gamma_2} = \frac{\Delta H}{RT^2} \frac{dT}{dx} . \qquad (42)$$

The final integrated form for isobaric condition is

$$\int_{x_1=o}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} \, dx = - \int_{T \text{ at } x_1=o}^{T \text{ at } x_1=1} \frac{\Delta H}{RT^2} \, dT \qquad (43)$$

because of

$$\int_{x_1=o}^{x_1=1} dQ = 0$$

In this equation, γ_1 and γ_2 can be calculated from experimentally determined values of the equilibrium temperature and composition. If $\ln \frac{\gamma_1}{\gamma_2}$ is plotted against x_1, the left-hand side of equation (44) can be evaluated graphically. If ΔH is known as an analytical function of temperature, the right-hand side of equation (44) can be integrated or if ΔH is experimentally determined, then the right-hand side can be evaluated graphically.

5. Adjustment of data

Redlich and Kister[7] have developed an expression for the function Q as a power series of (x_1-x_2) which is

$$Q = x_1 \ln\gamma_1 + x_2 \ln\gamma_2$$
$$= x_1 x_2 [B+C(x_1-x_2) + D(x_1-x_2)^2 + \ldots] \qquad (44)$$

On differentiating equation (44) with respect to x_1, one obtains

$$\frac{dQ}{dx_1} = \ln \frac{\gamma_1}{\gamma_2} = B(x_1-x_2) + C[6x_1(1-x_1)-1] + D(x_1-x_2)[1-8x_1(1-x_1)] + \ldots \qquad (45)$$

Equations (44) and (45) are for the condition of constant temperature and pressure. For isobaric condition, when the temperature range is small, equation (44) may be used to represent the relationship between the activity coefficient and the liquid composition. Because the temperature coefficient of γ is small within small temperature range, it is sometimes justified to use equation (45) for representing isobaric data. The constants B, C, D etc. may be calculated by using the

experimentally determined liquid compositions and the calculated values of γ_1 and γ_2 from the experimentally determined data of temperature, vapor and liquid compositions. From the evaluated constants, the curves for $\ln \frac{\gamma_1}{\gamma_2}$ vs. x_1 can be further adjusted. By analogy with the binary system,

$$Q_{12} = x_1 x_2 [B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2 + \ldots] , \qquad (46)$$

Redlich and Kister proposed that the Q function for the ternary may be also represented by

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3[C + D_1(x_2-x_3) + D_2(x_3-x_1) + D_3(x_1-x_2) + \ldots] \qquad (47)$$

and

$$\begin{aligned} \ln \frac{\gamma_1}{\gamma_2} = {} & B_{12}(x_1-x_2)+C_{12}[(x_1-x_2)^2 - 2x_1x_2 \\ & + D_{12}(x_1-x_2)[(x_1-x_2)^2 - 4x_1x_2] + \ldots \\ & + x_3 [B_{23}-B_{31} + C_{23}(2x_2-x_3) + C_{31}(2x_1-x_3) \\ & + D_{23}(3x^2-4x_2x_3+x_3^2) - D_{31}(3x_1^2-4x_1x_3+x_3^2) \\ & + C(x_1-x_2) + D_1(-x_1x_3+2x_1x_2+x_2x_3-x_2^2) \\ & + D_2(x_3x_1+2x_1x_2-x_2x_3-x_1^2) \\ & + D_3(x_1^2 - 4x_1x_2 + x_2^2) + \ldots \quad . \end{aligned} \qquad (48)$$

Cyclic permutation of the subscripts gives the corresponding expressions for $\ln \gamma_2/\gamma_3$ or $\ln \gamma_1/\gamma_3$. The constants in the equation (47) or (48) may be determined in the same way as for the binary systems.

IV - EXPERIMENTAL DETAILS

1. Apparatus

There are several types of the equilibrium still commonly used for the determination of the vapor-liquid equilibrium at atmospheric pressure, vacuum and elevated pressures. [9, 12, 13,] Gillespie[9] was the first person proposing to circulate both the vapor and the liquid phase by means of a Cottrell pump which brings up a mixture of vapor-liquid onto the outside wall of the thermowell. Thus the temperature measured is close to the true equilibrium one. Furthermore, the partial condensation and entrainment of the liquid in the vapor sample are eliminated. Besides supplying heat for boiling, the internal heater also forms vapor bubbles that will thoroughly stir the contents of the boiling flask. The vapor then carries some liquid into the Cottrell pump. The mixture is separated in the equilibrium chamber. The equilibrium still used in the present work is illustrated in Fig. 1. It is a recirculating still of Gillespie type, modified by Fowler and Morris. They modified the original Gillespie still by the addition of a liquid receiver. The liquid separated in the equilibrium chamber flows to the liquid receiver and returns to the boiling flask. A sample withdrawn from this receiver is the liquid that is in equilibrium with the vapor in the equilibrium chamber. The capillary placed in the return line of the vapor condensate

FOWLER — NORRI'S STILL OF GILLESPIE TYPE WITH MODIFICATIONS

A. BOILING FLASK

B. RECEIVER FOR CONDENSATE

C. RECEIVER FOR LIQUID

R. EQUILIBRIUM CHAMBER

S. CONDENSER

P. COTTRELL PUMP

H. INTERNAL HEATER

T. THERMO WELL

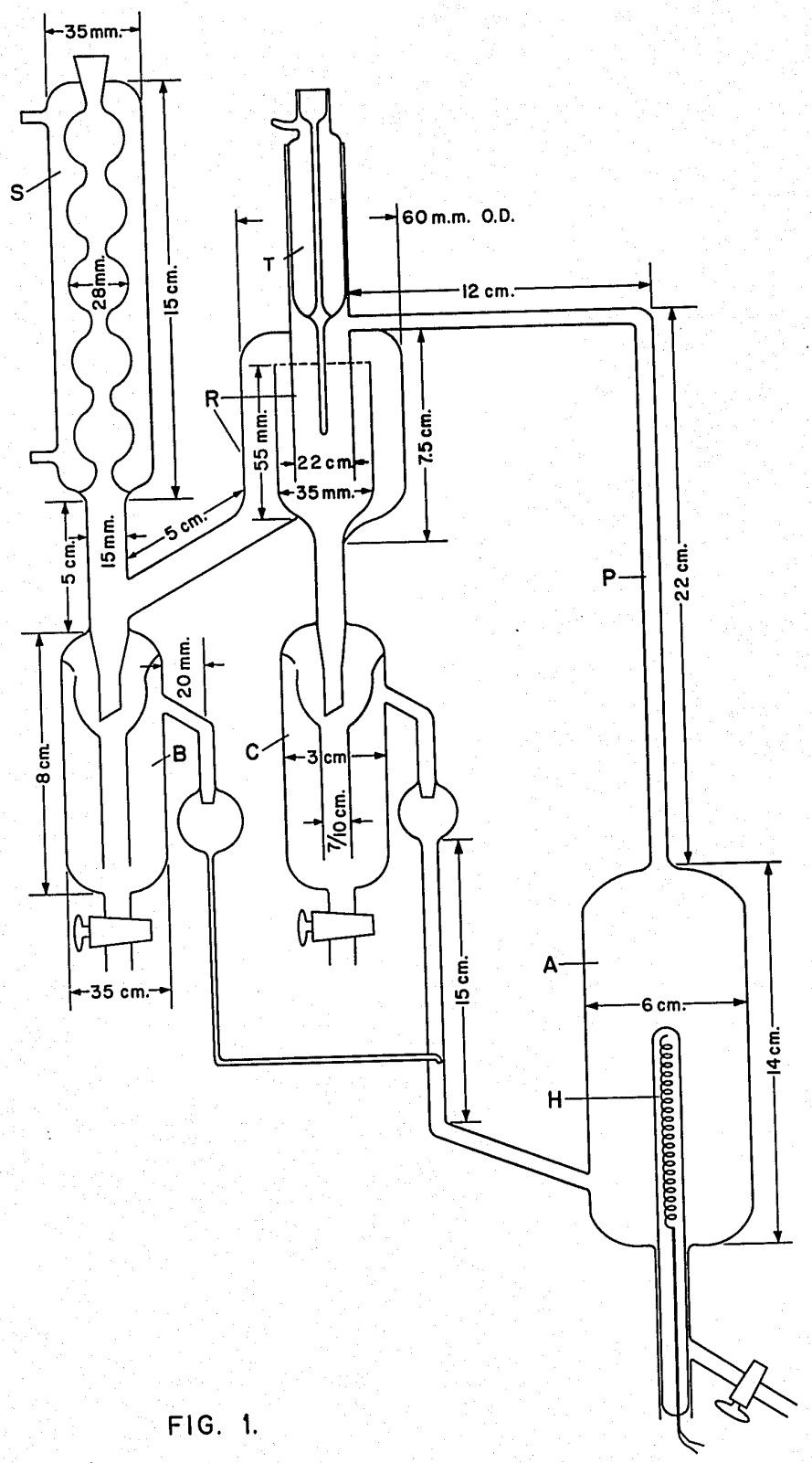


FIG. 1.

decreases the holdup of the liquid and minimizes the fluctuation of the level of the liquid during boiling. The present apparatus differs from the modified model in three essential aspects.

(1) To obtain better measurement of equilibrium temperature, a vacuum-sealed double-jacket glass thermowell was used for the insertion of the hot junction of the thermocouple.

(2) For better mixing in the liquid and the vapor condensate receivers, a double-jacket tube was used instead of the simple tubing.

(3) The internal heater in the original still is placed at the top of the boiler. Air bubbles may form around the opening where the heater is inserted and also the liquid might come out of the opening. The internal heater used for the present investigation was placed at the bottom of the boiler to avoid these phenomena.

The still was made of Pyrex glass. The boiler was heated both externally and internally. The internal heater was a 100-watt Brown and Co. total immersion glass-sealed wire-wound A.C. resistor, provided by the United Glassblowing Laboratory. The external heater consisted of 1/2 inch electrothermal heating tape having a resistance of five ohms per foot, wound evenly around the boiler. The heating elements were connected to separate variable-voltage autotransformers from a 110-volt A.C. power supply. The Cottrell tube and the equilibrium chamber were insulated with asbestos and raw silk. The temperature of

the equilibrium mixture was measured by a copper-constantan thermocouple. The cold junction was immersed in an ice-water bath in a Dewar flask. The hot junction was placed in the thermowell of the still. In the thermowell a few drops of silicone 704 of Dow Corning Silicones Ltd was added to provide a good contact for the lead of the thermocouple. The thermocouple was calibrated by the courtesy of the Physical Testing Department of the National Research Council of Canada. The accuracy was of ± 0.02° C. over the required temperature range. For interpolation, a table was kindly supplied by Dr. T.W. Dauphinee of the National Research Council. Densities were determined at the temperature of the sample by weighing pycnometers with a Gram-atic balance. Refractive indices were determined with a Bausch and Lomb ABBE-3L precision refractometer using a sodium vapor lamp illuminator. The glass-piece of the refractometer was maintained at 25° C ± 0.05° C by circulating water of a constant temperature from a water bath in a tubing under the glass-piece.

Auxiliary apparatus included the following items:

(1) Potentiometer

The Potentiometer used was a Leeds and Northrup Universal Type K-3 potentiometer with limits of error of ± 0.01 + 20μv for the high range (0-1.611 volt); ± 0.015% + 2μv for the medium range (0-0.6110 volt) and ± 0.015% + 0.5μv for the low range (0-0.016110 volt).

(2) A galvanometer

The galvanometer used was a Tinsley type SRI suspension model.

(3) A working cell

The working cell was an Exide Tytex 2-volt lead-acid battery made by the Electric Storage Co. Canada Ltd.

(4) A standard cell

The standard cell was an 1149-type saturated cell of Tinsley Instrument Ltd., Smith Falls, Ontario, Canada. Its EMF was 1.01859 absolute volts at 20° C.

2. Material

Carbon tetrachloride, cyclohexane and isopropyl alcohol of the spectroquality of Matheson Coleman and Bell were used. The refractive indices, and normal boiling points of these liquids were determined and the comparions of these values with the accepted ones[14] are listed in Table 2.

TABLE 2

Physical Properties of the Chemicals

	Normal Boiling Point		Refraction Index	
	Observed	Literature	Observed	Literature
Carbon tetrachloride	76.61° C	76.75° C	1.4570	1.45704
Cyclohexane	80.70° C	80.73° C	1.4235	1.42354
Isopropyl Alcohol	82.01° C	82.19° C	1.3750	1.3749

3. Measurement

(1) Charging the still

The still was dried with filtered dry air and rinsed with one of the pure components of the liquid to be used. Then it was filled with the liquid. Distilled water, ethanol and the mixture of both were used for testing the performance of the still and the accuracy of the temperature measurement. Excellent agreement was found for the boiling point of ethanol and water with the accepted values for them and with the data of Otsuki and Williams[14] for the system: ethanol and water as shown in Table 3.

TABLE 3

Experimental Vapor-liquid Equilibrium Data

of the System: Ethanol-water at the Pressure of 760mm Hg.

Equilibrium Temperature in °C	Vapor Mole Fraction of Ethanol	Liquid Mole Fraction of Ethanol
95.34	0.162	0.015
89.92	0.334	0.052
85.07	0.470	0.134
80.95	0.610	0.386
78.46	0.792	0.759

Normal Boiling Point

	Observed	Literature
Ethanol	78.24° C	78.33° C
Water	99.91° C	100.0° C

For the binary systems, the still was filled with the less volatile component first. The boiling point of the pure component was determined. Then mixtures of increasing amount of the more volatile component were used for successive runs.

For the ternary systems, mixtures of fixed composition of isopropyl alcohol and cyclohexane were prepared and increasing amount of carbon tetrachloride was added for successive runs.

(2) Procedure

a) The boiler, the liquid receiver and the vapor condensate receiver were filled with the mixture for the run.

b) The two heaters were switched on simultaneously. The external heater was adjusted to supply slightly less heat than that from the internal heater. As soon as the Cottrell tube started pumping liquid and vapor into the equilibrium chamber, cooling water was admitted to the condenser, on top of which a reducing tube with a small amount of silica gel was placed to prevent the moisture in the air from contaminating the condensate. The heating was adjusted until the liquid in the enlarged tube around the drop counter gently pulsates and the condensed vapor and the liquid dropped into the drop counter at a desired rate of approximately 30 drops a minute. The heating was continued until temperature showed no change on successive potentiometer reading. To ensure true equilibrium, ample time was allowed for each run. On the average, five hours was allowed.

c) Observations made during operations:

(i) Take barometer reading.

(ii) Check the reference junction temperature.

(iii) Take potentiometer reading.

(iv) Withdraw the liquid and the vapor samples simultaneously into separate volumetric bottles which were kept in ice. A small amount of liquid from each receiver was first discarded.

(v) Take readings of the refractive indices of the samples, each time checking the temperature of the water bath which should be at 25° C.

(vi) Weigh the samples in a pycnometer and take the temperature of the sample in the pycnometer.

(3) Calibration

a) Analysis of the samples of the binary systems

Refractive index readings were taken for binary mixtures of known composition at 25° C as given in Tables 4, 5, 6.

TABLE 4

Calibration: Refractive Index of the Mixtures: Carbon Tetrachloride and Cyclohexane

	Mole Fraction of CCl_4	N_D^{25}
1.	0.063	1.4247
2.	0.150	1.4272
3.	0.202	1.4290
4.	0.272	1.4314
5.	0.352	1.4344
6.	0.379	1.4351
7.	0.463	1.4381
8.	0.540	1.4409
9.	0.623	1.4437
10.	0.736	1.4478
11.	0.758	1.4500
12.	0.889	1.4537

TABLE 5

Calibration: Refractive Index of the Mixtures: Carbon Tetrachloride and Isopropyl Alcohol

	Mole Fraction of CCl_4	N_D^{25}
1.	0.036	1.3788
2.	0.065	1.3814
3.	0.105	1.3854
4.	0.149	1.3895
5.	0.172	1.3913
6.	0.273	1.4000
7.	0.309	1.4031
8.	0.464	1.4167
9.	0.551	1.4234
10.	0.694	1.4342
11.	0.735	1.4374
12.	0.748	1.4382
13.	0.852	1.3891
14.	0.877	1.4473

TABLE 6

Calibrations Refractive Index of the Mixtures:

Cyclohexane and Isopropyl Alcohol

	Mole Fraction of CCl_4	n_D^{25}
1.	0.044	1.3770
2.	0.078	1.3787
3.	0.120	1.3810
4.	0.156	1.3824
5.	0.190	1.3846
6.	0.297	1.3901
7.	0.400	1.3955
8.	0.516	1.4007
9.	0.544	1.4022
10.	0.600	1.4048
11.	0.709	1.4094
12.	0.775	1.4125
13.	0.861	1.4165

Charts were prepared from the Tables for the analysis of the samples.

Densities were measured from the same mixtures at the temperature of the mixture as given in Tables 7, 8, 9.

TABLE 7

Density of the Mixture:

Carbon Tetrachloride and Cyclohexane

Density of Mixture: C_6H_{12} and CCl_4 27.5% CCl_4

Refractive Index 1.4314

Temperature in Degree Centigrade	Density in gr./cc.
19.8	0.98544
18.8	0.98658
22.3	0.98250
21.4	0.98335
15.3	0.99047
16.5	0.98918

Density of Mixture: C_6H_{12} and CCl_4 35.3% CCl_4

Refractive Index 1.4344

Temperature in Degree Centigrade	Density in gr./cc.
19.7	1.06025
19.1	1.06920
15.6	1.06538
22.2	1.05726
21.7	1.05757

Density of Mixture: C_6H_{12} and CCl_4 45.8% CCl_4

Refractive Index 1.4381

Temperature in Degree Centigrade	Density in gr./cc.
20.1	1.14633
18.9	1.14789
16.5	1.15076
22.3	1.14329
21.8	1.14394
15.3	1.15226

Density of Mixture: C_6H_{12} and CCl_4 62.4% CCl_4

Refractive Index 1.4437

Temperature in Degree Centigrade	Density in gr./cc.
19.7	1.28612
19.1	1.28725
16.0	0.88571
18.7	0.88178
22.4	0.87621
21.3	1.28350

Density of Mixture: C_6H_{12} and CCl_4 73.3% CCl_4

Refractive Index 1.4478

Temperature in Degree Centigrade	Density in gr./cc.
20.4	1.37822
19.0	1.37893
22.1	1.37516
21.3	1.37671
15.5	1.38627
16.8	1.38438

TABLE 8

Density of the Mixtures:

Carbon Tetrachloride and Isopropyl Alcohol

Density of Mixtures: C_3H_8O and CCl_4 19.9% CCl_4

Refractive Index 1.3937

Temperature in Degree Centigrade	Density in gr./cc.
22.7	0.97614
20.0	0.97886
20.1	0.97785
23.4	0.97649
19.7	0.97899
19.3	0.97942
18.0	0.98059
17.1	0.98036

Density of Mixtures: C_3H_8O and CCl_4 36.4% CCl_4

Refractive Index 1.4081

Temperature in Degree Centigrade	Density in gr./cc.
18.8	1.1068
19.8	1.1054
22.3	1.1020
21.1	1.1036

Density of Mixtures: C_3H_8O and CCl_4 38.6% CCl_4

Refractive Index 1.4100

Temperature in Degree Centigrade	Density in gr./cc.
23.0	1.1448
21.9	1.1466
17.6	1.1534
20.4	1.1487
23.8	1.1437
19.9	1.1487
19.1	1.1495

Density of Mixtures: C_3H_8O and CCl_4 45.3% CCl_4

Refractive Index 1.4156

Temperature in Degree Centigrade	Density in gr./cc.
19.4	1.1691
18.0	1.1710
18.9	1.1698
22.5	1.1647
22.3	1.1657
20.2	1.1680

Density of Mixtures: C_3H_8O and CCl_4 58.9% CCl_4

Refractive Index 1.4264

Temperature in Degree Centigrade	Density in gr./cc.
20.5	1.3070
22.2	1.3044
23.7	1.3021
21.3	1.3052
19.4	1.3085
17.9	1.3107

Density of Mixtures: C_3H_8O and CCl_4 79.7% CCl_4

Refractive Index 1.4420

Temperature in Degree Centigrade	Density in gr./cc.
22.5	1.4524
23.6	1.4513
20.1	1.4582
19.4	1.4590
21.4	1.4555
17.6	1.4620
17.7	1.4619
21.6	1.0994
19.4	1.1036
17.9	1.1076

TABLE 9

Density of the Mixture:

Cyclohexane and Isopropyl Alcohol

Density of Mixtures: C_3H_8O and C_6H_{12} 27.4 Mole % C_6H_{12}

Refractive Index 1.3890

Temperature in Degree Centigrade	Density in gr./cc.
22.5	0.77773
22.8	0.77730
19.8	0.77995
22.9	0.77713
19.9	0.78008
19.4	0.78060
20.7	0.77934
20.5	0.77957
19.5	0.78032
19.7	0.78025
28.3	0.77243
27.9	0.77278
20.1	0.77980
19.9	0.78003
19.5	0.78041
17.8	0.78146

24.5	0.77596
21.7	0.77872
26.6	0.77407
23.5	0.77698

Density of Mixture: C_3H_8O and C_6H_{12} 39.7 Mole % of C_6H_{12}

Refractive Index 1.3953

Temperature in Degree Centigrade	Density in gr./cc.
18.4	0.77923
21.2	0.77724
25.6	0.77322
23.8	0.77496
18.2	0.77979
25.1	0.77371
18.9	0.77941
24.4	0.77424
22.1	0.77639
23.3	0.79010
22.9	0.77602
15.9	0.78194
20.3	0.77794

Density of Mixtures: C_3H_8O and C_6H_{12} 49.4 Mole % C_6H_{12}

Refractive Index 1.4000

Temperature in Degree Centigrade	Density in gr./cc.
22.0	0.77468
25.3	0.77165
18.8	0.77784
19.9	0.77682
21.3	0.77554
23.5	0.77354
17.8	0.77869

Density of Mixtures: C_3H_8O and C_6H_{12} 51.5 Mole % C_6H_{12}

Refractive Index 1.4009

Temperature in Degree Centigrade	Density in gr./cc.
19.2	0.77710
21.3	0.77501

Density of Mixtures: C_3H_8O and C_6H_{12} 75.8 Mole % C_6H_{12}

Refractive Index 1.4117

Temperature in Degree Centigrade	Density in gr./cc.
20.4	0.77546
22.5	0.77346
25.0	0.77124

Density of Mixture: C_3H_8O and C_6H_{12} 64.8 Mole % C_6H_{12}

Refractive Index 1.4069

Temperature in Degree Centigrade	Density in gr./cc.
20.2	0.77494
24.4	0.77117
20.3	0.77503
18.3	0.77679
28.4	0.76733
20.3	0.77511
21.2	0.77396
19.6	0.77565
22.4	0.77317
25.8	0.76985
23.7	0.77186

Density of Mixture: C_3H_8O and C_6H_{12} 80 mole % of C_6H_{12}

Refractive Index 1.4134

Temperature in Degree Centigrade	Density in gr./cc.
21.0	0.77433
18.6	0.77654
21.5	0.77360
20.4	0.77520
15.4	0.77931
16.8	0.77822

Density of Mixture: C_3H_8O and C_6H_{12} 86 Mole % C_6H_{12}
Refractive Index 1.4165

Temperature in Degree Centigrade	Density in gr./cc.
21.2	0.77447
15.6	0.77960
16.9	0.77847
17.6	0.77675
19.3	0.77617
21.2	0.77441

Density of Mixture: C_3H_8O and C_6H_{12} 86.1 Mole % C_6H_{12}
Refractive Index 1.4165

Temperature in Degree Centigrade	Density in gr./cc.
21.2	0.77447
15.6	0.77960
16.9	0.77847
17.6	0.77675
19.3	0.77617
21.2	0.77441

A chart was drawn of temperature vs. log of density with composition as an additional parameter for each mixture. In the temperature ranges used the relationship was found to be linear. From these lines, a curve for density vs. composition was drawn for the particular temperature at which the density was determined. From this curve the composition of the sample was read.

The composition of the vapor and the liquid samples of the binary systems was read from the refractive index charts and the density charts. The two readings were found to be in agreement.

b) Analysis of the samples of the ternary system.

Thirty-five testing mixtures were prepared from five binary mixtures of cyclohexane and isopropyl alcohol and different amount of carbon tetrachloride. Refractive Indices and densities were determined for each mixture as were for the binary mixtures. The refractive indices and the densities of the ternary mixtures were given in Table 10.

TABLE 10

Refraction Index and the Denisty of the Mixture: Carbon Tetrachloride, Cyclohexane and Isopropyl Alcohol

Calibration for the System: 1. Carbon Tetrachloride CCl_4

2. Cyclohexane C_6H_{12}

and 3. Isopropyl Alcohol C_3H_8O

	Composition in mole fraction			Ref. Index		Density in gr./cc.		
	CCl_4	C_6H_{12}	C_3H_8O					
1.	0.1106	0.2225	0.6669	1.3957	Temp.	26.8°C 0.87324	26.7°C 0.87332	26.0°C 0.87422
					Temp.	23.9°C 0.87646	23.6°C 0.87639	
2.	0.2125	0.1969	0.5906	1.4035	Temp.	25.7°C 0.96376	25.1°C 0.96460	24.1°C 0.96563
3.	0.3371	0.1657	0.4972	1.4126	Temp.	25.0°C 1.07087	19.9°C 1.07689	21.7°C 1.07508
						22.9°C 1.07323		
4.	0.4643	0.1339	0.4018	1.4210	Temp.	24.2°C 1.17705	20.0°C 1.17948	22.5°C 1.17991
					Temp.	23.2°C 1.17797	15.7°C 1.19270	

(Table 10, continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.		
	CCl_4	C_6H_{12}	C_3H_8O				
5.	0.5864	0.1034	0.3102	1.4293	Temp. 20.7°C 1.27958	22.7°C 1.27594	23.6°C 1.27420
					Temp. 22.5°C 1.27671	20.4°C 1.28082	15.1°C 1.29062
					Temp. 19.5°C 1.28215		
6.	0.7302	0.0675	0.2023	1.4390	Temp. 20.0°C 1.39167	18.3°C 1.39592	21.2°C 1.39043
					Temp. 22.0°C 1.38941	23.0°C 1.38649	
7.	0.8640	0.03399	0.1020	1.4479	Temp. 14.2°C 1.50816	19.6°C 1.49428	21.6°C 1.49129
					Temp. 22.3°C 1.48993	24°C 1.48583	23.1°C 1.48783
8.	0.1119	0.3330	0.5551	1.4020	Temp. 21.8°C 0.873357	19.9°C 0.875922	20.3°C 0.874856
					Temp. 22.4°C 0.872664	23.1°C 0.871199	19.2°C 0.877426
9.	0.1977	0.3009	0.5014	1.4095	Temp. 20.1°C 0.977880	21.6°C 0.976111	22.1°C 0.975024
					Temp. 23.0°C 0.972052	23.3°C 0.973105	20.1°C 0.978256

(Table 10, continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.		
	CCl_4	C_6H_{12}	C_3H_8O				
10.	0.3516	0.2432	0.4053	1.4172	Temp. 16.1°C	19.9°C	21.3°C
					1.08602	1.08048	1.07878
					Temp. 21.4°C	23.1°C	22.8°C
					1.07819	1.07482	1.07596
11.	0.4750	0.1969	0.3281	1.4249	Temp. 19.3°C	20.2°C	22.4°C
					1.18282	1.17984	1.17799
					Temp. 22.2°C	23.1°C	20.3°C
					1.17726	1.17647	1.18191
12.	0.6097	0.1464	0.2440	1.4329	Temp. 16.5°C	18.4°C	18.8°C
					1.295595	1.29277	1.29165
					Temp. 19.6°C	20.7°C	21.9°C
					1.28996	1.28782	1.28570
13.	0.7375	0.0985	0.1641	1.4410	Temp. 19.5°C	19.5°C	21.7°C
					1.39292	1.39233	1.38744
					Temp. 22.3°C	23.0°C	19.4°C
					1.38638	1.38495	1.39277
14.	0.8689	0.0491	0.0819	1.4492	Temp. 18.4°C	18.9°C	19.8°C
					1.49701	1.49634	1.49354
					Temp. 22.3°C	22.4°C	20.9°C
					1.48927	1.48872	1.49295

(Table 10), continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.			
	CCl_4	C_6H_{12}	C_3H_8O					
15.	0.1164	0.4418	0.4418	1.4065	Temp.	20.5°C	19.5°C	20.4°C
						0.875510	0.876474	0.875817
					Temp.	21.9°C	21.6°C	
						0.873388	0.872958	
16.	0.2436	0.3762	0.3782	1.4131	Temp.	20.4°C	21.6°C	22.0°C
						0.981690	0.980036	0.978734
					Temp.	23.7°C	17.9°C	23.4°C
						0.976790	0.983670	0.976729
17.	0.3640	0.3180	0.3180	1.4211	Temp.	18.9°C	18.9°C	21.4°C
						1.08182	1.08117	1.07726
					Temp.	21.7°C	23.7°C	24.4°C
						1.07675	1.07375	1.07269
18.	0.4937	0.2532	0.2532	1.4280	Temp.	21.5°C	18.9°C	20.1°C
						1.17855	1.18423	1.18151
					Temp.	21.0°C	22.4°C	24.7°C
						1.18060	1.17725	1.17332
19.	0.6175	0.1912	0.1912	1.4355	Temp.	20.3°C	18.6°C	20.5°C
						1.28752	1.29114	1.28784
					Temp.	20.5°C	23.6°C	
						1.28708	1.28200	

(Table 10, continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.			
	CCl_4	C_6H_{12}	C_3H_8O					
20.	0.7457	0.1215	0.1215	1.4426	Temp.	19.8°C	19.4°C	21.6°C
						1.39313	1.39235	1.38794
					Temp.	23.0°C	19.5°C	22.0°C
						1.38591	1.39471	1.38796
21.	0.8751	0.06245	0.06245	1.4501	Temp.	20.1°C	19.1°C	21.4°C
						1.49596	1.49759	1.49204
					Temp.	23.2°C	20.8°C	21.5°C
						1.48875	1.49414	1.49309
22.	0.1210	0.5494	0.3296	1.4120	Temp.	19.8°C	20.2°C	21.2°C
						0.87425	0.87359	0.87203
					Temp.	21.6°C	22.9°C	19.3°C
						0.87172	0.87025	0.87533
23.	0.2501	0.4687	0.2812	1.4183	Temp.	20.9°C	20.1°C	21.5°C
						0.97821	0.97912	0.97712
					Temp.	18.2°C	19.7°C	21.9°C
						0.981873	0.97976	0.97644
24.	0.3809	0.3870	0.2322	1.4246	Temp.	20.1°C	17.9°C	20.8°C
						1.08727	1.08912	1.08434
					Temp.	20.0°C	21.0°C	23.9°C
						1.08602	1.08443	1.07947

(Table 10, continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.			
	CCl_4	C_6H_{12}	C_3H_8O					
25.	0.4996	0.3128	0.1876	1.4316	Temp.	18.6°C	16.7°C	21.1°C
						1.18517	1.18901	1.18184
					Temp.	21.7°C	22.6°C	23.1°C
						1.18038	1.17862	1.17307
26.	0.6234	0.2354	0.1412	1.4380	Temp.	20.6°C	19.3°C	21.2°C
						1.28199	1.28524	1.28210
					Temp.	18.8°C	19.9°C	22.5°C
						1.28630	1.28325	1.27891
27.	0.7535	0.1540	0.0924	1.4441	Temp.	18.9°C	19.6°C	20.6°C
						1.39386	1.39163	1.38911
					Temp.	21.2°C	22.0°C	22.6°C
						1.38842	1.38647	1.38548
28.	0.8788	0.0720	0.0492	1.4508	Temp.	19.6°C	20.9°C	21.9°C
						1.49538	1.49319	1.49115
					Temp.	22.2°C	23.0°C	23.3°C
						1.49101	1.48846	1.48791
29.	0.1243	0.6568	0.2189	1.4165	Temp.	21.2°C	19.7°C	22.2°C
						0.87232	0.87397	0.87085
					Temp.	22.8°C	22.8°C	21.6°C
						0.86942	0.86974	0.87222

(Table 10, continued)

	Composition in mole fraction			Ref. Index	Density in gr./cc.			
	CCl_4	C_6H_{12}	C_3H_6O					
30.	0.2269	0.5798	0.1933	1.4228	Temp.	20.2°C	22.5°C	22.8°C
						0.82589	0.97428	0.97400
					Temp.	23.2°C	21.1°C	
						0.97221	0.97809	
31.	0.3845	0.4616	0.1539	1.4280	Temp.	22.6°C	20.6°C	21.4°C
						1.07736	1.08048	1.07975
					Temp.	21.7°C	20.7°C	21.8°C
						1.07899	1.08104	1.07834
32.	0.5133	0.3651	0.1217	1.4335	Temp.	22.1°C	23.2°C	24.1°C
						1.18278	1.18122	1.17899
					Temp.	24.7°C	25.1°C	21.7°C
						1.17815	1.17538	1.18426
33.	0.6312	0.2766	0.09220	1.4390	Temp.	19.4°C	21.9°C	22.5°C
						1.28422	1.28075	1.27979
					Temp.	23.8°C	24.7°C	21.7°C
						1.27631	1.27450	1.28195
34.	0.7596	0.1903	0.0601	1.4456	Temp.	17.9°C	19.7°C	20.1°C
						1.39404	1.39102	1.39040
					Temp.	22.2°C	21.5°C	20.9°C
						1.38352	1.38750	1.38863
35.	0.8751	0.09370	0.03124	1.4512	Temp.	18°C	19.0°C	20.4°C
						1.49218	1.48953	1.48669
					Temp.	21.4°C	20.8°C	23.1°C
						1.48469	1.48625	1.48195

Graphs drawn to provide the analysis of the ternary systems were listed as following:

First set: Refractive index vs. mole fraction of carbon tetrachloride with the five binary mixtures as an additional parameter.

Second set: Temperature vs. log of density with mole fraction of CCl_4 as an additional parameter. Five sets of this graph were drawn, one for each binary mixtures of cyclohexane and isopropyl alcohol.

Third set: Density vs. mole fraction of carbon tetrachloride with the five binary mixtures as an additional parameter.

Fourth set: Compositions read from curve of the first set corresponding to the refractive index determined for the samples were joined in a curve in a triangular graph paper. Another curve was drawn on the same graph paper with compositions read from the third set of graphs. The composition corresponding to the intersection of the two curves in the triangular graph paper was read as the composition of the sample analyzed.

V - RESULTS

1. Binary systems

The measured composition of the liquid and the vapor in equilibrium and the equilibrium temperature are presented in Tables 11, 12 and 13 and Fig. 2, 3, 4, 5, 6 and 7.

Azeotropes were found for the system: carbon tetrachloride and isopropyl alcohol and the system: cyclohexane and isopropyl alcohol. Values are listed in Table 14. The values are in close agreement with literature values.[15]

TABLE 11

Experimental Data of the System 1 2

Carbon Tetrachloride and Cyclohexane

Run	Equilibrium Temperature in Degree Centigrade at 760mm Hg. Pressure	Composition in Mole Fraction of Carbon Tetrachloride	
		Vapor y_1	Liquid x_1
1	80.34	0.068	0.045
2	79.60	0.155	0.124
3	79.66	0.163	0.134
4	79.17	0.230	0.201
5	58.88	0.273	0.256
6	79.10	0.220	0.201
7	76.74	0.805	0.791
8	77.06	0.693	0.675
9	77.07	0.696	0.685
10	77.40	0.600	0.579
11	77.53	0.569	0.540
12	77.63	0.545	0.519
13	78.06	0.436	0.412
14	78.46	0.345	0.314
15	78.80	0.285	0.260
16	79.25	0.230	0.198
17	79.54	0.171	0.146
18	79.73	0.135	0.113
19	78.07	0.427	0.404

TABLE 12

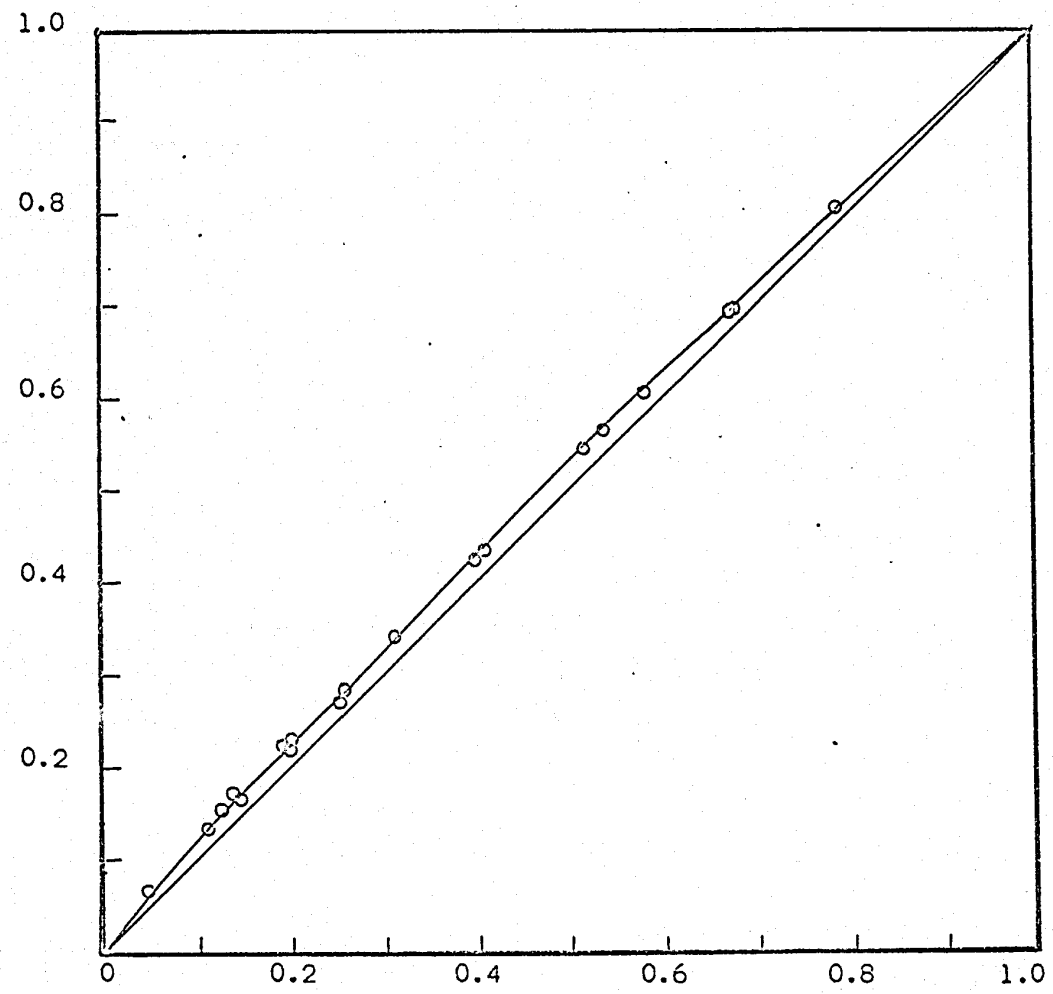
Experimental Data of the System:
Carbon Tetrachloride[1] and Isopropyl Alcohol[2]

Run	Equilibrium Temperature in Degree Centigrade at 760 mm Hg Pressure	Composition in Mole Fraction of Carbon Tetrachloride	
		Vapor y_1	Liquid x_1
1	79.15	0.138	0.058
2	75.71	0.283	0.104
3	74.90	0.210	0.138
4	71.62	0.438	0.236
5	69.28	0.742	0.847
6	69.00	0.708	0.789
7	68.75	0.629	0.603
8	69.15	0.584	0.422
9	71.78	0.433	0.225
10	70.12	0.497	0.317
11	70.63	0.473	0.289
12	70.51	0.483	0.294
13	72.54	0.399	0.190
14	74.27	0.306	0.140
15	69.54	0.500	0.343
16	71.40	0.842	0.946
17	74.79	0.940	0.989

TABLE 13

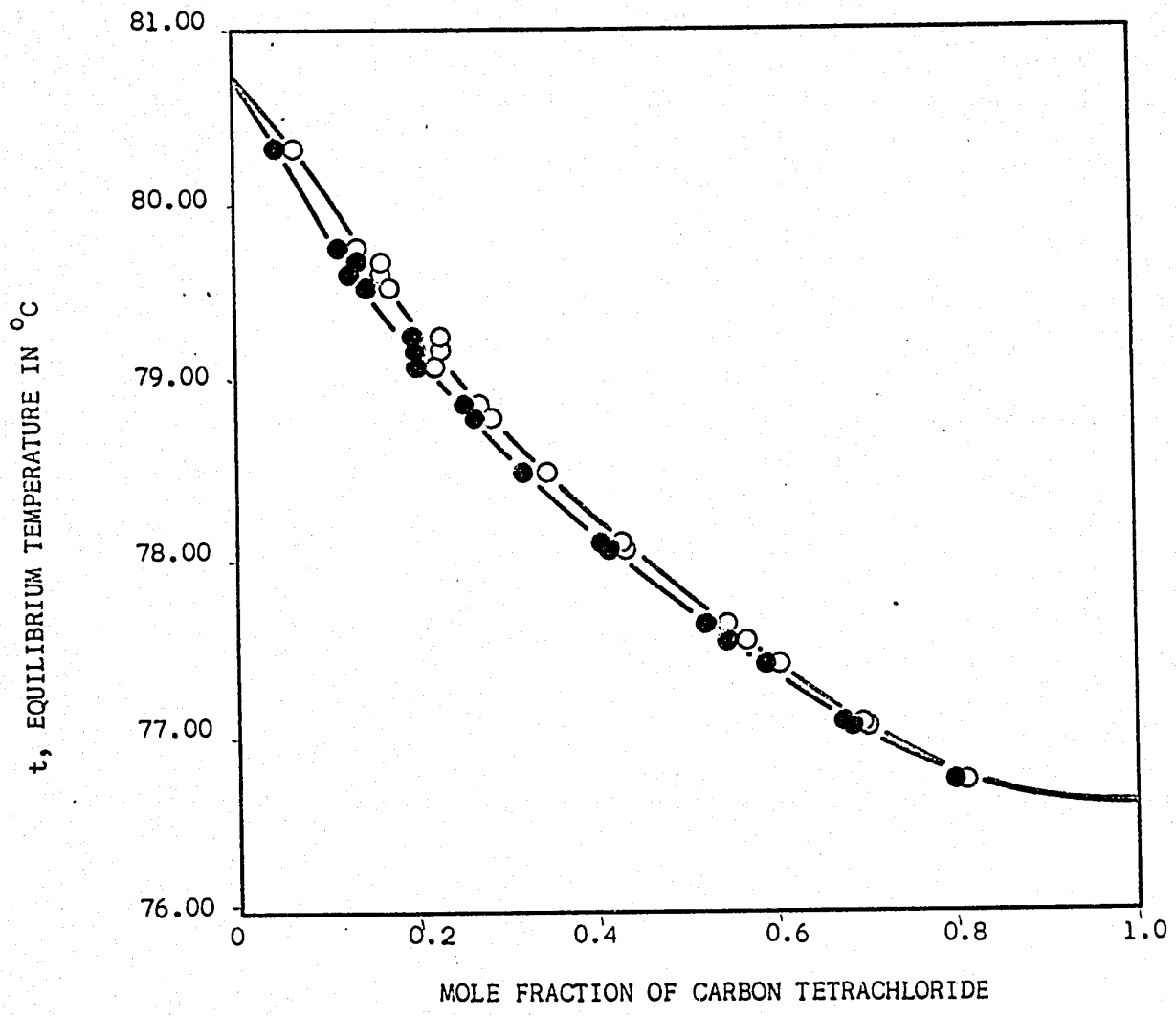
Experimental Data of the System:
1 2
Cyclohexane and Isopropyl Alcohol

Run	Equilibrium Temperature in Degree Centigrade at 760 mm Hg Pressure	Composition in Mole Fraction of Carbon Tetrachloride	
		Vapor y_1	Liquid x_1
1	69.35	0.555	0.473
2	69.37	0.550	0.442
3	69.01	0.582	0.538
4	69.10	0.627	0.708
5	69.45	0.660	0.784
6	69.20	0.570	0.516
7	68.80	0.583	0.528
8	69.21	0.605	0.631
9	69.42	0.649	0.742
10	69.66	0.673	0.807
11	70.11	0.697	0.862
12	71.50	0.773	0.921
13	74.01	0.838	0.990
14	76.73	0.893	0.995
15	74.96	0.283	0.116
16	74.80	0.276	0.120
17	72.28	0.271	0.191
18	70.19	0.489	0.306
19	69.11	0.568	0.518
20	69.14	0.572	0.516
21	69.02	0.548	0.485
22	69.08	0.582	0.571
23	69.06	0.595	0.640
24	74.74	0.850	0.978
25	70.31	0.709	0.873
26	78.71	0.112	0.027
27	76.91	0.218	0.070



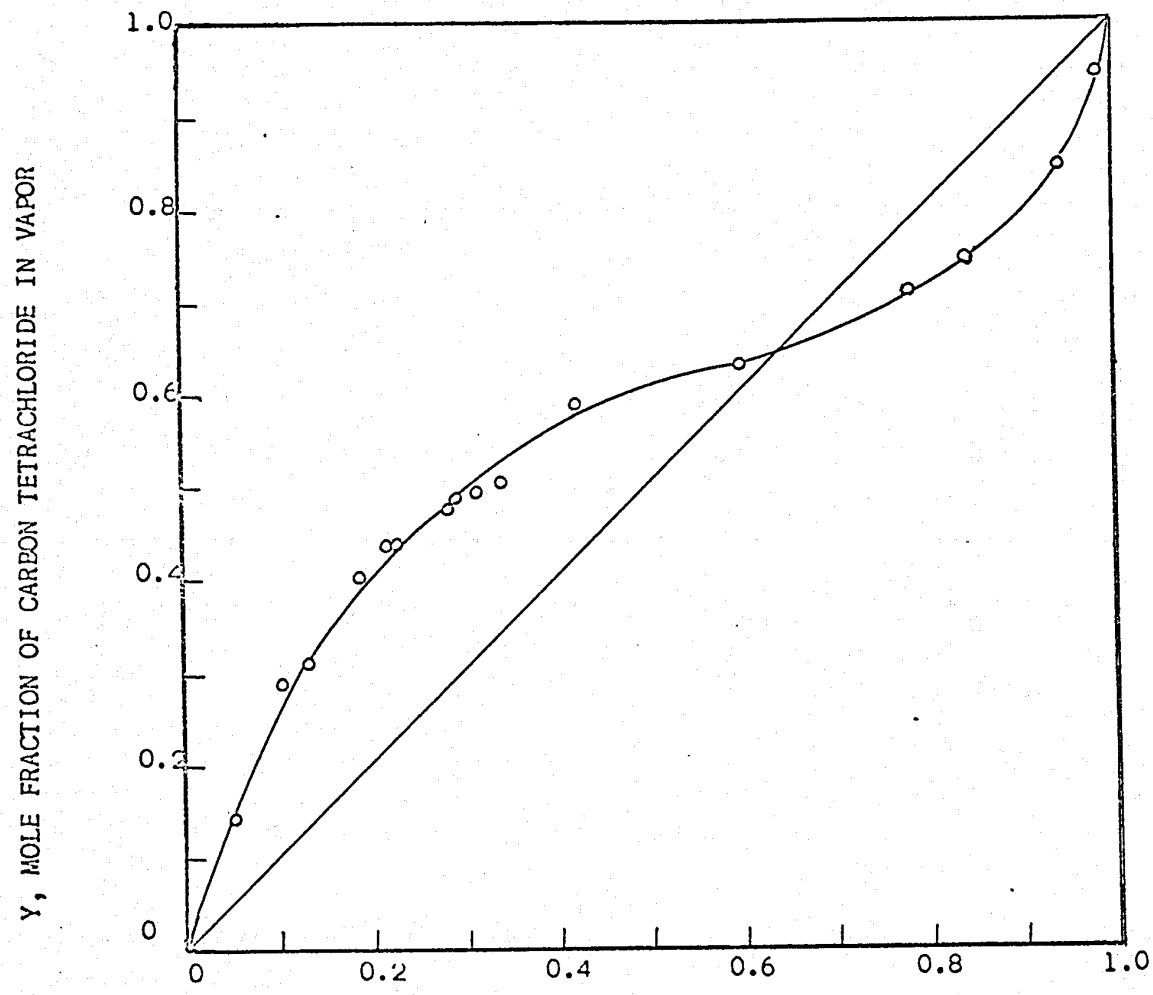
VAPOR-LIQUID PHASE EQUILIBRIUM DIAGRAM FOR THE SYSTEM: CARBON TETRALCHLORIDE AND CYCLOHEXANE AT PRESSURE OF 760 m m Hg.

FIG. 2



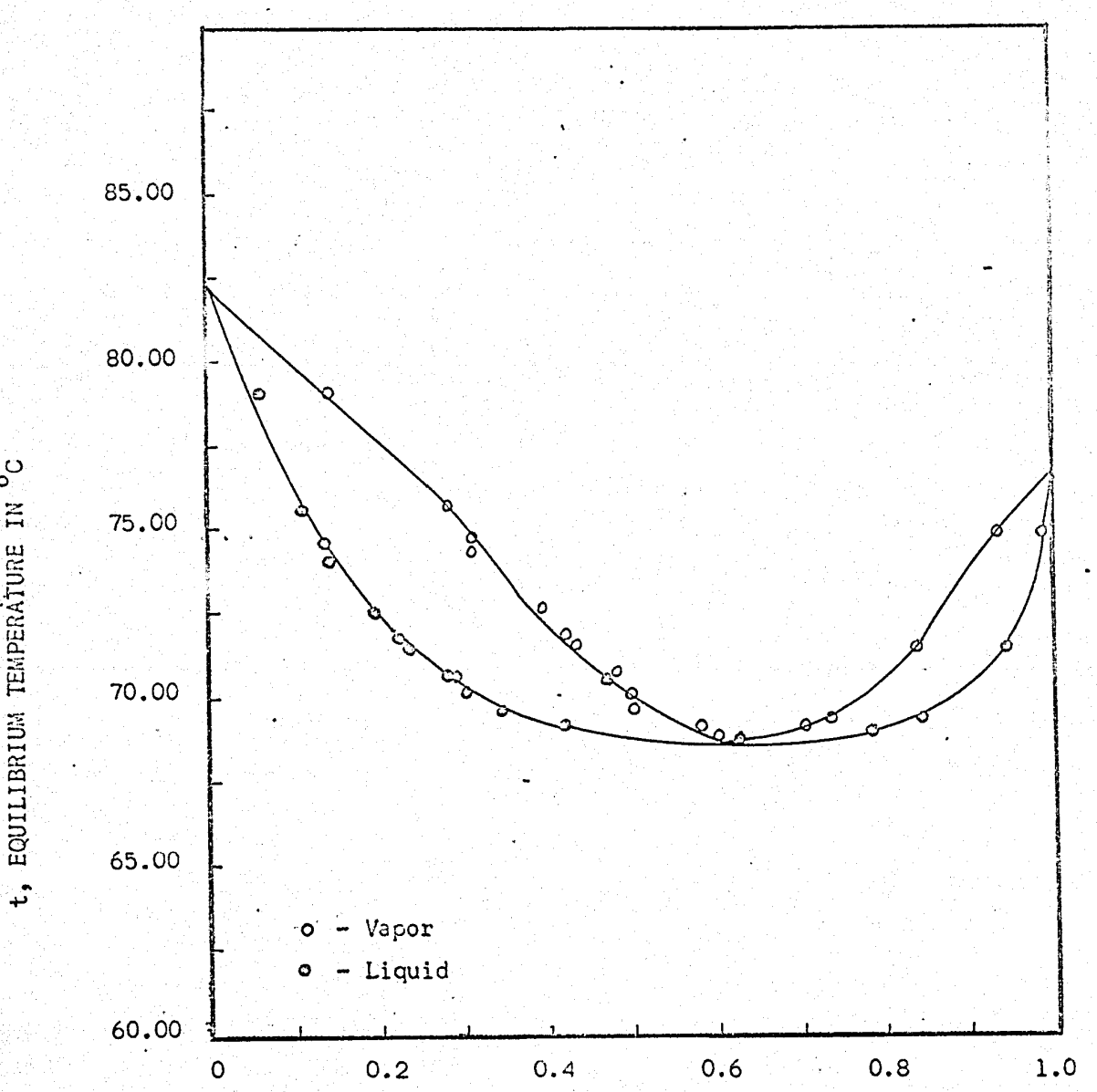
TEMPERATURE-COMPOSITION DIAGRAM FOR THE SYSTEM: CARBON TETRACHLORIDE AND CYCLOHEXANE AT PRESSURE OF 760 m m Hg

FIG. 3



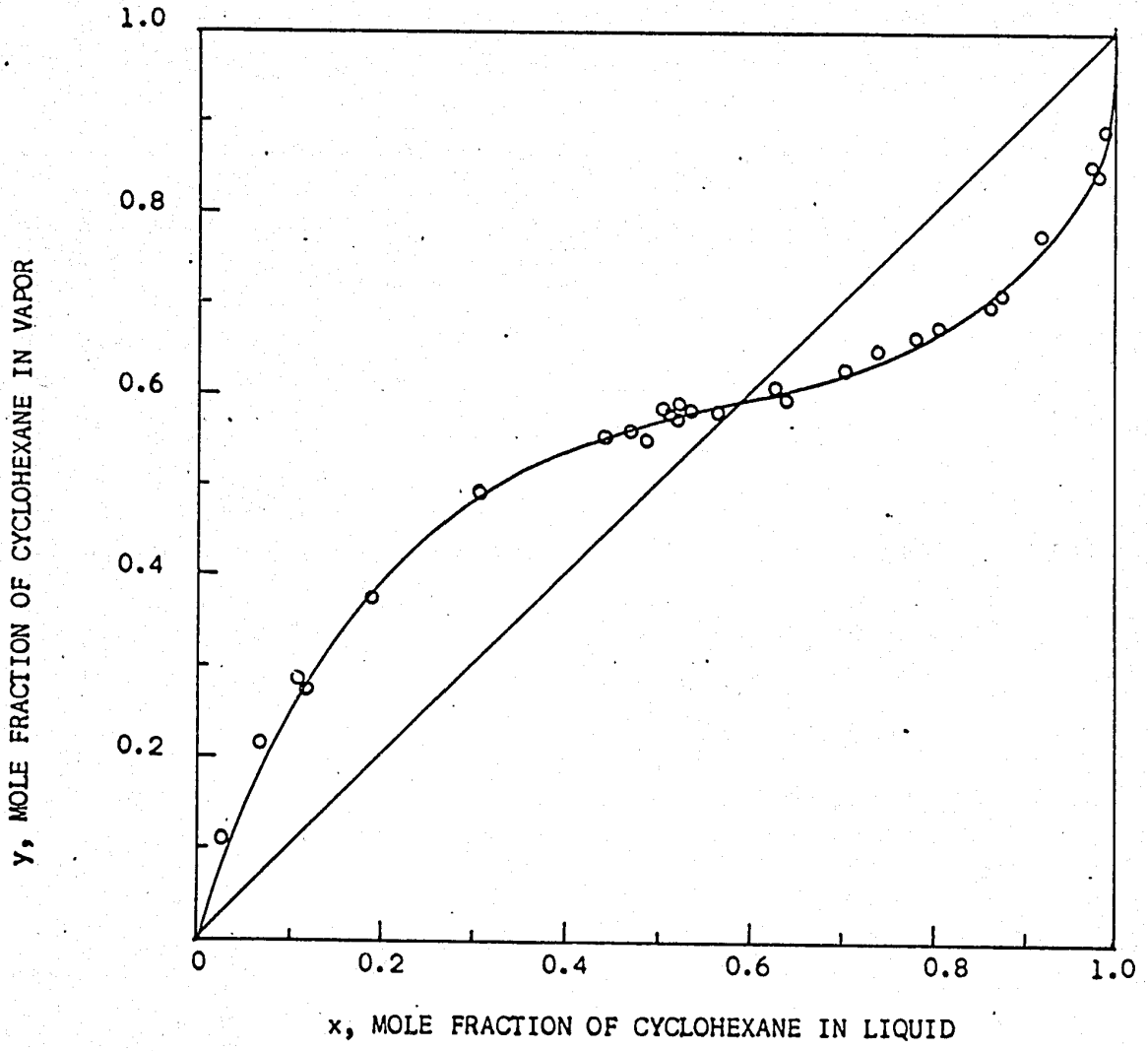
VAPOR-LIQUID PHASE EQUILIBRIUM DIAGRAM FOR THE SYSTEM: CARBON TETRACHLORIDE AND ISOPROPYL ALCOHOL AT PRESSURE OF 760 mm Hg.

FIG. 4



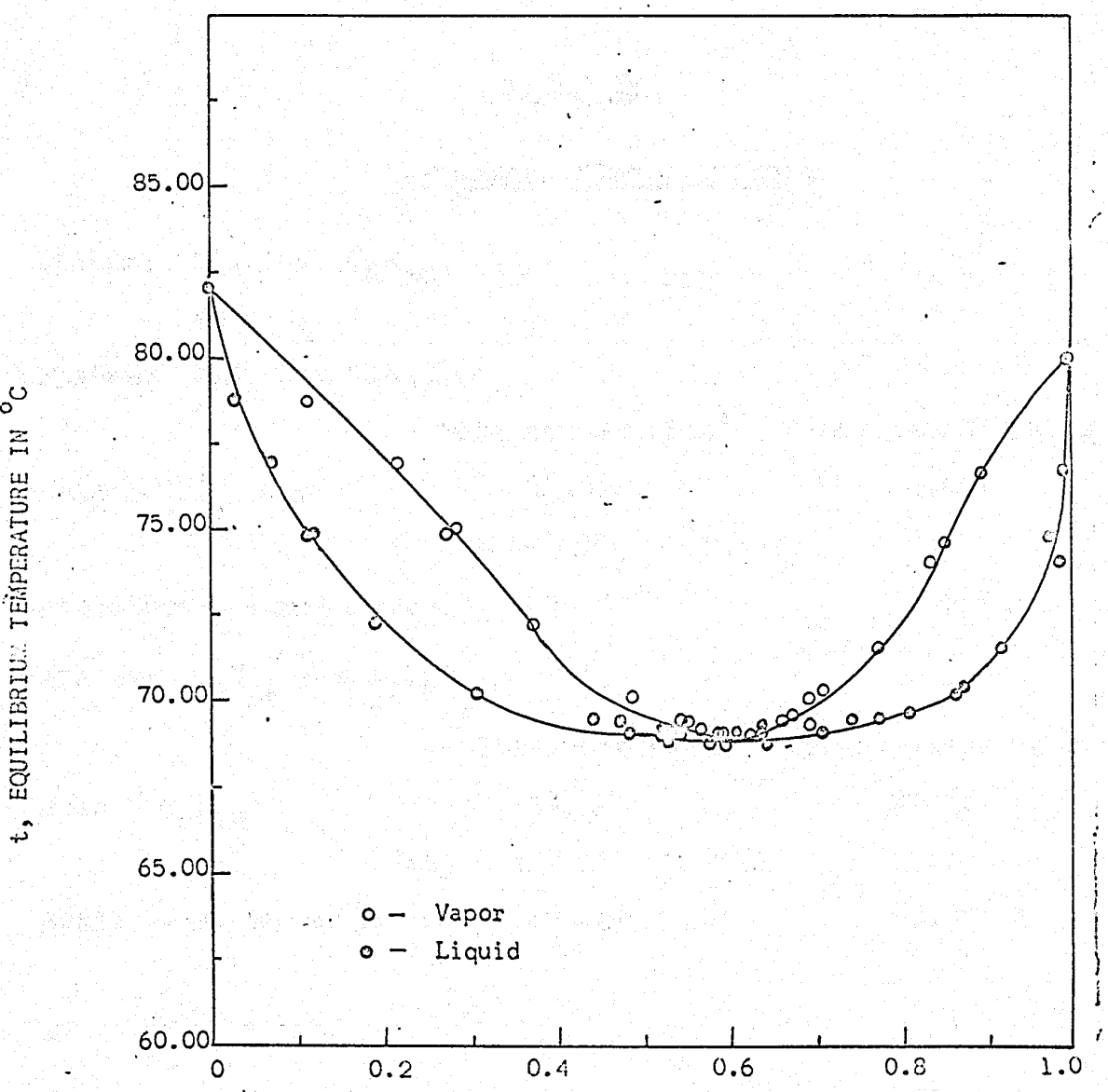
TEMPERATURE-COMPOSITION DIAGRAM FOR THE SYSTEM: CARBON TETRACHLORIDE AND ISOPROPYL ALCOHOL AT PRESSURE OF 760 mm Hg.

FIG. 5



VAPOR-LIQUID PHASE EQUILIBRIUM DIAGRAM FOR THE SYSTEM:
CYCLOHEXANE AND ISOPROPYL ALCOHOL AT PRESSURE OF 760 m m Hg.

FIG. 6



TEMPERATURE-COMPOSITION DIAGRAM FOR THE SYSTEM: CYCLOHEXANE AND ISOPROPYL ALCOHOL AT PRESSURE OF 760 m m Hg.

FIG. 7

TABLE 14

Azeotropes Binary Systems

System: CCl_4 and C_6H_{12}

None

System: CCl_4 and C_3H_8O

	Literature value[15]	Experimental value
Mole % CCl_4 =	64.02%	64.0%
	(wt. % of CCl_4 = 82%)	
Equilibrium temperature	68.95° C	68.65° C

System: C_6H_{12} and C_3H_8O

	Literature value[15]	Experimental value
Mole % C_6H_{12}	59.25%	59.2%
	(wt. % of C_3H_8O = 33%)	
Equilibrium temperature	68.60° C	68.80° C

2. Ternary system

The measured composition of the liquid and the vapor in equilibrium and the equilibrium temperature of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol are presented in Table 15 and Fig. 8, 9, 10, 11, 12 and 13.

There is an azeotrope in the neighborhood of the mixture of composition 0.48 mole fraction of carbon tetrachloride, 0.18 mole fraction of cyclohexane and 0.34 mole fraction of isopropyl alcohol where a lowest equilibrium temperature of 68.40°C was recorded.

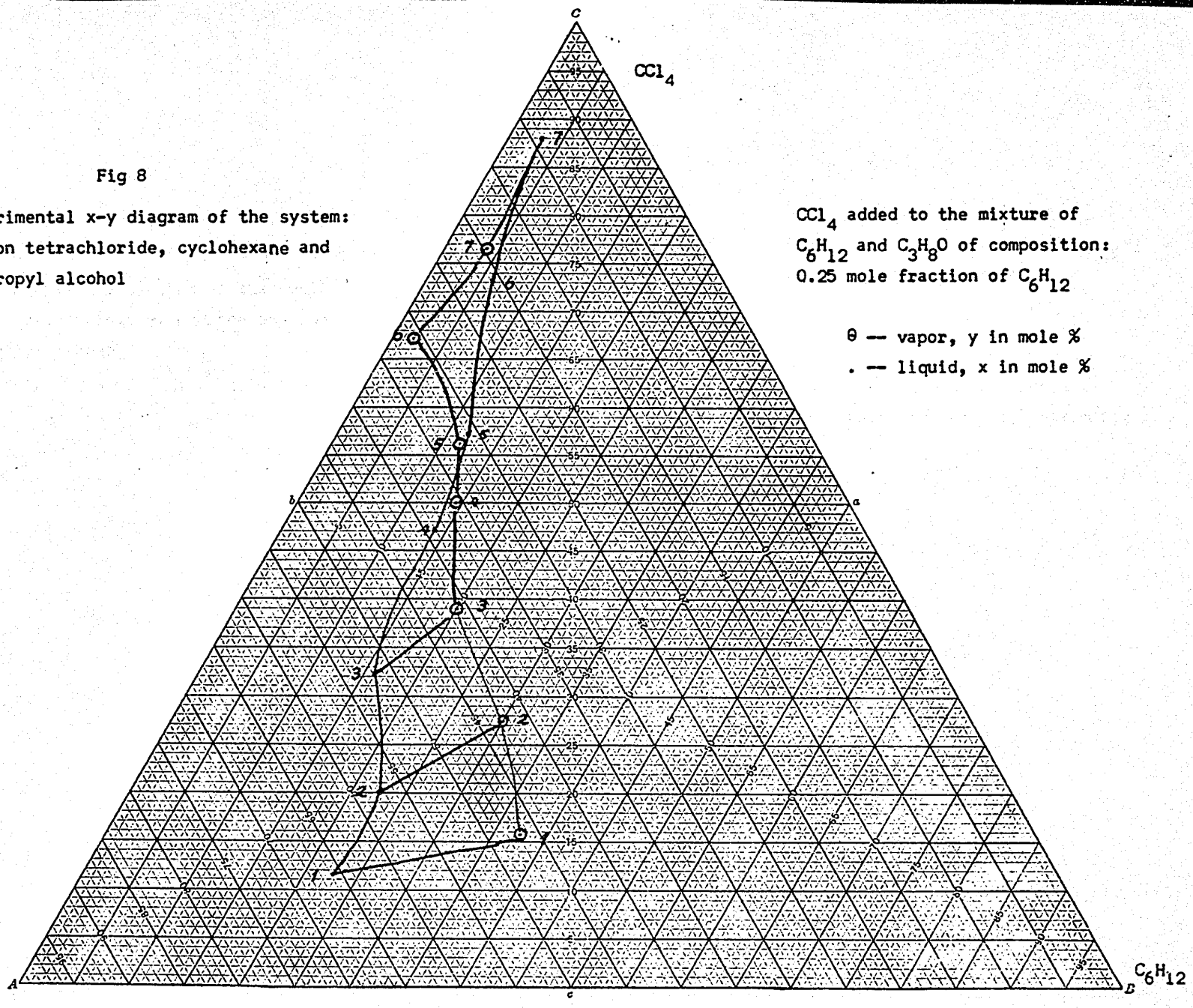
TABLE 15

Experimental Data of the System:
1 2 3
Carbon Tetrachloride, Cyclohexane and Isopropyl Alcohol

Run	Equilibrium Temperature	Composition of Vapor in Mole Fraction			Composition of Liquid in Mole Fraction		
	in °C	y_1	y_2	y_3	x_1	x_2	x_3
1	70.17	0.155	0.376	0.469	0.118	0.224	0.658
2	69.28	0.273	0.294	0.433	0.202	0.219	0.579
3	68.82	0.389	0.198	0.413	0.326	0.154	0.520
4	68.55	0.502	0.139	0.359	0.473	0.135	0.392
5	68.45	0.563	0.111	0.326	0.567	0.118	0.315
6	68.80	0.672	0.013	0.315	0.730	0.055	0.215
7	70.10	0.763	0.037	0.200	0.875	0.032	0.093
8	69.10	0.147	0.428	0.425	0.119	0.367	0.514
9	68.40	0.413	0.233	0.354	0.307	0.223	0.390
10	68.44	0.338	0.337	0.325	0.406	0.163	0.431
11	68.45	0.480	0.172	0.348	0.483	0.172	0.345
12	68.60	0.577	0.132	0.291	0.622	0.145	0.233
13	69.00	0.661	0.086	0.253	0.757	0.103	0.140
14	72.90	0.893	0.021	0.086	0.952	0.022	0.026
15	68.80	0.133	0.485	0.382	0.117	0.447	0.436
16	68.60	0.229	0.403	0.368	0.222	0.379	0.399
17	68.50	0.344	0.309	0.347	0.351	0.320	0.329
18	68.62	0.451	0.215	0.434	0.489	0.240	0.271
19	68.84	0.551	0.165	0.284	0.617	0.192	0.191
20	69.55	0.650	0.108	0.242	--	--	--
21	71.50	0.801	0.063	0.136	0.884	0.058	0.058
22	68.75	--	--	--	0.122	0.561	0.317
23	68.60	0.231	0.441	0.328	0.253	0.473	0.274
24	68.60	0.343	0.346	0.311	0.380	0.394	0.226
25	68.40	0.477	0.195	0.328	0.481	0.179	0.340
26	68.30	0.560	0.201	0.239	0.630	0.241	0.129
27	69.00	0.586	0.252	0.162	0.725	0.090	0.185
28	72.30	0.827	0.066	0.107	0.893	0.068	0.039
29	69.10	0.126	0.557	0.317	0.133	0.667	0.200
30	69.10	0.224	0.486	0.290	0.356	0.399	0.245
31	69.40	0.345	0.388	0.267	0.397	0.472	0.131
32	69.60	0.457	0.292	0.251	0.524	0.379	0.097
33	70.20	0.653	0.077	0.270	--	--	--
34	71.60	0.699	0.163	0.138	0.770	0.179	0.051
35	72.16	0.848	0.078	0.074	0.889	0.077	0.034

Fig 8

Experimental x-y diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol



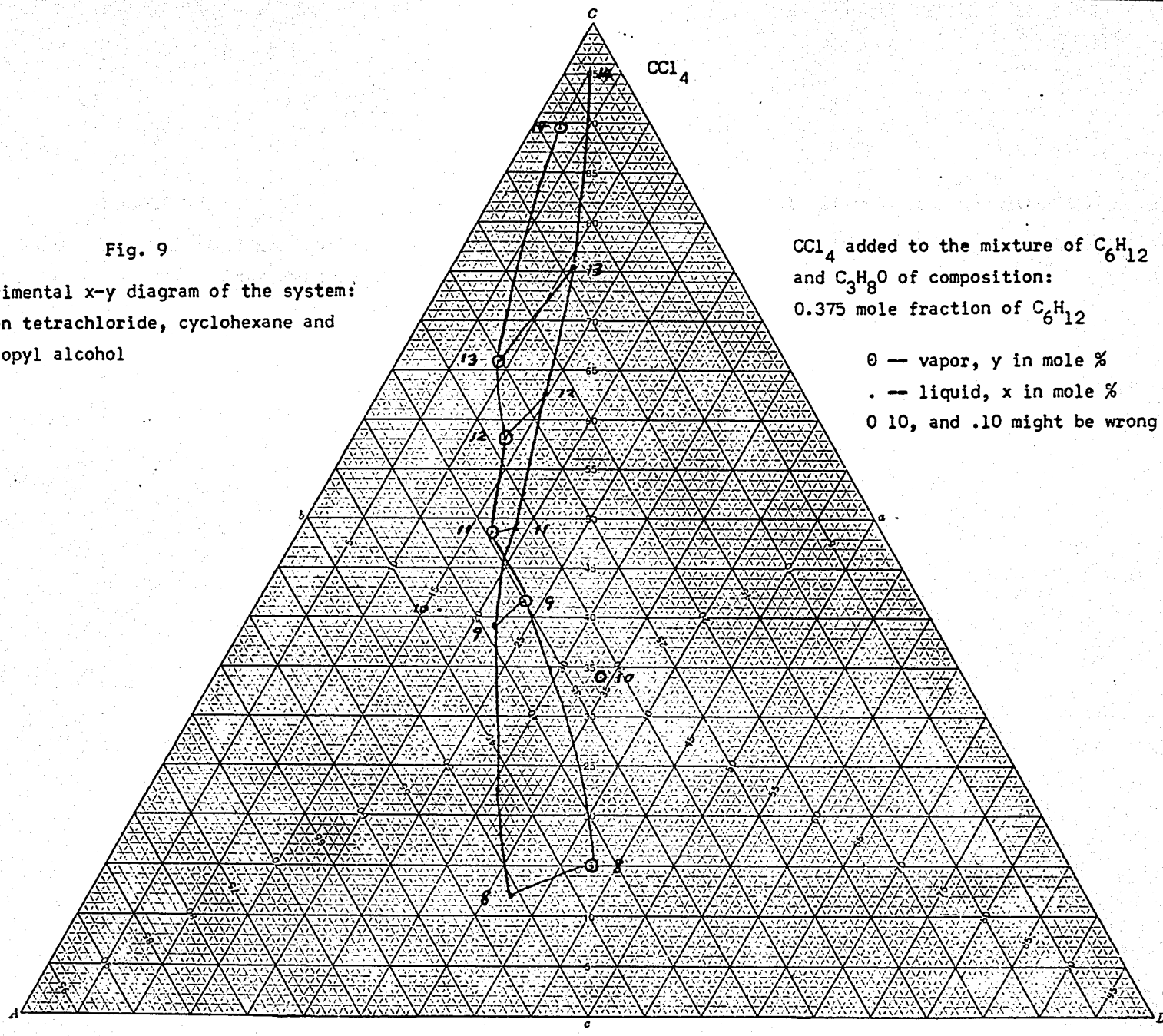
CCl_4 added to the mixture of C_6H_{12} and C_3H_8O of composition: 0.25 mole fraction of C_6H_{12}

θ — vapor, y in mole %

. — liquid, x in mole %

Fig. 9

Experimental x-y diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol

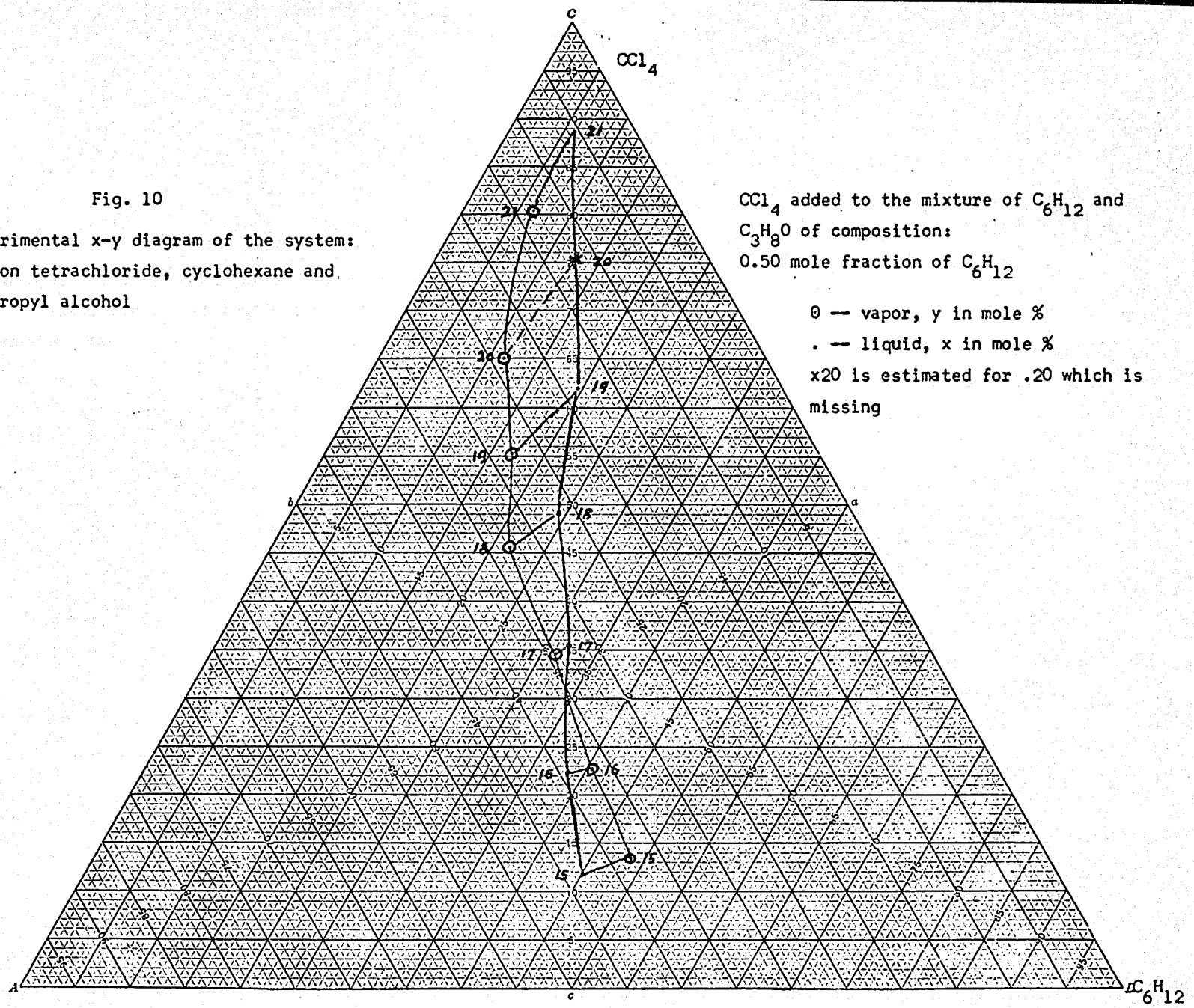


CCl_4 added to the mixture of C_6H_{12} and C_3H_8O of composition:
0.375 mole fraction of C_6H_{12}

0 — vapor, y in mole %
. — liquid, x in mole %
0 10, and .10 might be wrong

Fig. 10

Experimental x-y diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol



CCl_4 added to the mixture of C_6H_{12} and C_3H_8O of composition:
0.50 mole fraction of C_6H_{12}

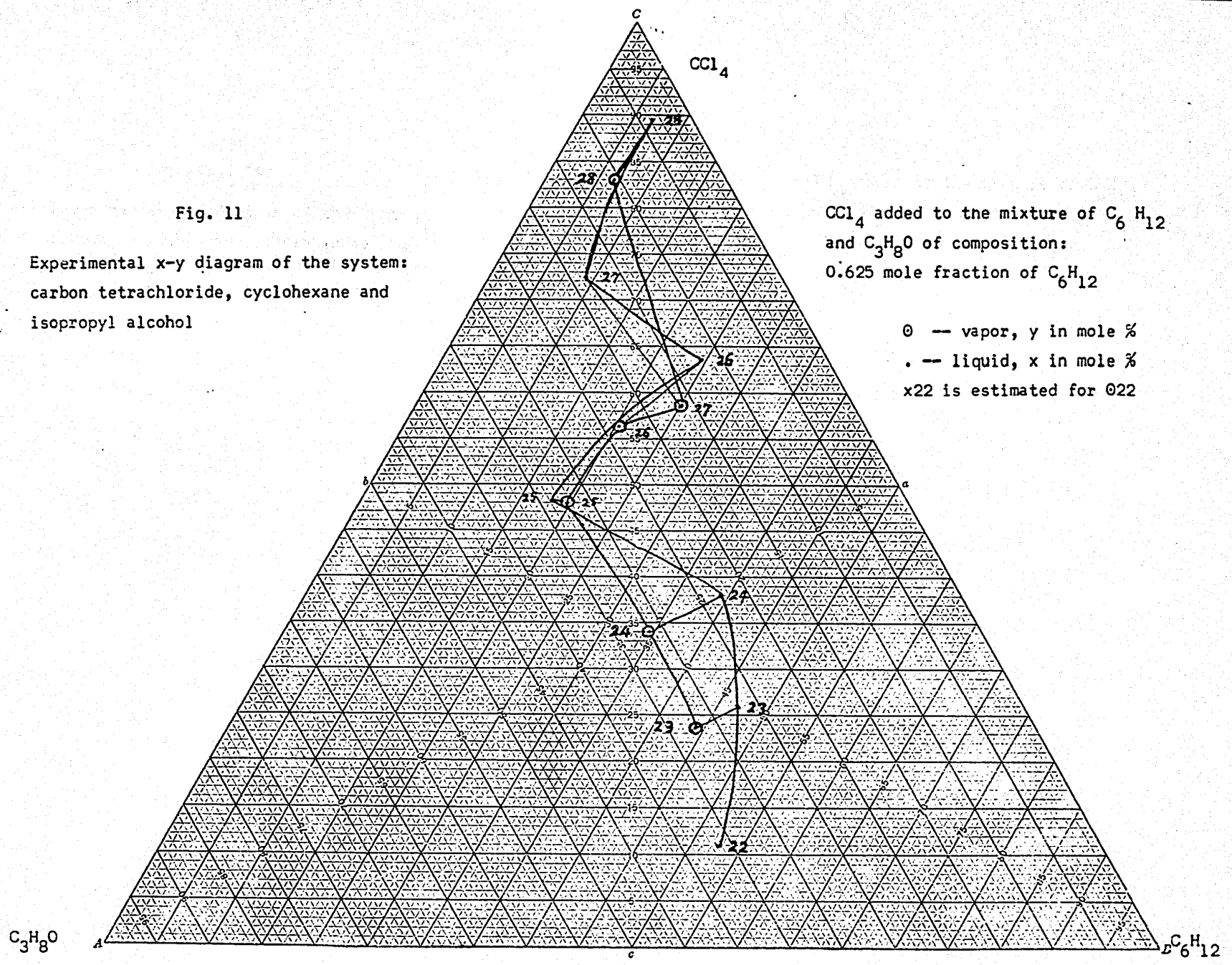
0 — vapor, y in mole %

. — liquid, x in mole %

x20 is estimated for .20 which is missing

Fig. 11

Experimental x-y diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol

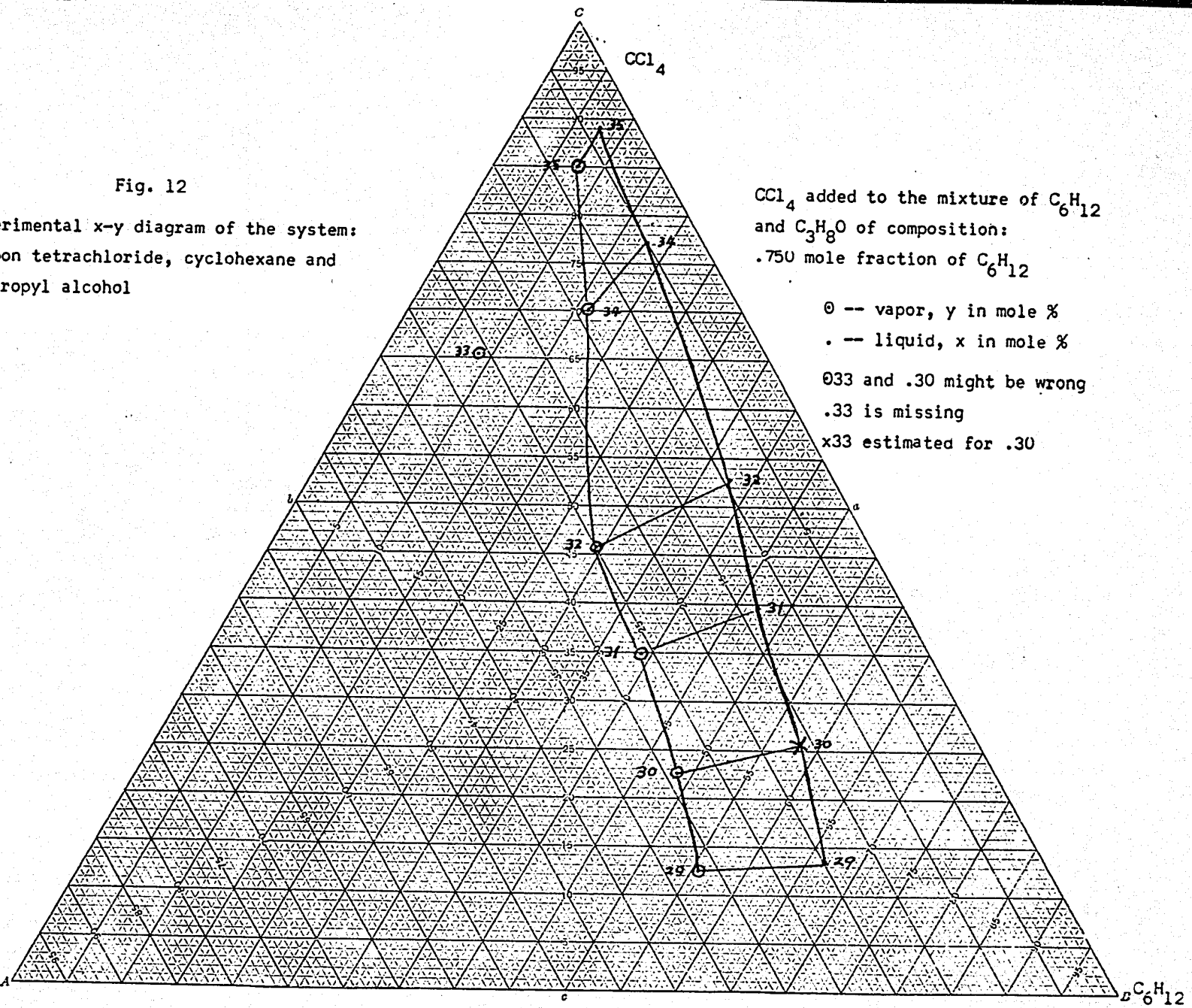


CCl_4 added to the mixture of C_6H_{12} and C_3H_8O of composition:
0.625 mole fraction of C_6H_{12}

⊙ — vapor, y in mole %
. — liquid, x in mole %
x22 is estimated for ⊙22

Fig. 12

Experimental x-y diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol



CCl_4 added to the mixture of C_6H_{12} and C_3H_8O of composition:
.750 mole fraction of C_6H_{12}

0 -- vapor, y in mole %

. -- liquid, x in mole %

033 and .30 might be wrong

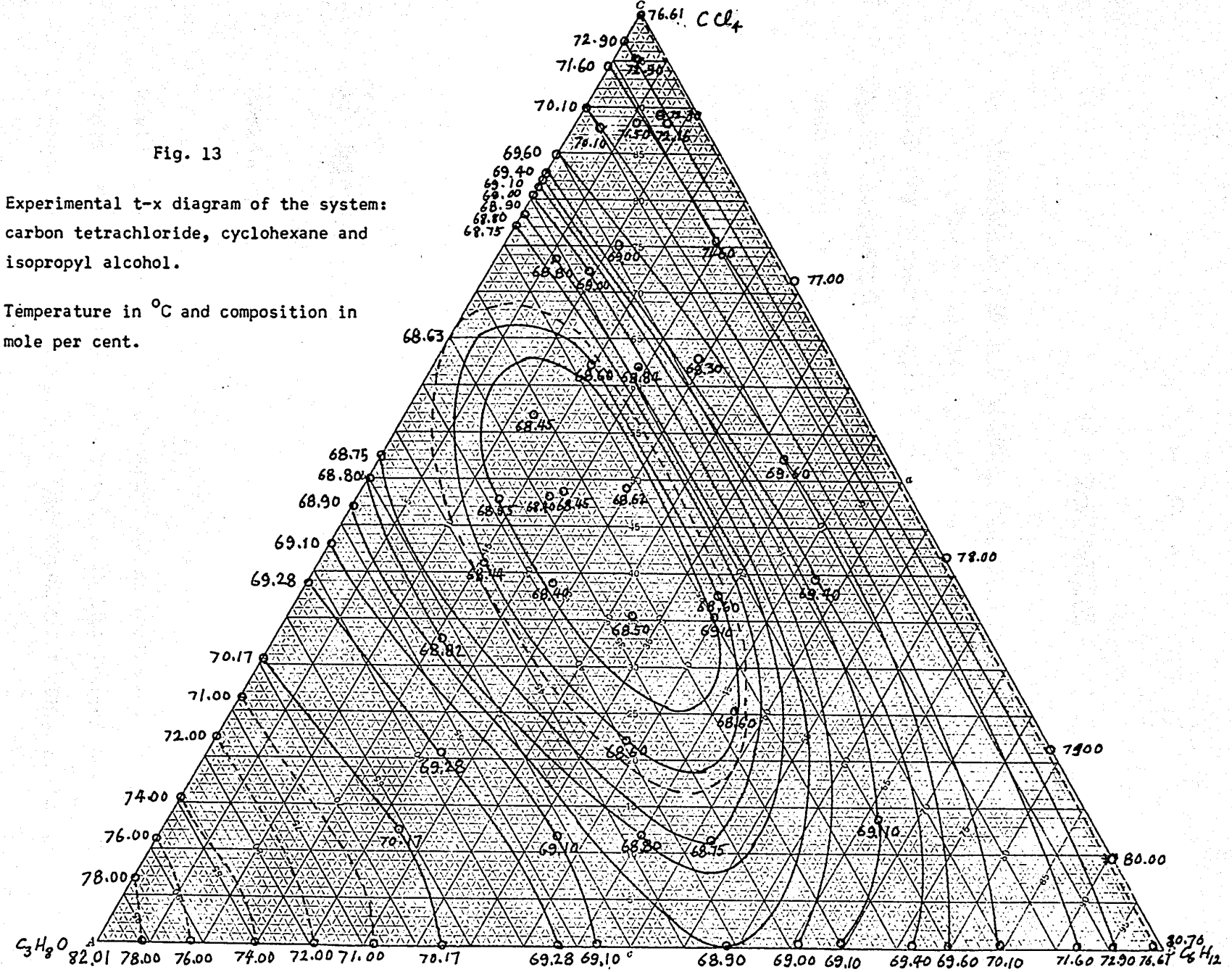
.33 is missing

x33 estimated for .30

Fig. 13

Experimental t-x diagram of the system: carbon tetrachloride, cyclohexane and isopropyl alcohol.

Temperature in ^{o}C and composition in mole per cent.



VI - CALCULATION

1. Correction for equilibrium temperature

The still was operated under atmospheric pressure which may differ slightly from the standard pressure of 760 mm Hg. A correction to the measured equilibrium temperature was made according to the Craft's Rule[16] which is

$$\Delta t = c\,(760 - P)\,T \qquad (49)$$

where T is the measured equilibrium temperature in ^{o}K at pressure P taken from a barometer and c is an empirical constant. For this investigation, c was taken as 0.0001.

Sample calculation:

Run 1 of the ternary system.

$T = 70.20 + 273.16 = 343.36\ ^{o}K$

Barometer reading = 761mm Hg.

$\Delta t = 0.0001\ (760 - 761)(273.16 + 70.20) = -0.03^{o}C.$

2. Calculation of log γ

If the vapor phase is considered ideal at low pressure, we have

$$P_i = y_i P = \gamma_i x_i P_i^{o} \qquad (50)$$

where P_i is the partial pressure of component i, P_i^{o} is the vapor pressure of pure component i at the temperature and pressure of the system, P is the total pressure, γ_i is the

liquid activity coefficient, y_i is the composition of component i in vapor phase and x_i is the composition of component i in liquid phase.

From equation (50), one obtains

$$\log \gamma_i = \log \frac{y_i}{x_i} \times \frac{P}{P_i^o} \quad . \qquad (51)$$

In order to take into consideration the imperfection of the vapor phase, Wohl's[4] equation is used to calculate log γ, which is

$$\log \gamma_i = \log \frac{y_i}{x_i} \times \frac{P}{P_i^o} + \frac{(P - P_i^o)(\beta_i^o - V_i^o)}{2.303 \times 760 \times R \times T} \qquad (52)$$

where P = 760mm Hg.

R is the gas constant = 82.057 (atm) (cm^3)/g mole ^oK,

Y_i and x_i are measured vapor and liquid composition of component i in mole fraction,

T is the equilibrium temperature in ^oK at the standard pressure of 760mm Hg.,

P_i^o is the vapor pressure of the pure component i at the equilibrium temperature and pressure of the system.

V_i^o is the liquid molal volume of component i and β_i^o is the second virial coefficient of component i.

The second term on the right hand of equation (52) is the correction for vapor imperfection.

In using equation (52) to calculate log γ, for the

binary and the ternary systems in this investigation, the vapor pressures were taken from charts drawn with experimental values from literatures[18,19] as given in Table 16.

The second virial coefficient of carbon tetrachloride was calculated according to the equation given by Black.[17] Those for the cyclohexane and isopropyl alcohol were taken from literatures.[17,21]

TABLE 16

Vapor Pressure of Pure Substances

Temperature in °C	Carbon Tetrachloride	Cyclohexane in mm	Isopropyl Alcohol in mm
30	141.55	121.60	
40	213.34	184.61	
50	312.04	271.80	176.8
55			227.4
60	444.28	389.29	288.5
65			363.1
70	617.43	543.93	454.8
75			561.4
80		743.27	691.8
85			845.6

The liquid molal volume was calculated by Lindersen, Greenkorn and Haugen's[21] method given in Reid and Sherwood's Properties of Gases and Liquids.

Sample Calculation.

(1) The second virial coefficient for carbon tetrachloride.

The equation[17] used to calculate the second virial coefficient is

$$\beta = b - a\xi/RT \qquad (53)$$

where $b = \frac{RT_c}{8P_c}$, $a = \frac{27}{8} bRT_c$

and

$$\xi = A' + \frac{B'}{T_r} - \frac{C'}{T_r^2} + \frac{D'}{T_r^3} + \frac{64E'}{27T_r^m} . \qquad (54)$$

For carbon tetrachloride, $T_c = 556.4^{\circ}K$, $P_c = 45$ atm.

$$b = \frac{82.06 \times 556.4}{8 \times 45} = 126.83,$$

$$a = \frac{27 \times 126.83 \times 82.06 \times 556.4}{8} = 19,544,000,$$

$A' = 0.396, B' = 1.181, C' = 0.864, D' = 0.384, E' = 0$

Substituting the constant in (54), one obtains

$$= 0.396 + \frac{1.181}{T_r} - \frac{0.864}{T_r^2} + \frac{0.384}{T_r^3} .$$

In Run 1 of the system: carbon tetrachloride and isopropyl alcohol.

$$T = 352.31\ ^{o}K$$

$$T_r = 0.63329$$

$$\xi = 0.396 + \frac{1.181}{0.6333} - \frac{0.864}{0.6333^2} + \frac{0.384}{0.6333^3}$$

$$= 1.6184$$

Substituting the calculated values for a, b and ξ in equation (53), one obtains the second virial coefficient of carbon tetrachloride as

$$\beta = b - a\xi/RT$$

$$= 126.83 - \frac{19,544,000 \times 1.6184}{82.06 \times 352.31} = -967.2$$

(b) Liquid molal volume

The equation used is

$$V_1 \rho_{r_1} = V_2 \rho_{r_2} \qquad (55)$$

In equation (55) V_1 and V_2 are liquid molal volumes at two different temperatures and ρ_{r_1} and ρ_{r_2} are the corresponding reduced density which is defined as

$$\rho_r = \frac{\rho_T}{\rho_c}$$

In using equation (55) to calculate liquid molal volume, reliable experimental value of liquid molal volume is taken for V_1, usually volume at normal boiling point, V_2 is calculated by taking readings of ρ_{r_1} and ρ_{r_2} from the table for Reduced Density of Liquids which is a function of Tr and $Z_c = \frac{P_c V_c}{RT_c}$.

There is such a table on P. 61 of Reid and Sherwood: Properties of Gases and Liquids.

When $V_{N.B.P.}$ is not available, liquid molal volume at any other temperature is used as V_1 and $V_{N.B.P.}$ is calculated as V_2 by using equation (55). The calculated $V_{N.B.P.}$ is then used as V_1 to calculate liquid molal volume at any other temperature by using the same equation.

The liquid molal volume at normal boiling point for carbon tetrachloride and cyclohexane were taken from literature[22] 102 cc/g mole was taken for carbon tetrachloride and 117 cc/g mole for cyclohexane.

The $V_{N.B.P.}$ for isopropyl alcohol was calculated from liquid molal volume at 30°C. The calculated $V_{N.B.P.}$ was 84.11 cc/g mole. For Run 1 of the system carbon tetrachloride and isopropyl alcohol,

$$T_r = 0.693, \quad Z_c = 0.278, \quad V_{N.B.P.} = V_1 = 84.110.$$

and $r_1 = 2.533$, $r_2 = 2.547$ read from Table 3 - 4 P. 61 Reid and Sherwood; Properties of Gases and Liquids, the liquid molal volume for isopropyl alcohol at $T = 353.16°K$ is given as

$$V_2 = \frac{\rho_{r_1}}{\rho_{r_2}} V_1 = \frac{2.533}{2.547} \times 84.110 = 83.647 \text{ cc/g mole.}$$

(c) Calculation of log γ

In Run 1 of the system carbon tetrachloride and isopropyl alcohol

$T = 352.31^{\circ}K$, $P_1^{\circ} = 812.0$ mm $P - P_1^{\circ} = -52.0$ mm

$\beta_1^{\circ} = -967.2$ cc/g mole, $V_1^{\circ} = 102.34$ cc/g mole $\beta_1^{\circ} - V_1^{\circ}$

$= -1069.5$ cc/g mole.

The correction term for vapor imperfection is

$$\frac{(P - P_1^{\circ})(\beta_1^{\circ} - V_1^{\circ})}{760 \times 2303\ RT} = \frac{(-52.0) \times (-1069.5)}{760 \times 2.303 \times 82.06 \times 352.32} = +0.0011$$

$$y_1 = 0.138, \quad x_1 = 0.058,$$

$$\frac{y_1}{x_1} \times \frac{P}{P_1^{\circ}} = \frac{0.138}{0.058} \times \frac{760}{812} = 2.2268$$

$$\log \frac{y_1}{x_1} \times \frac{P}{P_1^{\circ}} = 0.34768$$

and

$$\log \gamma = \log \frac{y_1}{x_1} \times \frac{P}{P_1^{\circ}} + \frac{(P - P_1^{\circ})(\beta_1^{\circ} - V_1^{\circ})}{760 \times 2.303\ RT}$$

$$= 0.3477 + 0.0011 = 0.3488.$$

All the values taken from charts prepared with literature values and values calculated for the vapor pressures, the liquid molal volumes, the second virial coefficients and the corrections for vapor imperfection for the binary systems are presented in Tables 17, 18, 19, 20, 21, 22 for the ternary system in Tables 23, 24, 25.

The calculated $\log \gamma$ and $\log \frac{\gamma_1}{\gamma_2}$ for the binary systems are presented in Tables 26, 27, 28, 29, 30, 31, 32, 33, 34 and Fig. 14, 15, 16, 17, 18, 19.

The calculated $\log \gamma$ and $x \log \gamma$ for the ternary system are presented in Tables 35, 36, 37.

TABLE 17

Correction for Vapor Imperfection for the System:

Carbon Tetrachloride and Cyclohexane

Run	Equilibrium Temperature in °K	Carbon Tetrachloride					
		Vapor Pressure in mm Hg. P_1°	$P-P_1^\circ$	Second Virial Coefficient β_1°	Liquid Molal Volume V_1°	$\beta_1^\circ - V_1^\circ$	$\frac{(P-P_1^\circ)(\beta_1^\circ - V_1^\circ)}{760 \times 2.303\ RT}$
1.	353.50	836.5	-76.5	-958.8	102.53	-1061.3	+0.0014
2.	352.76	821.0	-61.0	-964.6	102.42	-1067.0	+0.0016
3.	352.82	822.0	-62.0	-963.6	102.42	-1066.0	+0.0012
4.	352.33	812.0	-52.0	-967.1	102.34	-1069.4	+0.0010
5.	352.04	805.7	-45.7	-969.1	102.34	-1071.4	+0.0008
6.	349.60	753.5	- 6.5	-986.8	101.92	-1088.7	+0.0011
7.	349.90	760.0	- 0.0	-984.8	102.00	-1086.8	0
8.	350.22	767.0	- 7.0	-982.2	102.08	-1084.3	+0.0002
9.	350.23	767.0	- 7.0	-982.2	102.08	-1084.3	+0.0002
10.	350.56	776.0	-10.0	-981.8	102.08	-1083.8	+0.0002
11.	350.69	778.0	-18.0	-978.9	102.08	-1081.0	+0.0003
12.	350.79	780.0	-20.0	-978.1	102.15	-1080.2	+0.0004
13.	351.22	789.0	-29.0	-975.0	102.15	-1077.1	+0.0006
14.	351.62	797.0	-37.0	-972.1	102.27	-1074.3	+0.0007
15.	351.96	804.0	-44.0	-971.0	102.27	-1073.2	+0.0013
16.	352.41	814.0	-54.0	-966.5	102.34	-1068.8	+0.0011
17.	352.70	820.0	-60.0	-964.4	102.42	-1066.8	+0.0012
18.	352.89	823.0	-63.0	-963.1	102.42	-1065.5	+0.0013
19.	351.23	989.0	-29.0	-975.0	102.15	-1077.1	+0.0006

TABLE 18

Correction for Vapor Imperfection for the System:

Carbon Tetrachloride and Cyclohexane

Run	Equilibrium Temperature in °K	Cyclohexane					
		Vapor Pressure in mm Hg. P_2^o	$P-P_2^o$	Second Virial Coefficient β_2^o	Liquid Molal Volume V_2^o	$\beta_2^o - V_2^o$	$\frac{(P-P_2^o)(\beta_2^o - V_2^o)}{760 \times 2.303\ RT}$
1.	353.50	750.0	10.0	-1079	116.87	-1195.9	-0.0002
2.	352.68	733.0	27.0	-1085	116.69	- 120.17	-0.0006
3.	352.82	735.0	25.0	-1082	116.78	-1198.8	-0.0006
4.	352.33	722.5	37.5	-1088	116.69	-1202.0	-0.0009
5.	352.04	717.0	43.0	-1091	116.56	-1207.6	-0.0010
6.	349.60	720.0	93.5	-1109	116.17	-1225.2	-0.0022
7.	349.90	670.5	86.5	-1106	116.17	-1222.2	-0.0021
8.	350.22	679.5	80.5	-1104	116.30	-1220.3	-0.0020
9.	350.23	679.8	80.2	-1104	116.30	-1220.3	-0.0020
10.	350.29	687.0	73.0	-1103	116.30	-1219.3	-0.0018
11.	350.69	690.3	69.7	-1100	116.39	-1216.4	-0.0017
12.	350.79	692.0	68.0	-1099	116.39	-1215.4	-0.0016
13.	351.22	701.0	59.0	-.096	116.47	-1212.5	-0.0014
14.	351.62	708.0	52.0	-1094	116.56	-1210.6	-0.0012
15.	351.78	715.0	45.0	-1092	116.56	-1208.6	-0.0011
16.	352.41	725.0	35.0	-1088	116.69	-1204.7	-0.0008
17.	352.70	732.0	28.0	-1085	116.69	-1201.7	-0.0007
18.	352.89	735.5	24.5	-1084	116.78	-1200.8	-0.0006
19.	351.23	701.0	59.0	-1096	116.47	-1212.5	-0.0014

TABLE 19

Correction for Vapor Imperfection for the System:

Carbon Tetrachloride and Isopropyl Alcohol

Run	Equilibrium Temperature in °K	Carbon Tetrachloride					
		Vapor Pressure in mm Hg. P_1^o	$P-P_1^o$	Second Virial Coefficient β_1^o	Liquid Molal Volume V_1^o	$\beta_1^o - V_1^o$	$\frac{(P-P_1^o)(\beta_1^o - V_1^o)}{760 \times 2.303\ RT}$
1.	352.31	812.0	-52.0	-967.2	102.34	-1069.5	+0.0011
2.	348.87	735.0	25.0	-992.3	101.88	-1094.2	-0.0006
3.	348.06	720.0	40.0	-998.3	101.81	-1100.1	-0.0009
4.	344.78	650.0	110.0	-1023.0	101.40	-1124.8	-0.0026
5.	342.44	603.7	156.3	-1042.0	101.06	-1143.1	-0.0036
6.	342.16	598.5	161.5	-1045.0	101.06	-1146.0	-0.0036
7.	341.91	594.0	166.0	-1060.0	100.99	-1161.3	-0.0039
8.	342.31	600.0	160.0	-1042.0	101.06	-1146.0	-0.0035
9.	344.94	653.5	107.5	-1022.0	101.40	-1123.6	-0.0024
10.	343.28	620.0	140.0	-1035.0	101.13	-1136.5	-0.0031
11.	343.79	629.5	130.5	-1031.0	100.84	-1131.7	-0.0030
12.	343.67	627.0	133.0	-1032.0	101.21	-1133.4	-0.0031
13.	345.70	669.0	91.0	-1016.0	101.47	-1117.6	-0.0021
14.	347.43	705.0	55.0	-1003.0	101.66	-1104.6	-0.0012
15.	342.70	608.5	151.5	-1040.0	101.06	-1140.9	-0.0035
16.	344.56	646.0	114.0	-1036.0	101.40	-1137.4	-0.0026
17.	347.95	718.0	42.0	- 998.0	101.66	-1099.7	-0.0009

TABLE 20

Correction for Vapor Imperfection for the System:

Carbon Tetrachloride and Isopropyl Alcohol

R Run	Equilibrium Temperature in $^{\circ}$ K	Isopropyl Alcohol					
		Vapor Pressure in mm Hg. P_2°	$P-P_2^{\circ}$	Second Virial Coefficient β_2	Liquid Molal Volume V_2	$\beta_2^{\circ}-V_2^{\circ}$	$\frac{(P-P_2^{\circ})(\beta_2^{\circ}-V_2^{\circ})}{760 \times 2.303 RT}$
1.	352.31	66.5	93.5	-1285	83.65	-1368.6	-0.0025
2.	348.87	578.5	181.5	-1366	83.13	-1448.1	-0.0053
3.	346.06	559.0	201.0	-1385	83.03	-1468.0	-0.0058
4.	344.78	486.0	274.0	-1469	82.55	-1550.5	-0.0086
5.	342.44	440.5	319.5	-1533	82.26	-1612.2	-0.0105
6.	342.16	434.8	325.2	-1536	82.24	-1619.1	-0.0108
7.	341.91	430.5	329.5	-1545	82.20	-1627.2	-0.0109
8.	342.31	437.0	323.0	-5135	82.25	-1617.3	-0.0106
9.	344.94	489.2	270.8	-1465	82.61	-1536.6	-0.0085
10.	343.28	455.5	304.5	-1506	83.39	-1586.4	-0.0098
11.	343.79	466.2	293.8	-1493	82.45	-1574.5	-0.0094
12.	343.67	463.5	296.5	-1495	82.39	-1577.4	-0.0095
13.	345.70	505.4	254.6	-1443	82.67	-1525.7	-0.0112
14.	347.43	544.0	216.0	-1402	82.96	-1483.0	-0.0064
15.	342.70	445.3	314.7	-1523	82.26	-1604.3	-0.0103
16.	344.56	481.5	278.5	-1475	82.55	-1557.5	-0.0088
17.	347.95	556.5	203.5	-1388	82.03	-1470.0	-0.0060

TABLE 21

Correction for Vapor Imperfection for the System: Cyclohexane and Isopropyl Alcohol

Run	Equilibrium Temperature in °K	Cyclohexane					
		Vapor Pressure in mm Hg. P_1	$P-P_1^o$	Second Virial Coefficient β_1	Liquid Molal Volume V_1^o	$\beta_1^o-V_1^o$	$\frac{(P-P_1^o)(\beta_1^o-V_1^o)}{760 \times 2.303\ RT}$
1.	342.51	532.50	227.50	-1163	115	-1278	-0.0059
2.	342.53	532.86	227.14	-1163	115	-1278	-0.0059
3.	342.17	526.66	233.34	-1166	115	-1281	-0.0061
4.	342.26	528.20	231.80	-1165	115	-2180	-0.0060
5.	342.61	534.23	225.77	-1162	115	-1277	-0.0059
6.	342.36	529.92	230.08	-1164	115	-1279	-0.0060
7.	341.96	523.08	236.92	-1169	115	-1284	-0.0062
8.	342.37	530.09	229.91	-1164	115	-1279	-0.0060
9.	342.58	533.71	226.29	-1162	115	-1277	-0.0059
10.	342.82	537.89	222.11	-1161	115	-1277	-0.0058
11.	343.27	545.77	214.23	-1157	115	-1273	-0.0055
12.	344.66	570.70	189.30	-1146	115	-1287	-0.0049
13.	347.17	617.99	142.01	-1127	116	-2143	-0.0035
14.	349.89	672.63	87.37	-1105	116	-1221	-0.0021
15.	348.12	636.67	123.33	-1120	116	-1236	-0.0030
16.	347.96	633.47	126.53	-1121	116	-1236	-0.0031
17.	345.44	585.07	174.93	-1140	116	-1256	-0.0044
18.	343.35	547.10	212.90	-1156	115	-1271	-0.0055
19.	342.27	528.37	231.63	-1165	115	-1280	-0.0060
20.	342.30	528.89	231.11	-1165	115	-1280	-0.0060

(Table 21 continued)

21.	342.18	526.83	233.17	-1166	115	-1281	-0.0061
22.	342.24	527.86	232.14	-1166	115	-1281	-0.0061
23.	343.22	527.51	232.49	-1166	115	-1281	-0.0060
24.	347.90	632.30	127.70	-1121	116	-1237	-0.0032
25.	343.47	549.30	210.70	-1155	115	-1270	-0.0054
26.	351.87	714.77	45.23	-1091	117	-1208	-0.0011
27.	350.07	676.39	83.61	-1104	116	-1220	-0.0020

TABLE 22

Correction for Vapor Imperfection for the System:

Cyclohexane and Isopropyl Alcohol

Run	Equilibrium Temperature in °K	Vapor Pressure in mm Hg. P_2^o	$P-P_2^o$	Virial Second Coefficient β_2	Liquid Molal Volume V_2^o	$\beta_2^o-V_2^o$	$\frac{(P-P_2^o)(\beta_2^o-V_2^o)}{760 \times 2.303\ RT}$
				Isopropyl Alcohol			
1.	342.51	441.5	318.5	-1529	82.3	-1611.3	-0.0104
2.	342.53	441.7	318.3	-1529	82.3	-1611.2	-0.0104
3.	342.17	435.2	324.8	-1537	82.2	-1618.3	-0.0107
4.	342.26	436.8	323.2	-1535	82.3	-1616.3	-0.0106
5.	342.61	443.5	316.5	-1526	82.3	-1608.3	-0.0104
6.	342.36	438.5	321.5	-1531	82.3	-1612.3	-0.0105
7.	341.96	431.0	329.0	+1543	82.2	-1624.2	-0.0109
8.	342.37	439.0	321.0	-1531	82.3	-1612.3	-0.0105
9.	342.58	441.5	318.5	-1526	82.3	-1608.3	-0.0104
10.	342.82	443.0	317.0	-1521	82.3	-1601.3	-0.0102
11.	343.27	455.0	305.0	-1505	82.4	-1588.4	-0.0098
12.	344.66	482.5	277.5	-1471	82.5	-1552.5	-0.0086
13.	347.17	538.0	222.0	-1406	82.9	-1482.9	-0.0061
14.	349.89	602.3	158.0	-1342	83.4	-1410.4	-0.0042
15.	348.12	560.0	200.0	-1365	83.0	-1458.0	-0.0056
16.	347.96	556.0	204.0	-1388	83.0	-1471.0	-0.0058
17.	345.44	500.0	260.0	-1451	82.7	-1533.7	-0.0079
18.	343.35	457.0	303.0	-1506	82.4	-1587.4	-0.0097
19.	342.27	437.0	323.0	-1535	82.3	-1616.3	-0.0106

(Table 22 continued)

20.	342.30	437.5	322.5	-1535	82.3	-1616.3	-0.0103
21.	342.18	435.2	324.8	-1537	82.2	-1618.2	-0.0107
22.	342.24	436.8	323.2	-1537	82.2	-1616.2	-0.0106
23.	343.22	436.7	323.3	-1537	82.2	-1616.2	-0.0106
24.	347.90	555.0	205.0	-1391	83.0	-1473.0	-0.0059
25.	343.47	459.8	300.2	-1501	82.4	-1582.4	-0.0096
26.	351.87	653.5	106.5	-1293	83.5	-1376.5	-0.0026
27.	350.07	609.0	151.0	-1338	83.0	-1419.0	-0.0041

TABLE 23

Correction for Vapor Imperfection for the Systems
1 2 3
Carbon Tetrachloride, Cyclohexane and Isopropyl Alcohol

Run	$P - P_1^\circ$	$\beta_1^\circ - V_1^\circ$	$\frac{(P-P_1^\circ)(\beta_1^\circ-V_1^\circ)}{760 \times R \times 2.303 \times T}$
1.	139.5	-1139.1	-0.0032
2.	156.0	-1144.1	-0.0036
3.	165.0	-1148.0	-0.0039
4.	170.0	-1150.0	-0.0040
5.	171.5	-1150.9	-0.0040
6.	165.0	-1148.0	-0.0039
7.	140.0	-1133.0	-0.0032
8.	160.0	-1146.0	-0.0037
9.	172.0	-1151.9	-0.0040
10.	171.5	-1150.9	-0.0040
11.	171.8	-1150.9	-0.0040
12.	169.0	-1150.9	-0.0040
13.	161.5	-1146.0	-0.0036
14.	84.0	-1114.5	-0.0019
15.	165.0	-1148.0	-0.0038
16.	169.0	-1148.9	-0.0039
17.	170.5	-1148.9	-0.0040
18.	168.5	-1148.9	-0.0039
19.	164.8	-1148.0	-0.0039
20.	151.5	-1150.0	-0.0035
21.	113.0	-1134.0	-0.0026
22.	166.0	-1148.0	-0.0039
23.	169.0	-1148.9	-0.0040
24.	168.0	-1149.2	-0.0039
25.	172.0	-1151.9	-0.0040
26.	174.5	-1151.9	-0.0041
27.	161.5	-1146.0	-0.0038
28.	96.0	-1119.5	-0.0022
29.	160.0	-1146.0	-0.0037
30.	160.0	-1146.0	-0.0037
31.	154.5	-1142.1	-0.0036
32.	150.5	-1141.1	-0.0035
33.	139.0	-1136.1	-0.0032
34.	110.0	-1125.4	-0.0025
35.	99.0	-1121.5	-0.0022

TABLE 24

Correction for Vapor Imperfection for the System: Carbon Tetrachloride[1], Cyclohexane[2] and Isopropyl Alcohol[3]

Run	$P - P_2^o$	$\beta_2^o - V_2^o$	$\frac{(P-P_2^o)(\beta_2^o-V_2^o)}{R \times 760 \times 2.303 \times T}$
1.	213.5	-1272.3	-0.0055
2.	228.5	-1279.1	-0.0060
3.	236.5	-1283.0	-0.0062
4.	240.5	-1285.0	-0.0063
5.	242.5	-1285.9	-0.0064
6.	236.6	-1282.0	-0.0062
7.	214.6	-1273.2	-0.0051
8.	231.8	-1280.1	-0.0060
9.	243.5	-1285.9	-0.0064
10.	242.6	-1285.9	-0.0064
11.	242.5	-1285.9	-0.0064
12.	240.1	-1284.1	-0.0063
13.	233.4	-1280.0	-0.0061
14.	162.5	-1251.6	-0.0041
15.	236.6	-1282.0	-0.0062
16.	240.3	-1284.1	-0.0063
17.	241.7	-1285.0	-0.0063
18.	239.6	-1284.1	-0.0063
19.	236.5	-1282.0	-0.0062
20.	224.0	-1285.0	-0.0059
21.	199.5	-1269.3	-0.0049
22.	237.6	-1283.0	-0.0062
23.	240.0	-1285.0	-0.0063
24.	240.0	-1285.0	-0.0063
25.	243.4	-1285.9	-0.0064
26.	243.0	-1286.9	-0.0060
27.	233.5	-1280.0	-0.0061
28.	174.0	-1255.5	-0.0044
29.	231.5	-1280.1	-0.0060
30.	231.5	-1280.1	-0.0060
31.	226.4	-1278.1	-0.0059
32.	223.0	-1276.2	-0.0058
33.	212.5	-1272.3	-0.0055
34.	185.0	-1260.5	-0.0048
35.	176.5	-1256.5	-0.0045

TABLE 25

Correction for Vapor Imperfection for the System: Carbon Tetrachloride[1], Cyclohexane[2] and Isopropyl Alcohol[3]

Run	$P - P_3^o$	$\beta_3^o - V_3^o$	$\frac{(P-P_3^o)\ (\beta_3^o-V_3^o)}{760 \times 2.303 \times R \times T}$
1.	303.4	-1587.3	-0.0098
2.	319.0	-1613.3	-0.0105
3.	329.0	-1625.1	-0.0109
4.	333.5	-1633.1	-0.0111
5.	335.0	-1635.1	-0.0116
6.	330.0	-1625.1	-0.0109
7.	305.0	-1588.3	-0.0098
8.	323.0	-1617.3	-0.0106
9.	336.5	-1635.1	-0.0113
10.	335.8	-1635.1	-0.0113
11.	335.7	-1635.1	-0.0113
12.	332.5	-1629.1	-0.0111
13.	325.2	-1619.1	-0.0108
14.	246.5	-1516.7	-0.0075
15.	330.0	-1625.1	-0.0109
16.	332.5	-1629.1	-0.0111
17.	334.4	-1633.1	-0.0112
18.	332.3	-1629.1	-0.0111
19.	328.0	-1625.1	-0.0109
20.	214.5	-1626.4	-0.0105
21.	276.7	-1578.3	-0.0088
22.	329.8	-1628.2	-0.0110
23.	332.5	-1633.1	-0.0111
24.	332.5	-1633.1	-0.0111
25.	336.5	-1637.1	-0.0113
26.	338.5	-1638.1	-0.0113
27.	325.2	-1619.2	-0.0108
28.	258.7	-1532.6	-0.0080
29.	323.0	-1617.2	-0.0106
30.	323.0	-1617.6	-0.0107
31.	317.4	-1616.6	-0.0105
32.	313.8	-1602.3	-0.0102
33.	305.8	-1585.3	-0.0098
34.	274.8	-1550.5	-0.0086
35.	263.0	-1537.6	-0.0081

TABLE 26

Log γ_1 of the System:

Carbon Tetrachloride (1) and Cyclohexane (2)

Run	Carbon Tetrachloride y_1	Carbon Tetrachloride x_1	P_1^o	$\frac{y_1}{x_1} \times \frac{P}{P_1^o}$	$\text{Log}\frac{y_1}{x_1} \times \frac{P}{P_1^o}$	Vapor Correction	Log γ_1
1.	0.068	0.045	836.5	1.3728	.1376	+0.0014	0.1390
2.	0.155	0.124	821.0	1.1571	.0634	+0.0016	0.0649
3.	0.163	0.134	822.0	1.1246	.0510	+0.0012	0.0523
4.	0.230	0.201	812.0	1.0709	.0298	+0.0010	0.0308
5.	0.273	0.256	805.7	1.0347	.0148	+0.0008	0.0140
6.	0.220	0.201	753.5	1.1039	.0429	+0.0011	0.0440
7.	0.805	0.791	761.5	1.0156	.0067	0.	0.0067
8.	0.693	0.675	767.0	1.0173	.0075	+0.0002	0.0079
9.	0.696	0.685	767.0	1.0068	.0029	+0.0002	0.0031
10.	0.606	0.585	776.0	1.0145	.0063	+0.0002	0.0065
11.	0.569	0.540	778.0	1.0293	.0125	+0.0003	0.0128
12.	0.545	0.519	780.0	1.0232	.0100	+0.0004	0.0103
13.	0.436	0.412	789.0	1.0194	.0083	+0.0006	0.0089
14.	0.345	0.314	797.0	1.0477	.0202	+0.0007	0.0209
15.	0.285	0.260	804.0	1.0362	.0154	+0.0010	0.0164
16.	0.230	0.198	814.0	1.0845	.0352	+0.0010	0.0362
17.	0.171	0.146	820.0	1.0855	.0356	+0.0010	0.0366
18.	0.135	0.113	823.0	1.1032	.0427	+0.0010	0.0437
19.	0.427	0.404	790.0	1.0168	.0072	+0.0010	0.0082

TABLE 27

Log γ of the System:
Carbon Tetrachloride (1) and Cyclohexane (2)

Run	Cyclohexane						
	y_2	x_2	P_2^o	$\frac{y_2 P}{x_2 P_2^o}$	$\log \frac{y_2 P}{x_2 P_2^o}$	Vapor Correction	$\log \gamma_2$
1.	0.932	0.955	750.0	0.98889	1.99515	-0.0002	-0.0050
2.	0.845	0.876	733.0	1.0001	0.00004	-0.0006	-0.0006
3.	0.837	0.866	735.0	0.99937	1.99973	-0.0006	-0.0003
4.	0.770	0.799	722.5	1.0137	0.00591	-0.0009	+0.0050
5.	0.727	0.744	717.0	1.0358	0.01427	-0.0010	+0.0133
6.	0.780	0.799	720.0	1.0304	0.01301	-0.0020	+0.0110
7.	0.195	0.209	673.0	1.0536	0.02268	-0.0020	+0.0224
8.	0.307	0.325	679.5	1.0565	0.02387	-0.0019	+0.0220
9.	0.304	0.315	679.8	1.0789	0.03298	-0.0019	+0.0310
10.	0.394	0.415	687.0	1.0503	0.02131	-0.0017	+0.0203
11.	0.431	0.460	690.3	1.0316	0.01351	-0.0017	+0.0120
12.	0.455	0.481	692.0	1.0389	0.01657	-0.0016	+0.0150
13.	0.564	0.588	701.0	1.0399	0.01699	-0.0014	+0.0166
14.	0.655	0.686	708.0	1.0249	0.01068	-0.0012	+0.0095
15.	0.715	0.740	715.0	1.0270	0.01157	-0.0011	+0.0105
16.	0.770	0.802	725.0	1.0065	0.00281	-0.0008	+0.0020
17.	0.829	0.854	732.0	1.0079	0.00342	-0.0006	+0.0038
18.	0.865	0.887	735.5	1.0077	0.00333	-0.0006	+0.0027
19.	0.573	0.596	701.0	1.0423	0.01799	-0.0014	+0.0176

TABLE 28

Log γ_1/γ_2 of the System:

1 2
Carbon Tetrachloride and Cyclohexane

Run	x_1	log γ_1	log γ_2	log γ_1/γ_2
1.	0.045	0.1390	-0.0050	+0.1440
2.	0.124	0.0649	-0.0006	+0.0655
3.	0.134	0.0522	-0.0003	+0.0525
4.	0.201	0.0308	-0.0050	+0.0258
5.	0.256	0.0140	0.0133	+0.0007
6.	0.201	0.0440	0.0110	+0.0330
7.	0.791	0.0067	0.0224	-0.0157
8.	0.675	0.0079	0.0220	-0.0141
9.	0.685	0.0031	0.0310	-0.0279
10.	0.585	0.0065	0.0203	-0.0138
11.	0.540	0.0128	0.0120	+0.0008
12.	0.519	0.0103	0.0150	-0.0047
13.	0.412	0.0089	0.0166	-0.0077
14.	0.314	0.0209	0.0095	+0.0114
15.	0.260	0.0164	0.0105	+0.0059
16.	0.198	0.0362	0.0020	+0.0342
17.	0.146	0.0366	0.0038	+0.0328
18.	0.113	0.0437	0.0027	+0.0410
19.	0.404	0.0082	0.0176	-0.0094

TABLE 29

Log γ of the Systems:
1 2
Carbon Tetrachloride and Isopropyl Alcohol

Run	Carbon Tetrachloride						
	y_1	x_1	P_1^o	$\log \frac{y_1 P}{x_1 P_1^o}$	$\log_{x_1} \frac{y_1 P}{P_1^o}$	Vapor Correction	log γ_1
1.	0.138	0.058	812.0	2.2268	0.34768	+0.0011	0.3478
2.	0.283	0.104	735.0	2.8136	0.44926	-0.0006	0.4487
3.	0.310	0.138	720.0	2.3713	0.37498	-0.0009	0.3741
4.	0.438	0.236	650.0	2.1699	0.33644	-0.0026	0.3338
5.	0.742	0.847	603.7	1.1028	0.04250	-0.0036	0.0389
6.	0.708	0.789	598.5	1.1394	0.05668	-0.0036	0.0531
7.	0.629	0.603	594.0	1.3346	0.12535	-0.0039	0.1215
8.	0.584	0.422	600.0	1.7576	0.24492	-0.0035	0.2414
9.	0.433	0.225	653.5	2.2381	0.34988	-0.0024	0.3475
10.	0.497	0.317	620.0	1.9218	0.28371	-0.0031	0.2806
11.	0.473	0.289	629.5	2.1233	0.32700	-0.0030	0.3240
12.	0.483	0.294	627.0	1.9914	0.29916	-0.0031	0.2961
13.	0.399	0.190	669.0	2.3856	0.37760	-0.0021	0.3755
14.	0.306	0.140	705.0	2.3562	0.37222	-0.0012	0.3710
15.	0.500	0.343	608.5	1.8278	0.26193	-0.0035	0.2584
16.	0.842	0.946	646.0	1.0472	0.01903	-0.0026	0.0164
17.	0.940	0.989	718.0	1.0061	0.00264	-0.0009	0.0017

TABLE 30

Log γ of the System:
Carbon Tetrachloride[1] and Isopropyl Alcohol[2]

Run	Isopropyl Alcohol						
	y_2	x_2	P_2^o	$\frac{y_2}{x_2} \times \frac{P}{P_2^o}$	$\log \frac{y_2}{x_2} \times \frac{P}{P_2^o}$	Vapor Correction	Log γ_2
1.	0.862	0.942	666.5	1.0435	0.01849	-0.0025	0.0160
2.	0.717	0.896	578.5	1.0512	0.02169	-0.0053	0.0164
3.	0.690	0.862	559.0	1.0683	0.03675	-0.0058	0.0310
4.	0.562	0.764	486.0	1.1503	0.06081	-0.0086	0.0582
5.	0.258	0.153	440.5	2.9094	0.46380	-0.0105	0.4537
6.	0.292	0.211	434.8	2.4221	0.38419	-0.0108	0.3734
7.	0.371	0.397	430.5	1.6498	0.21743	-0.0109	0.2065
8.	0.416	0.578	437.0	1.2517	0.09750	-0.0106	0.0869
9.	0.567	0.775	489.2	1.1366	0.05561	-0.0085	0.0471
10.	0.503	0.683	455.5	1.2288	0.08948	-0.0098	0.0797
11.	0.527	0.711	466.2	1.2083	0.08218	-0.0094	0.0728
12.	0.517	0.706	463.5	1.2007	0.07943	-0.0095	0.0699
13.	0.601	0.810	505.4	1.1116	0.04595	-0.0112	0.0348
14.	0.694	0.860	544.0	1.1274	0.05208	-0.0064	0.0457
15.	0.500	0.657	445.3	1.2988	0.11354	-0.0103	0.1032
16.	0.158	0.054	481.5	4.6182	0.66447	-0.0088	0.6557
17.	0.060	0.011	556.5	7.4492	0.87211	-0.0060	0.8661

TABLE 31

Log γ_1/γ_2 of the System:

1 2
Carbon Tetrachloride and Isopropyl Alcohol

Run	x_1	log γ_1	log γ_2	log γ_1/γ_2
1.	0.058	0.3478	0.0160	+0.3318
2.	0.104	0.4487	0.0164	+0.4323
3.	0.138	0.3741	0.0310	+0.3431
4.	0.236	0.3338	0.0582	+0.2756
5.	0.847	0.0389	0.4537	0.4148
6.	0.789	0.0531	0.3734	-0.3203
7.	0.603	0.1215	0.2065	-0.0850
8.	0.422	0.2414	0.0869	+0.1545
9.	0.225	0.3475	0.0471	+0.3004
10.	0.317	0.2806	0.0797	+0.2009
11.	0.289	0.3240	0.0728	+0.2512
12.	0.294	0.2961	0.0699	+0.2262
13.	0.190	0.3755	0.0348	+0.3407
14.	0.140	0.3710	0.0457	+0.3253
15.	0.343	0.2584	0.1032	+0.1552
16.	0.946	0.0164	0.6557	-0.6393
17.	0.989	0.0017	0.8661	-0.8644

TABLE 32

Log γ_1 of the System:

1 2
Cyclohexane and Isopropyl Alcohol

Run	Cyclohexane						
	y_1	x_1	P_1^o	$\frac{y_1 \times P}{x_1 \times P_1^o}$	$\log \frac{y_1 \times P}{x_1 \times P_1^o}$	$\frac{(P-P_1^o)(\beta_1^o - V_1^o)}{760 \times 2.303RT}$	$\log \gamma_1$
1.	0.555	0.473	532.50	1.6747	0.2239	-0.0059	0.2180
2.	0.550	0.442	532.86	1.7748	0.2492	-0.0059	0.2473
3.	0.582	0.538	526.66	1.5611	0.1934	-0.0061	0.1873
4.	0.627	0.708	528.20	1.2742	0.1052	-0.0060	0.0992
5.	0.660	0.784	534.23	1.1976	0.0783	-0.0059	0.0724
6.	0.570	0.516	529.92	1.5843	0.1998	-0.0060	0.1938
7.	0.583	0.528	523.08	1.6043	0.2053	-0.0062	0.1991
8.	0.605	0.631	530.09	1.3746	0.1382	-0.0060	0.1322
9.	0.649	0.742	533.71	1.2455	0.0954	-0.0059	0.0895
10.	0.673	0.807	537.89	1.1703	0.0713	-0.0058	0.0655
11.	0.697	0.862	545.77	1.1260	0.0515	-0.0055	0.0460
12.	0.773	0.921	570.70	1.1177	0.0483	-0.0049	0.0434
13.	0.838	0.990	617.99	1.0410	0.0175	-0.0035	0.0140
14.	0.893	0.995	672.63	1.0141	0.0061	-0.0021	0.0040
15.	0.283	0.116	636.67	2.9122	0.4642	-0.0030	0.4612
16.	0.275	0.120	633.47	2.7494	0.4392	-0.0031	0.4361
17.	0.371	0.191	585.07	2.5232	0.4020	-0.0044	0.3976
18.	0.489	0.306	547.10	2.2199	0.3463	-0.0055	0.3408
19.	0.570	0.518	528.37	1.5828	0.1994	-0.0060	0.1924
20.	0.572	0.516	528.89	1.5929	0.2022	-0.0060	0.1962
21.	0.548	0.485	526.83	1.6300	0.2122	-0.0061	0.2061
22.	0.502	0.371	527.86	1.4675	0.1666	-0.0061	0.1605
23.	0.595	0.640	527.51	1.3394	0.1270	-0.0060	0.1210
24.	0.850	0.978	632.30	1.0446	0.0190	-0.0032	0.0158
25.	0.709	0.873	549.30	1.1236	0.0506	-0.0054	0.0452
26.	0.112	0.027	714.77	4.4106	0.6445	-0.0011	0.6434
27.	0.218	0.070	676.39	3.4992	0.5440	-0.0020	0.5420

TABLE 33

Log γ_2 of the System:

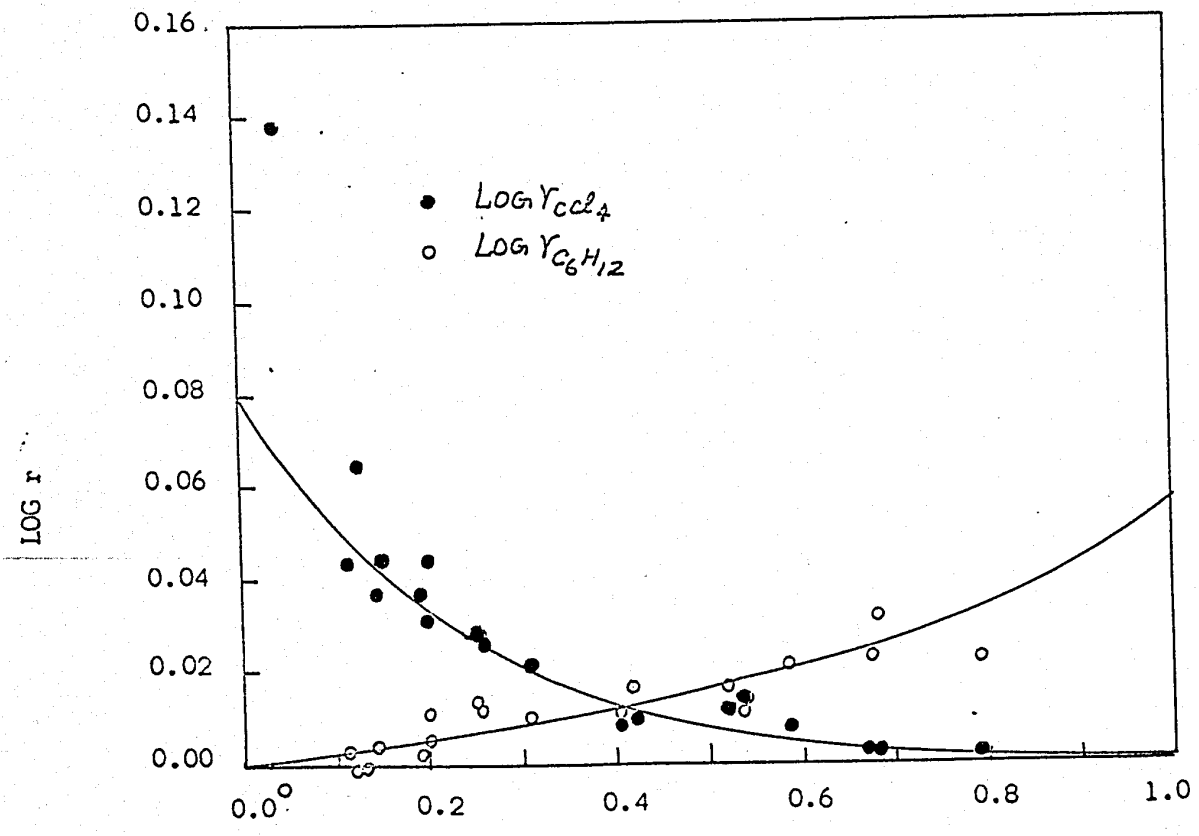
Cyclohexane and Isopropyl Alcohol

Run	Isopropyl Alcohol						
	y_2	x_2	P_2^o	$\frac{y_2 P}{x_2 P_2^o}$	$\log \frac{y_2 P}{x_2 P_2^o}$	$\frac{(P-P_2^o)(\beta_2^o - V_2^o)}{2.303 \times RT}$	log γ_2
1.	0.445	0.527	441.5	1.4536	0.1626	-0.0104	0.1522
2.	0.450	0.558	441.7	1.3875	0.1424	-0.0104	0.1320
3.	0.418	0.462	435.2	1.5799	0.1987	-0.0107	0.1880
4.	0.373	0.292	436.8	2.2224	0.3467	-0.0106	0.3361
5.	0.340	0.216	443.5	2.6972	0.4309	-0.0104	0.4205
6.	0.430	0.484	438.5	1.5397	0.1875	-0.0105	0.1770
7.	0.417	0.472	431.0	1.5577	0.1926	-0.0109	0.1817
8.	0.395	0.369	439.0	1.8531	0.2679	-0.0105	0.2574
9.	0.351	0.258	441.5	2.3418	0.3696	-0.0104	0.3592
10.	0.327	0.193	443.0	2.9066	0.4635	-0.0102	0.4533
11.	0.303	0.138	455.0	3.6673	0.5643	-0.0098	0.5645
12.	0.227	0.079	482.5	4.5253	0.6556	-0.0086	0.6470
13.	0.162	0.010	538.0	22.884	1.3595	-0.0061	1.3534
14.	0.107	0.005	602.3	27.003	1.4314	-0.0042	1.4272
15.	0.717	0.884	560.0	1.1007	0.0417	-0.0056	0.0361
16.	0.725	0.880	556.0	1.1261	0.0515	-0.0058	0.0457
17.	0.629	0.809	500.0	1.1818	0.0725	-0.0079	0.0646
18.	0.511	0.694	457.0	1.2245	0.0880	-0.0097	0.0783
19.	0.430	0.482	437.0	1.5515	0.1909	-0.0106	0.1793
20.	0.428	0.484	437.5	1.5359	0.1861	-0.0103	0.1758
21.	0.452	0.515	435.2	1.5326	0.1855	-0.0107	0.1748
22.	0.418	0.429	436.8	1.6952	0.2292	-0.0106	0.2186
23.	0.405	0.360	436.7	1.9578	0.2918	-0.0106	0.2812
24.	0.150	0.022	555.0	9.3338	0.9701	-0.0059	0.9642
25.	0.291	0.127	459.8	3.7871	0.5783	-0.0096	0.5687
26.	0.888	0.973	653.5	1.0613	0.0258	-0.0026	0.0232
27.	0.782	0.930	609.0	1.0492	0.0209	-0.0041	0.0168

TABLE 34

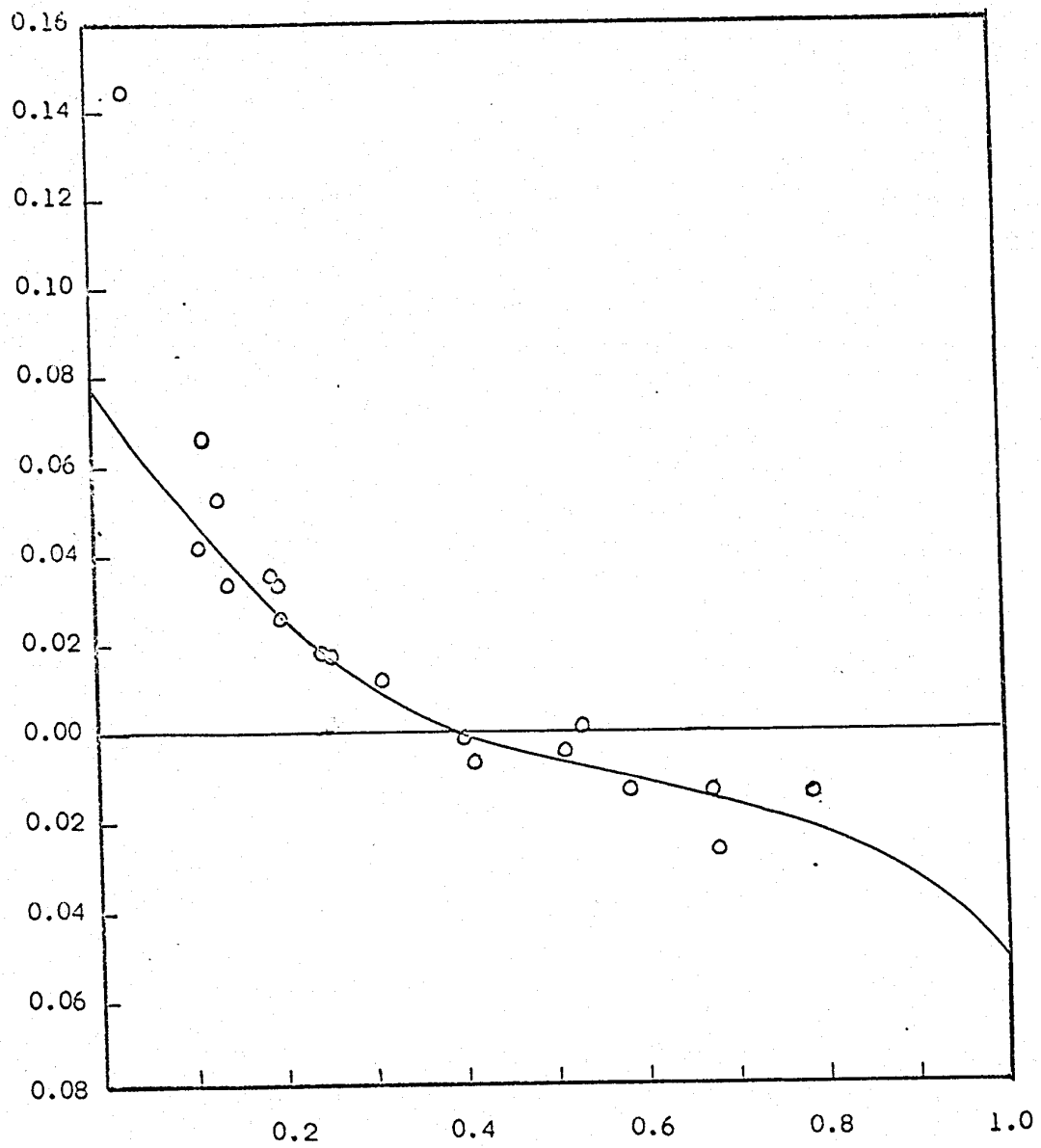
Log γ_1/γ_2 of the System:
1 2
Cyclohexane and Isopropyl Alcohol.

Run	x_1	log γ_1	log γ_2	log γ_1/γ_2
1.	0.473	0.2180	0.1522	+0.0658
2.	0.442	0.2433	0.1320	+0.1113
3.	0.538	0.1873	0.1880	-0.0007
4.	0.708	0.0992	0.3361	-0.2369
5.	0.784	0.0724	0.4205	-0.3481
6.	0.516	0.1938	0.1770	+0.0168
7.	0.528	0.1991	0.1817	+0.0174
8.	0.631	0.1322	0.2574	-0.1252
9.	0.742	0.0895	0.3592	-0.2697
10.	0.807	0.0655	0.4533	-0.3878
11.	0.862	0.0460	0.5645	-0.5185
12.	0.921	0.0434	0.6470	-0.6036
13.	0.990	0.0140	1.3534	-1.3394
14.	0.995	0.0040	1.4272	-1.4232
15.	0.116	0.4612	0.0361	+0.4251
16.	0.120	0.4361	0.0457	+0.3904
17.	0.191	0.3976	0.0646	+0.3330
18.	0.306	0.3408	0.0783	+0.2625
19.	0.518	0.1924	0.1793	+0.0131
20.	0.516	0.1962	0.1758	+0.0204
21.	0.485	0.2061	0.1748	+0.0313
22.	0.571	0.1605	0.2186	-0.0581
23.	0.640	0.1210	0.2812	-0.1602
24.	0.978	0.0158	0.9642	-0.9484
25.	0.873	0.0452	0.5687	-0.5235
26.	0.027	0.6434	0.0232	+0.6202
27.	0.070	0.5420	0.0168	+0.5252



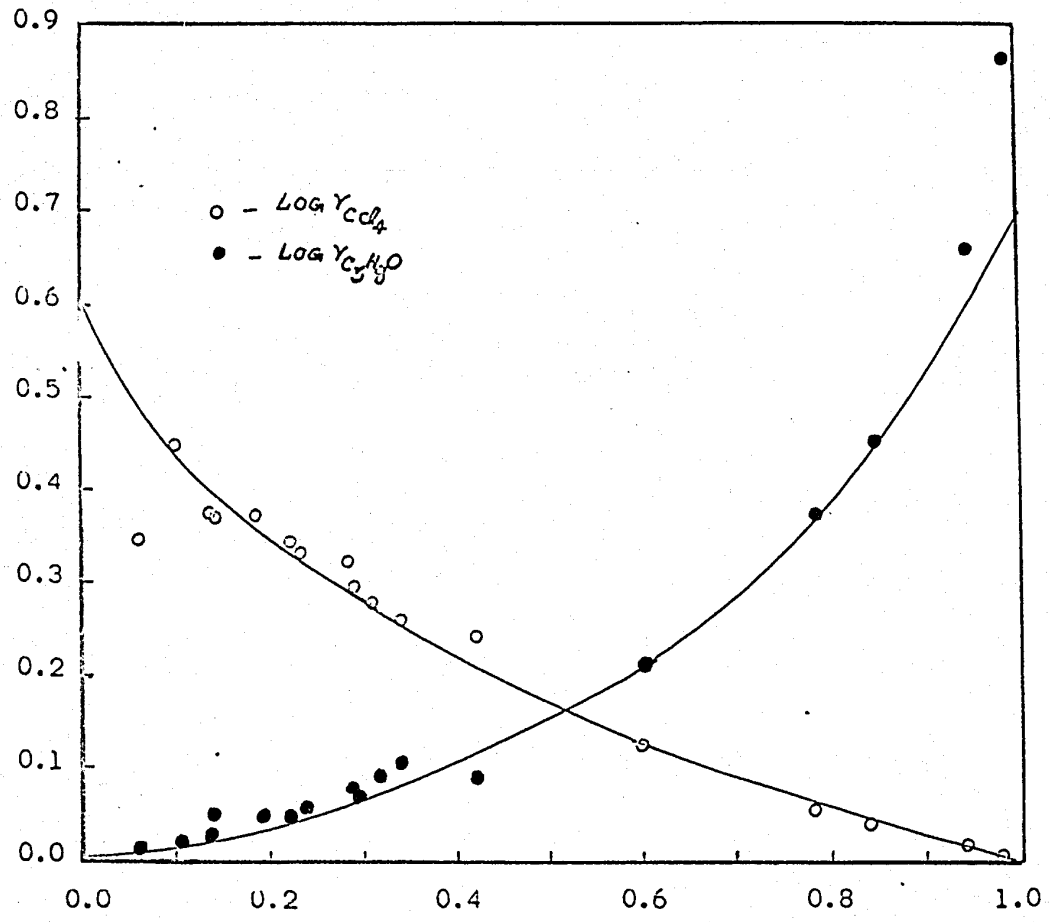
LOG r vs COMPOSITION DIAGRAM FOR THE SYSTEM:
CARBON TETRACHLORIDE AND CYLCLOHEXANE

FIG. 14



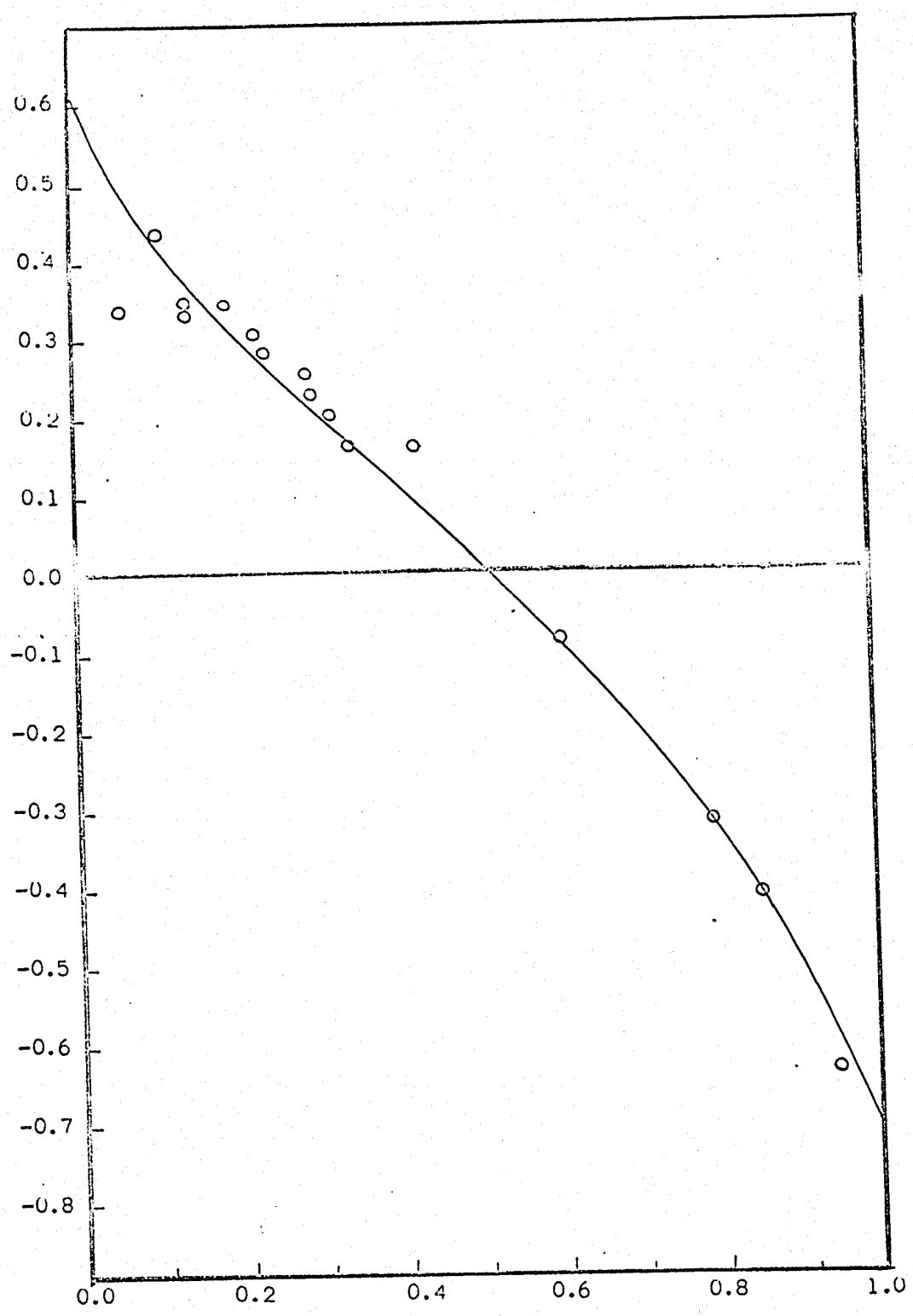
LOG $\frac{f_{CCl_4}}{f_{C_6H_{12}}}$ vs COMPOSITION DIAGRAM FOR THE SYSTEM: CARBON TETRALCHLORIDE AND CYCLOHEXANE.

FIG. 15



LOG r vs. COMPOSITION DIAGRAM FOR THE SYSTEM: CARBON TETRALCHLORIDE AND ISOPROPYL ALCOHOL.

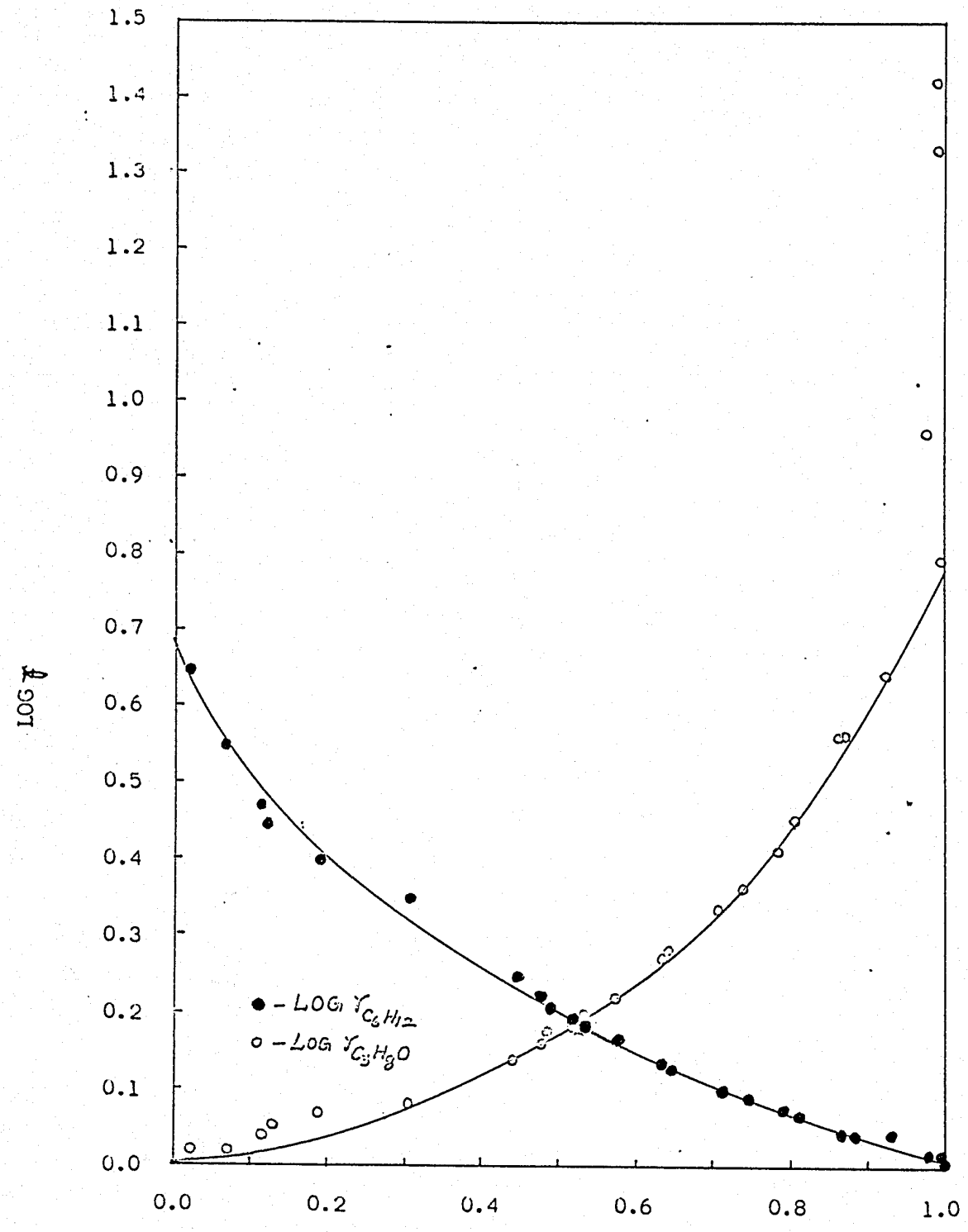
FIG. 16



LOG $\frac{\gamma_{CCl_4}}{\gamma_{C_3H_8O}}$ vs. COMPOSITION DIAGRAM FOR THE SYSTEM:

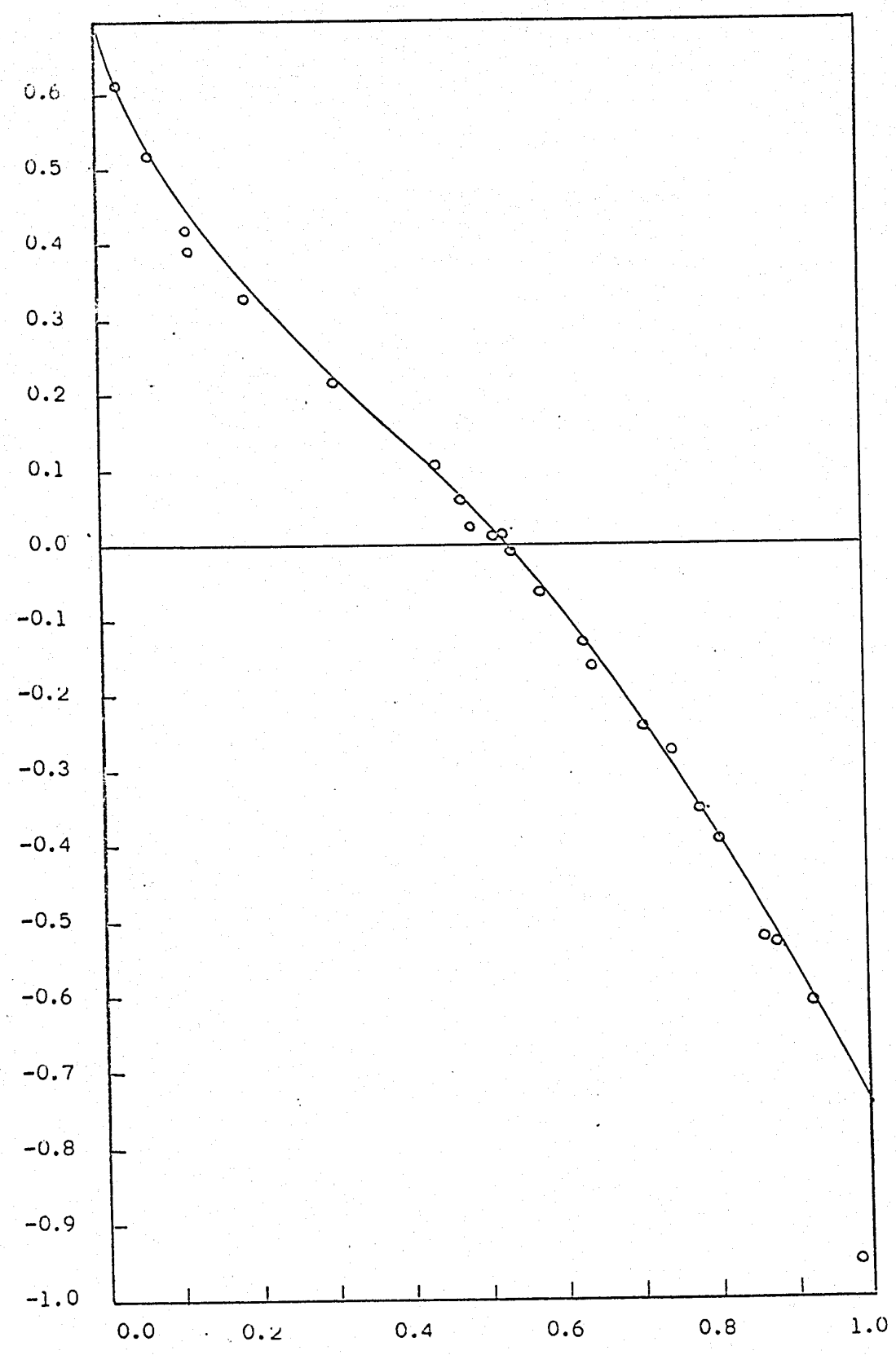
CARBON TETRACHLORIDE AND ISOPROPYL ALCOHOL.

FIG. 17



LOG γ vs. COMPOSITION DIAGRAM OF THE SYSTEM: CYCLOHEXANE AND ISOPROPYL ALCOHOL

FIG. 18



LOG $\frac{\gamma_{C_6H_{12}}}{\gamma_{C_3H_8O}}$ vs. COMPOSITION DIAGRAM FOR THE SYSTEM: CYCLOHEXANE

TABLE 35

Log γ of the System: 1 Carbon Tetrachloride, 2 Cyclohexane and 3 Isopropyl Alcohol

Run	y_1	x_1	P_1^o	$\frac{y_1}{x_1} \times \frac{P}{P_1^o}$	Log $\frac{y_1}{x_1} \times \frac{P}{P_1^o}$	log γ_1	x_1 log γ_1
1.	0.155	0.118	620.5	1.6088	0.2065	0.2033	0.02399
2.	0.273	0.202	604.0	1.7006	0.2306	0.2270	0.04585
3.	0.389	0.326	595.0	1.5242	0.1830	0.1791	0.05839
4.	0.502	0.473	590.0	1.3671	0.1358	0.1310	0.06196
5.	0.563	0.567	588.5	1.2823	0.1079	0.1039	0.05891
6.	0.672	0.730	595.0	1.1758	0.0704	0.0665	0.04855
7.	0.763	0.875	620.0	1.0689	0.0290	0.0258	0.02240
8.	0.147	0.119	600.0	1.5648	0.1945	0.1908	0.02271
9.	0.413	0.387	588.0	1.3794	0.1396	0.1356	0.05248
10.	0.338	0.406	588.5	1.0751	0.0314	0.0274	0.01112
11.	0.480	0.483	588.2	1.2841	0.1086	0.1046	0.05052
12.	0.577	0.622	591.0	1.1930	0.0766	0.0726	0.04516
13.	0.611	0.757	589.5	1.0249	0.0107	0.0071	0.00538
14.	0.893	0.952	676.0	1.0546	0.0233	0.0214	0.02037
15.	0.133	0.117	595.0	1.4520	0.1620	0.1581	0.01850
16.	0.229	0.222	591.0	1.3265	0.1227	0.1187	0.02635
17.	0.344	0.351	589.5	1.2635	0.1016	0.0976	0.03426
18.	0.451	0.489	591.5	1.1851	0.0738	0.0699	0.03418
19.	0.551	0.617	595.2	1.1403	0.0570	0.0531	0.03276
20.	0.650		608.5				
21.	0.801	0.884	647.0	1.0644	0.0270	0.0244	0.02157
22.		0.122	594.0				
23.	0.231	0.253	591.0	1.1682	0.0675	0.0635	0.01607
24.	0.343	0.380	591.0	1.1608	0.0648	0.0608	0.02310
25.	0.477	0.481	588.0	1.2817	0.1079	0.1039	0.04998

(cont'd next page)

TABLE 36

Log γ of the System: 1 Carbon Tetrachloride 2 Cyclohexane and 3 Isopropyl Alcohol

Run	y_2	x_2	P_2^o	$\frac{y_2}{x_2} \times \frac{P}{P_2^o}$	Log $\frac{y_2}{x_2} \times \frac{P}{P_2^o}$	Log γ_2	x_2 log γ_2
1.	0.376	0.224	546.5	2.3344	0.3682	0.3567	0.07990
2.	0.294	0.219	531.5	1.9196	0.2832	0.2770	0.06066
3.	0.198	0.154	523.5	1.8666	0.2711	0.2649	0.04079
4.	0.139	0.135	519.5	1.5062	0.1779	0.1716	0.02317
5.	0.111	0.118	517.5	1.3815	0.1404	0.1340	0.01581
6.	0.013	0.055	523.4	0.3432	T.5356	0.5294	0.02912
7.	0.037	0.032	545.4	1.6113	0.2072	0.2021	0.00647
8.	0.428	0.367	528.2	1.6779	0.2248	0.2188	0.08030
9.	0.233	0.233	516.5	1.5373	0.1867	0.1803	0.04021
10.	0.337	0.163	517.4	3.0370	0.4824	0.4760	0.07759
11.	0.172	0.172	517.5	1.4686	0.1669	0.1605	0.02761
12.	0.132	0.145	519.9	1.3308	0.1242	0.1179	0.01710
13.	0.086	0.103	527.6	1.2064	0.0815	0.0754	0.00784
14.	0.021	0.022	597.5	1.2142	0.0843	0.0802	0.00176
15.	0.485	0.447	523.4	1.5754	0.1974	0.1912	0.08547
16.	0.403	0.379	519.7	1.5550	0.1917	0.1854	0.07027
17.	0.309	0.320	518.3	1.4159	0.1511	0.1448	0.04634
18.	0.215	0.240	520.4	1.3083	0.1167	0.1104	0.02650
19.	0.165	0.192	523.5	1.2476	0.0961	0.0899	0.01726
20.	0.108		536.0				
21.	0.063	0.058	570.4	1.4473	0.1605	0.1556	0.00902
22.		0.561	522.4				
23.	0.441	0.473	520.0	1.3626	0.1344	0.1281	0.06059
24.	0.346	0.394	520.0	1.2834	0.1084	0.1021	0.04023
25.	0.195	0.179	517.6	1.6027	0.2048	0.1984	0.03551

(cont'd next page)

(Table 36, continued)

26.	0.201	0.241	515.0	1.2308	0.0901	0.0841	0.02027
27.	0.252	0.090	527.5	4.0418	0.6066	0.6005	0.05405
28.	0.066	0.068	586.0	1.2587	0.0999	0.0955	0.00649
29.	0.557	0.667	528.5	1.2008	0.0795	0.0735	0.04902
30.	0.486	0.399	528.5	1.7515	0.2434	0.2374	0.09472
31.	0.387	0.472	533.6	1.1708	0.0685	0.0626	0.02955
32.	0.292	0.379	537.0	1.0904	0.0376	0.0318	0.01205
33.	0.077		547.5				
34.	0.163	0.179	575.0	1.2036	0.0805	0.0750	0.01343
35.	0.078	0.077	583.5	1.3194	0.1204	0.1159	0.00892

TABLE 37

Log γ of the System:

1 Carbon Tetrachloride — 2 Cyclohexane — and — 3 Isopropyl Alcohol

Run	y_3	x_3	P_3^o	$\frac{y_3}{x_3} \times \frac{P}{P_3^o}$	$\text{Log} \frac{y_3}{x_3} \times \frac{P}{P_3^o}$	$\text{Log } \gamma_3$	$x_3 \text{ log } \gamma_3$
1.	0.469	0.658	456.6	1.1864	0.0742	0.0844	0.05238
2.	0.433	0.579	441.0	1.2888	0.1102	0.0997	0.05773
3.	0.413	0.520	434.0	1.4005	0.1463	0.1354	0.07041
4.	0.359	0.392	426.5	1.6319	0.2127	0.2016	0.07903
5.	0.326	0.315	425.0	1.8506	0.2673	0.2557	0.08054
6.	0.315	0.215	430.0	2.5894	0.4132	0.4023	0.08649
7.	0.200	0.093	455.0	3.5920	0.5553	0.5455	0.05073
8.	0.425	0.514	437.0	1.4300	0.1578	0.1472	0.07566
9.	0.354	0.390	423.5	1.6289	0.2119	0.2006	0.07823
10.	0.325	0.431	424.2	1.3510	0.1307	0.1194	0.05146
11.	0.348	0.327	424.3	1.9180	0.2829	0.2716	0.08827
12.	0.291	0.233	429.5	2.2203	0.3464	0.3353	0.07812
13.	0.253	0.140	434.8	3.1586	0.4995	0.4867	0.06842
14.	0.086	0.026	513.5	4.8954	0.6998	0.6923	0.01800
15.	0.383	0.436	430.0	1.5526	0.1910	0.1801	0.07852
16.	0.368	0.399	427.5	1.6397	0.2147	0.2036	0.08124
17.	0.347	0.329	425.6	1.8834	0.2750	0.2638	0.08679
18.	0.434	0.271	427.8	2.8451	0.4541	0.4430	0.12005
19.	0.284	0.191	432.0	2.6159	0.4176	0.4067	0.07768
20.	0.242		445.5				
21.	0.136	0.058	483.3	3.6872	0.5667	0.5579	0.03236
22.		0.317	430.2				
23.	0.328	0.274	427.5	2.1148	0.3253	0.3142	0.08609
24.	0.311	0.226	427.5	2.4464	0.3886	0.3775	0.08532
25.	0.328	0.340	423.5	1.7313	0.2384	0.2271	0.07721

(cont'd next page)

(Table 37, continued)

26.	0.239	0.129	421.5	3.3406	0.5238	0.5125	0.06611
27.	0.162	0.185	434.8	1.5306	0.1849	0.1741	0.03221
28.	0.107	0.039	500.3	4.1677	0.6199	0.6119	0.02386
29.	0.317	0.200	437.0	2.7565	0.4404	0.4298	0.08596
30.	0.290	0.245	437.0	2.0586	0.3136	0.3029	0.07421
31.	0.267	0.131	442.6	3.4998	0.5440	0.5335	0.06989
32.	0.251	0.097	446.2	4.4075	0.6442	0.6340	0.06150
33.	0.270	454.2					
34.	0.138	0.051	485.2	4.2384	0.6272	0.6186	0.03155
35.	0.074	0.034	497.0	3.3283	0.5222	0.5141	0.01748

3. Calculation of B, C, D of Redlich and Kester's[7] equation for log γ_1/γ_2 for the three binary systems.

Characteristic points were used as suggested by Redlich and Kister. Value of log γ_1/γ_2 were read from diagrams of log γ_1/γ_2 vs x at x = 0.5, x = 0.1464, x = 0.8536, x = 0.2956 x = 0.7041. At these points, the equation for log γ_1/γ_2 in terms of x becomes

$$x = 0.5, \quad \log \frac{\gamma_1}{\gamma_2} = 1/2\ C, \tag{56}$$

$$x = 0.1464, \log \frac{\gamma_1}{\gamma_2} = 0.7071B - \frac{C}{4}, \tag{57}$$

$$x = 0.8536, \log \frac{\gamma_1}{\gamma_2} = -0.7071B - \frac{C}{4}, \tag{58}$$

$$x = 0.2956, \log \frac{\gamma_1}{\gamma_2} = 0.4082\ (B - \frac{2}{3} D) + \frac{C}{4}, \tag{59}$$

$$x = 0.7041, \log \frac{\gamma_1}{\gamma_2} = -0.4082\ (B - \frac{2}{3} D) + \frac{C}{4}, \tag{60}$$

(a) B_{12}, C_{12} and D_{12} for the system: carbon tetrachloride and cyclohexane.

At $x = 0.5$, $\log \frac{\gamma_1}{\gamma_2} = -0.006$.

Substituting -0.006 in equation (56) for log γ_1/γ_2, one obtains

$$-0.0060 = \frac{1}{2}\ C_{12},$$

and hence

$$C_{12} = -0.0120.$$

At $x = 0.1464$, $\log \frac{\gamma_1}{\gamma_2} = 0.037$.

Substituting 0.037 in equation (57) for $\log \gamma_1/\gamma_2$, one obtains

$$0.037 = 0.7071 B_{12} - \frac{C_{12}}{4},$$

and hence

$$B_{12} = \frac{0.037 - 0.003}{0.7071} = 0.0495$$

At $x = 0.8536$, $\log \frac{\gamma_1}{\gamma_2} = -0.027$.

Substituting -0.027 in equation (58) for $\log \gamma_1/\gamma_2$, one obtains

$$-0.027 = -0.7071 B_{12} - \frac{C}{4},$$

and hence

$$B_{12} = \frac{-0.027 - 0.003}{0.7071} = 0.0424.$$

An average value was taken from the two values of B_{12} calculated as:

$$B_{12\ ave.} = \frac{1}{2} (0.0495 + 0.0424) = 0.0460.$$

At $x = 0.2959$, $\log \frac{\gamma_1}{\gamma_2} = 0.0095$

Substituting 0.0095 in equation (59) for $\log \gamma_1/\gamma_2$, one obtains

$$0.0095 = 0.4082 \left(B_{12} - \frac{2}{3} D_{12}\right) + \frac{C_{12}}{4}$$

$$0.003 + 0.0095 - 0.01878 = \frac{2}{3} \times 0.4082\ D_{12}.$$

hence

$$D_{12} = 0.0231.$$

$$\text{At} \quad x = 0.7041, \log \frac{\gamma_1}{\gamma_2} = -0.017$$

Substituting -0.017 in equation (60) for $\log \gamma_1/\gamma_2$, one obtains

$$-0.017 = -0.4082\ (B_{12} - \frac{2}{3} D_{12}) + \frac{C_{12}}{4}$$

$$0.003 - 0.017 + 0.01878 = \frac{2}{3} \times 0.4082\ D_{12},$$

hence

$$D_{12} = \frac{0.01434}{0.8164} = 0.01756,$$

and

$$D_{12\ \text{ave.}} = \frac{0.0231 + 0.0176}{2} = 0.0203.$$

(b) B_{31}, C_{31} and D_{31} for the systems carbon tetrachloride and isopropyl alcohol.

$$\text{At} \quad x = 0.5, \quad \log \frac{\gamma_1}{\gamma_2} = 0.024$$

and

$$\frac{1}{2} C_{31} = 0.024, \quad C_{31} = 0.048$$

$$\text{At} \quad x = 0.1464, \quad \log \frac{\gamma_1}{\gamma_2} = 0.363$$

and

$$0.7071 B_{31} - \frac{C_{31}}{4} = 0.363, \quad B_{31} = \frac{0.363 + 0.012}{0.7071} = 0.530$$

$$\text{At} \quad x = 0.8536, \quad \log\frac{\gamma_1}{\gamma_2} = 0.425$$

$$-0.7071 B_{31} - \frac{C_{31}}{4} = -0.425 \qquad B_{31} = \frac{0.425 - 0.012}{0.7071} = 0.584$$

and hence

$$B_{31\ \text{ave}} = \frac{0.530 + 0.584}{2} = 0.557$$

$$\text{At} \quad x = 0.2959, \quad \log\frac{\gamma_1}{\gamma_2} = 0.200$$

$$0.4082\ (B_{31} - \tfrac{2}{3} D_{31}) + \frac{C}{4} = 0.200$$

$$D_{31} = \frac{-0.200 + 0.012 + 0.4082 \times 0.557}{0.2722} = 0.108$$

$$\text{At} \quad x = 0.7041, \quad \log\frac{\gamma_1}{\gamma_2} = -0.193$$

$$-0.4082\ (B_{31} - \tfrac{2}{3} D_{31})\ \frac{C_{31}}{4} = -0.193$$

$$D_{31} = \frac{-0.193 - 0.012 + 0.2274}{0.2722} = 0.0827,$$

and

$$D_{31\ \text{ave.}} = \frac{0.0827 + 0.1080}{2} = 0.0917.$$

(c) B_{23}, C_{23} and D_{23} for the system: cyclohexane and isopropyl alcohol.

$$\text{At } x = 0.5, \quad \log\frac{\gamma_1}{\gamma_2} = 0.03$$

and

$$\frac{1}{2} C_{23} = 0.0300, \quad C_{23} = 0.0600$$

$$\text{At} \quad x = 0.1464, \quad \log\frac{\gamma_1}{\gamma_2} = 0.397$$

$$0.7071 B_{23} - \frac{C_{23}}{4} = 0.397,$$

and

$$B_{23} = \frac{0.397 + 0.015}{0.7071} = 0.5826.$$

At $x = 0.8536$, $\log \frac{\gamma_1}{\gamma_2} = -0.465$

$$-0.7071 B_{23} - \frac{C_{23}}{4} = -0.465,$$

$$B_{23} = \frac{0.465 - 0.015}{0.7071} = 0.6364,$$

and

$$B_{23\ ave.} = \frac{0.5826 + 0.6364}{2} = 0.6100.$$

At $x = 0.2959$, $\log \frac{\gamma_1}{\gamma_2} = 0.230,$

$$0.4082\ B_{23} - \frac{2}{3} D_{23} + \frac{C_{23}}{4} = 0.230,$$

$$D_{23} = \frac{(0.4082 \times 0.610 + 0.015 - 0.230)3}{0.8164} = 0.1249.$$

At $x = 0.7041$, $\log \frac{\gamma_1}{\gamma_2} = -0.22$

$$-0.4082(B_{23} - \frac{2}{3} D_{23}) + \frac{C_{23}}{4} = -0.220,$$

$$D_{23} = \frac{(0.2490 - 0.015 - 0.220)\ 3}{0.8164} = 0.0514,$$

and

$$D_{23\ ave.} = \frac{0.1249 + 0.0514}{2} = 0.0881.$$

4. Calculation of ternary constants C, D_1, D_2 and D_3 of Redlich and Kister's equation for the ternary system.

Redlich and Kister's equation of four ternary constants for the free energy function is represented by

$$Q = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3 [C + D_1 (x_2 - x_3) + D_2 (x_3 - x_1) + D_3 (x_1 - x_2)] \qquad (61)$$

where

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3.$$

In this equation, x_1, x_2 and x_3 are experimentally determined liquid composition and $\log r_1$, $\log r_2$ and $\log r_3$ are the calculated values for the carbon tetrachloride, cyclohexane and isopropyl alcohol respectively. These values are presented in Table 15 and Tables 35, 36, 37.

Q_{12}, Q_{23} and Q_{31} are calculated by the equations:

$$Q_{12} = x_1x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2],$$

$$Q_{23} = x_2x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2],$$

and

$$Q_{31} = x_3x_1 [B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2].$$

In these equations, x_1, x_2 and x_3 are experimentally determined liquid composition of the ternary system and the constants B, C, D are the calculated constants for the three binary systems.

The calculated values for Q_{12}, Q_{23} and Q_{31} are presented in Tables 38, 39, 40.

For calculating the ternary constants, equation (61) is rearranged as

$$\frac{Q - Q_{12} - Q_{23} - Q_{31}}{x_1 x_2 x_3} = C + (x_2 - x_3) D_1 + (x_3 - x_1) D_2 + (x_1 - x_2) D_3 \qquad (62)$$

The values of the term on the lefthand side of equation (62) are tabulated in Table 41.

Eighteen runs were chosen for the calculations of the ternary constants by means of the least square I.B.M. programming. Equations are listed in Table 42. The constants obtained from the I.B.M. programming are:

$$C = 1.1720240$$

$$D_1 = 1.3034932$$

and

$$D_2 = -0.13315090$$

$$D_3 = 1.1892104.$$

TABLE 38

Calculation of Q_{12}

$B_{12} = 0.0460$ $C_{12} = -0.0120$ $D_{12} = 0.0203$

$$Q_{12} = x_1 x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2]$$

Run	x_1x_2	x_1-x_2	$C_{12}(x_1-x_2)$	$(x_1-x_2)^2$	$D_{12}(x_1-x_2)^2$	Q_{12}
1.	0.0264	-0.106	0.00127	0.0112	0.000227	0.00125
2.	0.0442	-0.017	0.000204	0.000289	0.00000587	0.00204
3.	0.0502	0.172	-0.00206	0.0295	0.000599	0.00224
4.	0.0639	0.338	-0.00406	0.114	0.00231	0.00283
5.	0.0669	0.449	-0.00539	0.202	0.00410	0.00299
6.	0.0402	0.675	-0.00810	0.456	0.00926	0.00190
7.	0.0280	0.843	-0.01010	0.711	0.0144	0.00141
8.	0.0437	-0.248	+0.00298	0.0615	0.00125	0.00220
9.	0.0863	0.164	-0.00197	0.0270	0.000550	0.00385
10.	0.0662	0.243	-0.00292	0.0590	0.00120	0.00293
11.	0.0831	0.311	-0.00373	0.0967	0.00196	0.00368
12.	0.0902	0.477	-0.00572	0.228	0.00463	0.00405
13.	0.0780	0.654	-0.00785	0.428	0.00869	0.00365
14.	0.0209	0.930	-0.0112	0.865	0.0176	0.00110
15.	0.0523	-0.330	+0.00396	0.109	0.00221	0.00273
16.	0.0841	-0.157	+0.00188	0.0246	0.000500	0.00407
17.	0.1123	0.031	-0.000372	0.000961	0.0000195	0.00513
18.	0.1174	0.249	-0.00299	0.0620	0.00126	0.00520
19.	0.1185	0.425	-0.00510	0.181	0.00367	0.00528
20.						

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(Table 38, continued)

21.	0.0513	0.826	-0.00991	0.682	0.0138	0.00256
22.	0.0684	-0.439	+0.00527	0.193	0.00392	0.00377
23.	0.1197	-0.220	+0.00264	0.0484	0.000983	0.00594
24.	0.1497	-0.014	+0.000168	0.000196	0.00000398	0.00691
25.	0.0861	0.302	-0.00362	0.0912	0.00185	0.00381
26.	0.1518	0.369	-0.00467	0.151	0.00307	0.00674
27.	0.0653	0.635	-0.00762	0.403	0.00818	0.00304
28.	0.0607	0.825	-0.00990	0.681	0.0138	0.00303
29.	0.0887	-0.534	+0.00641	0.285	0.00579	0.00516
30.	0.1420	-0.043	+0.000516	0.00185	0.0000376	0.00661
31.	0.1874	-0.075	+0.000900	0.00563	0.000114	0.00881
32.	0.1986	0.145	-0.00174	0.0210	0.000426	0.00887
33.						
34.	0.1378	0.591	-0.00709	0.349	0.00708	0.00634
35.	0.685	0.812	-0.00974	0.659	0.0134	0.00340

TABLE 39

Calculation of Q_{23}

$B_{23} = 0.610$ $C_{23} = 0.0600$ $D_{23} = 0.0881$

$$Q_{23} = x_2x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2]$$

Run	x_2x_3	x_2-x_3	$C_{23}(x_2-x_3)$	$(x_2-x_3)^2$	$D_{23}(x_2-x_3)^2$	Q_{23}
1.	0.1474	-0.434	-0.0262	0.188	0.0166	0.05290
2.	0.1268	-0.360	-0.0216	0.130	0.0115	0.07607
3.	0.0801	-0.366	-0.0220	0.134	0.0118	0.04804
4.	0.0529	-0.257	-0.0154	0.066	0.00581	0.03176
5.	0.0372	-0.197	-0.0118	0.0388	0.00342	0.02238
6.	0.0118	-0.160	-0.00960	0.0256	0.00226	0.00711
7.	0.0030	-0.061	-0.00366	0.00372	0.000328	0.00182
8.	0.1886	-0.147	-0.00882	0.0216	0.00190	0.11374
9.	0.0870	-0.167	-0.0100	0.0279	0.00246	0.05241
10.	0.0703	-0.268	-0.0161	0.0718	0.00633	0.04200
11.	0.0593	-0.173	-0.0104	0.0299	0.00263	0.03571
12.	0.0338	-0.088	-0.00528	0.00774	0.000682	0.02046
13.	0.0144	-0.037	-0.00222	0.00137	0.000121	0.00875
14.	0.0006	-0.004	-0.000240	0.0000160	0.00000141	0.00366
15.	0.1949	0.011	+0.000660	0.000121	0.0000107	0.11902
16.	0.1512	-0.020	-0.00120	0.000400	0.0000352	0.09206
17.	0.1053	-0.009	-0.000540	0.0000810	0.0000714	0.06418
18.	0.0650	-0.031	-0.00186	0.000961	0.0000847	0.03953
19.	0.0367	+0.001	+0.0000600	0.00000100	0.000000881	0.02239
20.						

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(Table 39, continued)

21.	0.0034	0.000	0.	0.000	0.	0.00207
22.	0.1778	0.244	0.0146	0.0595	0.00524	0.11200
23.	0.1296	0.199	0.0119	0.0396	0.00349	0.08105
24.	0.0890	0.168	0.0101	0.0282	0.00248	0.05541
25.	0.0609	-0.161	-0.00966	0.0259	0.00228	0.03670
26.	0.0311	0.112	0.00672	0.0125	0.00110	0.01921
27.	0.0167	-0.095	-0.00570	0.00903	0.000896	0.01011
28.	0.0027	0.029	+0.00174	0.000841	0.0000741	0.00165
29.	0.1334	0.467	+0.0280	0.218	0.0192	0.08768
30.	0.0978	0.154	+0.00924	0.0237	0.00209	0.06077
31.	0.0618	0.341	+0.0205	0.116	0.0102	0.03960
32.	0.0368	0.282	+0.0169	0.0795	0.00700	0.02333
33.						
34.	0.0091	0.128	+0.00768	0.0164	0.00144	0.00563
35.	0.0026	0.043	+0.00258	0.00185	0.000163	0.00159

TABLE 40

Calculation of Q_{31}

$B_{31} = 0.557$ $C_{31} = 0.048$ $D_{31} = 0.0917$

$$Q_{31} = x_3x_1 [B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2]$$

Run	x_3x_1	x_3-x_1	$C_{31}(x_3-x_1)$	$(x_3-x_1)^2$	$D_{31}(x_3-x_1)^2$	Q_{31}
1.	0.0776	0.540	0.02592	0.292	0.02678	0.04731
2.	0.1170	0.377	0.1810	0.142	0.01302	0.06881
3.	0.1695	0.194	0.00931	0.0376	0.00345	0.09657
4.	0.1854	-0.081	-0.00389	0.00656	0.000602	0.10266
5.	0.1786	-0.252	-0.01210	0.0635	0.00582	0.09836
6.	0.1570	-0.515	-0.02472	0.265	0.02430	0.08738
7.	0.0814	-0.782	-0.03754	0.612	0.05612	0.04685
8.	0.0612	0.395	0.01896	0.156	0.01431	0.03612
9.	0.1509	0.003	0.000144	0.00000900	0.00000	0.08407
10.	0.1750	0.025	0.00120	0.000025	0.00006	0.09770
11.	0.1666	-0.138	-0.00662	0.0190	0.00174	0.09198
12.	0.1449	-0.389	-0.01867	0.151	0.01385	0.08001
13.	0.1060	-0.617	-0.02962	0.381	0.03494	0.05961
14.	0.0248	-0.926	-0.04445	0.857	0.07859	0.01466
15.	0.0510	0.319	0.01531	0.102	0.00935	0.02966
16.	0.0886	0.177	0.00850	0.0313	0.00287	0.05036
17.	0.1155	-0.022	-0.00106	0.000484	0.00004	0.06446
18.	0.1325	-0.218	-0.01046	0.0475	0.00436	0.07299
19.	0.1178	-0.426	-0.02045	0.181	0.01660	0.06516
20.						

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(Table 40, continued)

21.	0.0513	-0.826	-0.03965	0.682	0.06254	0.02975
22.	0.0387	0.195	0.00936	0.0380	0.00348	0.02205
23.	0.0693	0.021	0.00101	0.00044	0.00004	0.03867
24.	0.0859	-0.154	-0.00739	0.0237	0.00217	0.04740
25.	0.1635	-0.141	-0.00677	0.0199	0.00182	0.09026
26.	0.0813	-0.501	-0.02405	0.251	0.02302	0.04520
27.	0.1341	-0.540	-0.02592	0.292	0.02678	0.07481
28.	0.0348	-0.854	-0.04099	0.729	0.01685	0.02028
29.	0.0266	0.067	0.00322	0.00449	0.00041	0.01491
30.	0.0872	-0.111	-0.00533	0.0123	0.00113	0.04829
31.	0.0520	-0.266	-0.01277	0.0708	0.00649	0.02864
32.	0.0508	-0.427	-0.02050	0.182	0.01669	0.02810
33.						
34.	0.0393	-0.719	-0.03451	0.517	0.04741	0.02240
35.	0.0302	-0.855	-0.04104	0.731	0.06703	0.01761

TABLE 41

Calculations of $\frac{Q - Q_{12} - Q_{23} - Q_{31}}{x_1 x_2 x_3}$

Run	$Q = x_1 \log\gamma_1 + x_2 \log\gamma_2 + x_3 \log\gamma_3$	$x_1 x_2 x_3$	$Q_{12}+Q_{23}+Q_{31}$	$Q-Q_{12}-Q_{23}-Q_{31}$	$\frac{Q-Q_{12}-Q_{23}-Q_{31}}{x_1 x_2 x_3}$
1.	0.14627	0.01737	0.10146	0.04481	2.5747
2.	0.16424	0.02559	0.14692	0.01732	0.6768
3.	0.16959	0.02610	0.14685	0.02274	0.8712
4.	0.16416	0.02505	0.13725	0.02691	1.0742
5.	0.15526	0.02107	0.12373	0.03153	1.4964
6.	0.16416	0.00864	0.09639	0.06777	7.8437
7.	0.07960	0.00260	0.05008	0.02952	11.3538
8.	0.17867	0.02246	0.15206	0.02661	1.1847
9.	0.17092	0.03366	0.14033	0.03059	0.9087
10.	0.14017	0.02853	0.14263		
11.	0.16640	0.02867	0.13137	0.03503	1.2218
12.	0.14038	0.02102	0.10452	0.03586	1.7059
13.	0.08164	0.01092	0.07201	0.00963	0.8818
14.	0.04013	0.00054	0.01942	0.02071	38.3518
15.	0.18249	0.00136	0.15141	0.03108	22.8529
16.	0.17786	0.03667	0.14649	0.03137	0.8554
17.	0.16739	0.03695	0.13377	0.03362	0.4098
18.	0.18073	0.03181	0.11772	0.06301	1.9808
19.	0.12770	0.02263	0.09283	0.03487	1.5408
20.					

(table 41, cont'd next page)

(Table 41, cont'd)

21.	0.06295	0.00298	0.03438	0.02857	9.5872
22.			0.13782		
23.	0.16275	0.03280	0.12566	0.03709	1.1307
24.	0.14865	0.03383	0.10972	0.03893	1.1507
25.	0,16270	0.02927	0.13077	0.03193	1.0908
26.	0.12298	0.01958	0.07115	0.05183	2.6470
27.	0.09163	0.01208	0.08796	0.00367	0.3038
28.	0.05098	0.00237	0.02496	0.02602	10.9789
29.	0.14502	0.01774	0.10775	0.03727	2.1004
30.	0.06306	0.03479	0.11558		
31.	0.11298	0.02455	0.07705	0.03593	1.4635
32.	0.09079	0.01926	0.06020	0.03049	1.5830
33.					
34.	0.00300	0.00703	0.03437	0.02863	4.2147
35.	0.06187	0.00233	0.02260	0.03927	16.8540

TABLE 42

Equations for Solving the Ternary Constants

Run		
2	$C - 0.360D_1 + 0.377D_2 - 0.017D_3$	= 0.6768
3	$C - 0.366D_1 + 0.194D_2 + 0.172D_3$	= 0.8712
4	$C - 0.257D_1 - 0.081D_2 + 0.388D_3$	= 1.0742
5	$C - 0.197D_1 - 0.252D_2 + 0.449D_3$	= 1.4964
8	$C - 0.147D_1 + 0.395D_2 - 0.248D_3$	= 1.1847
9	$C - 0.167D_1 + 0.003D_2 + 0.164D_3$	= 0.9087
11	$C - 0.173D_1 - 0.138D_2 + 0.311D_3$	= 1.2218
12	$C - 0.088D_1 - 0.389D_2 + 0.477D_3$	= 1.7059
16	$C - 0.020D_1 + 0.177D_2 - 0.157D_3$	= 0.8554
17	$C - 0.009D_1 - 0.022D_2 + 0.031D_3$	= 0.9098
18	$C - 0.031D_1 - 0.218D_2 + 0.249D_3$	= 1.9808
19	$C + 0.001D_1 - 0.426D_2 + 0.425D_3$	= 1.5408
23	$C + 0.199D_1 + 0.021D_2 - 0.220D_3$	= 1.1307
24	$C + 0.168D_1 - 0.154D_2 - 0.014D_3$	= 1.1507
25	$C - 0.161D_1 - 0.141D_2 + 0.302D_3$	= 1.0908
26	$C + 0.112D_1 - 0.501D_2 + 0.389D_3$	= 2.6470
31	$C + 0.341D_1 - 0.266D_2 - 0.075D_3$	= 1.4635
32	$C + 0.282D_1 - 0.427D_2 + 0.145D_3$	= 1.5830

VII - DISCUSSION

1. Testing the consistency of data

The Gibbs-Duhem equation

$$\int_{x=o}^{x=1} \log \frac{\gamma_1}{\gamma_2}\, dx = -\int_{T_o \text{ at } x_1=o}^{T_1 \text{ at } x_1=1} \frac{\Delta H}{RT^2}\, dt \qquad (43)$$

is to be used. The lefthand side of equation (43) is evaluated by measuring the area under the curve $\log \frac{\gamma_1}{\gamma_2}$ vs x from x=0 to x=1. The righthand term can be evaluated either analytically or graphically. If ΔH as a function of T is known, the integral can be evaluated by substituting this function for ΔH. Graphically, ΔH is taken from experimentally determined value for temperature near T_o and T_1 if $T_1 - T_o$ is small or an average value of ΔH for T_o and T_1 is used. $\frac{\Delta H}{RT^2}$ is then calculated and a curve of $\frac{\Delta H}{RT^2}$ vs T is drawn. The area under this curve from T_o to T_1 gives the value for the integral $\int_{T_o}^{T_1} \frac{\Delta H}{RT^2}\, dt$. If the values thus measured for the two integrals are nearly equal and opposite in sign, it may be concluded that the experimental data are consistent.

(i) Carbon tetrachloride-isopropyl alcohol

$$\int_{x=o}^{x=1} \log \frac{\gamma_1}{\gamma_2}\, dx = \text{area under the curve of Fig. 17}$$

$$= -0.0004$$

$\frac{1}{2.303R} \int_{T_o \text{ at } x=o}^{T_1 \text{ at } x=1} \frac{\Delta H}{RT^2} dT = 0.0013$ is taken from S.K. Jeun's[27] thesis on the vapor-liquid equilibrium submitted to the University of Ottawa, Ottawa, Canada.

(ii) Cyclohexane and isopropyl alcohol

$$\int_{x=o}^{x=1} \log \frac{\gamma_1}{\gamma_2} dx = \text{area under the curve of Fig. 19}$$

$$= -0.0002$$

$\frac{1}{2.303R} \int_{T_o \text{ at } x=o}^{T_1 \text{ at } x=1} \frac{\Delta H}{RT^2} dT = 0.0002$ is taken from the same paper of Jeun's.

(iii) Carbon tetrachloride-cyclohexane system

$$\int_o^1 \log \frac{\gamma_1}{\gamma_2} dx = \text{area under the curve of Fig. 15}$$

$$= o$$

ΔH measured by Coates, Sullivan and Ott's[28] for temperature $40^\circ C$ has a maximum value of 31 calories per mole. For approximation, ΔH is taken as 31 calories per mole, this value is considerably smaller than the values for the other two systems. As the value of the integral

$$\int_{T_o \text{ at } x=o}^{T_1 \text{ at } x=1} \frac{\Delta H}{RT^2} dT$$

for the other two systems is small and $T_1 - T_o$ is also small, the value for the integral is therefore negligible.

2. Checking of Redlich and Kister's three constants equation for the binary systems

By substituting ten values of x from 0.0 - 1.0 in Redlich and Kister's equation, as listed in Tables 43, 44, 45, 46, it is found that the three constants equation fit the binary system very well as shown by plotting the calculated values for $\log \frac{\gamma_1}{\gamma_2}$ in the diagrams for $\log \frac{\gamma_1}{\gamma_2}$ vs x in Fig. 20, 21, 22.

TABLE 43

Redlich and Kister Equation of Three Constants for x=0, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, 1.0 for the Binary System

X	$\log \frac{\gamma_1}{\gamma_2} = B(1-2x) + C[6x(1-x)-1] + D(1-2x)[1-8x(1-x)]$
0	$\log \frac{\gamma_1}{\gamma_2} = B - C + D$
.1	$\log \frac{\gamma_1}{\gamma_2} = 0.8B - 0.46C + 0.224D$
.2	$\log \frac{\gamma_1}{\gamma_2} = 0.6B - 0.04C - 0.168D$
.3	$\log \frac{\gamma_1}{\gamma_2} = 0.4B + 0.26C - 0.272D$
.4	$\log \frac{\gamma_1}{\gamma_2} = 0.2B + 0.44C - 0.184D$
.6	$\log \frac{\gamma_1}{\gamma_2} = -0.2B + 0.44C + 0.184D$
.7	$\log \frac{\gamma_1}{\gamma_2} = -0.4B + 0.26C + 0.272D$
.8	$\log \frac{\gamma_1}{\gamma_2} = -0.6B - 0.04C + 0.168D$
.9	$\log \frac{\gamma_1}{\gamma_2} = -0.8B - 0.46C - 0.224D$
1.0	$\log \frac{\gamma_1}{\gamma_2} = -B - C - D$

TABLE 44

Checking the Redlich Kister Equation for the System Carbon Tetrachloride[1] and Cyclohexane[2]

$B_{12} = 0.0460$ $C_{12} = 0.0120$ $D_{12} = 0.0203$

X	Log $\frac{\gamma_1}{\gamma_2}$
0	B - C + D = 0.0460 + 0.0120 + 0.0203 = +0.078
0.1	0.8B-0.46C+0.24D = 0.8 X 0.0460+0.46 X 0.0120+0.224 X 0.0203 = 0.0368 + 0.00552 + 0.004547 = 0.04687
0.2	0.6B-0.04C-0.168D = 0.6 X 0.0460+0.04 X 0.0120-0.168 X 0.0203 = 0.0276 + 0.00048 - 0.00341 = 0.02467
0.3	0.4B+0.26C-0.272D = 0.4 X 0.0460-0.26 X 0.0120-0.272 X 0.0203 = 0.0184 - 0.00312 - 0.00552 = 0.00976
0.4	0.2B+0.44C-0.184D = 0.2 X 0.0460-0.44 X 0.0120-0.184 X 0.0203 = 0.0092 - 0.00528 - 0.00374 = 0.00018
0.6	-0.2B+0.44C+0.184D = 0.0092 - 0.00528 + 0.00374 = -0.01074
0.7	-0.4B+0.26C+0.272D = -0.0184 - 0.00312 + 0.00552 = -0.0160
0.8	-0.6B-0.04C+0.168D = -0.0276 + 0.00048 + 0.00341 = -0.02371
0.9	-0.8B-0.46C-0.224D= -0.0368 + 0.00552 - 0.00455 = -0.003503
1.0	-B - C - D = -0.0460 + 0.0120 - 0.0203 = .0543

TABLE 45

Checking the Redlich-Kister Equation for the System Carbon Tetrachloride(1)-Isopropyl Alcohol(2)

$B_{31} = 0.557$ $C_{31} = 0.0480$ $D_{31} = 0.0920$

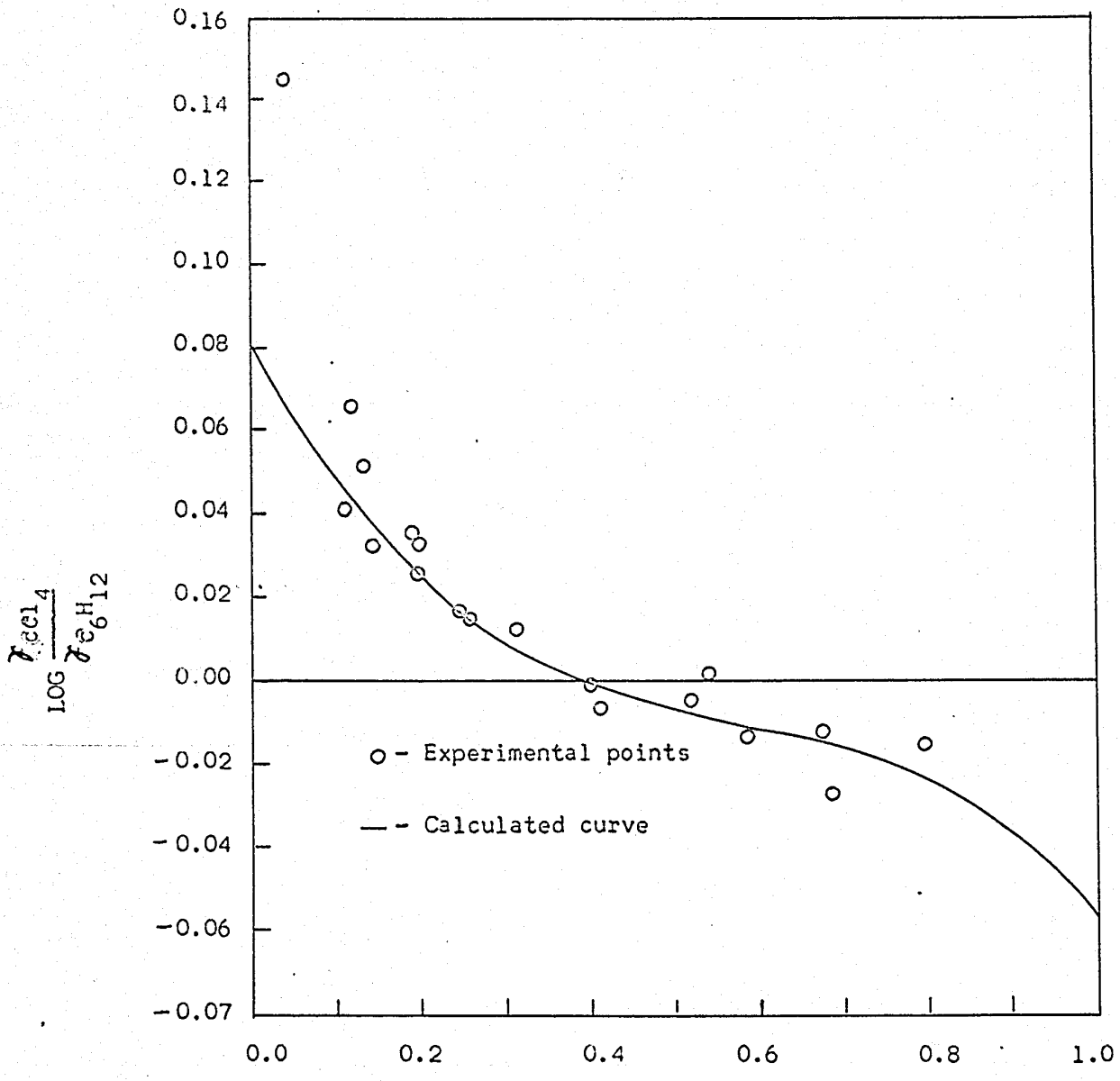
X	$\text{Log } \frac{\gamma_1}{\gamma_2}$
0	B - C + D = 0.6010
0.1	0.8 X 0.557 - 0.46 X 0.048 + 0.224 X 0.092 = 0.4456 - 0.02208 + 0.02061 = 0.4441
0.2	0.6 X 0.557 - 0.04 X 0.048 - 0.0168 X 0.092 = 0.3342 - 0.00192 - 0.01546 = 0.3168
0.3	0.4 X 0.557 + 0.26 X 0.048 - 0.272 X 0.092 = 0.2228 + 0.01248 - 0.02502 = 0.2103
0.4	0.2 X 0.557 + 0.44 X 0.048 - 0.184 X 0.092 = 0.1114 + 0.02112 - 0.01693 = 0.1156
0.6	-0.2 X 0.557 + 0.44 X 0.048 + 0.184 X 0.092 = -0.1114 + 0.02112 + 0.01693 = 0.07335
0.7	-0.4 X 0.557 + 0.26 X 0.048 + 0.272 X 0.092 = -0.2228 + 0.01248 + 0.02502 = -0.1853
0.8	-0.6 X 0.557 - 0.04 X 0.048 + 0.168 X 0.092 = -0.3342 - 0.00192 + 0.01546 = -0.2307
0.9	-0.8 X 0.557 - 0.46 X 0.048 - 0.224 X 0.092 = -0.4456 - 0.02208 - 0.02061 = -0.4883
1.0	- B - C - D = -0.557 - 0.048 - 0.092 = -0.6970

TABLE 46

Checking the Redlich-Kister Equation for the System
Cyclohexane[1] and Isopropyl Alcohol[2]

B_{23} = 0.610 C_{23} = 0.0600 D_{23} = 0.0881

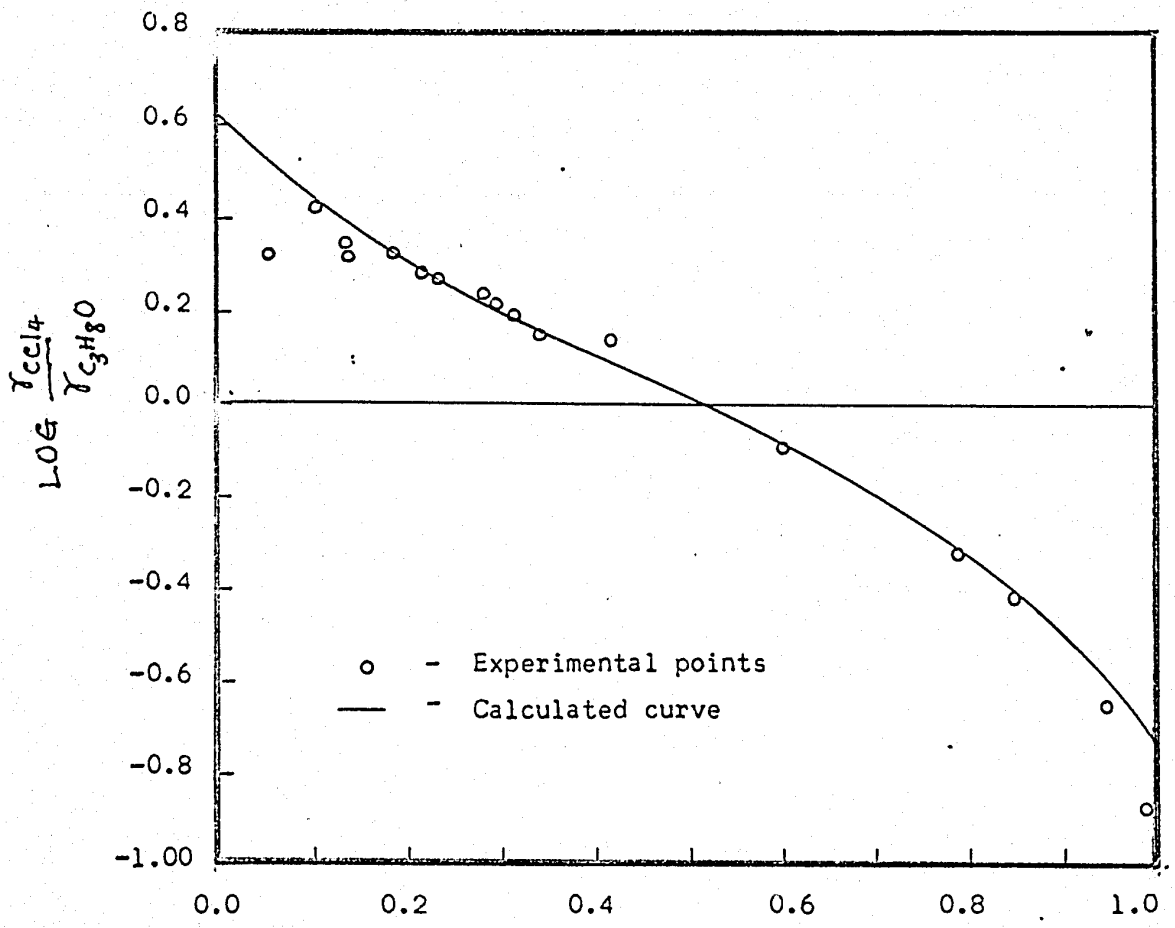
X	Log $\frac{\gamma_1}{\gamma_2}$
0	B - C + D = 0.610 - 0.0600 + 0.0881 = 0.6380
0.1	0.8 X 0.610 - 0.46 X 0.0600 + 0.224 X 0.0881 = 0.4880 - 0.0276 + 0.01971 = 0.4801
0.2	0.6 X 0.610 - 0.04 X 0.0600 - 0.168 X 0.0881 = 0.366 - 0.0024 - 0.01478 = 0.3488
0.3	0.4 X 0.610 + 0.26 X 0.0600 - 0.272 X 0.0881 = 0.244 + 0.0156 - 0.2394 = 0.2357
0.4	0.2 X 0.610 + 0.44 X 0.0600 - 0.184 X 0.0881 = 0.122 + 0.0264 - 0.01619 = 0.1322
0.6	-0.2 X 0.610 + 0.44 X 0.0600 + 0.184 X 0.0881 = 0.122 + 0.0264 + 0.01619 = -0.07941
0.7	-0.4 X 0.610 + 0.26 X 0.0600 + 0.272 X 0.0881 = -0.244 + 0.0156 + 0.02394 = -0.2045
0.8	-0.6 X 0.610 - 0.04 X 0.0600 + 0.168 X 0.0881 = -0.366 - 0.0024 + 0.01478 = -0.3536
0.9	-0.8 X 0.610 - 0.46 X 0.0600 - 0.224 X 0.0881 = -0.488 - 0.0276 - 0.01971 = -0.5353
1.0	-B -C -C = -0.7580



LOG $\frac{\gamma_{CCl_4}}{\gamma_{C_6H_{12}}}$ vs. COMPOSITION DIAGRAM FOR THE SYSTEM:

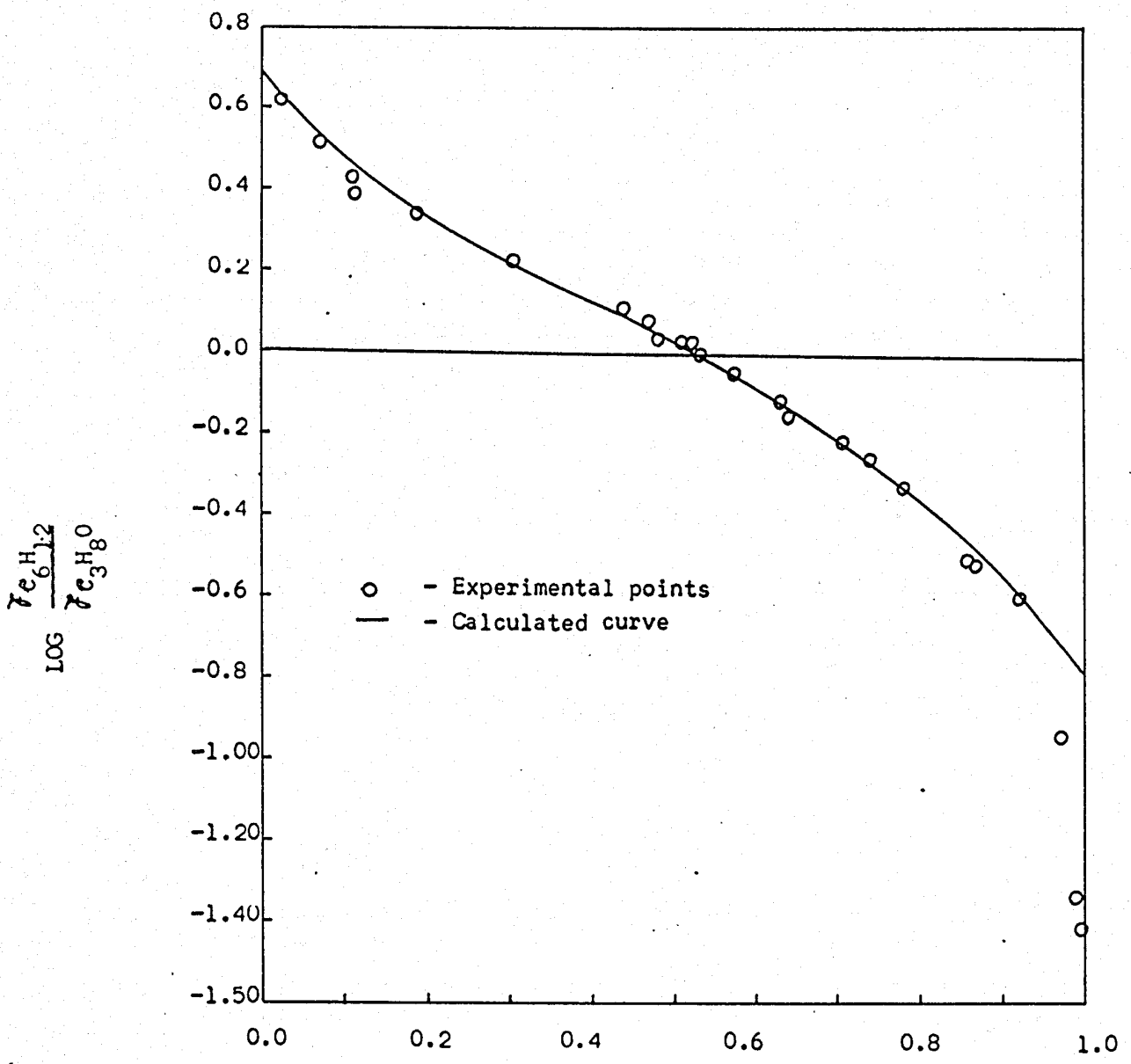
CARBON TETRALCHLORIDE AND CYCLOHEXANE

FIG. 20



LOG $\frac{\gamma_{CCl_4}}{\gamma_{C_3H_8O}}$ vs. COMPOSITION DIAGRAM FOR THE SYSTEMS CARBON TETRALCHLORIDE AND ISOPROPYL ALCOHOL.

FIG. 21



LOG $\frac{\gamma c_6H_{12}}{\gamma c_3H_8O}$ vs. COMPOSITION DIAGRAM FOR THE SYSTEM:

CYCLOHEXANE AND ISOPROPYL ALCOHOL

FIG. 22

3. Checking of Redlich and Kister's four ternary constants equation

Run 10 is chosen for checking.

Q calculated with experimental data is 0.14017.

Q from the Redlich and Kister equation:

$$Q = x_1x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2]$$
$$+ x_2x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2]$$
$$+ x_3x_1 [B_{31} + C_{31} (x_3 - x_1) + D_{31} (x_3 - x_1)^2]$$
$$+ x_1x_2x_3[C + D_1(x_2 - x_3) + D_2(x_3 - x_1) + D_3(x_1 - x_2)]$$

In Run 10, $x_1 = 0.406$ $x_2 = 0.163$ $x_3 = 0.431$

and the constants determined are

$B_{12} = 0.046$	$C_{12} = -0.012$	$D_{12} = 0.020$
$B_{23} = 0.610$	$C_{23} = 0.060$	$D_{23} = 0.088$
$B_{31} = 0.557$	$C_{31} = 0.048$	$D_{31} = 0.0917$
$C = 1.172$	$D_1 = 1.303$	$D_2 = -0.133$
		$D_3 = 1.189$
$x_1 = 0.406$	$x_2 = 0.163$	$x_3 = 0.431$

$$x_1x_2 [B_{12} + C_{12} (x_1 - x_2) + D_{12} (x_1 - x_2)^2]$$
$$= 0.406 \times 0.163 [0.046 + 0.012 \times 0.243 + 0.02 \times 0.243^2]$$
$$= 0.0662 [0.046 - 0.00292 + 0.00118]$$
$$= 0.0662 \times 0.0501 = \underline{0.00331}$$

$$x_2x_3 [B_{23} + C_{23} (x_2 - x_3) + D_{23} (x_2 - x_3)^2]$$

$$= 0.163 \times 0.431 \, [0.610 + 0.060 \times -.268 + 0.088 \times (.268)^2]$$

$$= 0.0703 \, [0.610 + (-0.0107) + 0.00632] = 0.0703 \times 0.6056$$

$$= \underline{0.00426}$$

$$x_3x_1 \, [B_{31} + C_{31} \, (x_3 - x_1) + D_{31} \, (x_3 - x_1)^2]$$

$$= 0.406 \times 0.431 \, [0.557 + 0.048 \times 0.025 + 0.0917 \, (0.025)^2]$$

$$= 0.1750 \, [0.557 + 0.00120 + 0.0917 \times 0.000625]$$

$$.0000573$$

$$= 0.1750 \times 0.55825 = \underline{0.0977}$$

$$x_1x_2x_3 \, [1.172 - 1.303 \times .268 - 0.133 \times 0.025 + 1.189 \times 0.243]$$

$$= .406 \times .163 \times .431 \, [1.172 - 0.349 - 0.00333 + 0.289]$$

$$= 0.0284 \times 1.109 = 0.0315$$

$$Q = 0.00331 + 0.00426 + 0.0977 + 0.0315$$

$$= 0.1368.$$

The value checks with the value 0.14017 obtained from the expression:

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 + x_3 \log \gamma_3$$

for the Run 10. It can be concluded that Run 10 is consistent.

Run 10 was the only point which was not an end point among the runs which were not taken in the calculation of the ternary constants.

4. A research was made of literature on the vapor-liquid equilibrium of the binary and the ternary systems of carbon tetrachloride, cyclohexane and isopropyl alcohol. Four articles[18,23,24,25] were of the system carbon tetrachloride and cyclohexane and one[26] the system carbon tetrachloride and isopropyl alcohol.

Scatchard, Wood and Mochel's[18] work was isothermal determination of vapor-liquid equilibrium at several temperatures. The data for 40°C and 70°C were extrapolated to obtain the isobaric composition and equilibrium temperature at atmospheric pressure. It was found that the expolated equilibrium temperature and composition in equilibrium of Scatchard el and that of the present investigation agreed very well as shown in Table 47.

TABLE 47

Comparison with the Expolated Isobaric Equilibrium Data of Scatchard, Wood and Mochel's Data for Isothermal Vapor-Liquid Equilibrium of the System: Carbon Tetrachloride and Cyclohexane

Composition of liquid in mole fraction of carbon tetrachloride	Equilibrium Temperature in °C		Difference in temperature in °C between the two determinations
X	Scatchard	Observed	
0.0	80.37	80.60	+0.23
0.1	80.03	79.83	-0.20
0.2	79.39	79.15	-0.24
0.3	78.64	78.58	-0.06
0.4	78.21	78.07	-0.14
0.5	77.80	77.68	-0.12
0.6	77.52	77.34	-0.18
0.7	77.07	77.02	-0.05
0.8	76.77	76.74	-0.03
0.9	76.44	76.53	+0.09
11.0	76.41	76.44	+0.03

Norrish and Twigg[24] have determined the vapor-liquid equilibrium composition of the system carbon tetrachloride and cyclohexane. Their data are presented in Table 48. A comparison with present investigation is shown in Fig. 23. The agreement is good for the entire composition range.

The isothermal vapor-liquid equilibrium of Brown and Edwald, Scatchard, Wood and Mochel are compared in Fig. 24. It is seen that their data are in good agreement with each other. From these comparisons for the system carbon tetrachloride and cyclohexane, it is seen that the results of the present investigation are consistent with all the available data on this system.

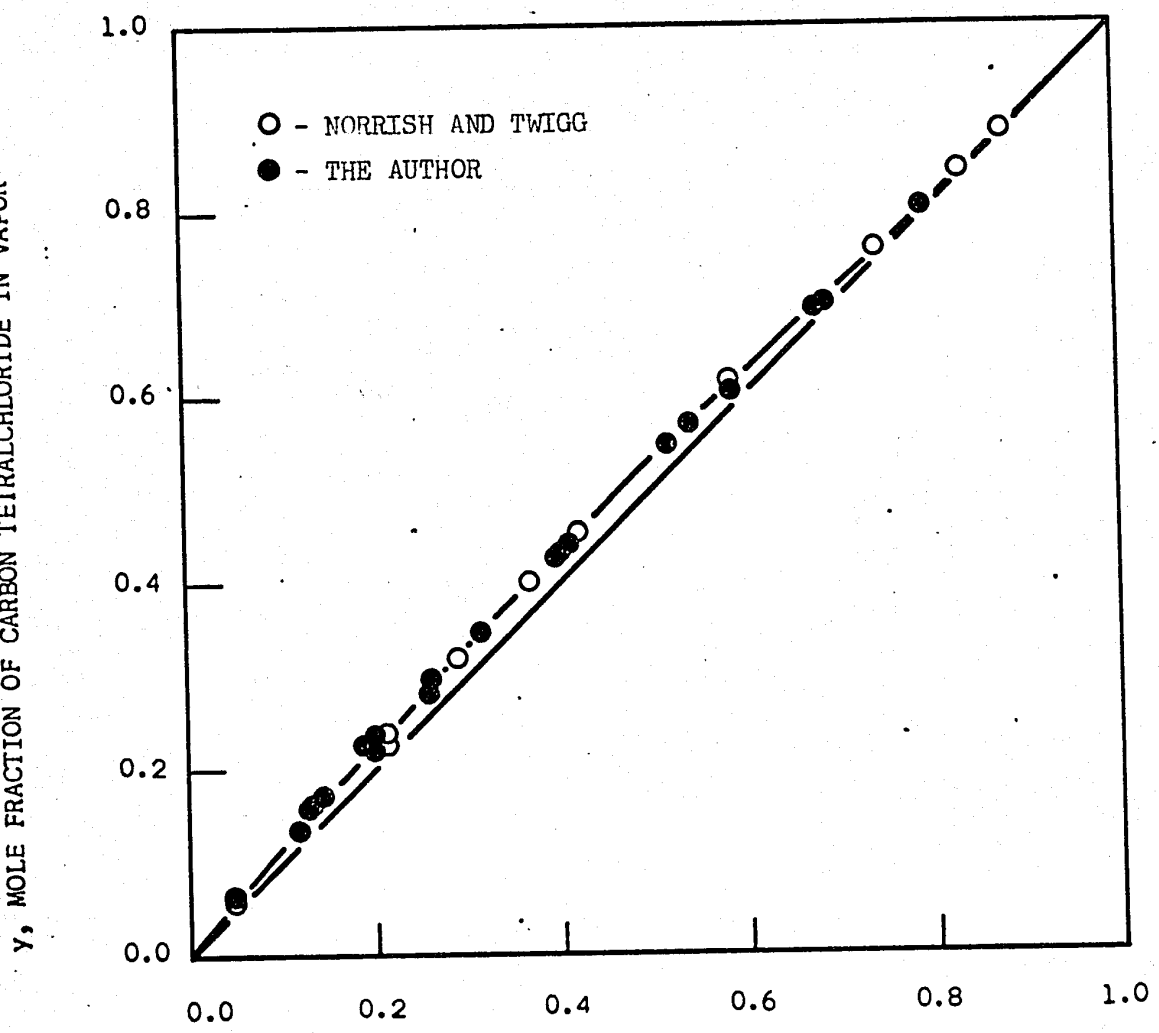
The isothermal data of Papousek, Papouskova and L. Page at 70°C for the system: carbon tetrachloride and isopropyl alcohol are presented in Fig. 25 for comparison with present investigation. The compositions read from Fig. 25 corresponding to a pressure of 760 mm. agree fairly well with the compositions corresponding to a temperature of 70°C of present investigation.

TABLE 48

Norrish and Twigg's data

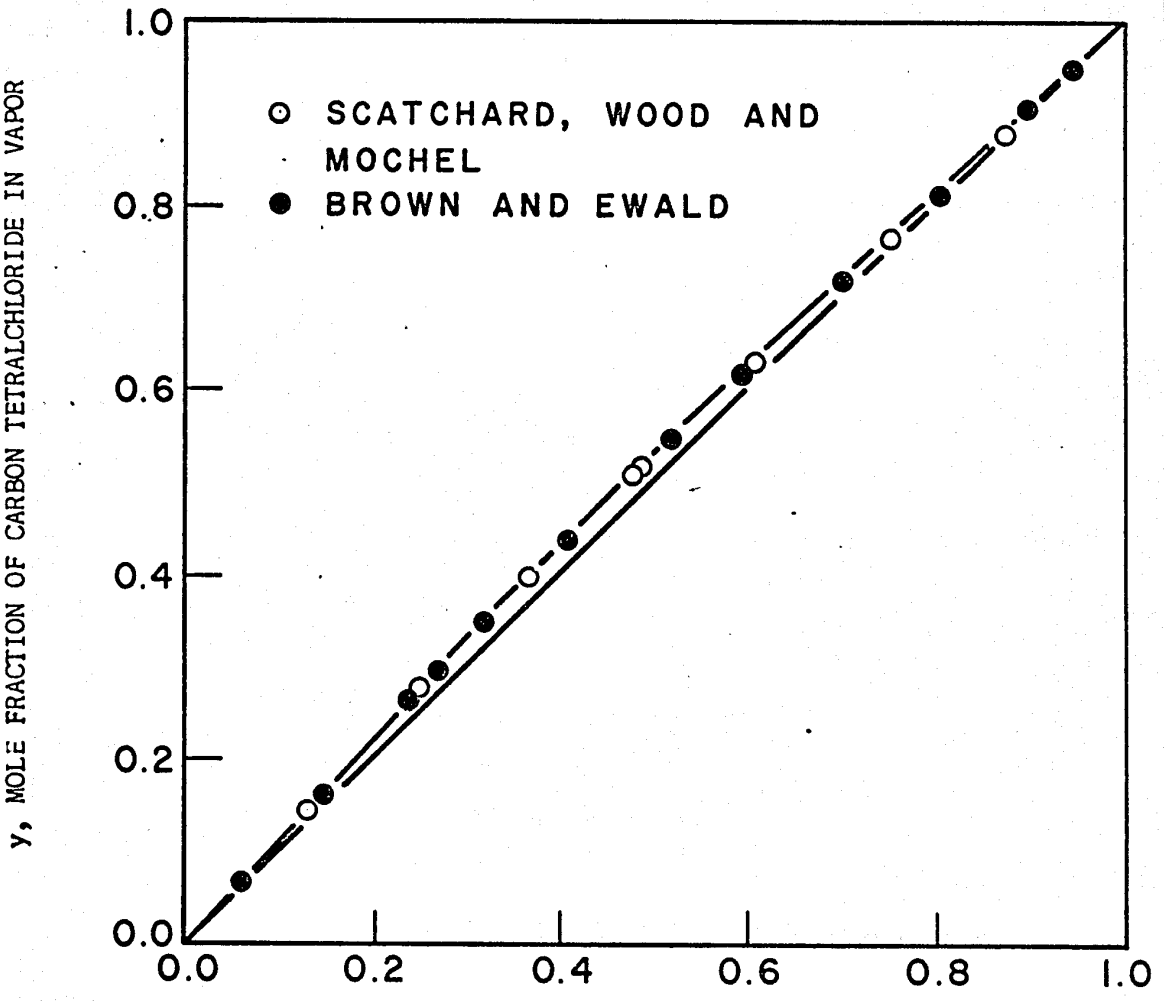
Carbon tetrachloride-Cyclohexane at pressure of 760 mm Hg.

Mole fraction of Carbon tetrachloride	
Liquid	Vapor
0.048	0.056
0.207	0.233
0.286	0.3195
0.366	0.396
0.4195	0.454
0.5845	0.6155
0.7425	0.7595
0.833	0.843
0.880	0.886



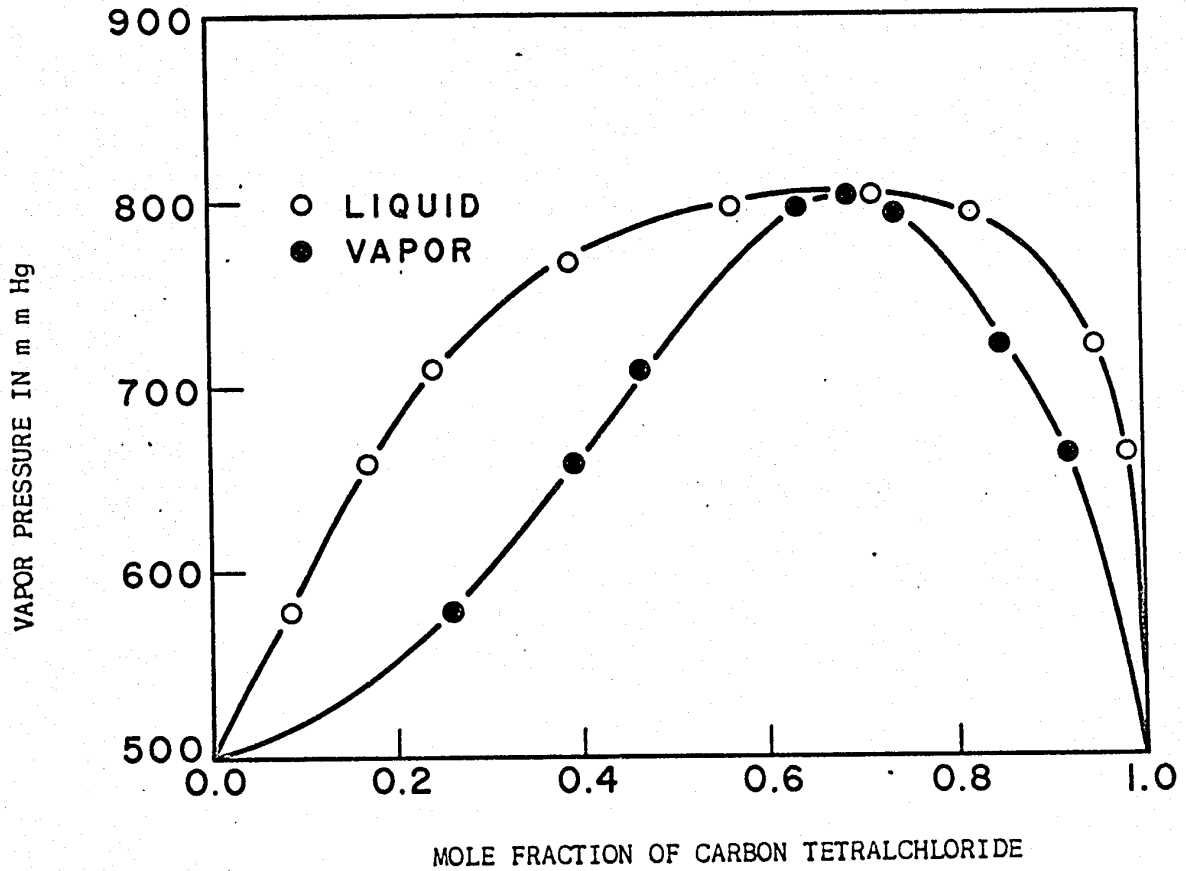
COMPOSITION IN VAPOR VS. COMPOSITION IN LIQUID DIAGRAM OF THE SYSTEM: CARBON TETRALCHLORIDE AND CYCLOHEXANE

FIG. 23



COMPOSITION IN VAPOR VS. COMPOSITION IN LIQUID DIAGRAM OF THE SYSTEM: CARBON TETRALCHLORIDE AND CYCLOHEXANE AT 70°C

FIG. 24



P-x-y DIAGRAM AT 70°C OF THE SYSTEM: CARBON TETRALCHLORIDE AND ISOPROPYL ALCOHOL OF PAPOUŠEK, PAPOUŠKOVÁ AND PAGO.

FIG. 25

5. Density of the binary mixtures

It was found that the density of the mixture carbon tetrachloride and cyclohexane, carbon tetrachloride and isopropyl alcohol increases with the concentration of carbon tetrachloride as shown in Table 49 and Fig. 26, 27. The density of the mixture cyclohexane and isopropyl alcohol decreases as the concentration of cyclohexane increases until the composition is that of the azeotrope. After this composition the density increases as the concentration of cyclohexane increases as shown in Table 50 and Fig. 28.

TABLE 49

Density of the Mixtures:

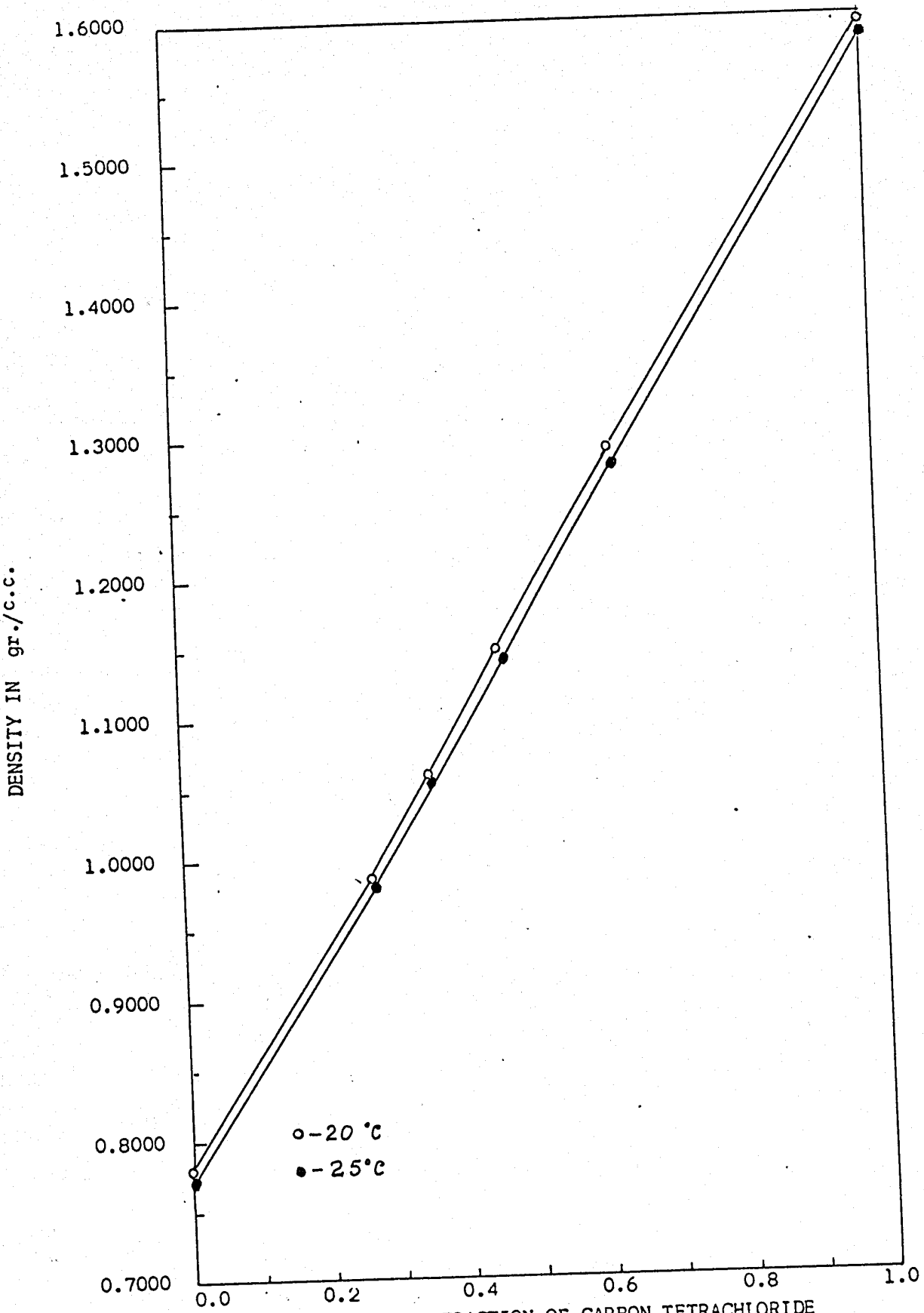
Carbon Tetrachloride and Cyclohexane

Mole fraction of Carbon Tetrachloride	Density in g/cc at 20°C	Density in g/cc at 25°C
0.000	0.77855	0.77389
0.271	0.9850	0.9800
0.353	1.0590	1.0540
0.458	1.1460	1.1400
0.623	1.2850	1.2770
1.000	1.59397	1.58429

Density of the Mixtures:

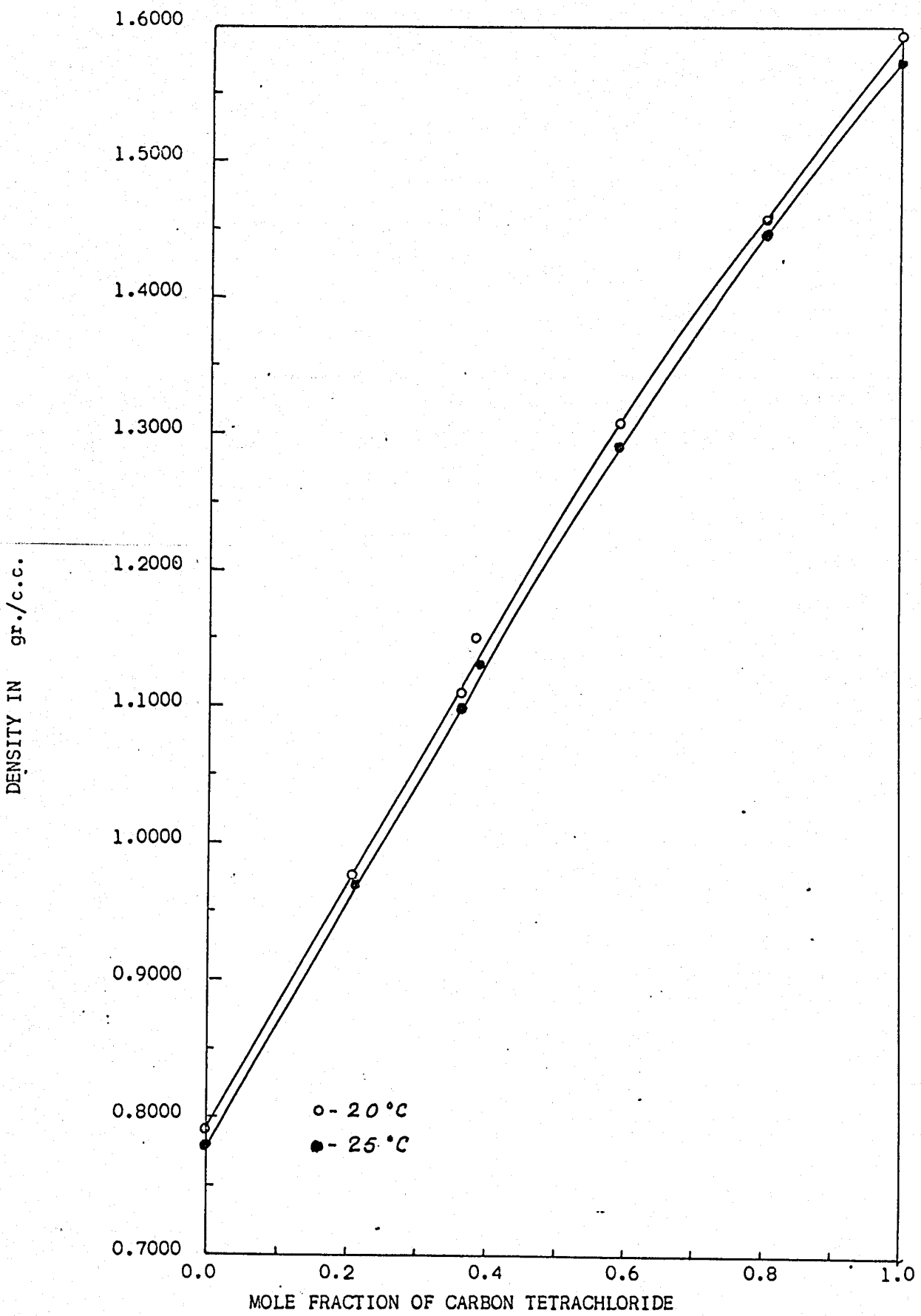
Carbon Tetrachloride and Isopropyl Alcohol

Mole fraction of Carbon Tetrachloride	Density in g/cc at 20°C	Density in g/cc at 25°C
0.000	0.78554	0.78091
0.205	0.97701	0.9780
0.367	1.1115	1.0960
0.389	1.1508	1.1300
0.455	1.1701	1.1360
0.590	1.3090	1.2940
0.803	1.4590	1.4481
1.000	1.59397	1.57458



DENSITY SIAGRAM OF THE MIXTURE: CARBON TETRACHLORIDE AND CYCLOHEXANE.

FIG. 26



DENSITY DIAGRAM OF THE MIXTURE: CARBON TETRACHLORIDE AND ISOPROPYL ALCOHOL

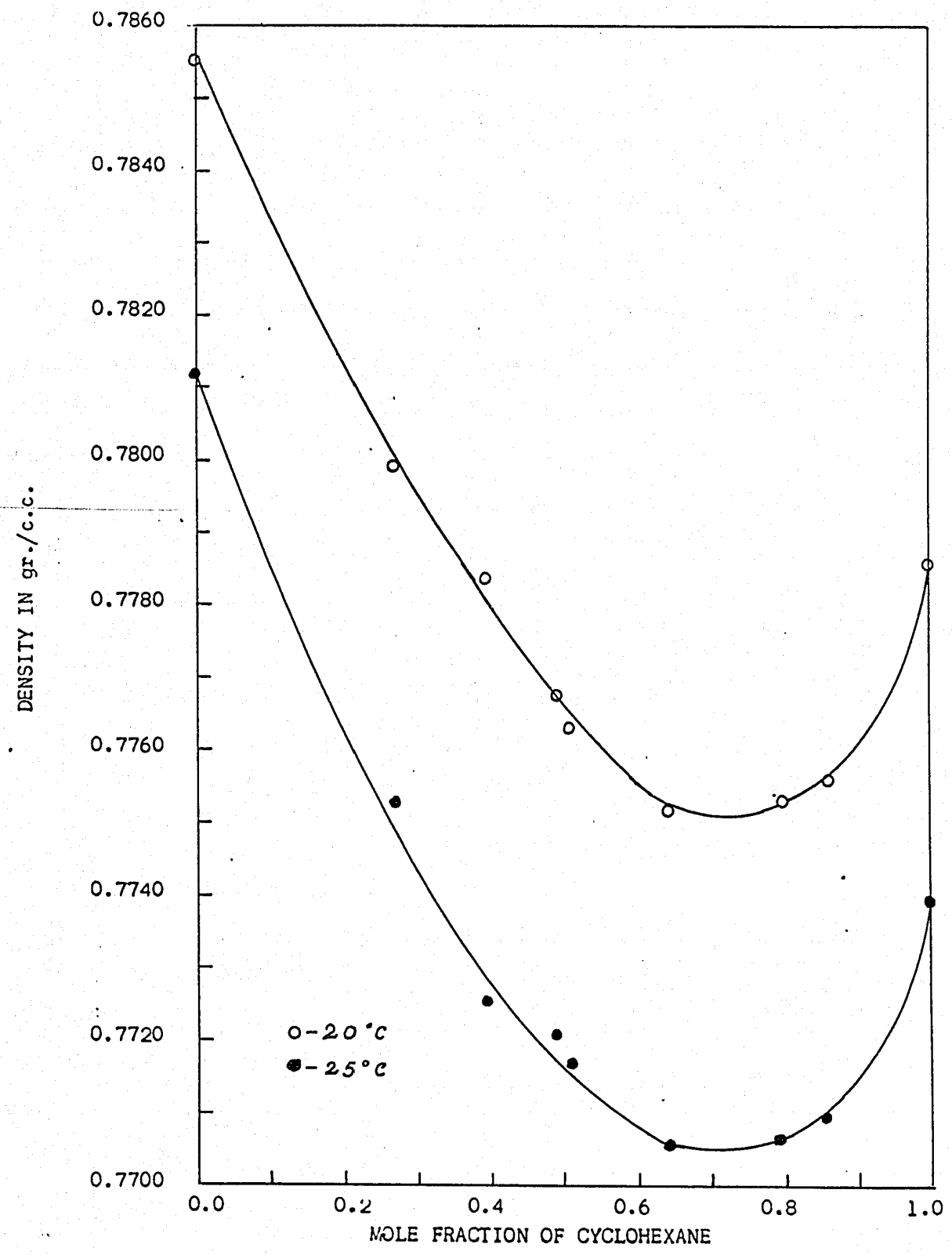
FIG. 27

TABLE 50

Density of the Mixture

Cyclohexane and Isopropyl Alcohol

Mole fraction of Cyclohexane	Density in g/c.c. at 20°C	Density in g/c.c. at 25°C
0.000	0.78554	0.78120
0.274	0.77992	0.77527
0.397	0.77838	0.77251
0.494	0.77674	0.77204
0.515	0.77630	0.77165
0.648	0.77518	0.77052
0.800	0.77528	0.77058
0.860	0.77553	0.77090
1.000	0.77860	0.77390



DENSITY DIAGRAM OF THE MIXTURE: CYCLOHEXANE AND ISOPROPYL ALCOHOL.

FIG. 28

VIII - CONCLUSION

1. The design of the still was improved for better temperature determination and better mixing of the liquid and the vapor condensate. Besides, the placing of the internal heater at the bottom of the boiler eliminated the disadvantages of having an opening at the top as in the original still.

2. In measuring the density for analyzing the mixtures, it was found that the logarithm of density is a linear function of temperature. This relationship furnished an easier and more accurate reading for analyzing. Studies have been made on other mixtures and it was found that the linear relationship holds for many mixtures for various range of temperatures. Further study is suggested to correlate density data for general application.

3. The density of the mixture cyclohexane-isopropyl alcohol as a function of the composition has a minimum value for a certain composition.

4. The azeotrope composition and the equilibrium temperature were found to agree closely with the values given in the litterature for the binary systems: carbon tetrachloride-isopropyl alcohol and cyclohexane-isopropyl alcohol. An azeotropic point was located for the ternary system. Further investigation is suggested to determine the composition and the equilibrium temperature of ternary mixtures in the neighborhood of the ternary azeotrope.

5. The Gibbs-Duhem equation for binary vapor-liquid equilibrium at constant pressure was used to test the consistency of the data. The data for all three binary systems were found to be consistent.

6. The three binary systems and the ternary system of carbon tetrachloride, cyclohexane and isopropyl can be represented by the Redlich-Kister's equation as follows:

$$\log \frac{\gamma_{CCl_4}}{\gamma_{C_6H_{12}}} = 0.0460\ (x_1-x_2) - 0.00120\ [6x_1\ (x_1-x_2) - 1] + 0.0200\ (x_1-x_2)\ [1 - 8x_1\ (x_1-x_2)],$$

$$\log \frac{\gamma_{C_6H_{12}}}{\gamma_{C_3H_8O}} = 0.610\ (x_1-x_2) + 0.0600\ [6x_1\ (x_1-x_2) - 1] + 0.0881\ (x_1-x_2)\ [1 - 8x_1\ (x_1-x_2)],$$

$$\log \frac{\gamma_{CCl_4}}{\gamma_{C_3H_8O}} = 0.577\ (x_1-x_2) + 0.0480\ [6x_1\ (x_1-x_2) - 1] + 0.0917\ (x_1-x_2)\ [1 - 8x_1\ (x_1-x_2)]$$

and

$$Q_{123} = Q_{12} + Q_{23} + Q_{31} + x_1x_2x_3\ [1.172 + 1.303\ (x_2-x_3) - 0.133\ (x_3-x_1) + 1.189\ (x_1-x_2)]$$

where $Q_{12} = x_1x_2\ [0.0460 - 0.0120\ (x_1-x_2) + 0.0200\ (x_1-x_2)^2]$

$Q_{23} = x_2x_3\ [0.610 + 0.0600\ (x_1-x_2) + 0.0881\ (x_1-x_2)^2]$

and

$$Q_{31} = x_3 x_1 \left[0.557 + 0.0480 (x_1 - x_2) + 0.0917 (x_1 - x_2)^2\right].$$

Since the values for the constants C_{12}, C_{23} and C_{31} are small, it is expected that the curve for log γ_1/γ_2 should have S-shape as shown in Fig. 15, 17 and 19 for the three binary systems.

IX - ACKNOWLEDGEMENT

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