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EVALUATION OF HERINGTON
GENERAL INTEGRAL TEST
FOR
VAPOR-LIQUID EQUILIBRIUM DATA
BY
RAJA GOPAL NORI
A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
OF
MASTER OF SCIENCE IN CHEMICAL ENGINEERING
AT
NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1974

ABSTRACT

A new set of general integral tests for the thermodynamic consistency of isothermal and isobaric equilibrium data of binary systems was proposed by E.F.G. Herington.

The systems Benzene-Cyclohexane and Benzene-n-Propanol were examined using Herington integral tests. The data used included sets of data known to be in error. One set was, in effect, at true vapor-liquid equilibrium (the data of literature) but the other data was obtained when the system was inadequately insulated and heated.

Herington test showed significantly different estimates for heats of mixing for the cases involved. The best data showed heats of mixing near the theoretical values. The data known to be erroneous showed heats of mixing at variance with observation. The Herington test is found to be a significant improvement over the standard area test.

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INTRODUCTION

Vapor-Liquid equilibrium data are important from a theoretical view and for utilization in industry. This data can be generally calculated for ideal solutions, but unfortunately most solutions are non-ideal in behaviour. There is no way in the absence of experimental data at present to predict quantitatively the deviation from ideality.

It is very difficult to get accurate Vapor-Liquid equilibrium data in the laboratory. The amount of time spent in gathering data and the results obtained are always in doubt as the methods used need highly sophisticated equipment. The data published in the literature as pointed out by Redlich and Kister (⁴) is questionable. A number of investigators (1) have developed special techniques for testing and expanding the data to improve the dependability of actual data taken in the laboratory for Vapor-Liquid equilibrium of binary solutions. These techniques are based on certain thermodynamic functions, such as activity coefficients which measure the degree of deviation from the ideality.

In the literature, the most widely applied test has been, the "area test". This consists of plotting $\ln \frac{\gamma_1}{\gamma_2}$ against composition where, γ_1 and γ_2 are the liquid phase activity coefficients of components 1 and 2. This test was developed by Bourne (5). The Gibbs-Duhem equation is used to check phase - equilibrium data for thermodynamic consistency. It is important that the consistency of the data be checked against the Gibbs-Duhem equation and not one of the integrated forms. All the integrated forms will produce $\ln \gamma$ Vs X curves which are consistent with Gibbs-Duhem data. However, a particular set of data may be thermodynamically consistent (that is, it agrees with the Gibbs-Duhem equation) and still not agree with any of the suggested integrated forms of the Gibbs-Duhem equation. Agreement with one of the integrated forms is sufficient to show that a set of data is consistent, but disagreement is not sufficient to show that the data are inconsistent. In the case of disagreement, the question arises as to whether the disagreement is due to inadequacy on the part of the integrated solution or to inherent inaccuracy in the data.

Since equilibrium data are always obtained at either constant temperature or constant pressure, a rigorous check on the data can be made using approximately integrated iso-

thermal and isobaric forms of the Gibbs-Duhem relation. The areas above and below the line $\ln \frac{\gamma_1}{\gamma_2} = 0$, should be equal to the equilibrium data taken at constant temperature. The areas differ by an amount depending on the integral heat of mixing and temperature forms. All the integrated forms will produce $\ln \gamma$ Vs X curves which are consistent with Gibb-Duhem data. However, a particular set of data may be thermodynamically consistent (that is, it agrees with the Gibbs-Duhem equation) and still not agree with any of the suggested integrated forms is sufficient to show that a set of data is consistent. In the case of disagreement, the question arises as to whether the disagreement is due to inadequacy on the part of the integrated solution or to inherent inaccuracy in the data.

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The area test is necessary for ideality but not sufficient. The test shows only that the data on a given system are consistent. The test in no way implies that the data are accurate. It is a matter of some importance to have either a test with indications of accuracy or a way of developing accuracy using some existing test procedure.

PURPOSE AND SCOPE

The criticism (5) of the area test is that departure from equilibrium in one part of the composition range may compensate deviations in another part. This is due to integrating across the whole concentration range. Then the area tests are satisfied but misleadingly indicate equilibrium for the data as a whole. The tests are not always misleading, but it is important to recognize that at least three practical situations exist where the test may be erroneous.

Most of the attention is given to determining the effect of predicted errors such as pressure, temperature and fractionation. Such errors exist if the vapor space is inadequately lagged and heated. Various types of systems were discussed by Bourne and two are selected for experimental purposes. The first system consists of an azeotrope at $X = 0.5$ for benzene-cyclohexane. The second system selected for study was benzene-n-propanol which has a highly non-ideal azeotrope at $X = 0.78$. To detect the small possible errors, three sets of experimental data taken by Patel (1966) on Vapor-Liquid equilibrium were used in this Thesis. For the data obtained, each introduced a different type of small error. The ability of different tests to detect various

types of departure from equilibrium then could be determined.

Most laboratory work concentrates on the effect of pressure, temperature and composition. The equipment used is complex and sensitive and there are many chances for errors to creep in. The principal error seems to be:

(a) Inadequate lagging of the Vapor Space:

The equilibrium data obtained by taking off insulation of 2 and 3 inches in thickness from the body of the equilibrium still.

(b) Maximum Boiling Azeotrope:

At high concentrations of the lower boiling component, the high boiling component becomes the more volatile constituent and has the larger activity coefficients due to fractionation.

(c) Minimum Boiling Azeotrope:

At low concentrations of the low boiling component, the activity coefficients of this component increased to values greater than those corresponding to equilibrium.

A new set of general integrated tests for the thermodynamic consistency of isothermal and isobaric Vapor-Liquid equilibrium data on binary and ternary systems proposed by E.F. Herington is used to evaluate experimental data taken by Patel (7). These tests can be used to examine compositions range as the error in one concentration range do not cancel errors in another but can be used to identify regions of poor observation. These tests can reveal the measured quantity is in error.

The data is unique in that the two systems were studied under special conditions. For each, accurate equilibrium data was measured and then, deliberate errors were introduced by removal of insulation. The value of a thermodynamic test lies in its ability to differentiate between good and poor data. Thus Patel's data will be used to evaluate Herington's proposed equation

THEORY

Binary Solutions are considered ideal in thermodynamics. All ideal binary systems should satisfy the following conditions:

1. The components must be soluble in one another in all proportions.
2. There should be no change in the average intermolecular forces of attractions on mixing.
3. There must be no change in volume or in internal energy.
4. No heat must be evolved or absorbed in mixing.
5. There should not be any hydrogen bonding.

All the above requirements have to satisfy the solution when the vapor pressure of the mixture is a linear function of the molar composition and expressed by Raoult's law as follows.

$$P_1 = P^\circ X_1 \quad (1)$$

where P_1 = Partial pressure of component 1.

P° = Vapor pressure of component 1 in pure state
at the temperature of system.

X_1 = Mole fraction of component 1 in the solution.

However, the most majority of binary mixtures encountered in practice have vapor pressures different from ideal values calculated by Raoult's law.

These non-ideal solutions are explained by difference in the attractive forces between the molecules of each component in the solution.

To compensate the deviations from Raoult's law, a correction factor is introduced. This correction factor, γ , is called the activity coefficient. Adding the activity coefficient, correction, γ , to Raoult's law the equation for both ideal and non-ideal solutions becomes:

$$P_1 = \gamma P_1^\circ X_1 \quad (2)$$

In equations (1) & (2) when $\gamma = 1$, the solutions are ideal.

The partial pressure of the component in the vapor phase of an ideal binary system is equal to the total pressure of the system multiplied by the mole fraction of the Component in the Vapor phase or:

$$P_1 = \pi Y_1 \quad (3)$$

Equating and rearranging (2) & (3) equations.

$$\gamma_1 = \frac{y_1 \pi}{P_1^0 X_1} \quad (4)$$

Similarly for Component 2

$$\gamma_2 = \frac{y_2 \pi}{P_2^0 X_2} \quad (5)$$

Equations (4) & (5) form the basis for determining the degree of non-ideality of binary systems, when considering the actual measurable properties of the system. Just as the assumption that vapor behaves as "ideal" gas, is true only at or near atmospheric pressure.

The fundamental concepts of activity coefficients equation (4) & (5) have been derived by many authors (11) from

the fugacity of the pure component at the temperature of the solution.

Accurate vapor liquid equilibrium data are difficult to obtain in the laboratory. The method of obtaining data require highly developed techniques which are time consuming and often yield questionable results. To improve the accuracy of actual laboratory vapor-liquid data for binary systems, a number of investigators (1,3,4,6) have developed special techniques for testing and expanding data. The more classical of these approaches are the Van Laar, Marguls, Redlich & Kister and Herington (1) solutions of the Gibbs-Duhem equation. Following is the derivation of Gibb-Duhem equation (10).

$$F_{pt} = (X_1 F_1 + X_2 F_2 + \dots) P_t \quad (6)$$

$$F_1 = \mu_1$$

Where F = free energy of components

\bar{F} = partial free energy of components

μ = chemical potential

from (6)

$$F_{pt} = (X_1 \mu_1 + X_2 \mu_2 + \dots) P_t \quad (7)$$

The total derivative of (6)

$$dF_{pt} = (X_1 d\mu_1 + \mu_1 dX_1 + X_2 d\mu_2 + \mu_2 dX_2 + \dots) \quad (8)$$

At constant temp and pressure equation (8) reduces to

$$dF_{pt} = (\mu_1 dX_1 + \mu_2 dX_2) \quad (9)$$

Subtracting equation (9) from (8)

$$(X_1 d\mu_1 + X_2 d\mu_2 + \dots) = 0 \quad (10)$$

$\therefore d\mu_i = (RT d \ln P_i)$, equation (10) becomes

$$X_1 \left(\frac{\partial \ln P_1}{\partial X_1} \right) + X_2 \left(\frac{\partial \ln P_2}{\partial X_1} \right) + X_3 \left(\frac{\partial \ln P_3}{\partial X_1} \right) + \dots = 0 \quad (11)$$

Equation (11) relates the pressure (fugacities) of various components in the solution to one another and to composition at constant temperature and pressure. This important relationship is termed the Gibbs-Duhem equation.

A more general form of this equation in terms of the activity coefficients can be derived in the following manner for binary system:

$$d X_1 = - dX_2$$

The equation (11) becomes:

$$X_1 \left(\frac{\partial \ln P_1}{\partial X_1} \right)_{P_T} = X_2 \left(\frac{\partial \ln P_2}{\partial X_2} \right)_{P_T} \quad (12)$$

$$\therefore \gamma_i a_i = \frac{P_i}{P_i^0}$$

where P_i^0 is a constant at given pressure and temperature.

Equation (12) becomes (13)

$$X_1 \left(\frac{\partial \ln a_1}{\partial X_1} \right)_{P_T} = X_2 \left(\frac{\partial \ln a_2}{\partial X_2} \right)_{P_T}$$

The activity coefficient, $\gamma_i = \frac{a_i}{x_i}$

$$X_1 \left(\frac{\partial \ln X_1 \gamma_1}{\partial X_1} \right)_{P_T} = X_2 \left(\frac{\partial \ln X_2 \gamma_2}{\partial X_2} \right)_{P_T} \quad (14)$$

$$X_1 \left(\frac{\partial \ln \gamma_1}{\partial X_1} \right) + X_1 \left(\frac{\partial \ln X_1}{\partial X_1} \right)_{P_T} = X_2 \left(\frac{\partial \ln \gamma_2}{\partial X_2} \right) + X_2 \left(\frac{\partial \ln X_2}{\partial X_2} \right)_{P_T} \quad (15)$$

$$\therefore x_1 \left(\frac{\partial \ln x_1}{\partial x_1} \right) = \frac{x_1 \partial x_1}{x_1 \partial x_1} = 1$$

Similarly

$$x_2 = \left(\frac{\partial \ln x_2}{\partial x_2} \right) = 1$$

$$\therefore x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right) = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right) \quad (16)$$

The equation (16) is called the Gibbs-Duhem equation for binary systems. It is very useful since activity coefficients measure directly the departure from an ideal solution.

The general form of eq (16) is written as follows:

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 + \dots = 0 \quad (17)$$

$$(x_i d \ln \gamma_i = 0)_{pt} \quad (18)$$

The more specific equation delivered by Herington from eq. (17) as follows:

$$x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0$$

$$X_1 d \ln \gamma_1 + d \ln \gamma_2 - X_1 d \ln \gamma_2 = 0$$

$$X_1 (d \ln \gamma_1 - d \ln \gamma_2) = - d \ln \gamma_2 \quad (19)$$

The total derivative

$$d (X_1 (\ln \gamma_1 - \ln \gamma_2)) = X_1 d \ln \gamma_1 - X_1 d \ln \gamma_2 + \ln \gamma_1 dX_1 - \ln \gamma_2 dX_2 \quad (20)$$

Rearranging equation (20)

$$X_1 (d \ln \gamma_1 - d \ln \gamma_2) + \ln \frac{\gamma_1}{\gamma_2} dX_1 = d(X_1 (\ln \frac{\gamma_1}{\gamma_2})) \quad (21)$$

Substituting eq. (19) into (21)

$$- d \ln \gamma_2 + \ln \frac{\gamma_1}{\gamma_2} dX_1 = d (X_1 \ln \frac{\gamma_1}{\gamma_2}) \quad (22)$$

Rearranging equation (22)

$$\ln \frac{\gamma_1}{\gamma_2} dX_1 = d \ln \gamma_2 + d (X_1 \ln \frac{\gamma_1}{\gamma_2}) \quad (23)$$

Integrating equation (23) and taking limits

At $X_1 = 0$ to $X_1 = 1$

$$\gamma_2 = 1 \quad \gamma_1 = 1$$

$$\int_{X_1=0}^{X_1=1} \ln \frac{\gamma_1}{\gamma_2} dX_1 = 0 \quad (24)$$

The preceding equation is used to check the consistency of the measured Vapor-Liquid equilibrium data. From equation (24) the total area under the curve with respect to the abscissa must be equal to zero, provided the obtained data satisfy the Gibbs-Duhem equation.

METHOD OF CALCULATION

In this Section we show how Herington's equation was used to evaluate and test laboratory data.

Benzene - Cyclohexane:

This data has been obtained by M. F. Patel. (Thesis of M. S. 1966) at constant pressure varying temperature and concentration.

TABLE NO. 1

EXPERIMENTAL DATA OF PATEL (7)

RUN #1 (BEST DATA)

PRESSURE 760 MM Hg

SYSTEM #1, Benzene - Cyclohexane

B - Benzene C - Cyclohexane

<u>Temp</u>	<u>Composition</u>	<u>Activity</u>	<u>Coefficients</u>
<u>°C</u>	<u>XB</u>	<u>γ_B</u>	<u>γ_C</u>
80.8	0.00	----	----
79.5	0.12	1.2840	1.001
78.5	0.23	1.219	1.019
77.7	0.40	1.1327	1.0615
77.6	0.55	1.08219	1.1013
77.6	0.63	1.0564	1.1458
78.0	0.76	1.0264	1.224
78.3	0.895	1.01379	1.2936
79.1	0.922	1.01379	1.3488
79.95	1.00	-----	-----

The heat of mixing data for the binary solutions at temperatures in the neighborhood of the normal boiling temperatures are known. The activity coefficients for an isothermal condition are calculated by means of the well-known equations connecting the temperature dependence of activity coefficients with the partial molal heats of mixing. Generally, the required heat quantities are rarely available and most calculations are made using only the experimental boiling temperatures and activity coefficients for the mixtures.

$$RT \sum X_1 d \ln \gamma_1 + (H^E/T) dT - V^E dP = 0 \quad (1)$$

For isobaric data $V^E dP = 0$

$$RT \sum X_1 d \ln \gamma_1 + (H^E/T) dT = 0 \quad (2)$$

For a binary mixture equation (2) becomes equation (3) after rearrangement:

$$X_1 d \ln \gamma_1 + X_2 d \ln \gamma_2 + (H^E/RT^2) dT = 0 \quad (3)$$

The composition of Benzene - Cyclohexane are plotted on the X - axis and $\ln \gamma_1$ and $\ln \gamma_2$ on the Y-axis as Fig. 1.

The boiling temperatures of components 1 and 2 are T_1 and T_2 and that of mixture of composition X_1 is T^1 .

After integration equation (3) becomes:

$$I_{1p} + I_{2p} + I_H = K_p \quad (4)$$

where the algebraic sum of the areas AFG and HJCE.

$$I_{1p} = \text{Area AFG} = \int_{X_1=0}^{X_1'} X_1 d \ln \gamma_1 = \int_{\ln \gamma_{1,0}}^{\ln \gamma_1, X_1'} X_1 d \ln \gamma_1 \quad (5)$$

$$I_{2p} = \text{Area HJCE} = \int_{X_1=1}^{X_1'} X_2 d \ln \gamma_2 = \int_{\ln \gamma_{2,1}}^{\ln \gamma_2, X_1'} X_2 d \ln \gamma_2 \quad (6)$$

$$I_H = \int_{T_1}^{T^1} (H^E/RT^2) dT \quad (7)$$

and K_p is constant.

Equations (5) and (6) refer to isobaric data (the P in I_{1p} , I_{2p} means at constant pressure), and the activity coefficients are calculated with respect to the pure components at the normal boiling temperatures.

Rewriting equation (4) as:

$$I_{1p} + I_{2p} = K_p - I_H \quad (8)$$

The rate of change of $I_{1p} + I_{2p}$ with X_1 is:

$$\frac{d(I_{1p} + I_{2p})}{dX_1} = - \left(\frac{H^E}{RT^2} \right) \left(\frac{dT}{dX_1} \right) \quad (9)$$

but $H^E + 0$ at $X_1 = 0$ or 1 and therefore

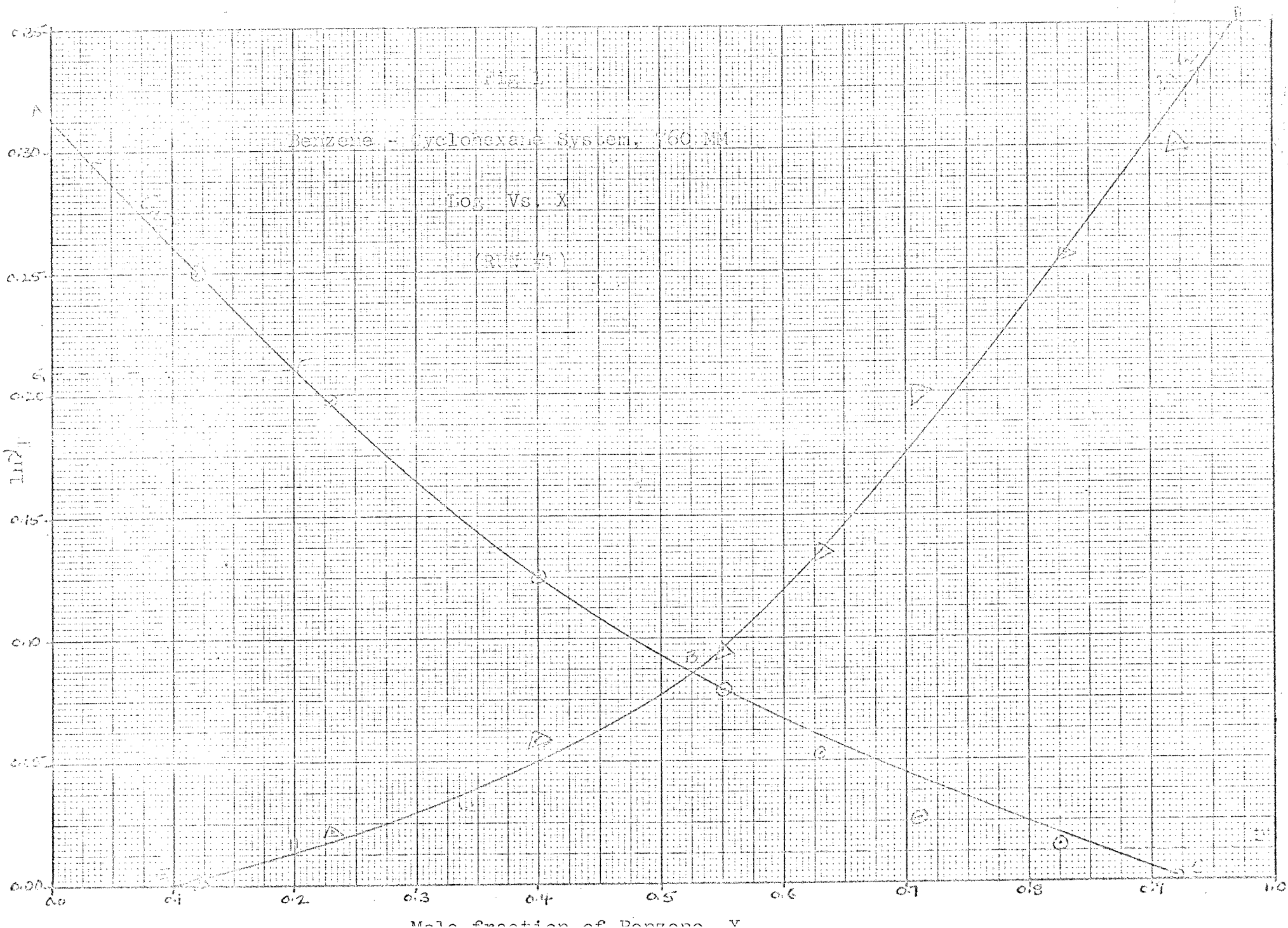
$$\frac{d(I_{1p} + I_{2p})}{dX_1} \rightarrow 0 \text{ as } X_1 \rightarrow 0 \text{ or } 1$$

The curve of $I_{1p} + I_{2p}$ against X_1 becomes horizontal as $X_1 \rightarrow 0$ and $X_1 \rightarrow 1$. The term $\frac{d(I_{1p} + I_{2p})}{dX_1}$ is zero at an azeotropic composition and therefore at such a composition

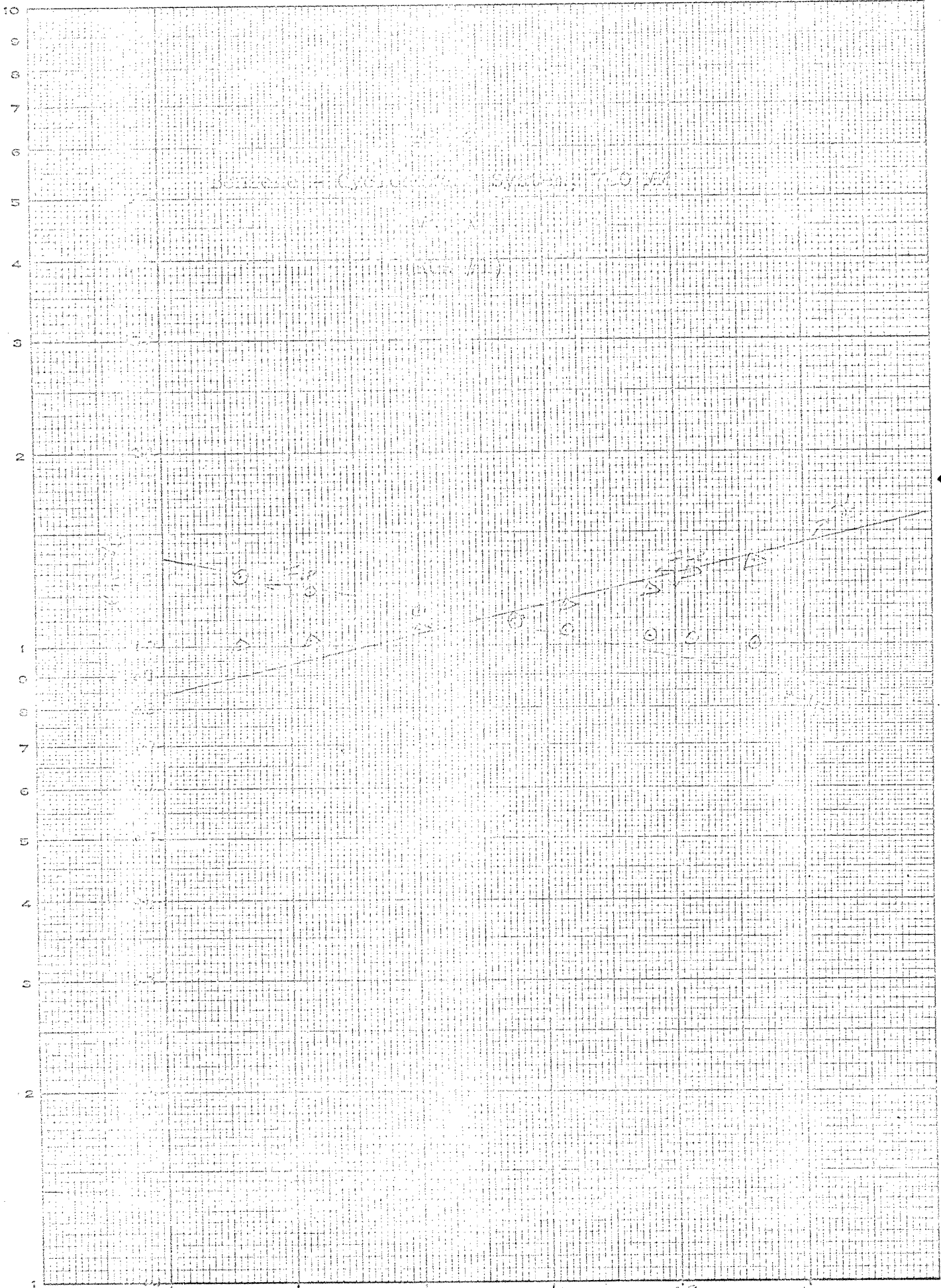
$$\frac{d(I_{1p} + I_{2p})}{dX_1} = 0$$

The curves of I_1 and I_2 are shown by plotting composition on the X-axis and $\ln \gamma$ on the Y-axis as shown in Fig. 2. The algebraic signs of I_1 and I_2 follow from the definitions of these quantities and are negative for the data shown on Fig. 1.

The composition of the Benzene - Cyclohexane mixtures are plotted on the X-axis and temperature, in $^{\circ}\text{C}$, on the Y-axis as shown in Fig. 3. The shape of the composition of boiling point vs temperature curve is entirely different when the azeotrope has formed and when it is not formed.

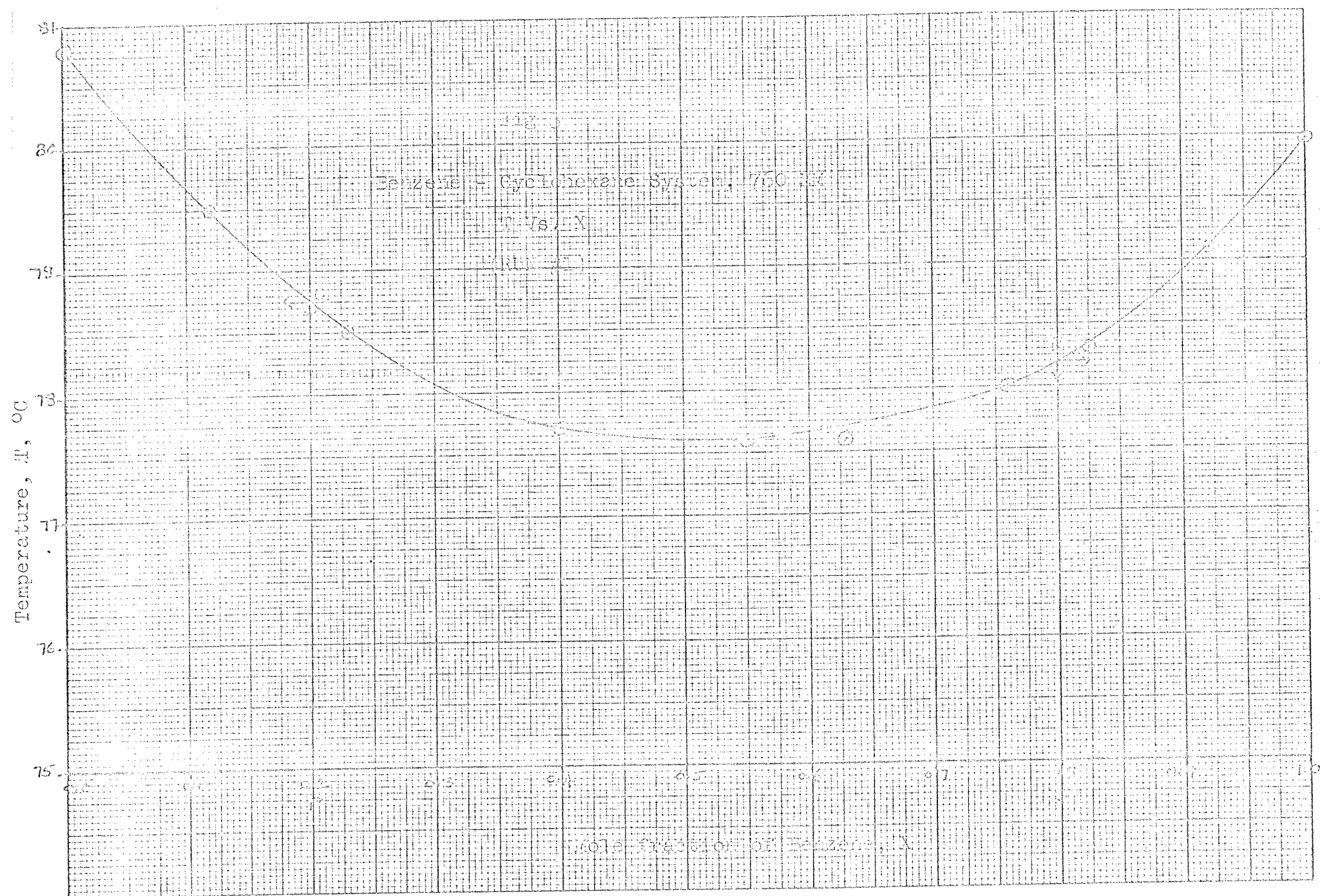


Int 2



Mole fraction of Benzene, X

In UT



The values of I_{1p} vary with composition and the heat of mixing is calculated using equation (10).

$$H^E = -RT^2 \left[\frac{d (I_{1p} + I_{2p})}{d X_1} \right] \left(\frac{dT}{d X_1} \right) \quad (10)$$

where

H^E = Heat of mixing in cal/mole.

R = Gas constant in $\frac{(\text{cals})}{(\text{deg } ^\circ\text{C}) (\text{gram mole})}$

T = Temperature in degrees Centigrade

The same technique is used for the other sets of data. The graphs developed for these other sets (Figs. 4 to 18) are in Appendix "D".

DISCUSSION

The area test examines the consistency of the vapor-liquid equilibrium data using a form of the Gibbs-Duhem equation. According to Redlich, Kister and Tranquist (4), the area under the curve should be zero, if the data are consistent. A new set of general integral tests for the thermodynamic consistency of isothermal and isobaric vapor-liquid equilibrium data of binary systems was proposed by E.F.G. Herington. This test calculates heat of mixing. The heats of mixing are compared to experimental values as a measure of the consistency of the data. The Herington tests seems a promising proposal.

The systems used are Benzene-Cyclohexane and Benzene-n-propanol and the vapor-liquid equilibrium data were obtained by Patel (7). This data was collected at a total pressure of 760 mm mercury and over the entire range of concentration. The data are in groups of three; good data that compares well with the literature, and two sets of data with errors. The errors were introduced by removing insulation from the equilibrium still after the best data were obtained. Two successive patches of insulation were removed, one for each set of data.

The test for vapor-liquid equilibria should be able to differentiate between the good and bad. Patel used his data and the usual area test. He could not find significant deviations of area between sets and showed the area test was inadequate. The Herington test tries to evaluate the heats of mixing. The Herington tests can be used to examine part of the composition range since errors in one concentration region need not cancel errors in another. This test then can be used to identify regions of poor observation, since the isobaric heats of mixing calculated will differ from heats of mixing from observation.

We first checked the good data of Patel which showed consistency in the Gibbs-Duhem sense. The Herington technique had a similar consistency. Sets of experimental vapor-liquid equilibrium data (from Patel) were used with Herington technique. The systems used were Benzene-Cyclohexane and Benzene-n-propanol at a total pressure of 760 mm mercury and over the entire range of concentrations. The best sets of data are considered first.

Fig 1 shows the plot of $\ln \gamma$ against X_1 for the isobaric data on the system Benzene-Cyclohexane with the boiling

range shown in Fig 3.

The area AFCE does not equal to area DBEC and the difference between them equals the value of the integral I_H with T' equal to T_2 . The curve of $\ln \gamma_1$ against X_1 has a maximum whereas the curve of $\ln \gamma_2$ against X_1 does not have a minimum.

Fig 2 shows I_{1p} and $I_{1p} + I_{2p}$ plotted against X_1 for the data shown on Fig 1. The boiling temperature variation for compositions from $X_1 = 0.2$ to $X_1 = 0.8$ has a very little effect on the value of $I_{1p} + I_{2p}$ because the temperature variation with composition was only 4°C over that range. The variation in the values of $I_{1p} + I_{2p}$ for real systems is likely to be small as shown here. By examination, the values of $I_{1p} + I_{2p}$ appear to vary with composition and an approximate calculation of H^E should be made by using equation (10).

$$H^E = - RT^2 \frac{d(I_{1p} + I_{2p})}{dX_1} \frac{dT}{dX_1} \quad (10)$$

The total change in temperature is 4°C for the systems but, the change in temperature from $X_1 = 0.2$ to $X_1 = 0.8$ is 0.5°C . The initial value of $\frac{dT}{dX_1}$ at $X_1 = 0.2$ is 78.7°C . However, since H^E is usually small near the

ends of the composition range the value of $\frac{d(I_{1p} + I_{2p})}{dX_1}$ will usually not be larger at the ends of the composition range.

From Fig 2, the areas AFCE and DEBC obtained by graphical integration are:

$$\begin{array}{ll} \text{At } X_1 = 0.2 & \text{then } I_{1p} = \ln 1.25 \\ \text{and } X_2 = 0.8 & \text{then } I_{2p} = \ln 1.30 \text{ mixing } X_1 = 0 \end{array}$$

$$\begin{aligned} \frac{d(I_{1p} + I_{2p})}{dX_1} &= \frac{d(I_{1p})}{dX_1} + \frac{d(I_{2p})}{dX_1} \\ &= \frac{\ln 1.25}{0.6} - \frac{\ln 1.30}{0.6} \\ &= \left(\frac{0.2231}{0.6} - 0.2624 \right) \\ &= - \frac{0.0393}{0.6} = - 0.0655 \end{aligned}$$

From Fig 3, the area PQRS obtained by graphical integration:

$$\begin{array}{ll} \text{At } X_1 = 0.2 & \text{then } T_1 = 78.75 \\ \text{and } X_2 = 0.8 & \text{then } T_2 = 78.20 \end{array}$$

$$\frac{dT}{dX_1} = \frac{(78.20 - 78.75)}{(0.8 - 0.2)} = \frac{-0.55}{0.66} = -0.917^\circ\text{C/mole}$$

The final step in calculating the heat of mixing for the systems is from equation (10):

$$H^E = - \frac{(1.987) (354.2)^2 (-0.0655)}{-0.917} = -17.81 \frac{\text{Kcals}}{\text{mole}}$$

Doing the calculation for Benzene-Cyclohexane using the "poor" data, we calculate the following heats of mixing: (using the same technique)

Run # 1	-17.81 Kcals/mole	good data
Run # 2	-37.43 Kcals/mole	poor data
Run # 3	-71.12 Kcals/mole	poorest data

The test has separated good from bad in this case, because the heats of mixing calculated for Run # 2 & 3 are not likely to be in this range for relatively ideal systems.

Doing similar calculations for the case of Benzene-n-Propanol which forms an azeotrope (data and calculation in Appendix C,D & E), we find:

Run #1	-5.24 Kcals/mole	good data
Run # 2	-3.44 Kcals/mole	poor data
Run # 3	-2.71 Kcals/mole	poorest data

These results were calculated for the range of X, from 0.2 to 0.8 in graphical integration.

The above results vary widely because the experimental data included deliberate errors in runs # 2 & 3. The data for runs # 2 & 3 were taken after removing 2 inches and 3 inches, thickness of the insulation from the equilibrium still. Thus the vapor space was inadequately lagged and heated. The calculated values for heats of mixing showed significant but inconsistent differences.

The table shows that the heat of mixing of the low boiling component for run #1 is good but increases to higher values as soon as the insulation is taken off (2 inches thickness for run #2). The heat of mixing value decreases considerably after one more inch thickness of the insulation is taken off (run #3 compared to run #2). This sequence was observed for both systems.

The decreases in heats of mixing may be due to the development of additional reflux in run #3 of the data compared run #2. In any case the inconsistent pattern of the heats of mixing values for runs #2 & 3 are beyond the normal ranges for the systems.

The integral test proposed by Herington for isobaric data is not consistent in the composition region where the temperature is changing rapidly. The test shows that the heat of mixing calculated from the isobaric data is quite large, when the data is not taken accurately. This conclusion of Herington holds true for our present experimental data. On the other hand the integral area test applied to runs #2 & 3 for both the systems indicates a consistency in data known to be incorrect. Thus, the integral test indicated all sets of data could be accurate while the Herington integral test showed significant differences.

CONCLUSION

The area test for Vapor-Liquid equilibrium data is basically inadequate to decide whether or not a set of data is good. Herington's test seems promising and was tested using both good and erroneous data.

The Herington test differentiated between good and poor data, but the trend was inconsistent. The test seems to be a real improvement over the area test. Additional sets of data should be studied to see if the variation of heats of mixing is random or is consistently in one direction from experimental values.

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APPENDIX A

NOMENCLATURE

P	Vapor pressure of pure component, mm Hg.
p	Partial pressure of binary system.
X	Mole fraction of liquid
Y	Mole fraction of vapor
F	Free energy of components
\bar{F}	Partial free energy of components
a	Activity of components
d	Differential
Q	Excess free energy
H^E	Molal heat of mixing
P_t	Total pressure of the system, mm Hg.
R	Gas constant
T	Temperature in °C
T_1	Boiling point of component 1
T_1	Boiling point of binary mixture containing X_1 mole fraction of component 1.
T_2	Boiling point of component 2
V^E	Molal volume of mixing
X_i	Molal fraction of the i th component in the liquid
γ_i	Activity coefficient of the i th component with the Standard State that the pure liquid component at the same temperature.
γ_{1,X_1}	Activity coefficient of component 1 at mole fraction X_1 of component 1 in the liquid mixture.
γ_{2,X_1}	Activity coefficient of component 2 at mole fraction X_1 of component 1 in the liquid mixture.

NOMENCLATURE (Cont'd)Subscripts:

- p At constant pressure
- t At constant temperature
- ln Logarithm to base e
- 1,2 Refers to components 1,2

APPENDIX B

PHYSICAL PROPERTIES OF THE PURE COMPONENTS

COMPONENT	REFRACTIVE	INDEX	BOILING POINT	
	EXP.	LIT.	(760 MM)	
	25°C.	25°C.	EXP.	LIT.
N - Propanol	1.3835	1.38335	97.2	97.2
Benzene	1.4986	1.4982	79.95	79.9
Cyclohexane	1.4235	1.4235	80.8	80.7

The physical properties and densities were also determined experimentally (7) by Patel and good agreement was obtained with literature values.

APPENDIX C

TABLE NO. 2
EXPERIMENTAL DATA OF PATEL (7)
PRESSURE 760 MM Hg.
RUN #2
SYSTEM #1, BENZENE - CYCLOHEXANE.
 B - BENZENE
 C - CYCLOHEXANE

<u>Temperature</u>	<u>Composition</u>	<u>Activity</u>	<u>Coefficients</u>
°C	X_B	γ_B	γ_C
76.45	0.088	1.440	1.03485
77.70	0.175	1.358	1.0432
77.20	0.290	1.2575	1.050
77.00	0.400	1.1688	1.072
76.80	0.500	1.08603	1.1499
76.80	0.580	1.07796	1.1677
77.40	0.790	1.03939	1.2912
78.20	0.890	1.0459	1.3745
78.60	0.95	1.0310	1.4935
79.90	1.00	- -	- -

TABLE NO. 3EXPERIMENTAL DATA OF PATEL (7)PRESSURE 760 MM Hg. 10RUN #3SYSTEM #1, BENZENE - CYCLOHEXANE

B - BENZENE

C - CYCLOHEXANE

<u>Temperature</u>	<u>Composition</u>	<u>Activity Coefficients</u>	
<u>°C</u>	<u>X_B</u>	<u>B</u>	<u>C</u>
78.9	0.050	1.4960	1.008
77.8	0.215	1.301	1.032
77.5	0.332	1.210	1.042
77.4	0.400	1.130	1.080
77.2	0.570	1.085	1.129
77.7	0.760	1.035	1.3117
78.0	0.860	1.0128	1.444
79.0	0.940	--	--

TABLE NO. 4
EXPERIMENTAL DATA OF PATEL (7)
PRESSURE 760 MM Hg
RUN #1
SYSTEM #2, BENZENE - n - PROPANOL

A - n - PROPANOL

B - BENZENE

<u>Temperature</u> °C	<u>Composition</u> X_B	<u>Activity Coefficients</u>	
		B	A
77.3	0.895	1.0316	3.223
76.7	0.800	1.085	2.571
76.9	0.600	1.21328	1.71876
77.7	0.540	1.5181	1.4255
79.2	0.432	1.549	1.288
82.4	0.290	1.8665	1.0803
83.9	0.249	1.9020	1.0706
85.3	0.150	2.3696	1.065
91.1	0.080	2.552	1.0265
93.9	0.040	2.832	1.001

TABLE NO.5
EXPERIMENTAL DATA OF PATEL (7)
PRESSURE 760 MM Hg.
RUN #2
SYSTEM #2, BENZENE - n - PROPANOL
 A - n - PROPANOL
 B - BENZENE

<u>Temperature</u>	<u>Composition</u>	<u>Activity</u>	<u>Coefficients</u>
<u>°C</u>	<u>X_B</u>	<u>γ_B</u>	<u>γ_A</u>
93.3	0.032	2.765	1.050
90.0	0.075	2.6010	1.080
85.2	0.160	2.182	1.148
82.2	0.230	2.080	1.148
81.0	0.290	1.922	1.162
78.5	0.440	1.561	1.363
77.5	0.540	1.375	1.422
76.85	0.690	1.193	1.813
76.6	0.792	1.112	2.361
77.0	0.900	1.045	3.228

TABLE NO. 6

EXPERIMENTAL DATA OF PATEL (7)

PRESSURE 760 MM Hg.RUN #3SYSTEM #2, BENZENE - n - PROPANOL

A - n - PROPANOL

B - BENZENE

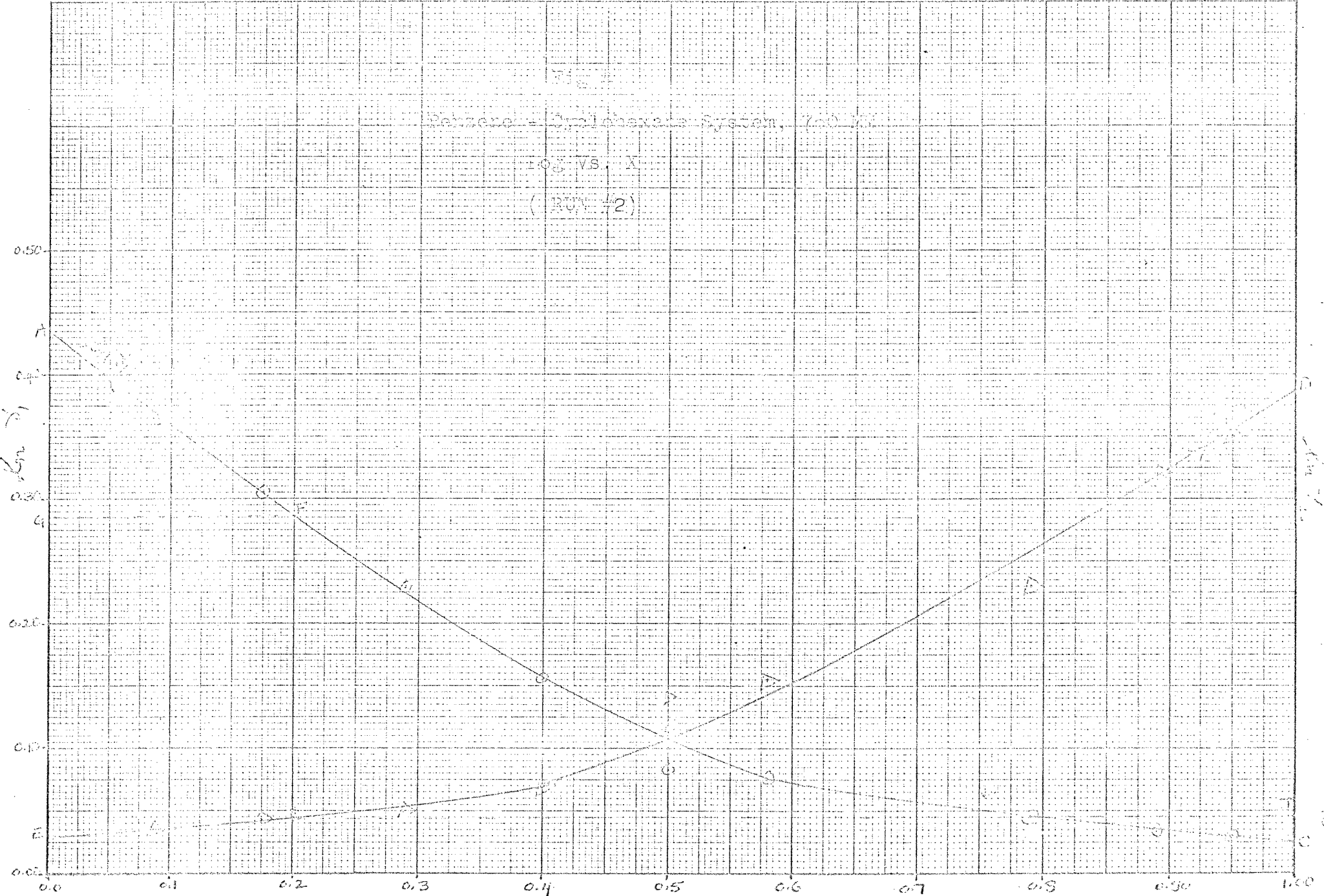
<u>Temperature</u>	<u>Composition</u>	<u>Activity</u>	<u>Coefficients</u>
<u>°C</u>	<u>X_B</u>	<u>γ_B</u>	<u>γ_A</u>
76.4	0.89	1.061	3.014
76.0	0.78	1.166	2.190
76.2	0.675	1.255	1.845
77.05	0.535	1.441	1.615
78.4	0.430	1.621	1.302
81.3	0.280	1.940	1.193
83.9	0.190	2.161	1.145
88.2	0.110	2.322	1.097
92.3	0.030	2.570	1.101

APPENDIX D

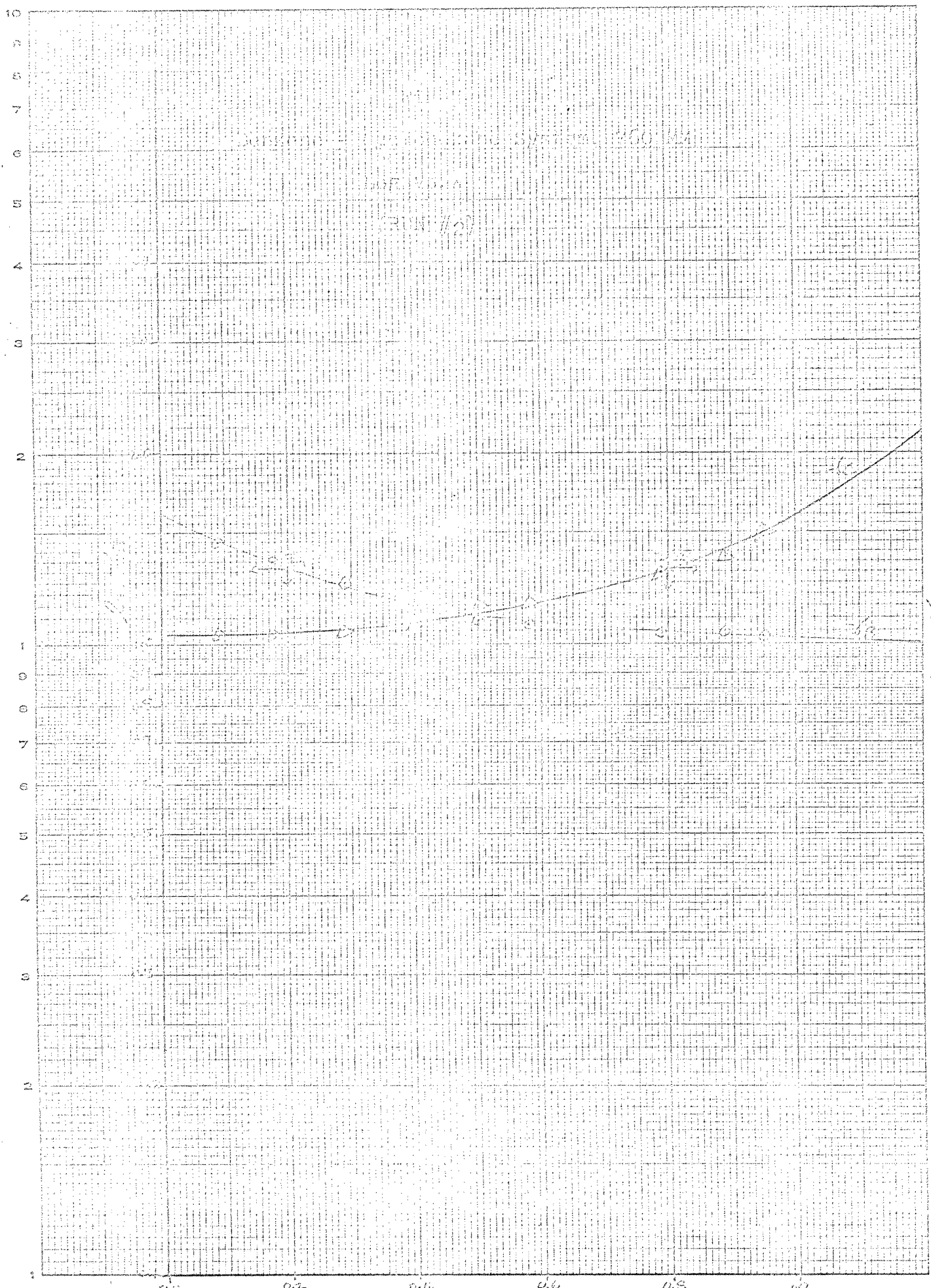
Benzene - Cyclohexane System, (60-10)

P_{10} vs. X

(ROY 42)



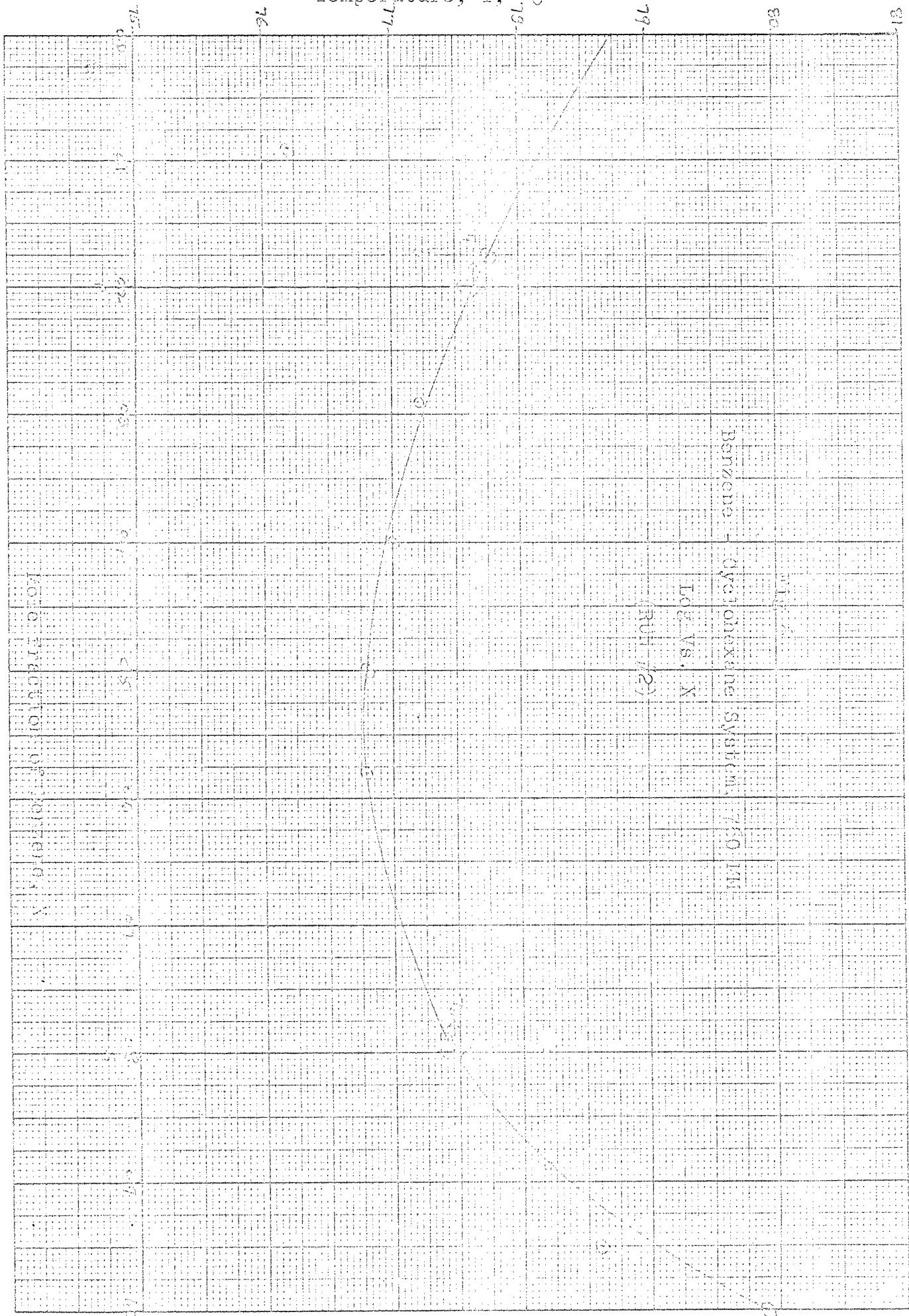
SCHEMATICALLY
2 CYCLES X 20 DIVISIONS PER INCH



Mole fraction of Benzene, X

Run #2

Temperature, T, °C

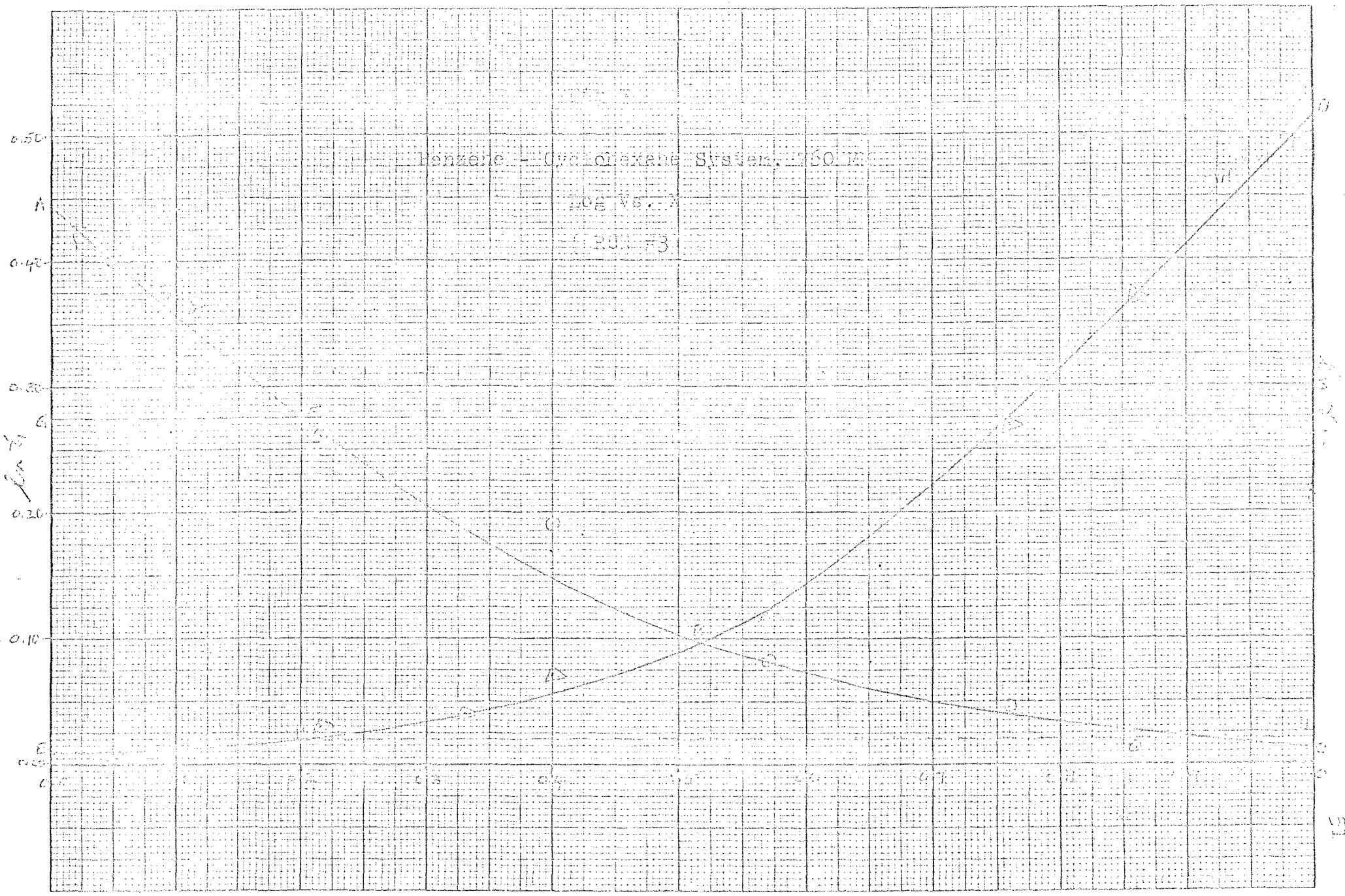


Benzene - Cyclohexane System (750 MM)

LOG. VS. X

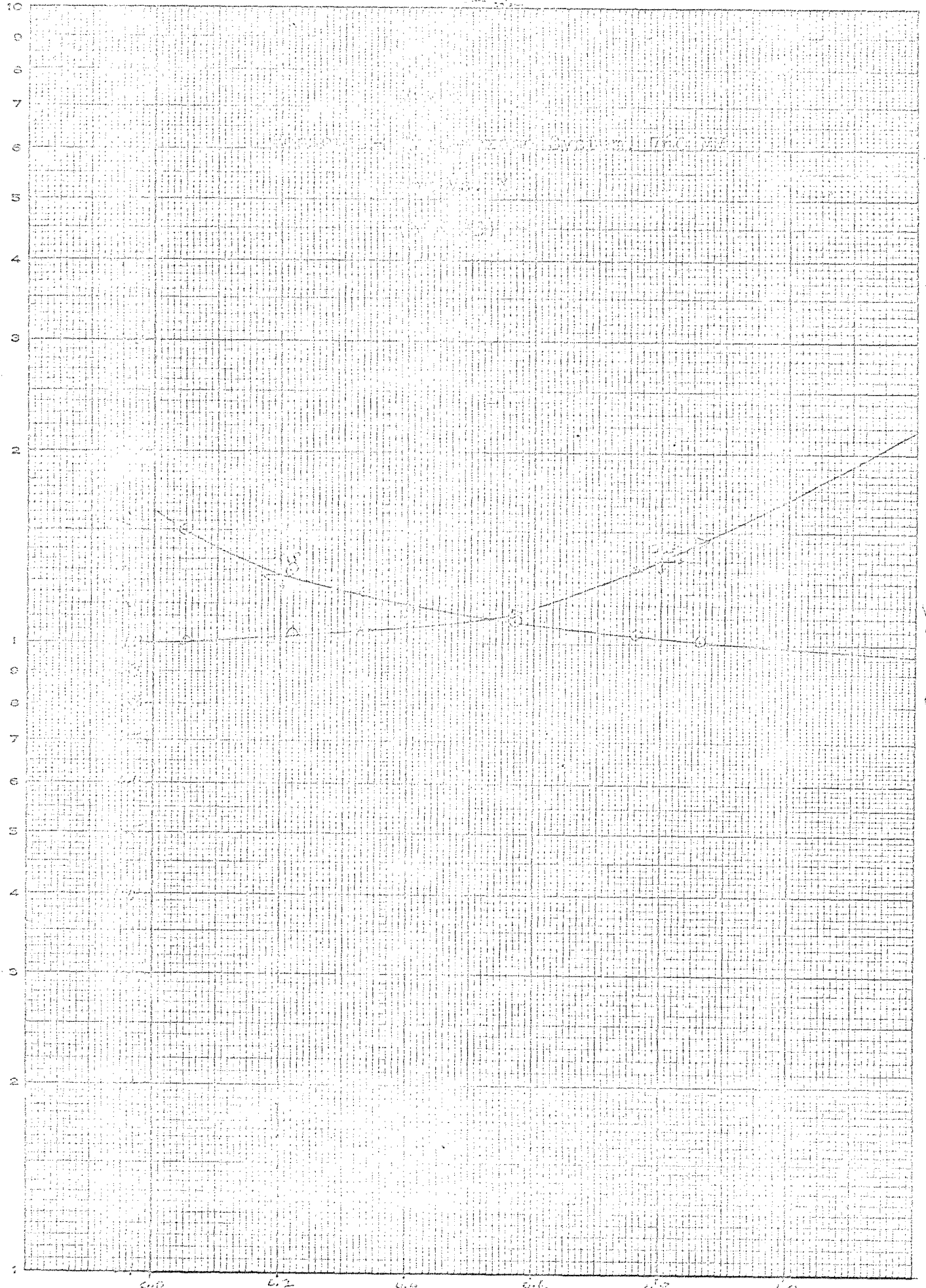
(RUI-72)

LOG. REDUCTION OF PRESSURE, X



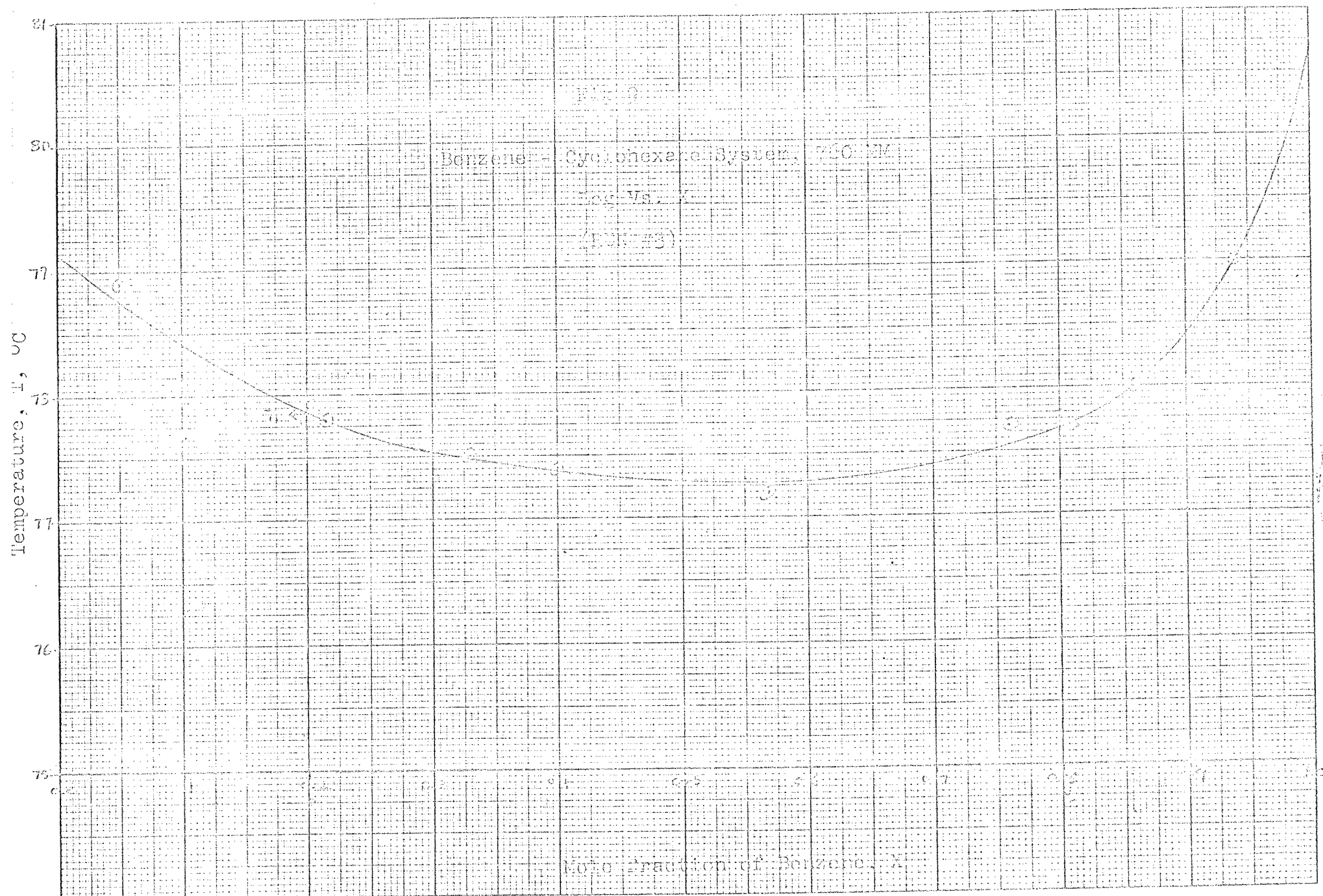
Mole fraction of Benzene, X

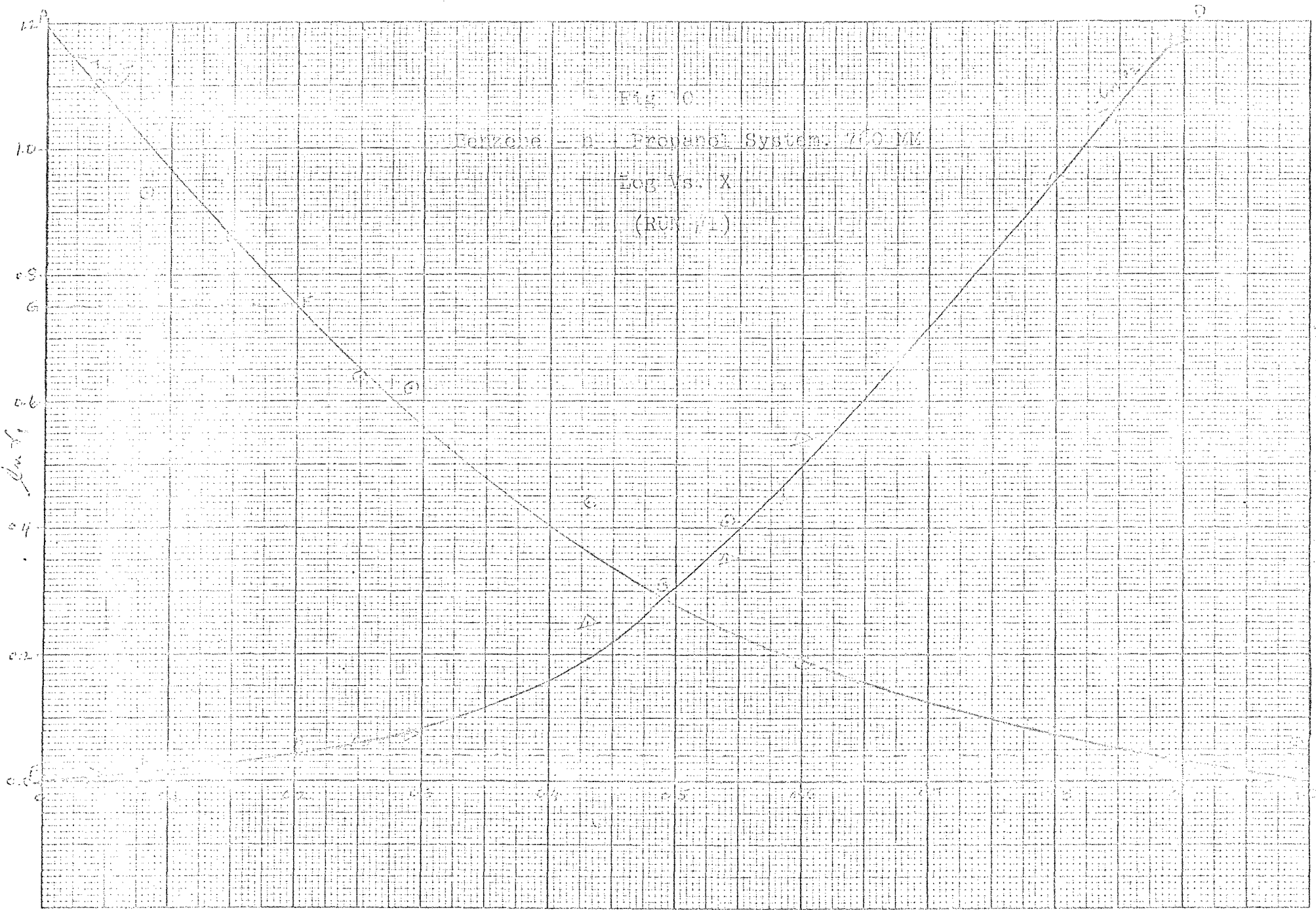
2 CYCLES X 20 DIVISIONS PER INCH



Mole fraction of Benzene, X

En 10





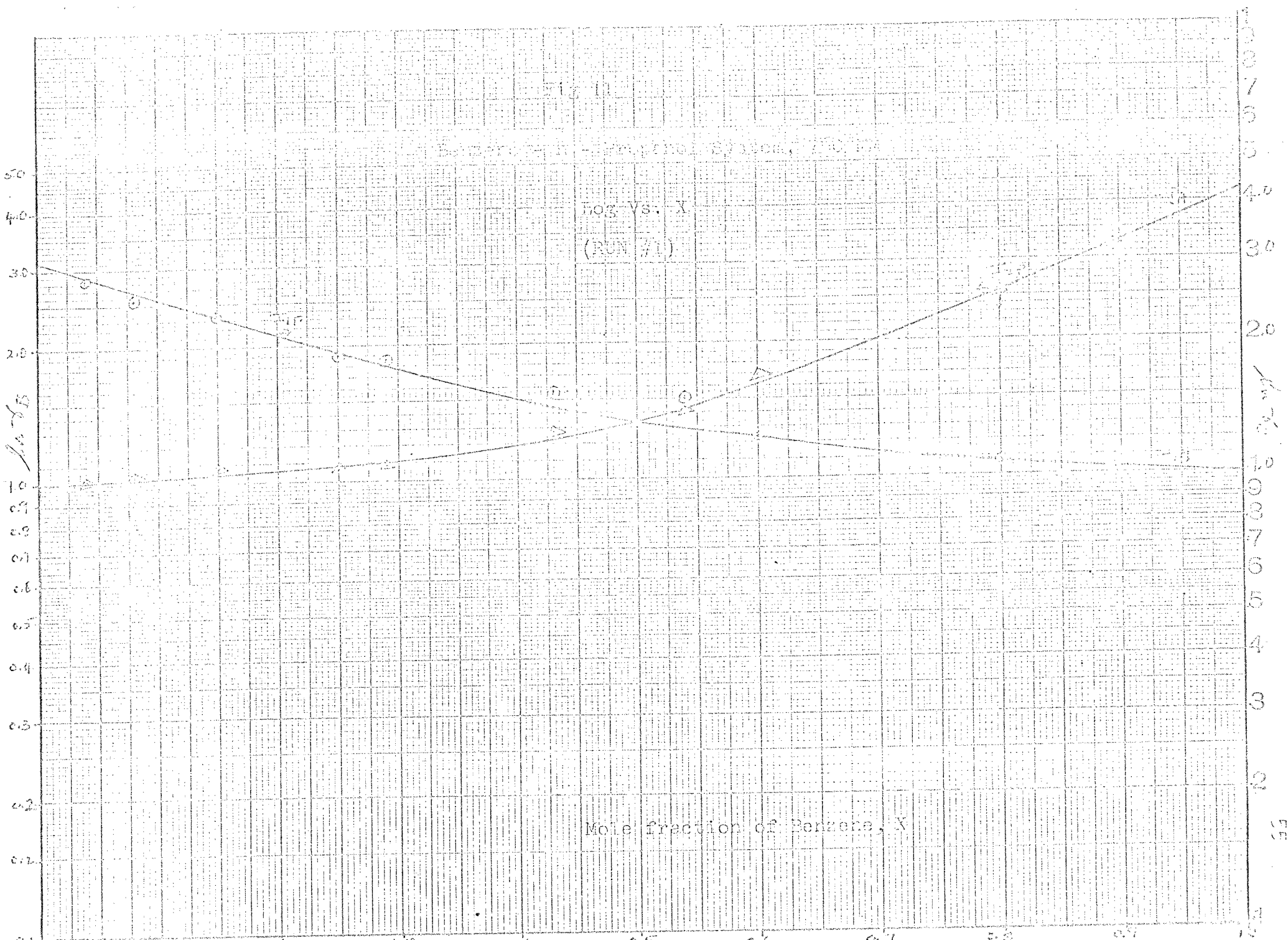
Mole fraction of Benzene, X

11.5
41

Fig. II

Temperature vs. Mole Fraction, 730 mm.

103 vs. X
(RUN 71)



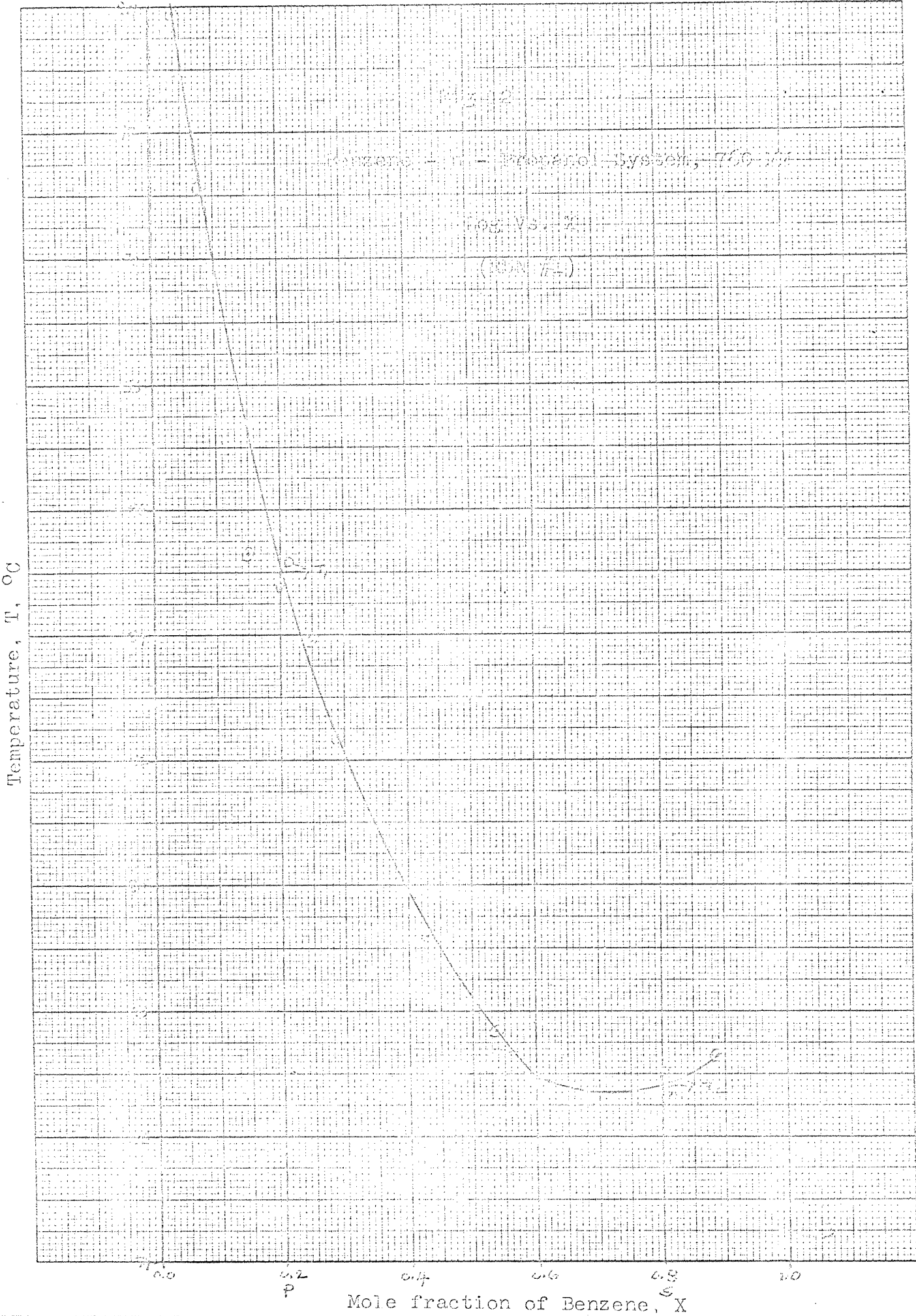
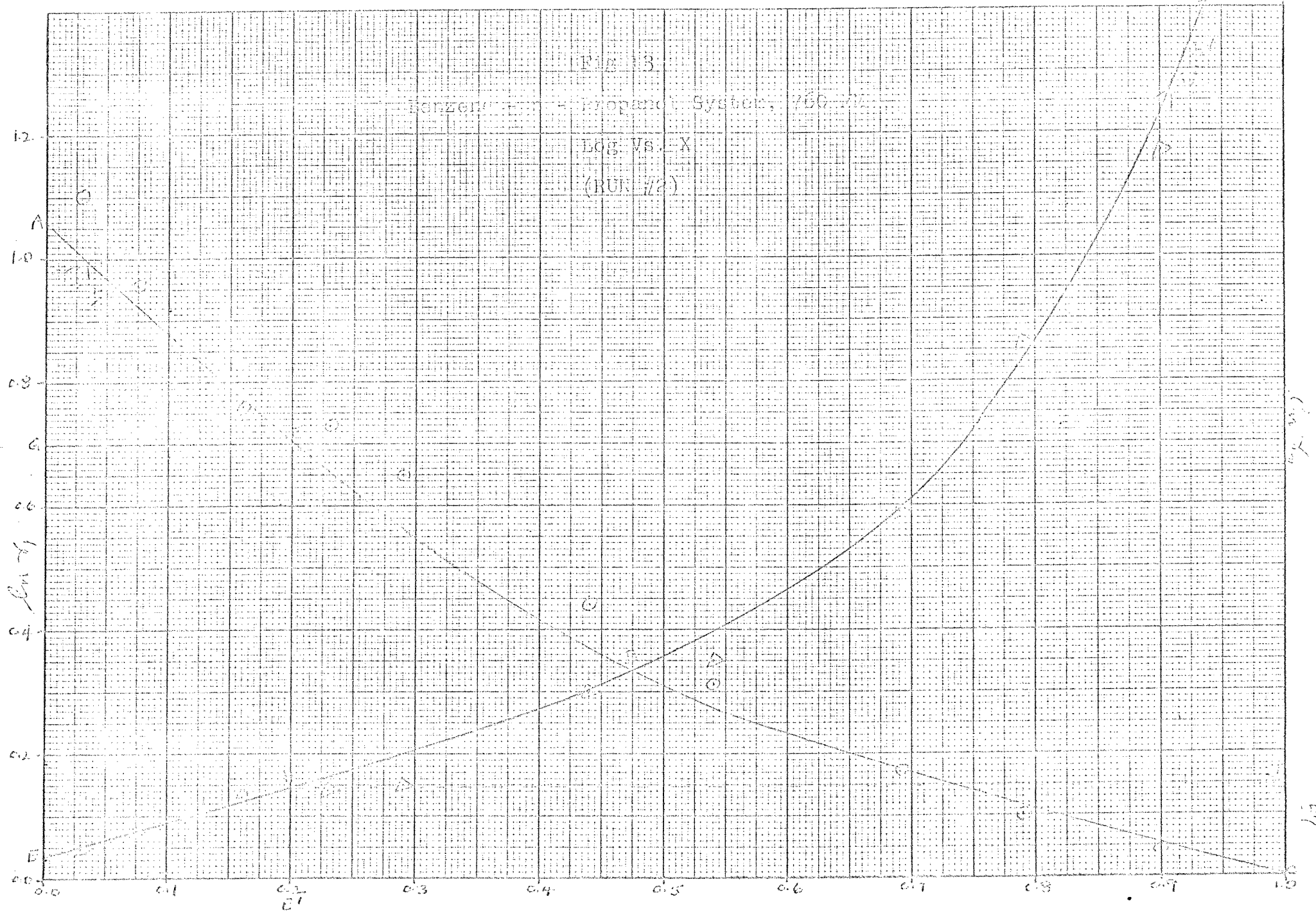


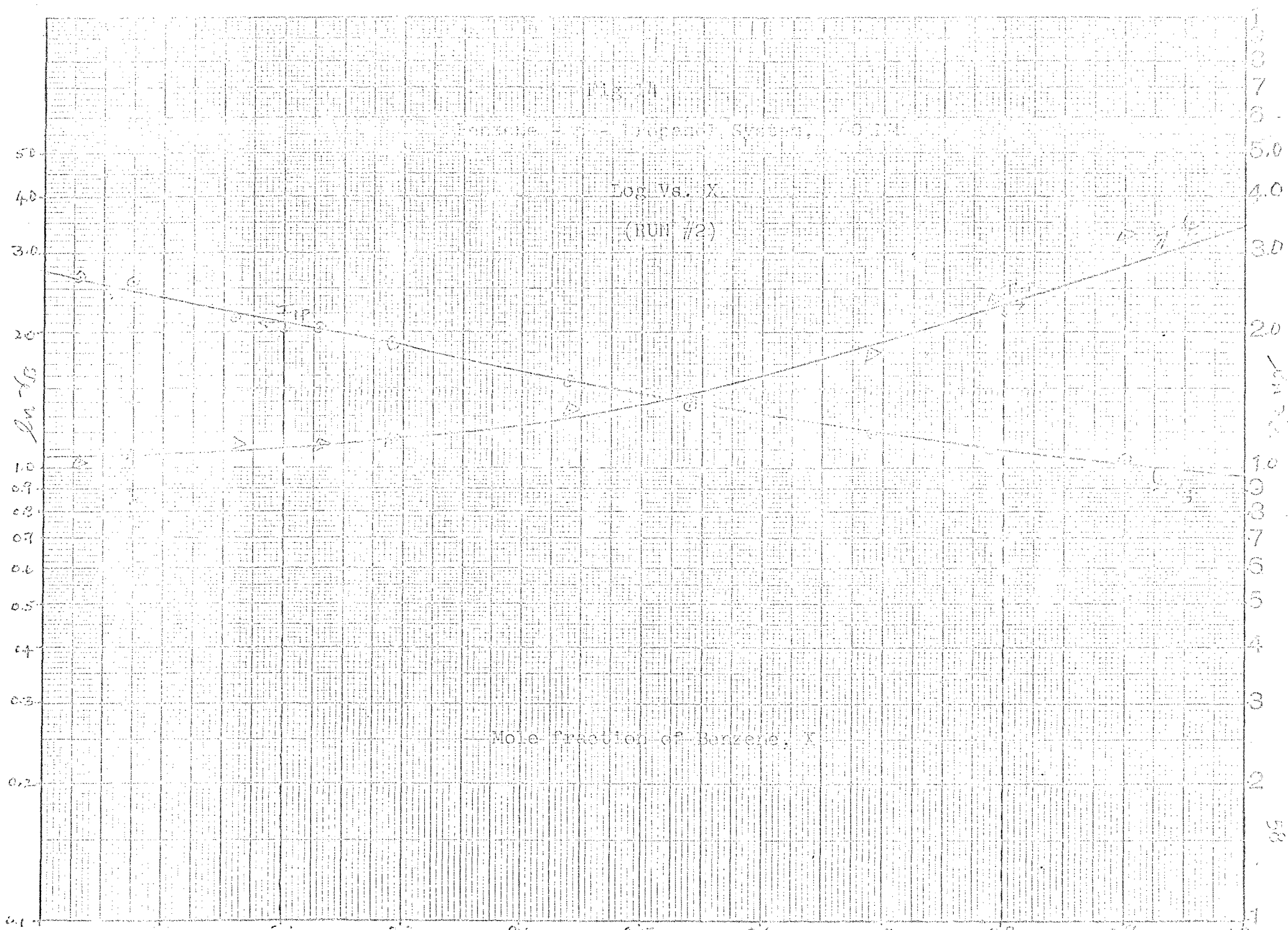
FIG. 13

BENZENE-ETHANE-PROPANE SYSTEM, 100°C.

LOG. VS. X

(BUN 72)



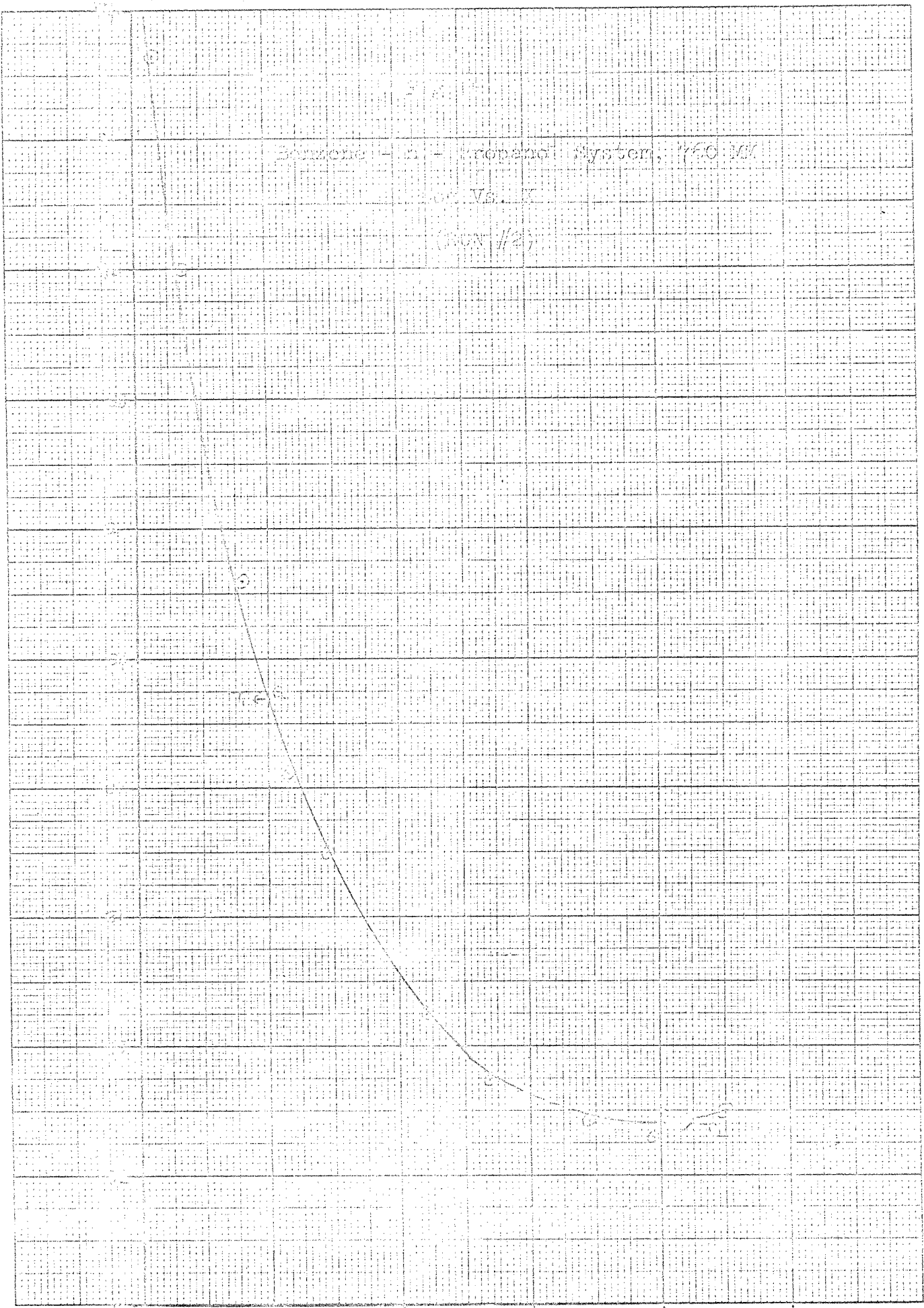


Benzene - n - Propane System, 160 mm

vs. X

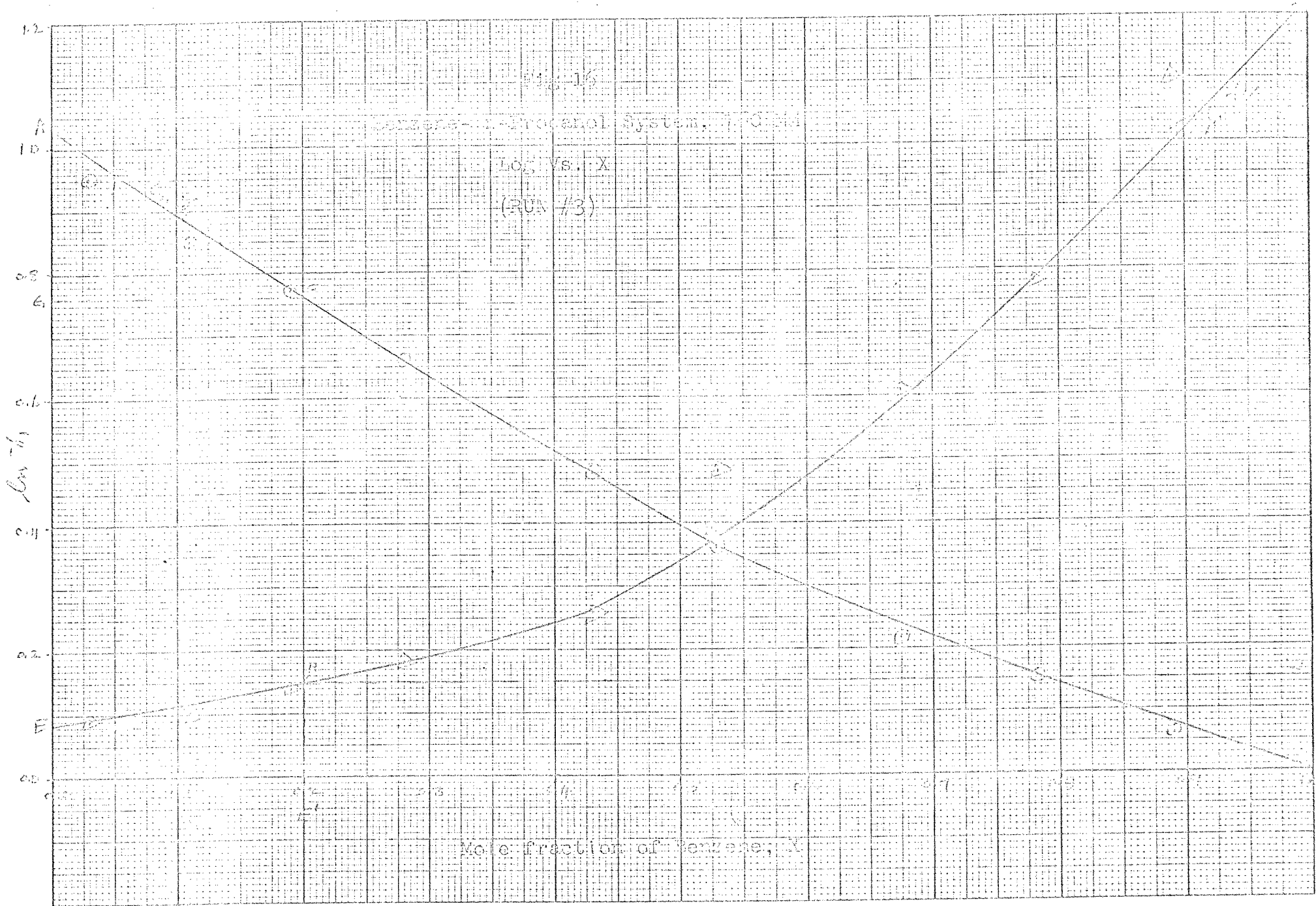
(WV 12)

Temperature, T, °C



0.0 0.2 0.4 0.6 0.8 1.0

Mole fraction of Benzene, X



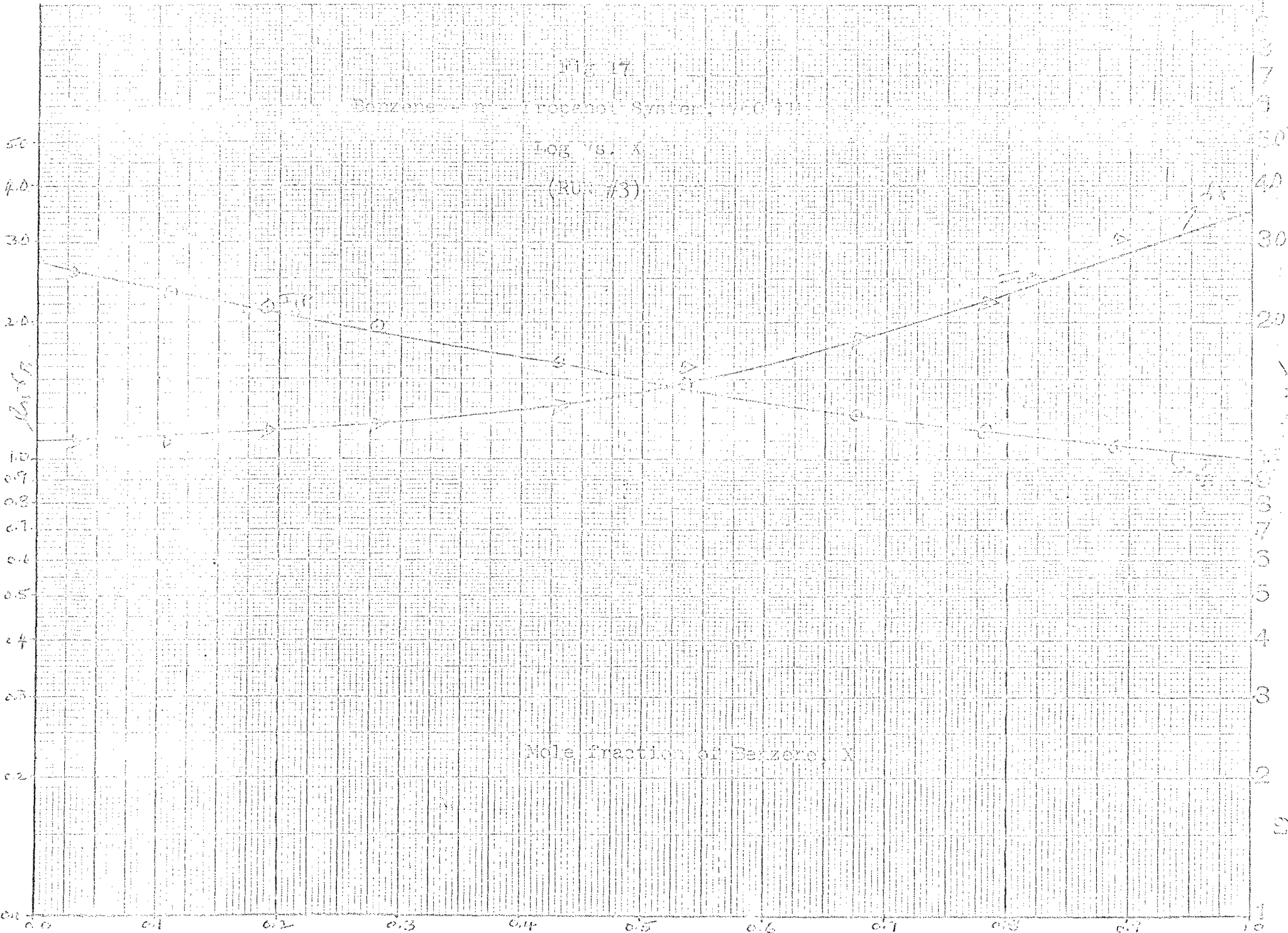
M. A.

Fig. 17

Benzene - n-Propanol System, 70°C (17)

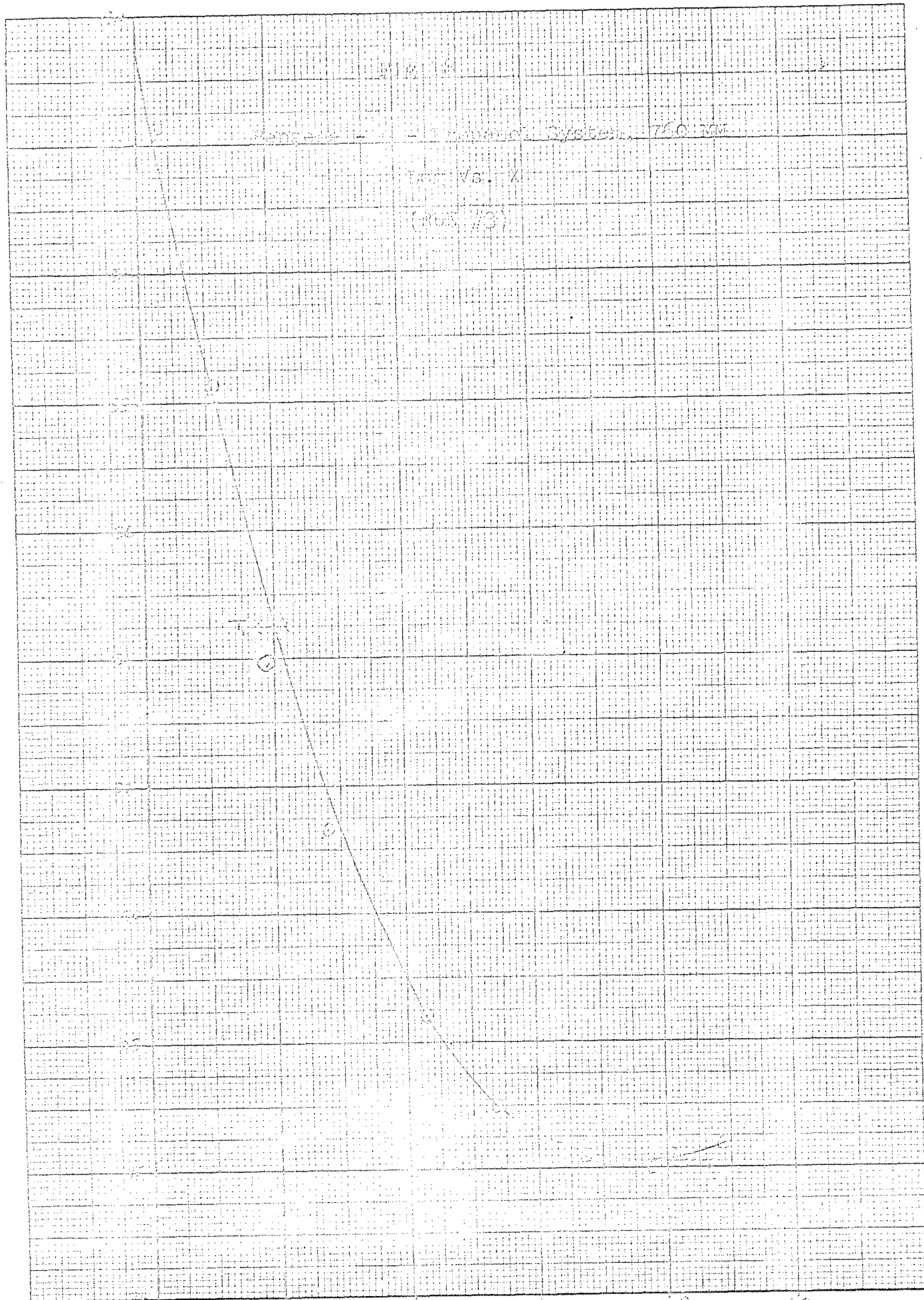
Log γ_B, A

(RU: 73)



Mole fraction of Benzene, X_B

Temperature, T, °C



Mole fraction of Benzene, X

APPENDIX E

CALCULATION OF RUN #2
SYSTEM #1 BENZENE-CYCLOHEXANE

From Fig 5, the areas AFCE and DBEC obtained by graphical integration are:

$$\text{At } X_1 = 0.2 \quad \text{then } I_{1p} = \ln 1.30$$

$$\text{and } X_2 = 0.8 \quad \text{then } I_{2p} = \ln 1.32$$

$$\begin{aligned} \frac{d(I_{1p} + I_{2p})}{dX} &= \frac{d(I_{1p})}{dX} + \frac{d(I_{2p})}{dX} \\ &= \frac{\ln 1.30}{0.6} - \frac{\ln 1.32}{0.6} \\ &= \frac{(0.2623 - 0.2776)}{0.6} \\ &= \frac{0.01533}{0.6} = -0.025 \end{aligned}$$

From Fig 6, the area PQRS obtained by graphical integration

$$\text{At } X_1 = 0.2 \quad \text{then } T_1 = 77.75$$

$$\text{and } X_2 = 0.8 \quad \text{then } T_2 = 77.45$$

CALCULATION OF RUN #2 (CONT'D)

$$\frac{dT}{dX} = \frac{(77.45-77.55)}{(0.8-0.2)} = -\frac{0.10}{0.60} = -0.1665 \text{ } ^\circ\text{C}/\text{mole}$$

The heat of mixing for the System is:

(from equation (10))

$$H^E = -\frac{(1.987)(354.2)^2(-0.025)}{(-0.1665)} = -37.43 \frac{\text{K cal}}{\text{mole}}$$

CALCULATION OF RUN #3
SYSTEM #1, BENZENE-CYCLOHEXANE

From Fig 8, the areas AFCE and DBEC obtained by graphical integration are:

$$\text{At } X_1 = 0.2 \quad \text{then } I_{1p} = \ln 1.275$$

$$\text{and } X_2 = 0.8 \quad \text{then } I_{2p} = \ln 1.35$$

$$\begin{aligned} \frac{d(I_{1p} + I_{2p})}{dX} &= \frac{d(I_{1p})}{dX} + \frac{d(I_{2p})}{dX} \\ &= \frac{\ln 1.275}{0.6} - \frac{\ln 1.35}{0.6} \\ &= \frac{(0.2429 - 0.3001)}{0.6} \\ &= - \frac{0.0572}{0.6} = - 0.095 \end{aligned}$$

From Fig 9, the area PQRS obtained by graphical integration

$$\text{At } X_1 = 0.2 \quad \text{then } T_1 = 77.85$$

$$\text{and } X_2 = 0.8 \quad \text{then } T_2 = 77.65$$

CALCULATION OF RUN #3 (CONT'D)

$$\frac{dT}{dx} = \frac{(77.65 - 77.85)}{(0.8 - 0.2)} = - \frac{0.20}{0.60} = - 0.333 \text{ } ^\circ\text{C/mole}$$

The heat of mixing for the System is:

(from equation (10))

$$H^E = - \frac{(1.987) (354.2)^2 (-0.095)}{(-0.333)} = 71.12 \frac{\text{K cal}}{\text{mole}}$$

CALCULATION OF RUN #1
SYSTEM #2, BENZENE-n-PROPANOL

From Fig 11, the areas AFCE and DBEC obtained by graphical integration are:

$$\text{At } X_1 = 0.2 \quad \text{then } I_{1p} = \ln 2.15$$

$$\text{and } X_2 = 0.8 \quad \text{then } I_{2p} = \ln 2.55$$

$$\begin{aligned} \frac{d(I_{1p} + I_{2p})}{dX} &= \frac{d(I_{1p})}{dX} + \frac{d(I_{2p})}{dX} \\ &= \frac{\ln 2.15}{0.6} - \frac{\ln 2.55}{dX} \\ &= \frac{(0.7655 - 0.9361)}{0.6} = \frac{0.1706}{0.6} = - 0.2843 \end{aligned}$$

From Fig 12, the area PQRS obtained by graphical integration:

$$\text{At } X_1 = 0.2 \quad \text{then } T_1 = 85.0$$

$$\text{and } X_2 = 0.8 \quad \text{then } T_2 = 77.9$$

CALCULATION OF RUN #1 (CONT'D)

$$\frac{dT}{dX} = \frac{(77.9 - 85.0)}{0.6} = - \frac{7.1}{0.6} = 13.5 \text{ } ^\circ\text{C/mole}$$

The heat of mixing for the System is:

(from equation (10))

$$H^E = - \frac{(1.987) (354.2)^2 (-0.2843)}{(-13.5)} = - 5.244 \frac{\text{K cal}}{\text{mole}}$$

CALCULATION OF RUN #2
SYSTEM #2, BENZENE-n-PROPANOL

From Fig 14, the areas AFCE and DBEC obtained by graphical integration are:

$$\text{At } X_1 = 0.2 \quad \text{then } I_{1p} = \ln 2.1$$

$$\text{and } X_2 = 0.8 \quad \text{then } I_{2p} = \ln 2.3$$

$$\begin{aligned} \frac{d(I_{1p} + I_{2p})}{dX} &= \frac{d(I_{1p})}{dX} + \frac{d(I_{2p})}{dX} \\ &= \frac{\ln 2.1}{0.6} - \frac{\ln 2.3}{0.6} \\ &= \frac{(0.7419 - 0.8329)}{0.6} \\ &= -\frac{0.091}{0.6} - 0.1516 \end{aligned}$$

From Fig 15, the area PQRS obtained by graphical integration:

$$\text{At } X_1 = 0.2 \quad \text{then } T_1 = 83.4$$

CALCULATION OF RUN #2 (CONT'D)

and $X_2 = 0.8$ then $T_2 = 76.8$

$$dT = \frac{(76.8 - 83.4)}{(0.8 - 0.2)} = -6.6 = -11.0 \text{ } ^\circ\text{C/mole}$$

The heat of mixing for the System is:

(from equation (10))

$$H^E = - \frac{(1.987) (354.2)^2 (-0.1516)}{(-11.00)} = -3.44 \text{ K cal/mole}$$

CALCULATION OF RUN #3
SYSTEM #2, BENZENE-n-PROPANOL

From Fig 17, the areas AFCE and DBEC obtained by graphical integration are:

$$\text{At } X_1 = 0.2 \quad \text{then } I_{1p} = \ln 2.1$$

$$\text{and } X_2 = 0.8 \quad \text{then } I_{2p} = \ln 2.3$$

$$\begin{aligned} \frac{d(I_p + I_{2p})}{dX} &= \frac{d(I_{1p})}{dX} + \frac{d(I_{2p})}{dX} \\ &= \frac{\ln 2.1}{0.6} - \frac{\ln 2.3}{0.6} \\ &= \frac{(0.742 - 0.833)}{0.6} = - \frac{0.091}{0.6} = -0.152 \end{aligned}$$

From Fig 18, the area PQRS obtained by graphical integration:

$$\text{At } X_1 = 0.2 \quad \text{then } T_1 = 84.5$$

(CALCULATION OF RUN #3 (CONT'D))

and $X_2 = 0.8$ then $T_2 = 76.1$

$$\frac{dT}{dX} = \frac{(76.1 - 84.5)}{(0.8 - 0.2)} = - \frac{8.4}{0.6} = - 14.0 \text{ } ^\circ\text{C/mole}$$

The heat of mixing for the System is:

(from equation (10))

$$H^E = - \frac{(1.987) (354.2)^2 (- 0.152)}{(- 14.0)} = - 2.71 \text{ K cal/mole}$$