AN INVESTIGATION OF THE BENEDICT EQUATION OF STATE AS A MEANS OF CORRELATING VOLUMETRIC DATA FOR LIGHT HYDROCARBONS

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Chemical Engineer

California Institute of Technology
Pasadena, California
1950

ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness and express his thanks to Dr. Bruce H. Sage for the guidance and inspiration, both technical and personal, which he has offered as director of this research. Also gratefully acknowledged is the considerable assistance of Dr. Stanley Frankel in development of the computational procedures.

Thanks are also due to V. Berry and B. Eldridge for invaluable assistance in preparation of the manuscript.

ABSTRACT

The problem of evaluating constants for the Benedict equation of state is discussed. It is concluded that a method must be found which is adaptable to high-speed digital computers and which is capable of precise analytical interpretation if the equation is to be made practical as a means of correlating data for mixtures of hydrocarbons.

A study has been made of the least squares criterion of best fit as a means of evaluating the Benedict constants from volumetric data alone. The necessary equations are presented and some analytical characteristics of the solution investigated. A procedure was developed for performing the calculations with commercial punched card equipment, and the results of two test calculations are presented. It is shown that a significantly better fit of volumetric data is possible than was obtained by Benedict. Computations are shown which indicate that the Benedict constants are determined by the experimentally observed behavior to four digits at most. Coefficients are presented for an equation by means of which the least squares measure of the precision of fit may readily be calculated for any arbitrary values of the constant.

It is concluded that the method used is suitable for digital-computer treatment and, as applied to volumetric data, gives both an improved fit and the desired precise interpretation of the fit.

INTRODUCTION

One of the most important and long-standing problems of the petroleum industry is that of obtaining adequate thermodynamic and volumetric data upon which to base engineering calculations. Because the processes upon which petroleum technology is based are largely physical rather than chemical, and because the physical properties of petroleum and its constituents are so notoriously non-ideal, progress in meeting this problem has largely been through the compilation of experimental data on numerous systems of interest. However, because of the almost unlimited number of constituents of petroleum and the great range of compositions which are encountered in the natural product and in its various derivatives, the now large body of available data is but a minute fraction of what is needed.

Coincident with the compilation of data, therefore, there have been devised numerous empirical techniques for correlation of the behavior of hydrocarbons with various measurable and predictable characteristics such as molecular weight, critical constants, viscosity, density and the like. These techniques, while by necessity much used, are subject to serious limitations in accuracy and applicability, and can hardly be considered to have solved the problem.

In recent years, however, the marked development in two fields rather far removed from petroleum engineering has shed new light on the problem. First, from statistical mechanics has come a greater understanding of the molecular interactions which determine the thermodynamic behavior of materials and an increased theoretical interest in thermodynamic equations of state; and secondly, the recent rapid development of high-speed computing equipment has made it possible to consider, for practical engineering computations, equations which would formerly have been considered as interesting, perhaps, but hopelessly cumbersome.

It was in the belief that the development of suitable equations of state offered the most promising approach to the problem of establishing the thermodynamic behavior of petroleum and its derivatives, and in the hope that a contribution could be made toward putting the development on a more precise basis that the present investigation was launched.

DISCUSSION OF OBJECTIVES

In 1940 Benedict(1)* showed that an equation of the form

$$P = RTd + (B_0RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{c}{T^2}(1 + \gamma d^2)\varepsilon^{-\gamma d^2} \quad (1)$$

would correlate volumetric data for methane, ethane, propane, and butane with an average error of less than 0.4%. In addition, he demonstrated that vapor pressure data for these hydrocarbons could be correlated with an average error of approximately 1.1% by means of a fugacity equation derived from it using the same constants. Subsequently(2) he showed that a partly theoretical, partly empirical set of rules for combination of the constants for pure hydrocarbons gave constants for mixtures which represented their behavior with a comparable though somewhat reduced accuracy.

However, the magnitude of the computations involved in evaluating suitable constants appears to have prevented any investigation of the Benedict equation as a means of correlating rather than predicting thermodynamic data for mixtures. Since the ability of the Benedict equation to correlate the data for mixture is hardly to be questioned in view of its proved utility for prediction, the only obstacle is the computational one. The ultimate objective of the project of which this work is the initial phase is to utilize the Benedict equation as a means of correlating data on hydrocarbon mixtures and if possible to improve upon the methods.

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*Here and throughout the text, superscript numbers in parenthesis are used to designate references.

for predicting the Benedict constants for mixtures.

In attempting to fit Benedict's equation to existing data for hydrocarbons, it was obvious that many evaluations would be required, and that accordingly a much more economical procedure than Benedict's was required. This, in fact, is the essence of the problem, and it was assumed from the beginning that a method was required which was sufficiently routine that available digital computer facilities could be utilized.

In addition, it was recognized that another important condition must be met. It can be seen that the requirements that both volumetric and vapor pressure data be fitted are quite independent, for no matter how accurately the equation describes the single phase volumetric data, there is no assurance that the change in fugacity integrated across the two phase region will be zero. Accordingly, some compromise was assumed to be required. In order that the variations with composition of calculated values of the constants have significance, or even consistency, some method for precise specification of the compromise must be found. This requires first that characteristics of the volumetric fit be investigated and answers found to the following question: First, how good is the "best" fit? Second, how well are the constants corresponding to the "best" fit defined? Third, how much is the "goodness" of the fit reduced by any arbitrary change in the constants from their "best" values?

Obviously, the first problem is then to establish a measure of the "goodness of fit" which will furnish the necessarily precise answers to the above questions by a computational procedure economically adaptable to digital computing equipment. In the following discussion are presented the results of the application of the least squares criterion of best fit.

CHOICE OF EQUATION

The compressibility factor, Z, was the function chosen for application of the least squares method. That is, values of the Benedict constants were found such that the sum of the squares of the errors in Z was minimized. The choice was a compromise in this respect: the minimization of the absolute errors in pressures would have placed an undesired weight on data for high pressure, whereas minimization of the relative errors in pressure involved repeated divisions by pressure. Such divisions were found to cause considerable difficulty in computation with the available machines due to the large range of pressures involved.

The Benedict equation as written for the compressibility factor is given below:

$$Z = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right)d + \left(b - \frac{a}{RT}\right)d^2 + a\alpha\frac{d^5}{RT} + \frac{cd^2}{RT^3}\left(1 + \gamma d^2\right)\varepsilon^{-\gamma d^2} \qquad (2)$$

In the following sections are discussed the analytical aspects of the problem of fitting experimental data with an equation of this form by the application of the least squares criterion.

MATHEMATICAL FORMALIZATION OF THE LEAST SQUARES PROBLEM

Let it be assumed that n simultaneous measurements of Z, d, and T have been made, and that the results are to be correlated with an equation of the form

$$Z_c(d,T) = 1 + \phi_7'(d,T)\,\Psi(\gamma d^2)K_7 + \sum_{i=1}^{6} \phi_i(d,T)K_i \tag{3}$$

in which $$\Psi(\gamma d^2) = (1+\gamma d^2)\mathcal{E}^{-\gamma d^2}. \tag{4}$$

As our measure of the "goodness of fit", we shall choose the sum, $\chi^2(\gamma,K)$, of the squares of the errors in Z, and shall seek values of γ and the K's such that $\chi^2(\gamma,K)$ has its minimum value. Using the subscript k to denote the value corresponding the k^{th} experiment and defining $\mathfrak{z}_k$ as the error, $Z_{ck} - Z_k$, in the calculated Z, $\chi^2(\gamma,K)$ can then be expressed as

$$\chi^2(\gamma,K) = \sum_{k=1}^{n} \mathfrak{z}_k^2 \tag{5}$$

Using these conventions, we can now write the conditions which we require on γ and the K's in the following implicit form:

$$\frac{\partial \chi^2(\gamma,K)}{\partial \gamma} = 0 \tag{6}$$

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} > 0 \tag{7}$$

$$\frac{\partial \chi^2(\gamma,K)}{\partial K_i} = 0 \tag{8}$$

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial K_i^2} > 0 \tag{9}$$

Of the above equations, (6) and (8) require that $\chi^2(\gamma, K)$ have an extreme value or saddle point and (7) and (9) insure that the $\chi^2(\gamma, K)$ defined by (6) and (8) is indeed a minimum. In the following sections the characteristics of the above derivatives will be investigated in some detail, and the equations will be expressed in forms suitable for computation.

It may be noted at this point, however, that such a treatment of the problem is necessary only because of the $\psi(\gamma d^2)$ term. Omission of this factor would reduce equation (3) to a form linear in the K's, and the least squares fit of data to linear equations has been discussed in general by many authors. (See for example Ref. 3). Accordingly, interest is centered primarily in equations (6) and (7).

INVESTIGATION OF $\frac{\partial \chi^2(\gamma,K)}{\partial \gamma}$

By differentiation of equation (5) with respect to γ with all K's held constant there results:

$$\frac{\partial \chi^2(\gamma,K)}{\partial \gamma} = 2 \sum_{k=1}^{n} \mathfrak{z}_k \frac{\partial \mathfrak{z}_k}{\partial \gamma} \tag{1}$$

It should be emphasized at this point that $\mathfrak{z}_k$ is here considered to be a function only of γ and the K's. We have adopted for convenience the viewpoint that to each of the n experiments there corresponds a function, $\mathfrak{z}_k$, defined by

$$\begin{aligned} \mathfrak{z}_k &\equiv Z_{ck} - Z_k = Z_c(d_k, T_k) - Z_k \\ &= (1 - Z_k) + \phi_7' \psi_k(\gamma) K_7 + \sum_{i=1}^{6} \phi_{ik} K_i \end{aligned} \tag{11}$$

in which

$$\phi_{ik} = \phi_i(d_k, T_k) \qquad i \neq 7 \tag{12}$$

$$\psi_k(\gamma) = \psi(\gamma d_k^2) = (1 + \gamma d_k^2)\, \varepsilon^{-\gamma d_k^2} \tag{13}$$

$$\phi_{7k}' = \phi_7'(d_k, T_k) \tag{14}$$

Utilizing now equation (11), $\frac{\partial \mathfrak{z}_k}{\partial \gamma}$ can be evaluated as

$$\frac{\partial \mathfrak{z}_k}{\partial \gamma} = \phi_{7k}' K_7 \frac{d \psi_k(\gamma)}{\partial \gamma} \tag{15}$$

By differentiation of (13)

$$\frac{d \psi_k(\gamma)}{d \gamma} = -\gamma d_k^4\, \varepsilon^{-\gamma d_k^2} \tag{16}$$

Equation (10) yields, by substitution of (15) and (16)

$$\frac{\partial \chi^2(\gamma,K)}{\partial \gamma} = -2 \gamma K_7 \sum_{k=1}^{n} \mathfrak{z}_k \phi_{7k}' d_k^4\, \varepsilon^{-\gamma d_k^2} \tag{17}$$

Elimination of $\mathcal{Z}_k$ from (17) by means of (11) and of $\psi_k(\gamma)$ by means of (13) yields

$$\begin{aligned}\frac{\partial \chi^2(\gamma,K)}{\partial \gamma} = &-2\gamma K_7 \sum_{k=1}^{n} (1-Z_k)\, \varphi'_{7k}\, d_k^4\, \varepsilon^{-\gamma d_k^2} \\ &-2\gamma K_7^2 \sum_{k=1}^{n} \varphi'^2_{7k}\, d_k^4 (1+\gamma d_k^2)\, \varepsilon^{-2\gamma d_k^2} \\ &-2\gamma K_7 \sum_{i=1}^{6} K_i \sum_{k=1}^{n} \varphi_{ik}\, \varphi'_{7k}\, d_k^4\, \varepsilon^{-\gamma d_k^2}\end{aligned} \qquad (18)$$

This is then the expression for $\frac{\partial \chi^2(\gamma,K)}{\partial \gamma}$ explicit in γ and the K's.

INVESTIGATION OF $\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2}$

From (17), by differentiation, is obtained

$$\begin{aligned}\partial^2 \chi^2(\gamma,K) = &-2K_7 \sum_{k=1}^{n} \mathfrak{z}_k \Phi'_{7k} d_k^4 \varepsilon^{-\gamma d_k^2} \\ &-2\gamma K_7 \sum_{k=1}^{n} \frac{\partial \mathfrak{z}_k}{\partial \gamma} \Phi'_{7k} d_k^4 \varepsilon^{-\gamma d_k^4} \\ &+2\gamma K_7 \sum_{k=1}^{n} \mathfrak{z}_k \Phi'_{7k} d_k^6 \varepsilon^{-\gamma d_k^2}\end{aligned} \qquad (19)$$

By substitution of (17) in the first term and (15) and (16) in the second term, (19) reduces to

$$\begin{aligned}\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} = &\frac{1}{\gamma} \frac{\partial \chi^2(\gamma,K)}{\partial \gamma} + 2\gamma^2 K_7^2 \sum_{k=1}^{n} \Phi'^2_{7k} d_k^8 \varepsilon^{-2\gamma d_k^2} \\ &+ 2\gamma K_7 \sum_{k=1}^{n} \mathfrak{z}_k \Phi'_{7k} d_k^6 \varepsilon^{-\gamma d_k^2}\end{aligned} \qquad (20)$$

By rearrangement this becomes

$$\begin{aligned}\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} = &\frac{1}{\gamma} \frac{\partial \chi^2(\gamma,K)}{\partial \gamma} \\ &+ 2\gamma K_7 \sum_{k=1}^{n} \Phi'_{7k} d_k^6 \varepsilon^{-\gamma d_k^2} \left(\mathfrak{z}_k + \gamma d_k^2 \Phi'_{7k} K_7 \varepsilon^{-\gamma d_k^2}\right)\end{aligned} \qquad (21)$$

As an alternative form, equation (17) can be used to eliminate $\frac{\partial \chi^2(\gamma,K)}{\partial \gamma}$, and (13) substituted after rearrangement to yield

$$\begin{aligned}\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} = &2\gamma K_7 \sum_{k=1}^{n} \Phi'_{7k} d_k^6 \varepsilon^{-\gamma d_k^2} \\ &\times \left[\left(\frac{\gamma d_k^2 - 1}{\gamma d_k^2}\right) \mathfrak{z}_k + \gamma d_k^2 \Phi'_{7k} K_7 \varepsilon^{-\gamma d_k^2} \right]\end{aligned} \qquad (22)$$

DISCUSSION OF MINIMIZATION WITH RESPECT TO γ

By substitution of equation (18) in equation (6) there results a necessary condition that $\chi^2(\gamma, K)$ be a minimum with respect to γ.

$$\begin{aligned} &2\gamma K_7^2 \sum_{k=1}^{n} \Phi'_{7k}\, d_k^4 \,(1+\gamma d_k^2)\, \varepsilon^{-\gamma d_k^2} \\ &\quad + 2\gamma K_7 \sum_{i=1}^{6} K_i \sum_{k=1}^{n} \Phi_{ik}\, \Phi'_{7k}\, d_k^4\, \varepsilon^{-\gamma d_k^2} \\ &\quad\quad = 2\gamma K_7 \sum_{k=1}^{n} (Z_k - 1)\, \Phi'_{7k}\, d_k^4\, \varepsilon^{-\gamma d_k^2} . \end{aligned} \tag{23}$$

This equation, though a valid condition for minimization of $\chi^2(\gamma, K)$ with respect to γ, is far too clumsy to consider for computational use. It was decided that trial values of γ would be selected, and values of the K's found such that $\chi^2(\gamma, K)$ was a minimum with respect to all K's. As will be shown, the computation for the K's is straight-forward on this basis. The equations derived above can be used to investigate the nature of the dependence of $\chi^2(\gamma, K)$ on γ. Since each set of trial values of γ used involves a large amount of computation, any information of this nature may be quite valuable.

LIMITING BEHAVIOR OF $\chi^2(\gamma, K)$

We shall consider first the behavior of $\chi^2(\gamma,K)$ as γ increases without limit.

By L'Hospital's Rule

$$\underset{\gamma\to\infty}{L}\,(1+\gamma d^2)\epsilon^{-\gamma d^2} = \underset{\gamma\to\infty}{L}\,\frac{\frac{d}{d\gamma}(1+\gamma d^2)}{\frac{d}{d\gamma}\,\epsilon^{\gamma d^2}} \qquad (24)$$

Hence, by (13)

$$\underset{\gamma\to\infty}{L}\,\Psi_k(\gamma) = \underset{\gamma\to\infty}{L}\,\frac{d_k^2}{d_k^2\,\epsilon^{\gamma d_k^2}} = 0 \qquad (25)$$

From equation (25) it follows that the effect of letting γ increase without limit is simply that of omitting the term $\Phi'_{7k}\,\Psi_k(\gamma)\,K_7$ in equation (2). Hence $\underset{\gamma\to\infty}{L}\,\chi^2(\gamma,K)$ is best obtained by evaluation of χ^2 with this term deleted. All partial derivatives of $\chi^2(\gamma,K)$ with respect to γ must of course approach zero for sufficiently large γ.

Next, it will be of interest to investigate the behavior of $\chi^2(\gamma,K)$ as γ approaches zero.

From equation (13)

$$\underset{\gamma\to 0}{L}\,\Psi(\gamma d^2) = \underset{\gamma\to 0}{L}\,(1+\gamma d^2)\epsilon^{-\gamma d^2} = 1 \qquad (26)$$

Then in the limit as γ approaches zero, the correlating equation (2) becomes

$$Z_c(d,T) = 1 + \Phi_7'(d,T)K_7 + \sum_{i=1}^{6}\Phi_i(d,T)K_i \qquad (27)$$

In this case the limiting value of $\chi^2(\gamma,K)$ may be evaluated by deleting the factor $\Psi(\gamma d^2)$ and carrying out the conventional least squares evaluation of the seven linear constants, K.

It is of interest to compare equation (27) with the equivalent limiting form of the correlating equation as increases without limit. The latter was found to differ from equation (27) only by omission of the K term. From this fact a simple deduction shows that

$$\lim_{\gamma \to 0} \chi^2(\gamma, K) \leq \lim_{\gamma \to \infty} \chi^2(\gamma, K) \quad . \tag{28}$$

for K's which satisfy the least squares criterion. Thus if K_7 in (27) is found to have a least squares value of zero, then the least squares value of $\chi^2(0, K)$ and of $\chi^2(\infty, K)$ are equal because the correlating equations are identical. However, if the least squares value of K_7 is non-zero, then $\chi^2(0, K)$ must be less than $\chi^2(\infty, K)$, since it is less than the $\chi^2(\gamma, K)$ for K equal to zero.

For the limiting value of $\frac{\partial \chi^2(\gamma, K)}{\partial \gamma}$ as γ approaches zero we consider equation (17). From equation (26) it follows that z_k is finite as γ approaches zero. Accordingly

$$\lim_{\gamma \to 0} \frac{1}{\gamma} \frac{\partial \chi^2(\gamma, K)}{\partial \gamma} = -2 K_7 \sum_{k=1}^{n} \Phi'_{7k} \, d_k^4 \left(\lim_{\gamma \to 0} z_k \right) \tag{29}$$

is also bounded for finite d_k's and K's and

$$\lim_{\gamma \to 0} \frac{\partial \chi^2(\gamma, K)}{\partial \gamma} = 0 \tag{30}$$

For the limiting value of $\frac{\partial^2 \chi^2(\gamma, K)}{\partial \gamma^2}$ as γ approaches zero we consider equation (21). Having already demonstrated that z_k and $\mathcal{E}^{-\gamma d^2}$ are bounded for small γ , then

$$\mathop{L}_{\gamma\to 0} \; 2\gamma K_7 \sum_{k=1}^{n} \Phi'_{7k}\, d_k^6\, \mathcal{E}^{\gamma d_k^2}\left(z_k + \gamma d_k^2\, \Phi'_{7k} K_7 \mathcal{E}^{-\gamma d_k^2}\right) = 0 \tag{31}$$

Hence

$$\mathop{L}_{\gamma\to 0} \frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} = \mathop{L}_{\gamma\to 0} \frac{1}{\gamma}\frac{\partial \chi^2(\gamma,K)}{\partial \gamma} \tag{32}$$

By application of equation (26) this becomes

$$\mathop{L}_{\gamma\to 0} \frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2} = -2K_7 \sum_{k=1}^{n} \Phi'_{7k}\, d_k^4 \left(\mathop{L}_{\gamma\to 0} z_k\right) \tag{33}$$

Thus we find that as γ approaches zero, $\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2}$ approaches some finite positive value with zero first derivative and a finite second derivative. Though this second derivative could be calculated by equation (32), no certain information as to its sign can be obtained without computation. However, since Φ'_{7k} is proportional to d_k^2/T_k , it is apparent that the factor $\Phi'_{7k}\, d_k^4$ gives a very heavy weight in the summation to the z's for large values of d, hence we can conclude that sign of $\frac{\partial^2 \chi^2(\gamma,K)}{\partial \gamma^2}$ is largely determined by the signs of the z's corresponding to the largest values of d, and is of the opposite sign for positive K .

BEHAVIOR OF $\chi^2(\gamma)$

It will now be convenient to define a new set of variables useful in discussion of the method proposed above for evaluating γ and the K's. As has been stated, trial values of γ are selected, and the best values of the K's computed corresponding to these γ's. The values of K_i will be denoted by $K_i(\gamma)$ to indicate their dependence upon the trial γ value. Similarly, we shall define $\chi^2(\gamma)$ such that

$$\chi^2(\gamma) = \chi^2(\gamma, K(\gamma)) \tag{34}$$

We can easily show that $\dfrac{d\,\chi^2(\gamma)}{d\gamma} = \left(\dfrac{\partial\,\chi^2(\gamma,K)}{\partial\gamma}\right)_{K_i = K_i(\gamma)}$ as follows:

$$d\,\chi^2(\gamma,K) = \frac{\partial\,\chi^2(\gamma,K)}{\partial\gamma}d\gamma + \sum_{i=1}^{7}\frac{\partial\,\chi^2(\gamma,K)}{\partial K_i}\,dK_i \tag{35}$$

But if $K_i = K_i(\gamma)$, then by equation (8)

$$\frac{\partial\,\chi^2(\gamma,K)}{\partial K_i} = 0 \tag{8}$$

Hence, if $K = K(\gamma)$, then for any arbitrary change in γ and the K's

$$\frac{d\chi^2(\gamma,K)}{d\gamma} = \frac{\partial\,\chi^2(\gamma,K)}{\partial\gamma} \tag{36}$$

and in particular along the path defined by equation (8), for which $\chi^2(\gamma,K)$ becomes $\chi^2(\gamma)$, equation (36) is valid. Hence

$$\frac{d\chi^2}{d\gamma} = \left(\frac{\partial \chi^2(\gamma,K)}{\partial \gamma}\right)_{K=K(\gamma)} \tag{37}$$

The conclusions previously arrived at in the preceding discussions regarding $\frac{\partial \chi^2(\gamma,K)}{\partial \gamma}$ are accordingly equally valid for $\frac{d\chi^2(\gamma)}{d\gamma}$.

From consideration of the power series expansion of $\Psi(\gamma d^2)$ for γ sufficiently small that γd^2 is small in comparison to unity, another useful conclusion regarding the variation of $\chi^2(\gamma)$ can be reached. It is easily shown that the first two terms in the power series expansion of $(1+\gamma d^2)\epsilon^{-\gamma d^2}$ are $1 - \frac{1}{2}\gamma^2 d^4$. Accordingly, the effect for small γ of the $\Psi(\gamma d^2)$ factor in the correlating equation is that of including an extra term of the form $-\phi_7' \gamma^2 d^4 K_7$. Since γ occurs only as the square, the effect of this term is the same for both positive and negative γ , and $\chi^2(\gamma)$ must be locally symmetric about the point $\gamma=0$. Consequently we can state that the point $\gamma=0$ must be a maximum or minimum in $\chi^2(\gamma)$, not a flex point. Further, if $\gamma=0$ is a maximum in $\chi^2(\gamma)$, at least one minimum must exist on either side.

As a summary of the conclusions reached in the preceding discussion, sketches of possible $\chi^2(\gamma)$ curves are shown in Figure 1. Curve A represents the case of a negative value of $\frac{d^2\chi^2(\gamma)}{d\gamma^2}$. This is expected to be the normal case. Curve B represents the case of a small positive value of $\frac{d^2\chi^2(\gamma)}{d\gamma^2}$

at $\gamma=0$, with one minimum only for a positive γ . Curve C is the degenerate case of positive value of $\frac{d^2 \chi^2(\gamma)}{d\gamma^2} = 0$ at $\gamma=0$ with no minima except at this point.

EVALUATION OF $K(\gamma)$

In this and the two following sections are derived a number of equations which will be of use in treatment of the least squares problem and in interpretation of the results. Since they are applicable to any least squares treatment of a linear equation, no claim to originality is made, and the derivations are included here only in order that all pertinent equations may be available in the same nomenclature as is used throughout the remainder of the text.

It is now desired to obtain suitable equations for evaluation of the best K's for a given value of γ, and for convenience we shall rewrite the correlating equations in the form

$$Z_c(d,T) = 1 + \sum_{i=1}^{7} \Phi_i(d,T) K_i \tag{38}$$

in which the coefficient of K_7 is now written as

$$\Phi_7(\gamma, d, T) = \Phi_7' \, \Psi(\gamma d^2) \tag{39}$$

On this basis

$$\mathfrak{z}_k = (1 - Z_k) + \sum_{j=1}^{7} \Phi_{jk} K_j \tag{40}$$

By substitution of (5) in (8) we have

$$2 \sum_{k=1}^{n} \mathfrak{z}_k \frac{\partial \mathfrak{z}_k}{\partial K_i} = 0 \tag{41}$$

But from (40)

$$\frac{\partial \mathfrak{z}_k}{\partial K_i} = \Phi_{ik} \tag{42}$$

Hence

$$\sum_{k=1}^{n} \phi_{ik} z_k = 0 \tag{43}$$

Substitution of (40) yields, after rearrangement,

$$\sum_{j=1}^{7} K_j \sum_{k=1}^{n} \phi_{ik} \phi_{jk} = \sum_{k=1}^{n} (Z_k - 1) \phi_{ik} \tag{44}$$

For simplicity we shall define the quantities

$$C_{ij} = \sum_{k=1}^{n} \phi_{ik} \phi_{jk} \tag{45}$$

and

$$b_i = \sum_{k=1}^{n} (Z_k - 1) \phi_{ik} \tag{46}$$

Substituting (45) and (46) in (44) we have

$$\sum_{j=1}^{7} C_{ij} K_j = b_i \tag{47}$$

Hence application of equation (8) is shown to lead to a set of simultaneous linear equations in the K's. The solutions of these equations are the values of $K(\vartheta)$.

SPECIAL EQUATION FOR EVALUATION OF $\chi^2(\gamma)$

After evaluation of the quantities, K(γ), a simple method exists for evaluation of $\chi^2(\gamma)$. The expression is derived below.

By substitution of (40) in (5)

$$\chi^2(\gamma, K) = \sum_{k=1}^{n} z_k \left[(1-Z_k) + \sum_{j=1}^{7} \phi_{jk} K_j\right] \tag{48}$$

By rearrangement this yields

$$\chi^2(\gamma, K) = \sum_{k=1}^{n} z_k (1-Z_k) + \sum_{j=1}^{7} K_j \sum_{k=1}^{n} \phi_{jk}\, z_k \tag{49}$$

If the K's in (49) are taken as K(γ), then $\chi^2(\gamma, K)$ becomes $\chi^2(\gamma)$, and by substitution of equation (43)

$$\chi^2(\gamma) = \sum_{k=1}^{n} z_k (1-Z_k) \tag{50}$$

Expanding (50) by means of (40), we have

$$\chi^2(\gamma) = \sum_{k=1}^{n} (Z_k-1)^2 + \sum_{j=1}^{7} K_j \sum_{k=1}^{n} \phi_{jk}(1-Z_k) \tag{51}$$

Utilizing (46) this can be written as

$$\chi^2(\gamma) = \sum_{k=1}^{n} (Z_k-1)^2 + \sum_{j=1}^{7} K_j\, b_j \tag{52}$$

Utilizing equation (52), $\chi^2(\gamma)$ can then be computed from the K(γ) values by computing $(Z_k-1)^2$ along with the other cross-products, $\phi_{ik}\phi_{jk}$ and $\phi_i(Z_k-1)$, summing the values of $(Z_k-1)^2$ over the data, and then the simple evaluation of equation (52). The value of this procedure over that of calculating and summing the z_k^2 values lies essentially in the fact that it requires multiplication by the $K(\gamma)$ values only after summation.

For the experimental calculations here reported, $\chi^2(\gamma)$ was calculated both by equation (5) and by equation (52), since z_h's were required for other purposes. However, in a regular routine use of this method for evaluation of the K's, only equation (52) need be used, and a considerable saving can thus be effected.

VARIATION OF $\chi^2(\gamma,K)$ WITH K

In order to insure that equations (9) are satisfied by the values of $K(\gamma)$, and to obtain an expression for $\chi^2(\gamma,K)$, the second partials of $\chi^2(\gamma,K)$ with respect to the K's will now be obtained.

By differentiation of (5) and substitution of (42)

$$\frac{\partial \chi^2(\gamma,K)}{\partial K_i} = 2 \sum_{k=1}^{n} \gamma_k \phi_{ik} \tag{53}$$

Differentiating again, with substitution of (42)

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial K_i \partial K_j} = 2 \sum_{k=1}^{n} \phi_{ik} \phi_{jk} \tag{54}$$

Substituting (42) yields

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial K_i \partial K_j} = 2 C_{ij} \tag{55}$$

For $i=j$, this becomes

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial K_i^2} = 2 C_{ii} \tag{56}$$

Since C_{ii} is a sum of squares and is therefore positive, it is seen that equation (9) is indeed satisfied, and hence that equation (8) does in fact minimize $\chi^2(\gamma,K)$ with respect to the K's.

Equation (55) is of considerable interest for another reason. In subsequent investigations regarding correlations of vapor pressure data, it will be of interest to know the effect of changing the K's from their least squares values. Such information is readily available by integration of equation (55).

It can be shown by differentiation that the resulting equation for $\chi^2(\gamma, K)$ is

$$\chi^2(\gamma,K) = \chi^2(\gamma) + \sum_{i=1}^{7}\sum_{j=1}^{7} C_{ij}\,\delta K_i\,\delta K_j \tag{57}$$

where

$$\delta K_i = K_i - K_i(\gamma) \tag{58}$$

Thus by differentiation of (57) and (58)

$$\frac{\partial \chi^2(\gamma,K)}{\partial K_r} = \sum_{i=1}^{7}\sum_{j=1}^{7} C_{ij}\left(\frac{\partial K_i}{\partial K_r}\delta K_j + \delta K_i \frac{\partial K_j}{\partial K_r}\right) \tag{59}$$

Since from equation (45)

$$C_{ij} = C_{ji} \tag{60}$$

then (59) reduces to

$$\frac{\partial \chi^2(\gamma,K)}{\partial K_r} = 2\sum_{i=1}^{7} C_{ir}\,\delta K_r \tag{61}$$

Further differentiation gives

$$\frac{\partial^2 \chi^2(\gamma,K)}{\partial K_r\,\partial K_s} = 2\,C_{rs} \tag{62}$$

Since (62) is identical to (55), (57) reduces to (34), and (61) reduces to (8) for $\delta K_i = 0$, equation (57) is proved.

Using (57), the effect of any change in the K's from their best values can be readily computed. By combining (57) with (52) an alternative expression of $\chi^2(\gamma,K)$ can be obtained.

$$\chi^2(\gamma,K) = \sum_{k=1}^{n}(Z_k - 1)^2 + \sum_{j=1}^{7} K_j(\gamma)\,b_j + \sum_{i=1}^{7}\sum_{j=1}^{7} C_{ij}\,\delta K_i\,\delta K_j \tag{63}$$

DESCRIPTION OF COMPUTATIONS

All data were first converted into English units, with temperature recorded to the nearest 0.01°R, pressure recorded to the nearest 0.01 psia, and specific volume recorded to the nearest 10^{-7} cu.ft. per lb. This choice of variables was in conformity with laboratory policy for original data. The significant figures were chosen so as to be adequate for the available data for methane, ethane, propane, and butane. It is to be noted that data originally recorded in these units was not necessarily significant to this many figures, but when converted from other units the indicated figures were retained to avoid rounding errors.

From the specific volumes, the molal densities, d, were calculated as 1/MV and recorded to seven decimals. Molecular weights were on the basis of 12.010 for carbon and 1.0080 for hydrogen. The values of (Z - 1) were calculated as (P/RTd)-1 with seven decimals retained. The value of R used was 10.73185 (psia)(cu.ft.)/(°R)(lb.mol.).

Since the maximum values of d and T/1000 were both near unity for the data used, it was found that the ϕ's were adequately expressed to the same number of decimals as (Z - 1) if calculated as $\phi(d, T/1000)$. All ϕ's were accordingly calculated to seven decimals on this basis, and decimal locations in all subsequent computations are discussed accordingly.

After calculation of the ϕ's and (Z - 1), all the cross-products, $\varphi_{ik}\varphi_{jk}$, $\varphi_{ik}(Z_k - 1)$, and $(Z_k - 1)^2$, were then calculated to seven decimals. In some cases it was found that these products were nine-digit numbers. The sums of each of these cross-products were obtained retaining all decimals, and were found to be as large as eleven digits in some cases.

The sets of simultaneous equations whose coefficients and constant terms were the above sums of cross-products were then solved by the procedure of reduction to unit diagonal form. That is, a pivot coefficient was selected, the equation in which it occurred was divided through by this coefficient, and a suitable multiple of the pivot equation was then subtracted from each of the other equations so that all other coefficients in the pivot column were reduced to zero. Successive application of this operation to a pivot in each row reduced all coefficients except the pivot in each equation to zero, and the pivot to unity. Prior to solution of the equations, however, each equation was divided by its largest coefficient and the quotients recorded to eleven decimals. This served to simplify the machine procedure and to buffer the coefficients against the accumulation of rounding errors. In solving the resulting equations all computations were carried to eleven decimals, and the resulting K's were thus obtained to ten or more digits.

Before rounding, these K's were proved by substitution. A check to within one in the tenth decimal was considered to be due only to rounding errors. This check by substitution was concurrent with the entirely analogous computation, to seven decimals, of $\chi^2(\gamma)$ by equation (52).

For all subsequent calculations, three digits were dropped in the values of the K's, the resulting values being seven to ten digit numbers. The errors of fit were then calculated to seven decimals by equation (40). These ζ values were squared and summed to give $\chi^2(\gamma)$ for check purposes and were divided by the experimental Z values to give the relative errors of fit, r . Both ζ's and r's were computed to seven decimals for consistency with the representation of Z. The ζ values were also summed with and without sign for calculation of $\overline{r}$ and $\overline{|r|}$ respectively. For all calculations of average values, the sums were rounded rather than the individual errors of fit.

NOTES ON COMPUTATIONAL PRECISION

At this point it is recognized that the emphasis in the preceding discussion upon decimals rather than digits carried and the apparent disregard for significance of the many digits carried may very reasonably be questioned. Though a thorough examination of the questions involved is not considered justified at this time, the following brief discussion of two pertinent points is considered appropriate.

First, it may be noted that in any least squares procedure it is necessary to consider the errors of fit as exact quantities which are to be evaluated as accurately as desired. In general, the errors will be evaluated to as many digits as have any experimental significance. Furthermore, it is characteristic of the least squares procedure that a great many digits must be carried in order that the experimental significance of the data not be lost in the course of the computations. Indeed, it was found that the range of variation of some of the φ's, notably d^5/T, is such that even the eight digits carried were not adequate to retain all the significance of the data, and it may be advisable to use more digits in the computations with the next set of trial γ values.

Secondly, this computation is very much an exploratory one, with information as to the accuracy obtainable with the equation and the accuracy required in the computation considered to be among the main results desired. Hence the choice of precision used in the computation was dictated to a considerable extent by convenience in scheduling the computation for machine operation. Since the IBM type 604 Electronic Calculating Punch, which was used for calculation of all the ϕ's and the cross-products, is best adapted to handling of numbers of eight or less digits, a considerable advantage was realized by the choice made.

RESULTS FOR PROPANE

For propane the set of data treated was that of Beattie, Kay, and Kaminsky.(4) This set was identically that treated by Benedict, Webb, and Rubin(3) except for some measurements by Kemp and Egan(5) which supplemented it in the sub-critical region. The data was converted into English units before application of the least-squares method. Conversion factors are given in Table I.

Three values of γ were treated. They were chosen to be the value published by Benedict and values 5% on either side. The Benedict constants and several overall measures of the fit are presented in Table II. As a comparison, Benedict's constants and the same measures of the fit using his constants are included. In addition, χ^2, the sum of the squares of the residuals, is plotted versus γ in Figure 2. The interpolation of this plot is on the basis of a constant second derivative. From Figure 2 it is evident that the best value of γ differs considerably from Benedict's value. On the basis of the parabolic extrapolation used, the minimum is estimated to occur at approximately 77% of Benedict's γ. Returning to Table II it will be noted that the best γ which was tried gave a root-mean-square error which was 0.00253, 28% of that obtained using Benedict's constants. A considerable improvement in the overall fit of this set of volumetric data is thus shown to be possible by the application of the least-squares method.

In Figures 3 through 11 are shown the individual errors of fit versus d as isotherms for all four sets of constants. Inspection of these plots shows that the least-squares constants fit only slightly better over most of the range. The principal improvement occurs in the region of high density and low pressure. It does not appear that the fit for low densities is sacrificed.

It may be seen that a few points deviate markedly from the otherwise smooth curves. These points appear to be slightly in error, demonstrating an additional utility of the plots.

The least-squares values of the average error in Z are seen to be better in a somewhat smaller ratio than the root-mean-square error. As an estimate this is extrapolated on a plot versus the root-mean-square error in Figure 12. A value of 0.17% is obtained for the estimated least-squares value. As a check on the computation, the average error in Z was also calculated omitting the three experimental values for a density of 6.24 lb./mols/cu.ft. Benedict likewise omitted these points when he computed the average error of 0.40% which he gives for propane. The value 0.408% obtained using Benedict's constants is considered to check satisfactorily.

One additional point regarding the plots shown in Figures 3 through 11 of the relative errors versus density is considered worthy of note. It can be seen that, as a group, the curves show a tendency to approach a finite value as the density approaches zero. Since the Benedict equation approaches the perfect gas equation as density approaches zero just as the gas itself approaches perfect gas behavior, the limiting value of the relative error should be zero. In view of this it appears possible that there exists a consistent error in the experimental measurements. An impure sample or an error in container volume are considered most likely. Since such an effect might also be a result of a trial γ value which was too large no definite conclusion is justified until minimization with respect to γ is completed.

In Table III are shown for reference the coefficients C_{ij} and b_i in the set of simultaneous equations for the trial γ's used. The values are on the basis previously discussed of temperatures in thousands of degrees Rankine.

METHANE

The set of data for methane which was treated consisted of 66 experimental measurements of pressure, volume, and temperature, covering a range of temperatures from 100° to 460° F and a range of pressures from 1500 to 10,000 psia. This is the original data used for a paper by Olds, Reamer, Sage, and Lacey.(6) The results of the least-squares calculation using Benedict's value of γ and values 5% on either side are shown in Table IV. In this case marked differences are noted in the values of constants obtained. The constants a, α, and c differ most radically from Benedict's values. This behavior is attributed to the fact that only temperatures well above the critical were considered.

A plot of $\chi^2(\gamma)$ versus γ is shown in Figure 13. It is apparent that the γ values used are far from the best for this set of data. From these results, however, no estimate can be made of the best γ. From Table IV it is seen that the least-squares constants give a root-mean-square error in Z of 0.0034, which is 40% of the 0.0086 obtained using Benedict's constants. The average fractional error in Z is 0.234%, which is 45% of the value obtained using Benedict's constants. Since the data treated covers a restricted temperature range, this rather favorable comparison is to be expected.

In Figures 14 through 20 are presented the percentage error versus d plots for the trial γ of 1.05 times Benedict's value and for Benedict's constants. In this case so little difference was found in the z's for the three γ trials that their plots are essentially coincident. Again it will be seen that essentially smooth curves are obtained, indicating that the random experimental errors are small in relation to the failure of the equation to fit the true behavior.

In Table V are shown for reference the coefficients, C_{ij} and b_i , in the set of simultaneous equations for the trial γ values used. The values are on the basis previously discussed of temperature in thousands of degrees Rankine.

PRECISION TO WHICH CONSTANTS ARE DETERMINED

From the results obtained in the treatment of the propane data, an approximate calculation can be made which sheds considerable light on the precision to which the Benedict constants may be uniquely determined. We shall assume that the smallest change in the root-mean-square error which can be considered to have any significance is 1×10^{-5}. From this we can compute the smallest significant change in χ^2 as follows:

$$(\text{r.m.s. error}) = \sqrt{z^2} = \sqrt{\frac{\chi^2}{n}}$$

hence

$$\chi^2 = n\,(\text{r.m.s. error})^2$$

$$\delta\chi^2 = 2n(\text{r.m.s. error})\,\delta(\text{r.m.s. error})$$

$$\frac{\delta\chi^2}{\chi^2} = \frac{2\delta(\text{r.m.s. error})}{(\text{r.m.s. error})}$$

Using the extrapolated least squares value of χ^2, the corresponding value of the r.m.s. error is estimated to be 2×10^{-3}.

Hence

$$\frac{\delta\chi^2}{\chi^2} = \frac{2\times10^{-5}}{2\times10^{-3}} = 10^{-2}$$

On the basis we have established, the smallest significant change in χ^2 is found to be 1% of its minimum value.

Next, from equation (63) we find that a change, δK_r, in any one K changes χ^2 from its minimum value by the amount

$$\delta\chi^2 = C_{rr}(\delta K_r)^2$$

From this

$$\delta K_r = \sqrt{\frac{\delta\chi^2}{C_{rr}}}$$

and

$$\frac{\delta K_r}{K_r} = \sqrt{\frac{\delta\chi^2}{C_{rr}K_r^2}}$$

Using now the above expression for the smallest significant change in χ^2 and the estimated minimum value of χ^2 of 4×10^{-4} we have

$$\frac{\delta K_r}{K_r} = \sqrt{\frac{(4\times10^{-4})(10^{-2})}{C_{rr}K_r^2}} = 2\times10^{-3}\sqrt{\frac{1}{C_{rr}K_r^2}}$$

However, from Table III it is seen that $10 \leq C_{rr}K_r^2 \leq 100.$ Accordingly, we can state that the smallest significant change in $\delta K_r/K_r$ is within the range

$$6\times10^{-4} \geqq \delta K_r/K_r \geqq 2\times10^{-4}$$

We can thus conclude that the constants need only be computed to four figures to give a root-mean-square error of fit for this set of data which is within 10^{-5} and a χ^2 within 1% of the least squares values.

The above calculations can be expressed as formulae in the following form:

$$\frac{\delta K_r}{K_r} = \sqrt{\frac{2\delta}{C_{rr}K_r^2}}\,\sqrt[4]{n\chi^2} = \sqrt{\frac{2n\delta}{C_{rr}K_r^2}(\text{r.m.s. error})}$$

and

$$\frac{\delta\chi^2}{\chi^2} = \frac{2\delta}{(\text{r.m.s. error})} = 2\delta\cdot\sqrt{\frac{n}{\chi^2}}$$

where δ is the change in the root-mean-square error of fit which is taken to be the smallest which is significant.

NOTES ON THE MACHINE PROCEDURE

A very considerable part of the effort devoted to this investigation was directed toward devising and generalizing the machine techniques for computation, and descriptions of the technical details are on file with the Department of Chemical Engineering. However, a full presentation of this material is not considered appropriate here, for it is only a method of computation and thus not in itself of any theoretical interest. Accordingly, a few general comments only are included here.

It is recognized that the extent of the computations required has not been emphasized thus far, and hence that the need for machine techniques of computation may not be evident. However, a few statistics will serve to demonstrate this point. We shall assume for example that a typical set of data consists of 100 measurements of Z versus d and T. In the course of carrying out a full evaluation of three sets of trial ϕ values, a total of 9600 multiplications and divisions by 8 digit numbers and 500 multiplications and divisions by 13 digit numbers are required, together with a comparable number of additions and subtractions. Furthermore, about two-thirds as many operations are required for each subsequent set of three trial ϕ values investigated. It is evident that such a computation would be very expensive and time-consuming by conventional methods using desk calculators.

By the machine procedure developed for this investigation a complete least squares treatment can be carried out in two to three weeks and it is believed that reduction of this time by a factor of two or more can be achieved if the procedure is put on a large scale basis. However, it should be emphasized that these statements are on the basis of an operator who is thoroughly familiar with the thermodynamic and mathematical problems, the computing equipment, and all details of the procedures used.

CONCLUSION

By calculations using a typical set of volumetric data it has been shown that least squares values of the Benedict constants correlate the data significantly better than the values published by Benedict. The values of both the root-mean-square and the mean fractional error in Z for this set of propane data were estimated to be 0.0017, or 18% and 28%, respectively, of the corresponding quantities used in Benedict's constants. The improvement in the fit was found to be particularly noticeable at the maximum densities, indicating that significant extension of the range of applicability may be possible.

As a criterion for measuring the degree to which the constants and the sum of the squares of the residuals are uniquely determined the concept of the smallest significant increment has been established. By this is meant the smallest increment which is considered to be significant as a measure of the true function. Taking as the smallest significant increment in Z the value 1 X 10^{-5}, it has been shown that the corresponding increment in is 1% of its least value and that the increments in the K's are in the range 0.02% to 0.06%. On this basis, the Benedict constants are concluded to be significant to no more than four figures.

By way of summary, it is concluded that the least squares method furnishes a practical digital computer procedure for evaluation of the Benedict constants for correlation of volumetric data for light hydrocarbons. A significantly better fit is possible than by previous methods, and information is obtained which permits easy calculation of the determinacy of the constants and of the degree to which the precision of fit is reduced by any arbitrary change of the constants from their best values.

TABLE I

CONVERSION FACTORS

PROPANE DATA

Quantity	From	To	Factor
Pressure	atmos.	psia	14.696
Temperature	°K	°R	1.8
Volume	liters	cu.ft	28.3168
Mass	g.	lb.	453.5924

TABLE II

PROPANE

FUNCTION	TRIAL 1	TRIAL 2	TRIAL 3	BENEDICT'S
	5.946290	5.653610	5.370930	5.653610
B_0	1.5913065	1.4480064	1.2756728	1.559992
$10^{-3}A_0$	28.223008	26.060274	23.513037	25.95383
$10^{-9}C_0$	5.0238934	5.5362459	6.1228970	6.219139
b	4.6556428	5.1574946	5.7401757	5.782101
$10^{-3}a$	35.088861	42.927363	51.846861	57.37567
α	3.0273172	2.6366092	2.3217096	2.501316
$10^{-9}c$	17.865402	19.713905	21.759351	25.30414
χ^2	0.00127724	0.00096298	0.00071161	0.00936535
$\overline{\mathfrak{z}^2}$	0.00339	0.00295	0.00253	0.00919
$\overline{\mathfrak{z}}$	-0.00018	-0.00011	-0.00004	-0.00043
$\overline{\lvert\mathfrak{z}\rvert}$	0.00273	0.00229	0.00191	0.00370
$\overline{\lvert\mathfrak{z}/z\rvert}$	0.00483 (0.00473)*	0.00401 (0.00391)*	0.00332 (0.00324)*	0.00617 (0.00408)*

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*Data at d of 6.24 lb. mols/cu. ft. omitted

TABLE III(a)

PROPANE

i No.	1	2	3	4	5	6	7*
j No. 1	10.6945384	13.9519372	24.8511076	4.5064459	5.9724358	0.7517428	6.3258076 6.5604459 6.7941778
j No. 2	13.9519372	18.4874005	33.8415965	5.9724351	8.0283019	1.0423095	8.5918720 8.9186127 9.2443996
j No. 3	24.8511076	33.8415965	64.8851880	10.9312212	15.0553160	2.0550831	16.3991200 17.0482662 17.6165012
j No. 4	4.5064459	5.9724351	10.9312212	2.1037546	2.8266889	0.4086022	2.7974842 2.9205840 3.0437242
j No. 5	5.9724358	8.0283019	15.0553160	2.8266889	3.8465148	0.5705994	3.8365803 4.0090695 4.1817638
j No. 6	0.7517428	1.0423095	2.0550831	0.4086022	0.5705994	0.1048029	0.4978623 0.5271461 0.5567172

---

*The three values correspond to $\gamma = 1.05\gamma_B$, $1.00\gamma_B$, and $0.95\gamma_B$ respectively.

TABLE III(b)

PROPANE

i No.		1	2	3	4	5	6	7
j No. 7		6.3258076	8.5918720	16.3991200	2.7974842	3.8365803	0.4978623	4.2639687
		6.5604459	8.9186127	17.0482662	2.9205840	4.0090695	0.5271461	4.5983040
		6.7941778	9.2443996	17.6965012	3.0437242	4.1817638	0.5567172	4.9487437
b_j		-11.8821647	-16.0832203	-30.5185822	-4.3990393	-6.0388425	-0.6040738	-7.6996588
K_i		1.5913065	-2.6298363	-0.4681293	4.6556428	-3.2696004	9.8981175	1.6647085
		1.4480064	-2.4283115	-0.5158706	5.1574946	-3.9999966	10.5464279	1.8369531
		1.2756728	-2.1909584	-0.5705351	5.7401757	-4.8311224	11.2164633	2.0275489
$C_{11}\ K_i^2$		27.1	128	13.6	45.6	41.1	10.3	11.8
		22.5	109	17.3	56.1	61.6	11.7	15.5
		17.4	93.5	21.1	69.3	89.7	13.2	20.4

TABLE IV

METHANE

FUNCTION	TRIAL 1	TRIAL 2	TRIAL 3	BENEDICT'S
γ	1.6187740	1.5416900	1.4646060	1.5416900
B_0	0.70336500	0.70223723	0.69791469	0.6828612
$10^{-3}A_0$	7.366808	7.333657	7.256538	7.004694
$10^{-9}C_0$	0.1307256	0.1464787	0.1709262	0.2761352
b	0.57060456	0.57487211	0.58476176	0.8684956
$10^{-3}a$	-0.5152522	-0.4184701	-0.2407344	2.990183
α	1.7397648	2.2371713	4.1126911	0.5122074
$10^{-9}c$	-0.2134281	-0.1729780	-0.1161582	0.4991189
$\chi^2(\gamma)$	0.00077752	0.00078564	0.000791816	0.00485803
$\overline{z^2}$	0.00343	0.00345	0.00346	0.00858
$\overline{z}$	-0.00025	-0.00026	-0.00026	0.00176
$\overline{\lvert z \rvert}$	0.00278	0.00278	0.00276	0.00640
$\overline{\lvert z/Z \rvert}$	0.00243	0.00242	0.00240	0.00541

TABLE V(a)

METHANE

i No.	1	2	3	4	5	6	7*
j No. 1	31.4726905	46.2577337	107.7799221	25.9763582	39.0880564	31.2370121	55.6638722 57.7179103 59.8227471
j No. 2	46.2577337	69.7757018	170.0415877	39.0880562	60.2392988	50.5329453	87.4120028 90.7665709 94.2088716
j No. 3	107.7799221	170.0413877	446.0903394	94.8371312	152.1125267	137.8033481	227.3746916 236.6524464 246.1938028
j No. 4	25.9763582	39.0880562	94.8371312	22.7619427	34.9761577	30.6754479	48.9614118 50.9577824 53.0090807
j No. 5	39.0880564	60.2392988	152.1125276	34.9761577	54.9152142	50.2180479	78.0629552 81.3558671 84.7436223
j No. 6	31.2370121	50.5329453	137.8033481	30.6754479	50.2180479	54.0771839	68.5540905 71.9923894 75.5503869

---

*The three values correspond to $\gamma = 1.05\gamma_B$, $1.00\gamma_B$, and $0.95\gamma_B$ respectively.

TABLE V (b)

METHANE

i No.	1	2	3	4	5	6	7
j No. 7	55.6638722 57.7179103 59.8227471	87.4120028 90.7665709 94.2088716	227.3746916 236.6524464 246.1938028	48.9614118 50.9577824 53.0090807	78.0629552 81.3558671 84.7436223	68.5540905 71.9923894 75.5503869	117.5488717 127.1198188 137.4204916
b_i	7.2716818	10.2462733	22.0572783	6.5397980	9.5257067	8.6726528	11.4529803 11.9736986 12.5101080
K_i	0.7033650 0.7022372 0.6979147	-0.6864434 -0.6833544 -0.6761685	-0.0121811 -0.0136490 -0.0159270	0.5706047 0.5748721 0.5847618	0.0480115 0.0389933 0.0224318	0.0835287 0.0872347 0.0922549	-0.0198874 -0.0161182 -0.0108237
$C_{ii} K_i^2$	15.6 15.5 15.3	32.9 32.6 32.0	0.0662 0.0831 0.113	7.41 7.53 7.79	0.127 0.0837 0.0277	0.377 0.411 0.460	0.0464 0.0330 0.0161

FIGURE 1

Possible $\chi^2(\gamma)$ Curves

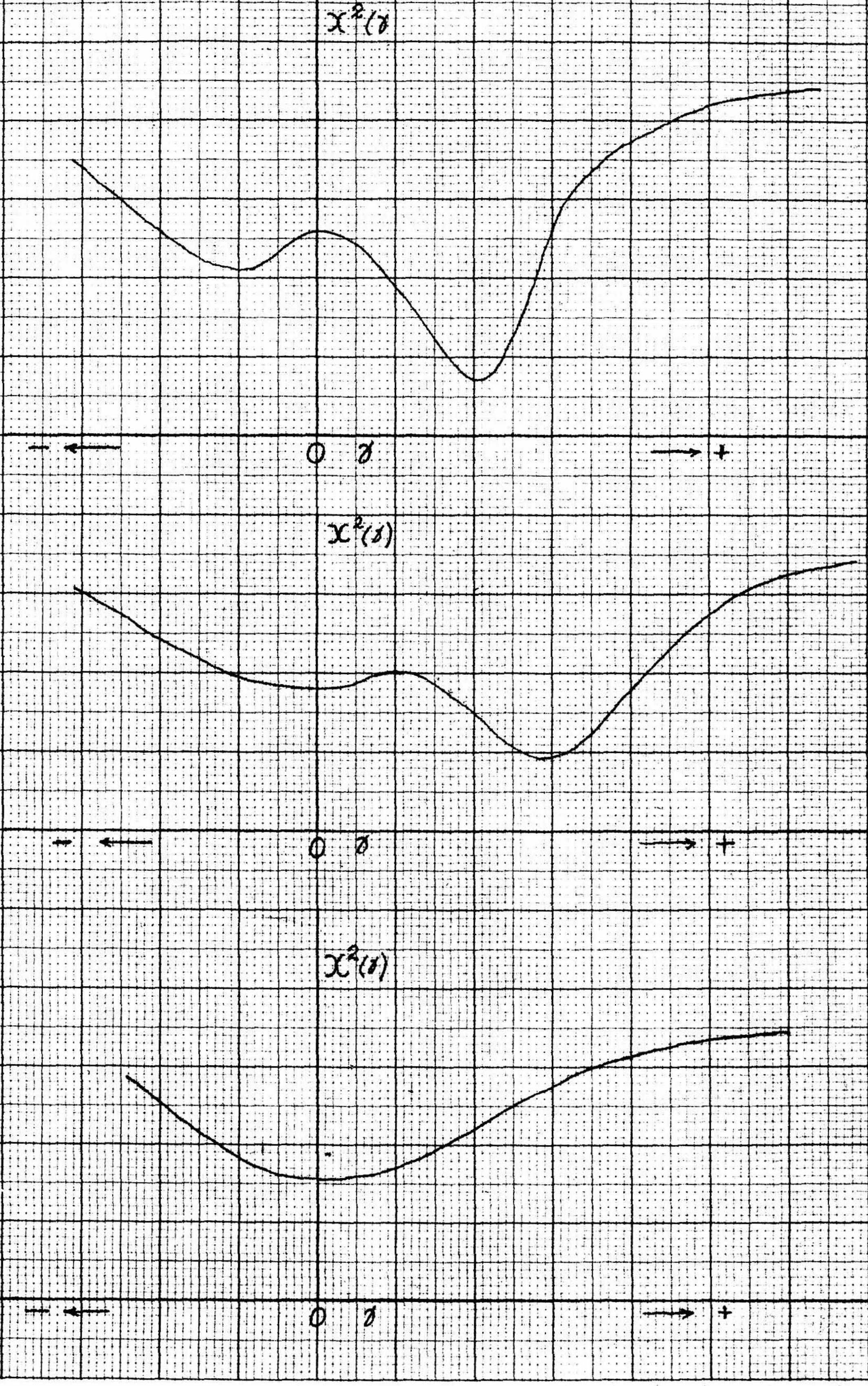
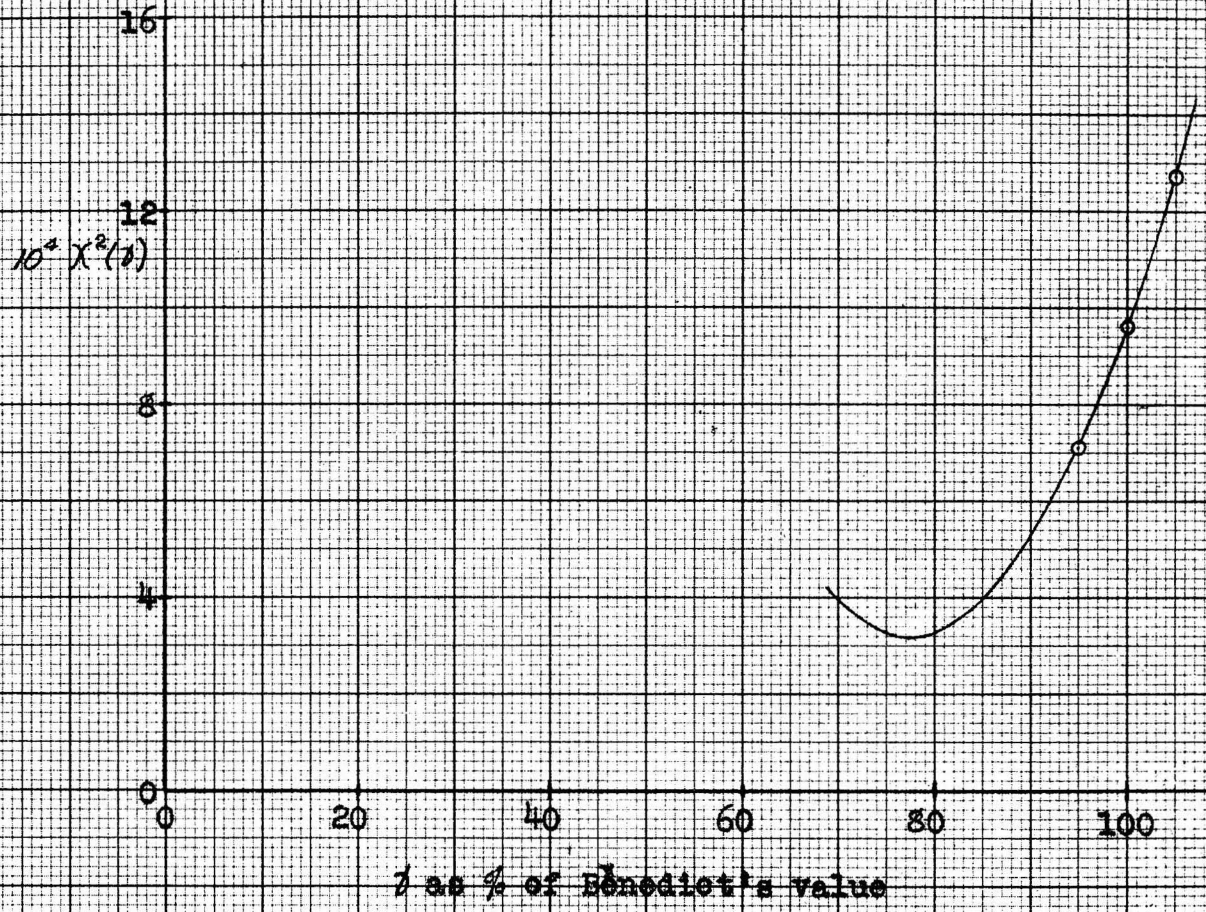


FIGURE 2

$\chi^2(\gamma)$ vs γ

PROPANE



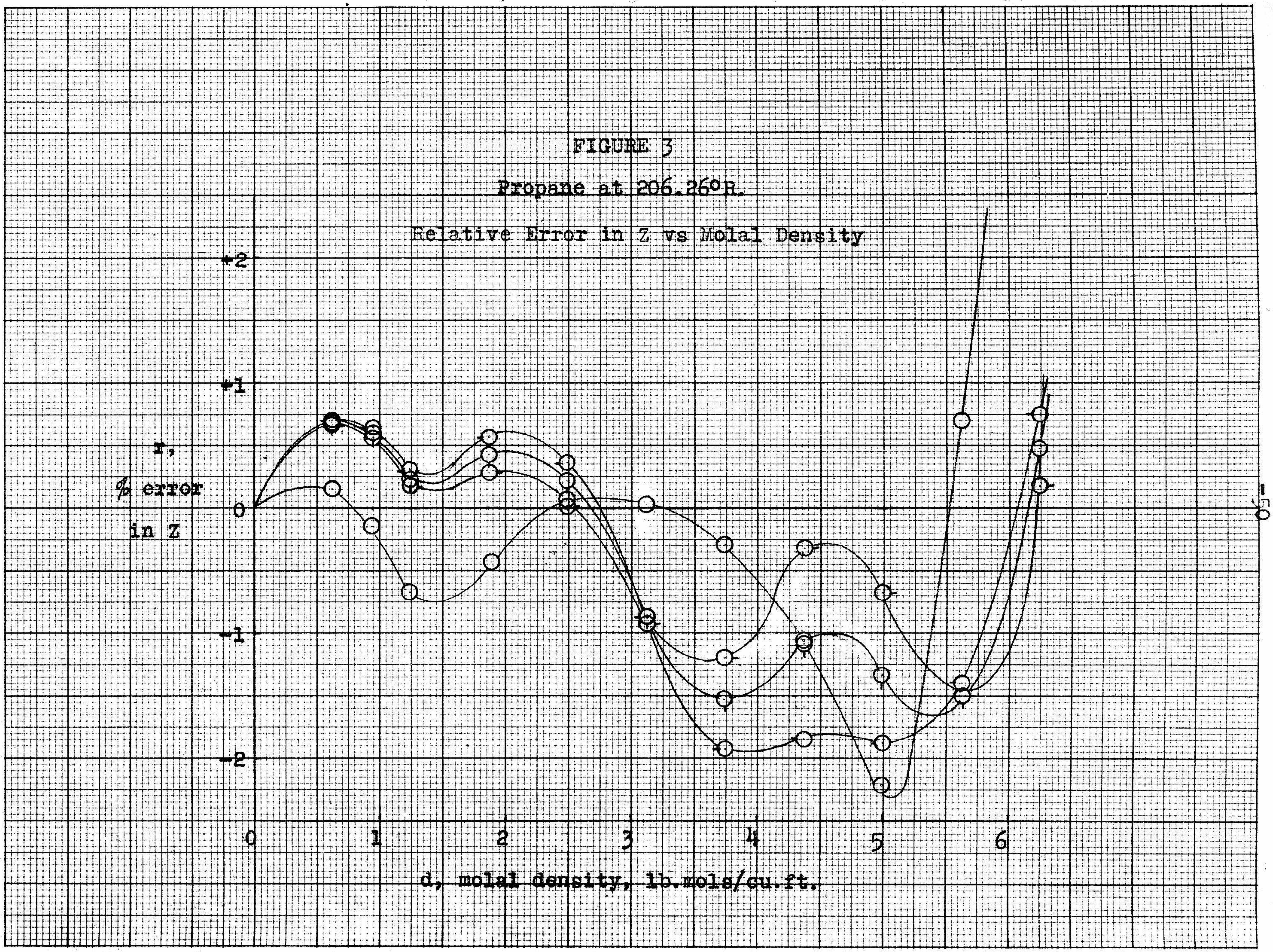


FIGURE 3

Propane at 206.26°R.

Relative Error in Z vs Molal Density

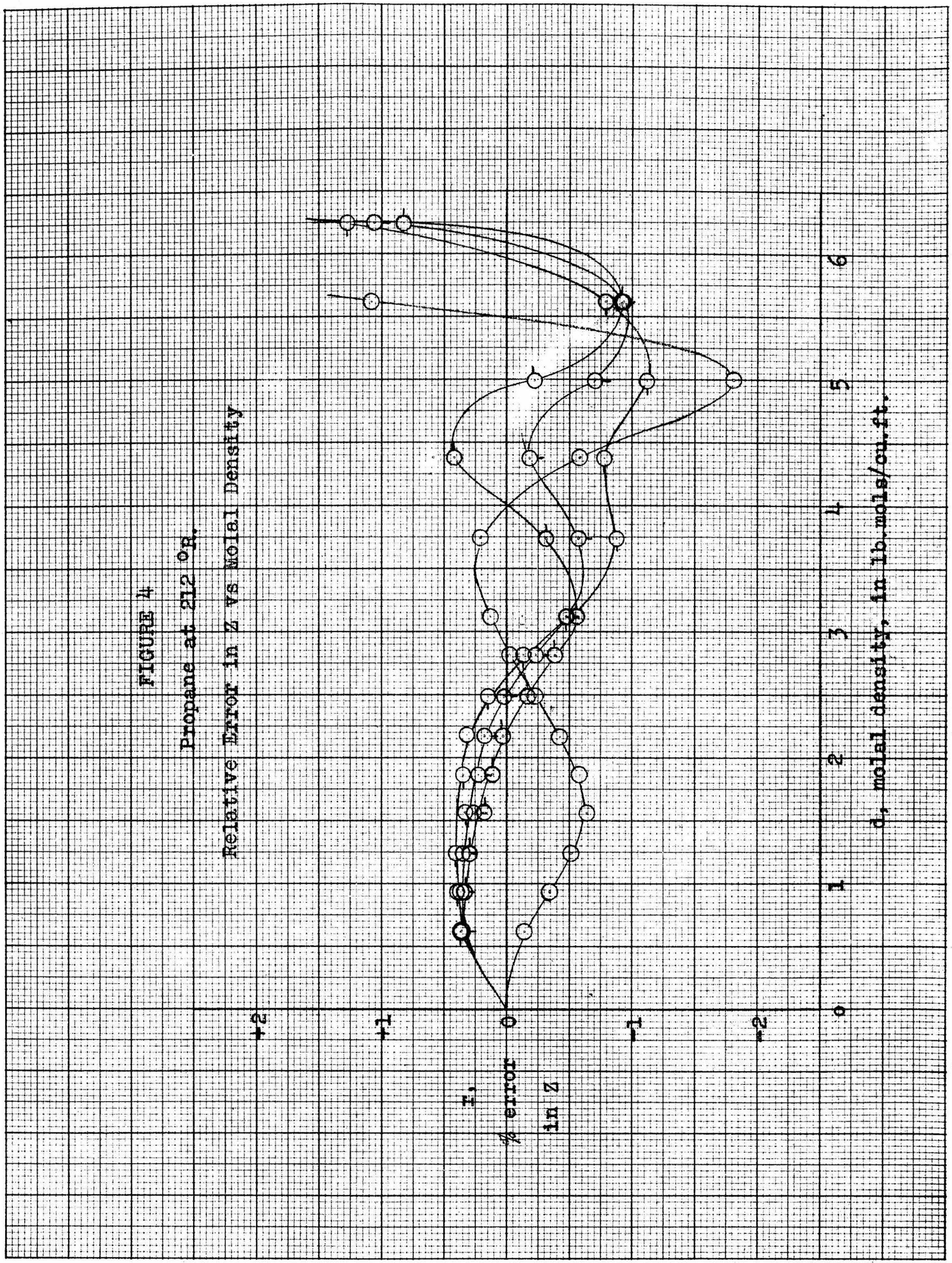


FIGURE 4

Propane at 212 °R.

Relative Error in Z vs Molal Density

FIGURE 5

Propane at 257 °R.

Relative Error in Z vs Molal Density

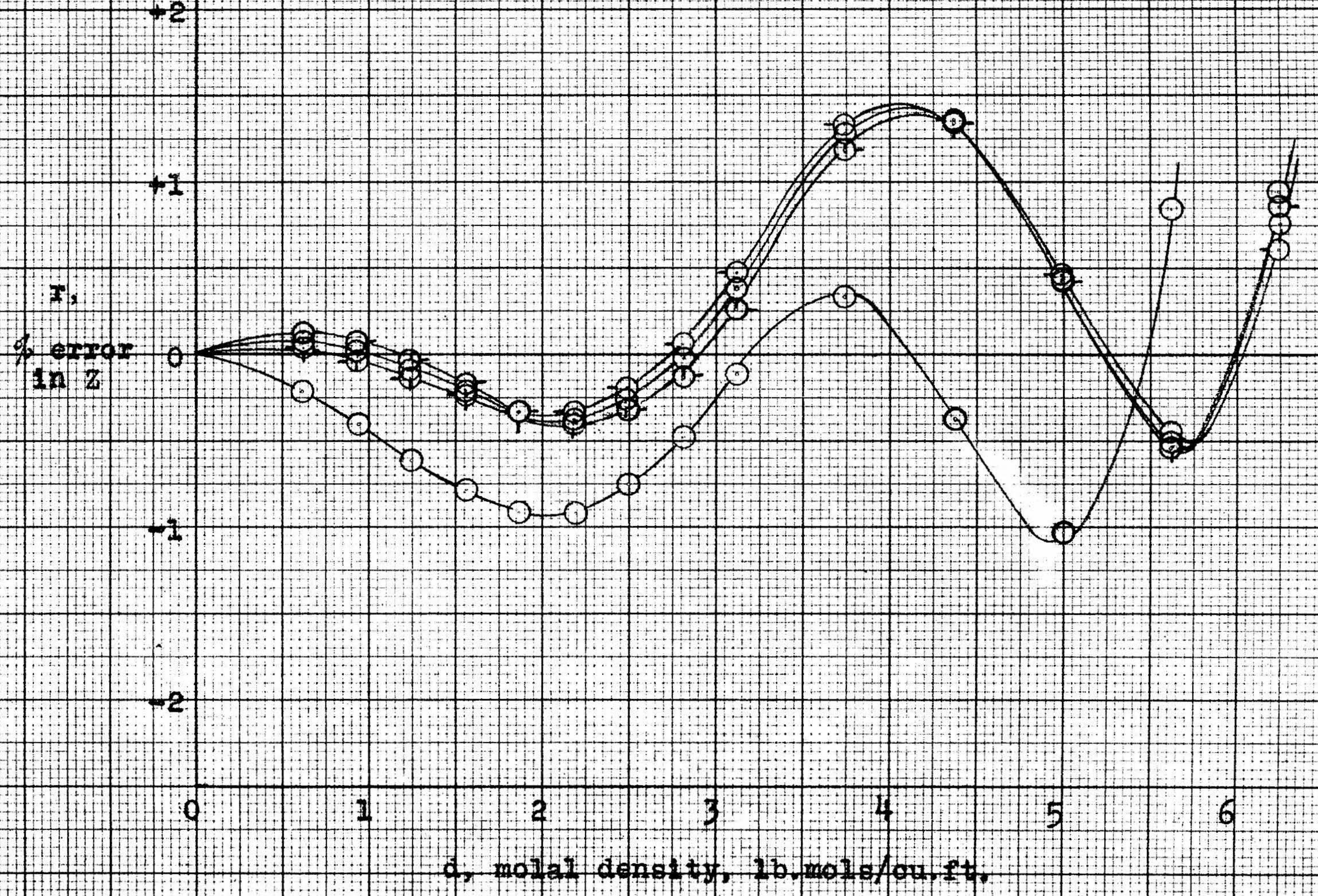
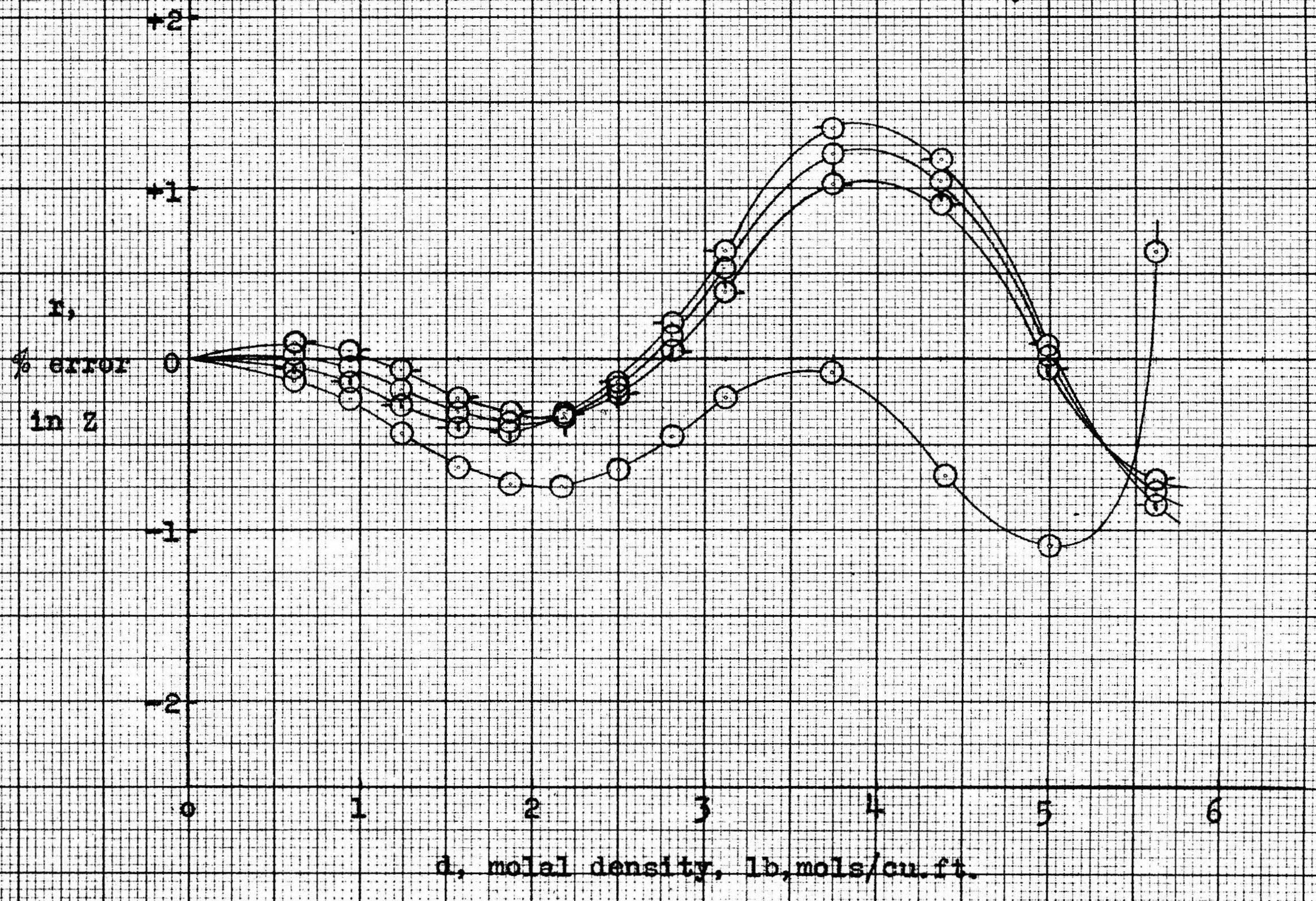


FIGURE 6

Propane at 302 °R.

Relative Error in Z vs Molal Density



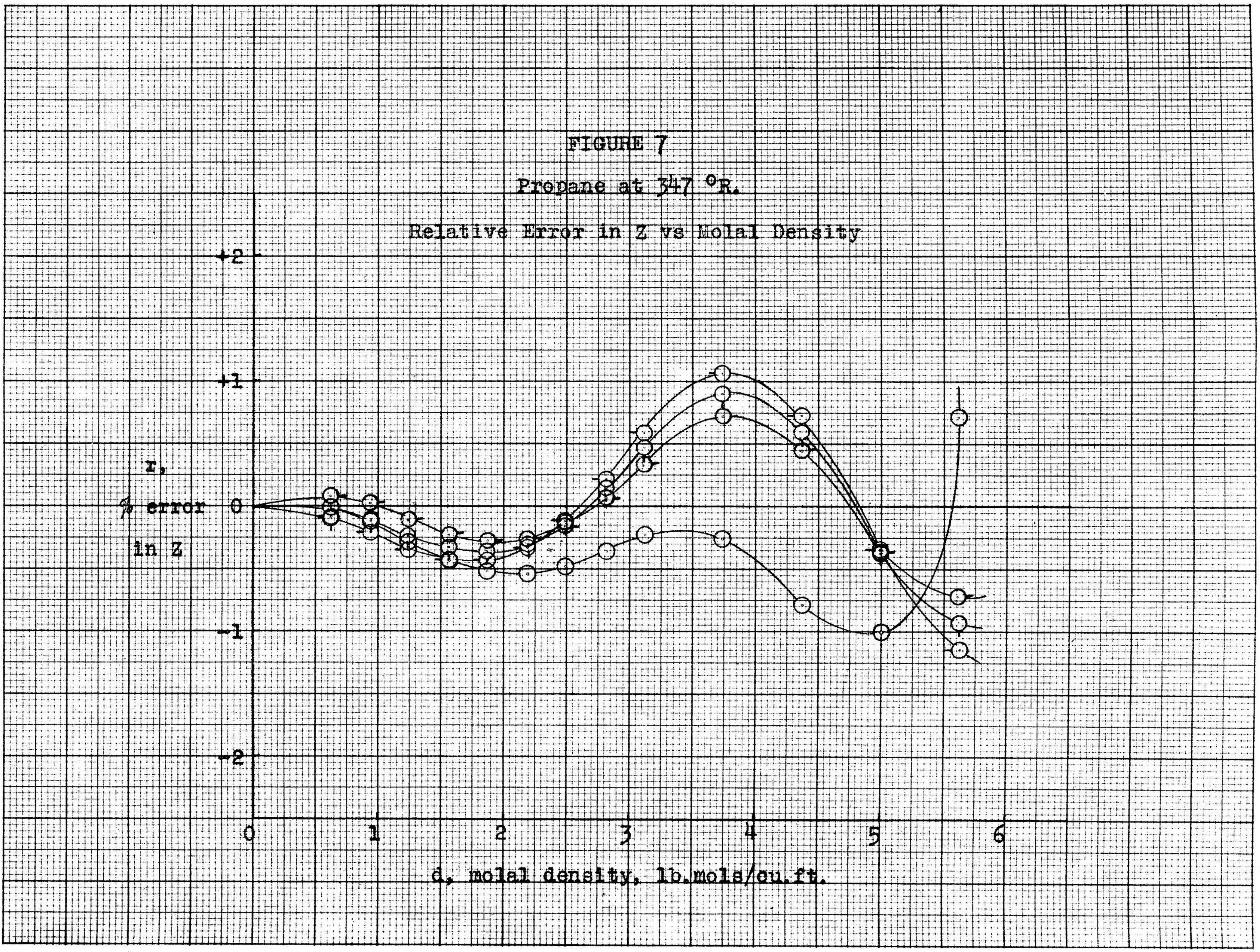


FIGURE 7

Propane at 347 °R.

Relative Error in Z vs Molal Density

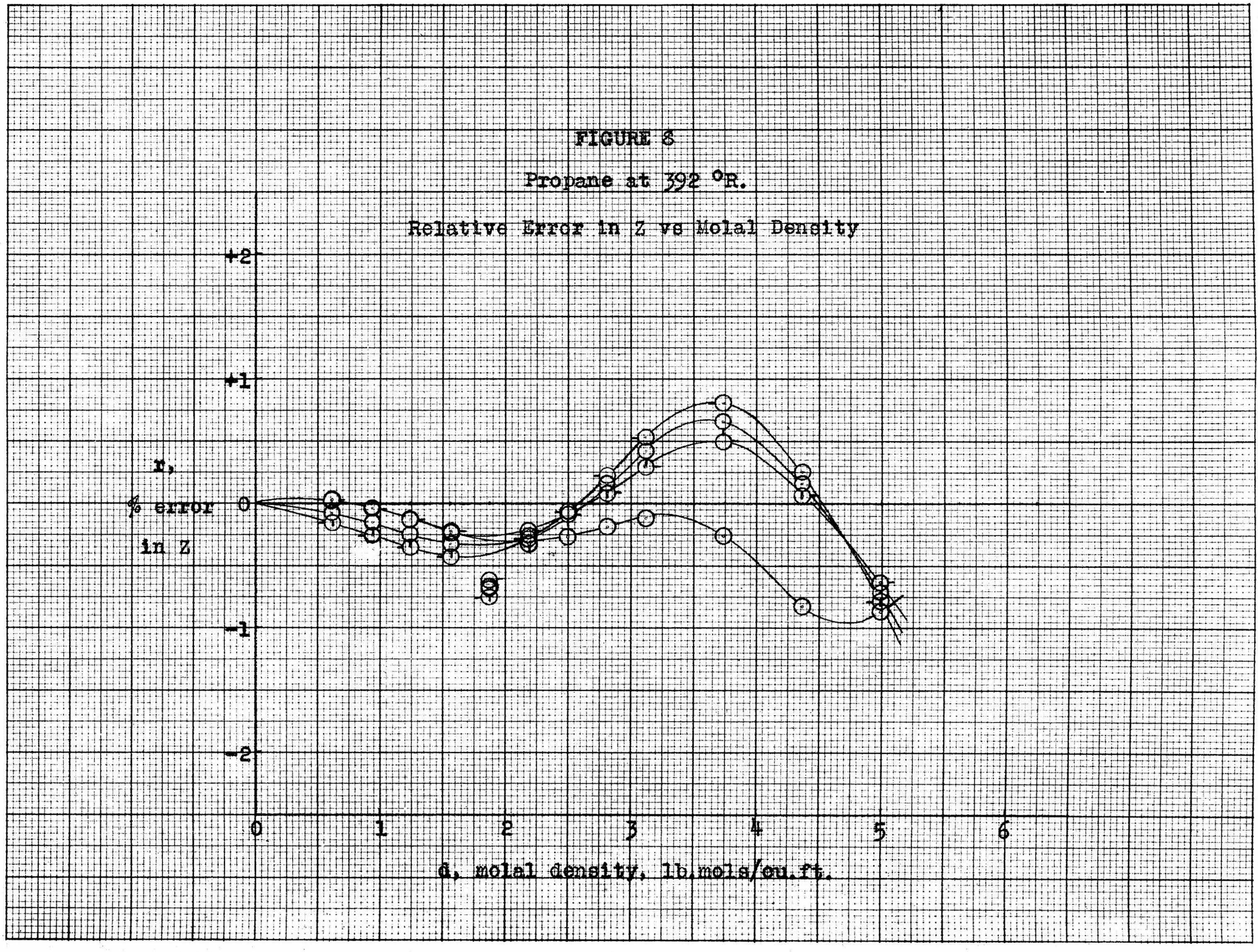


FIGURE 8

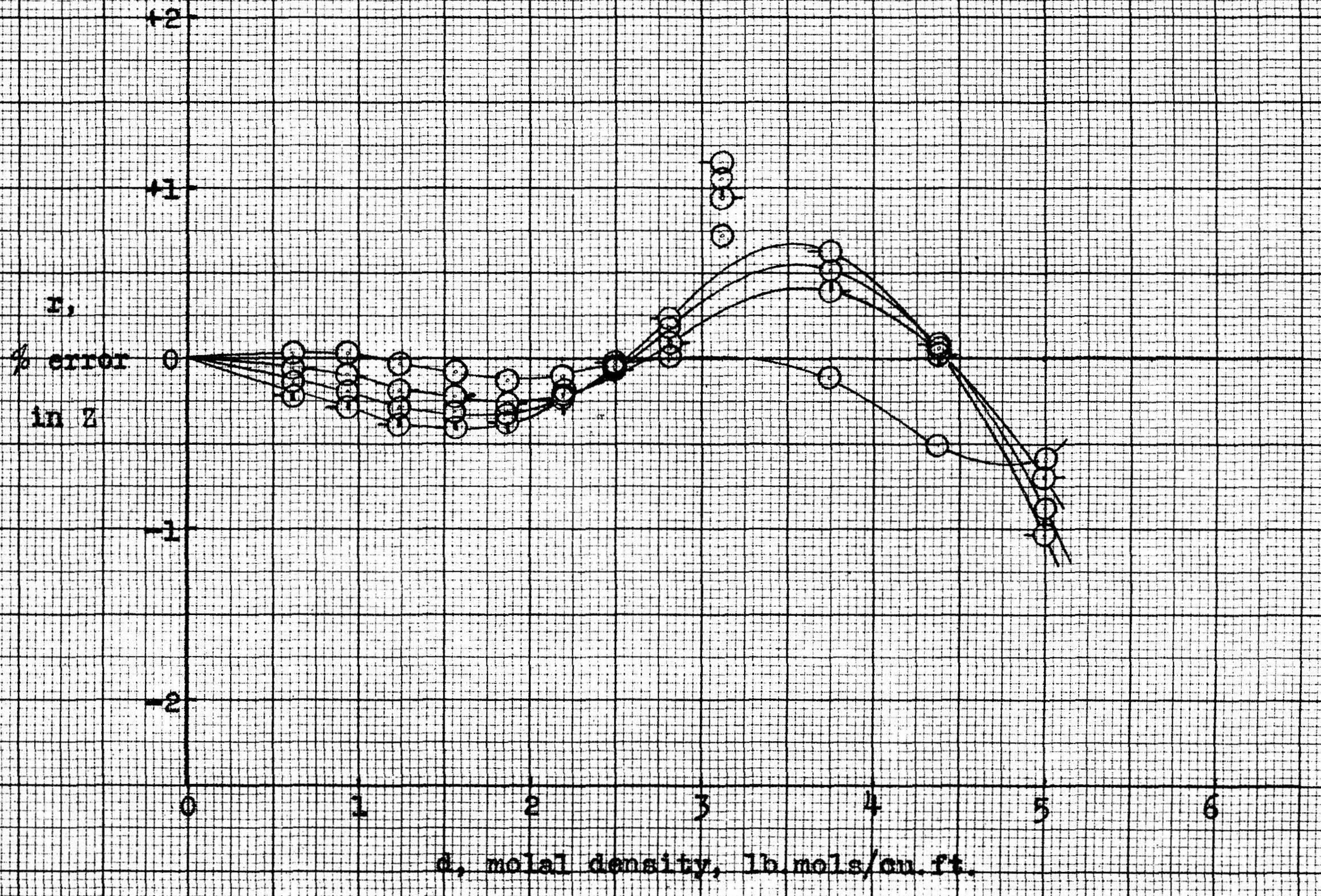
Propane at 392 °R.

Relative Error in Z vs Molal Density

FIGURE 9

Propane at 437 °R.

Relative Error in Z vs Molal Density



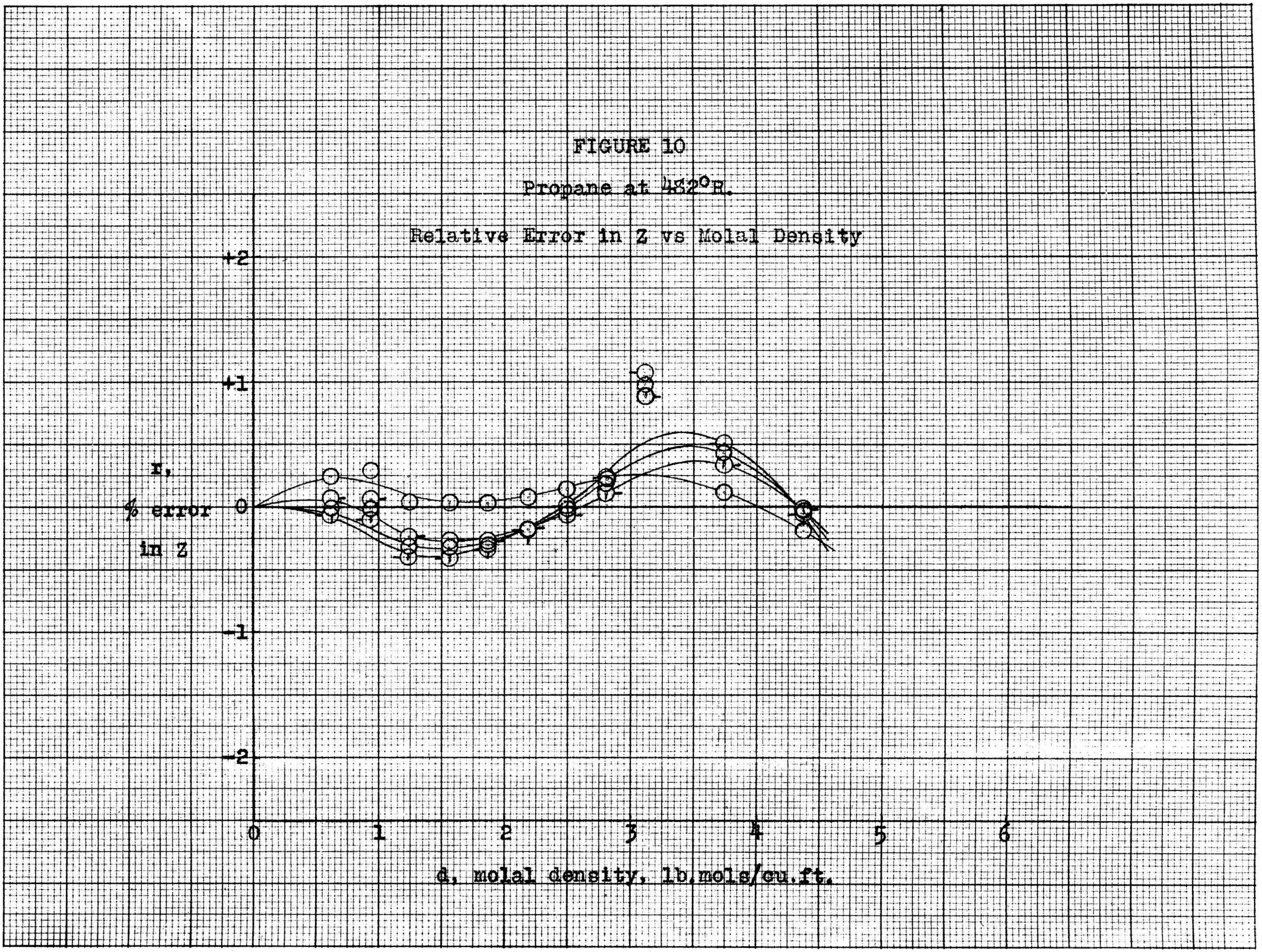


FIGURE 10

Propane at 482°R.

Relative Error in Z vs Molal Density

FIGURE 11

Propane at 527 °R.

Relative Error in Z vs Molal Density

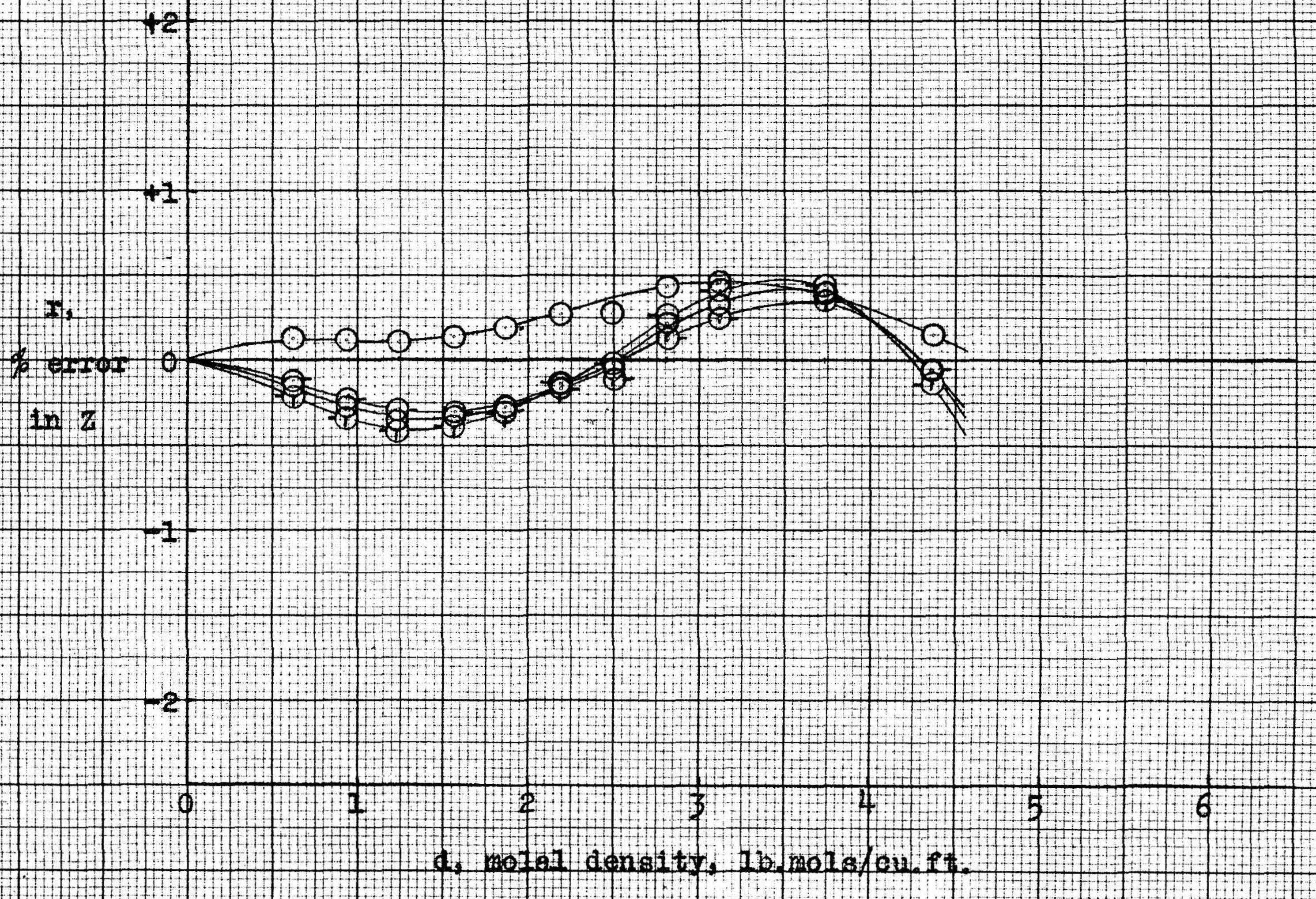


FIGURE 12

EXTRAPOLATION OF AVERAGE ERROR IN Z

PROPANE

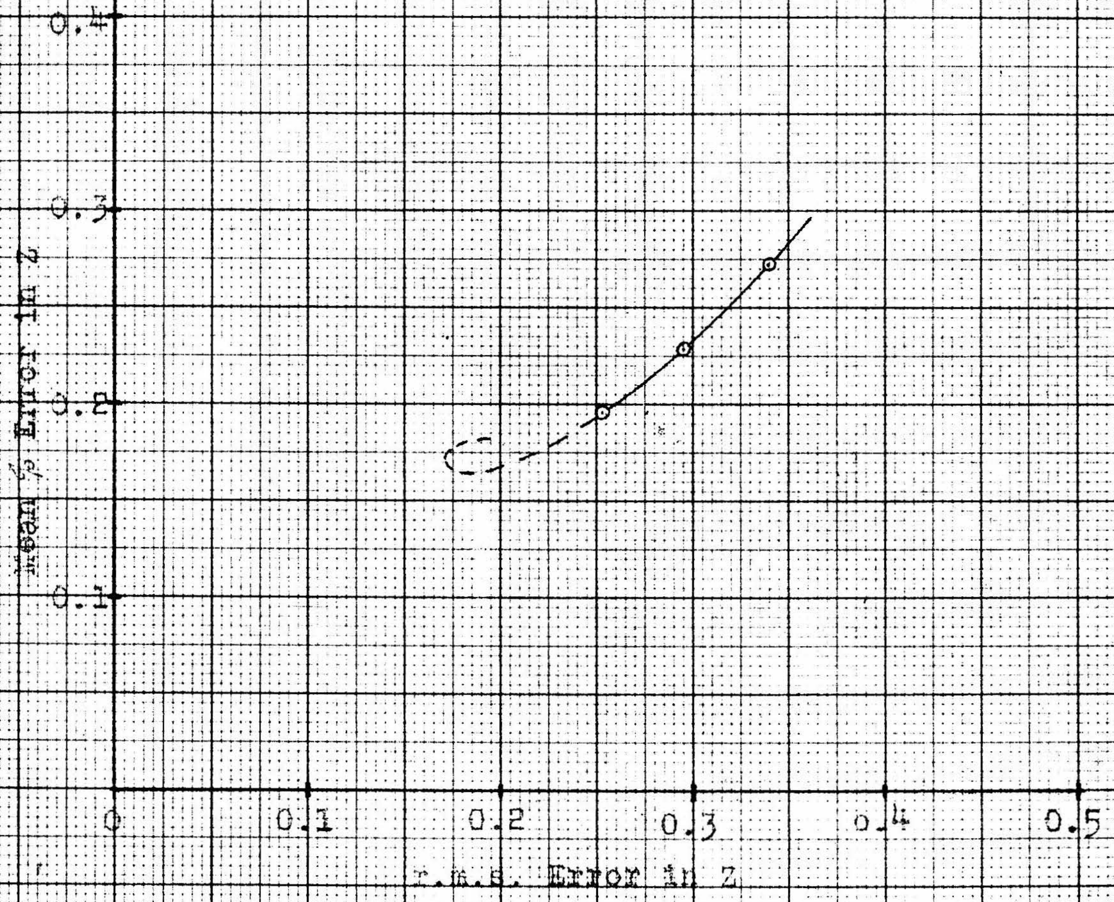


FIGURE 13

$\chi^2(\gamma)$ vs γ

METHANE

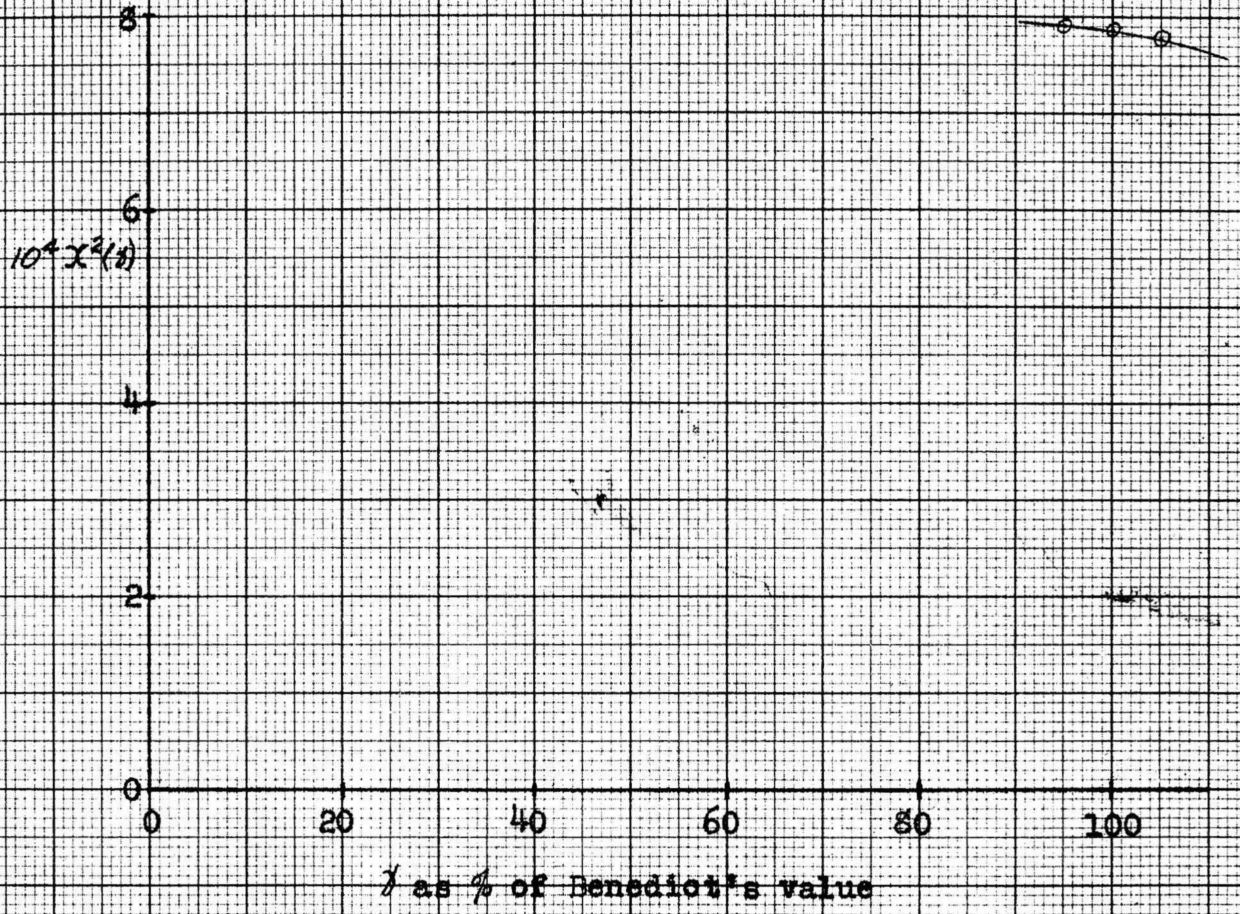


FIGURE 14

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
METHANE AT 100 °F.

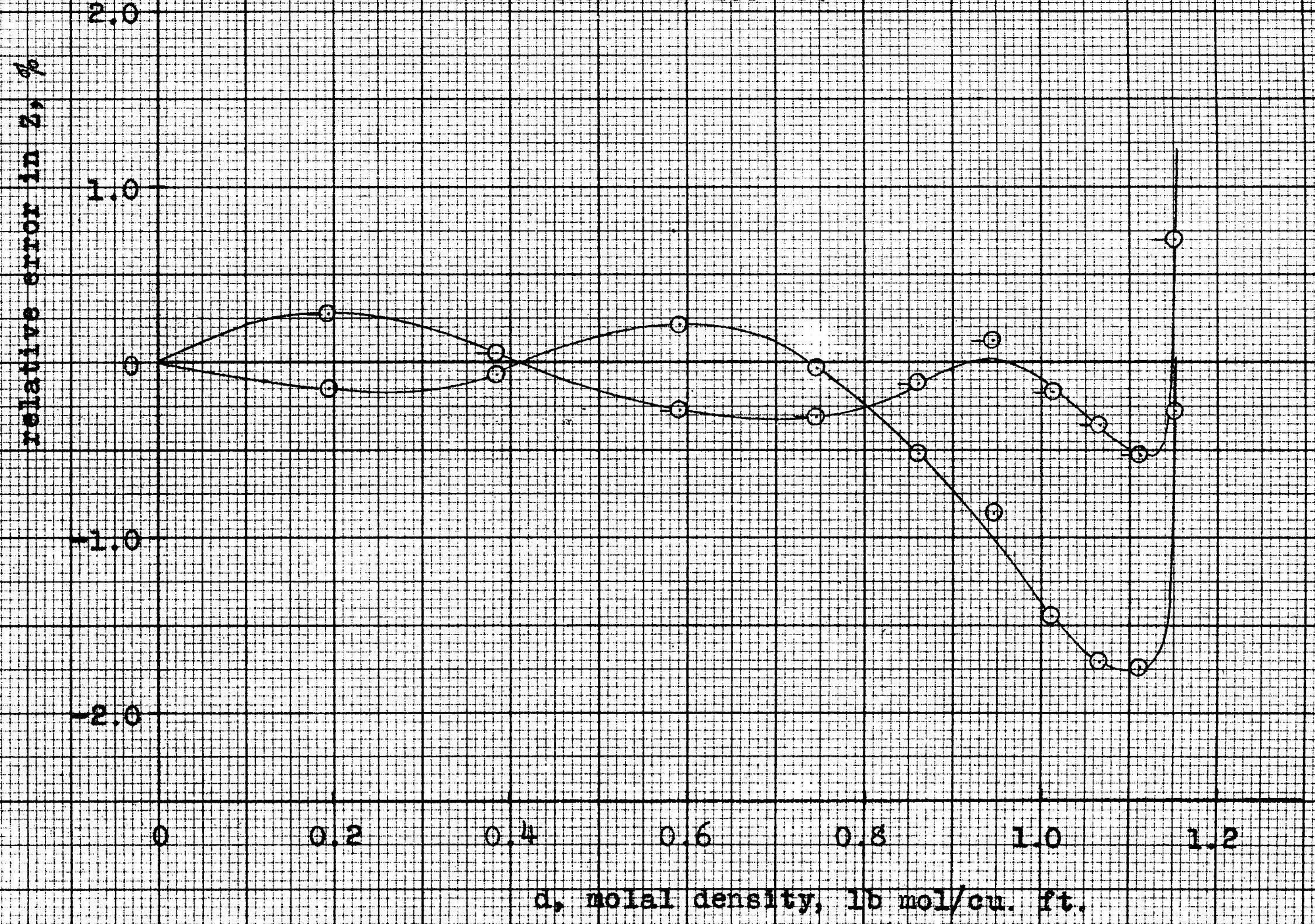


FIGURE 15

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
METHANE AT 160 °F.

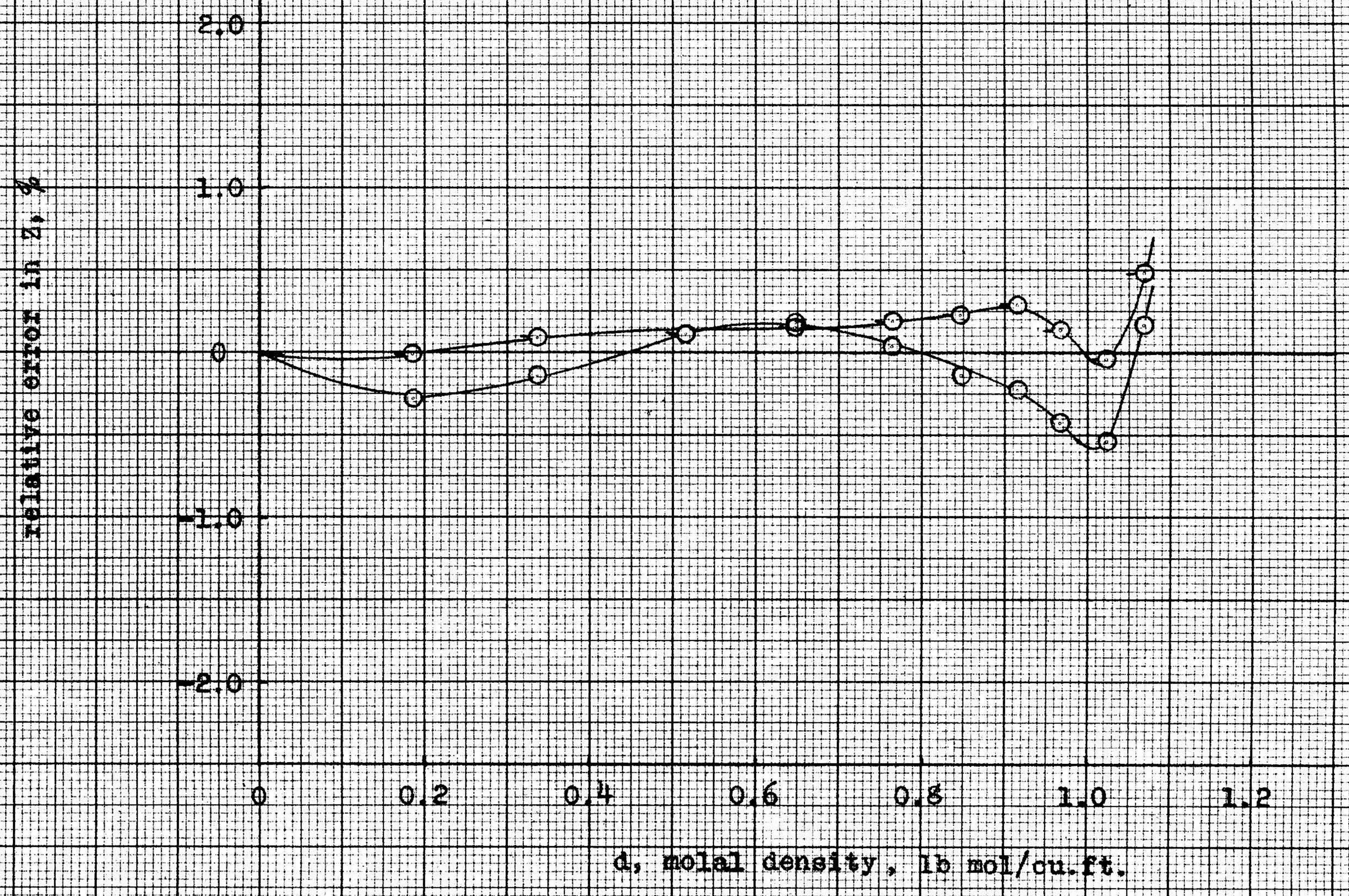


FIGURE 16

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
METHANE AT 220 °F.

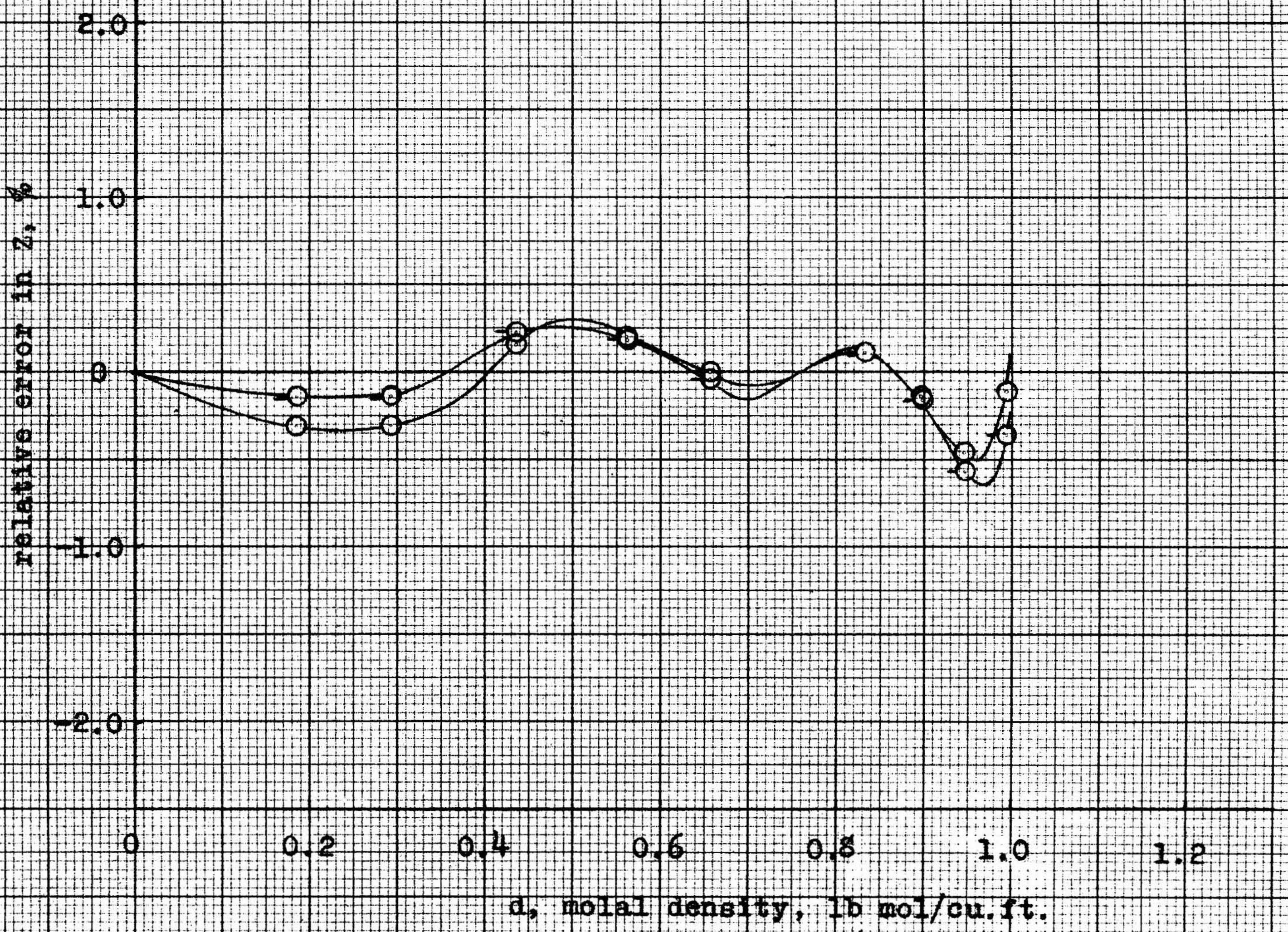


FIGURE 17

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
METHANE AT 280 °F.

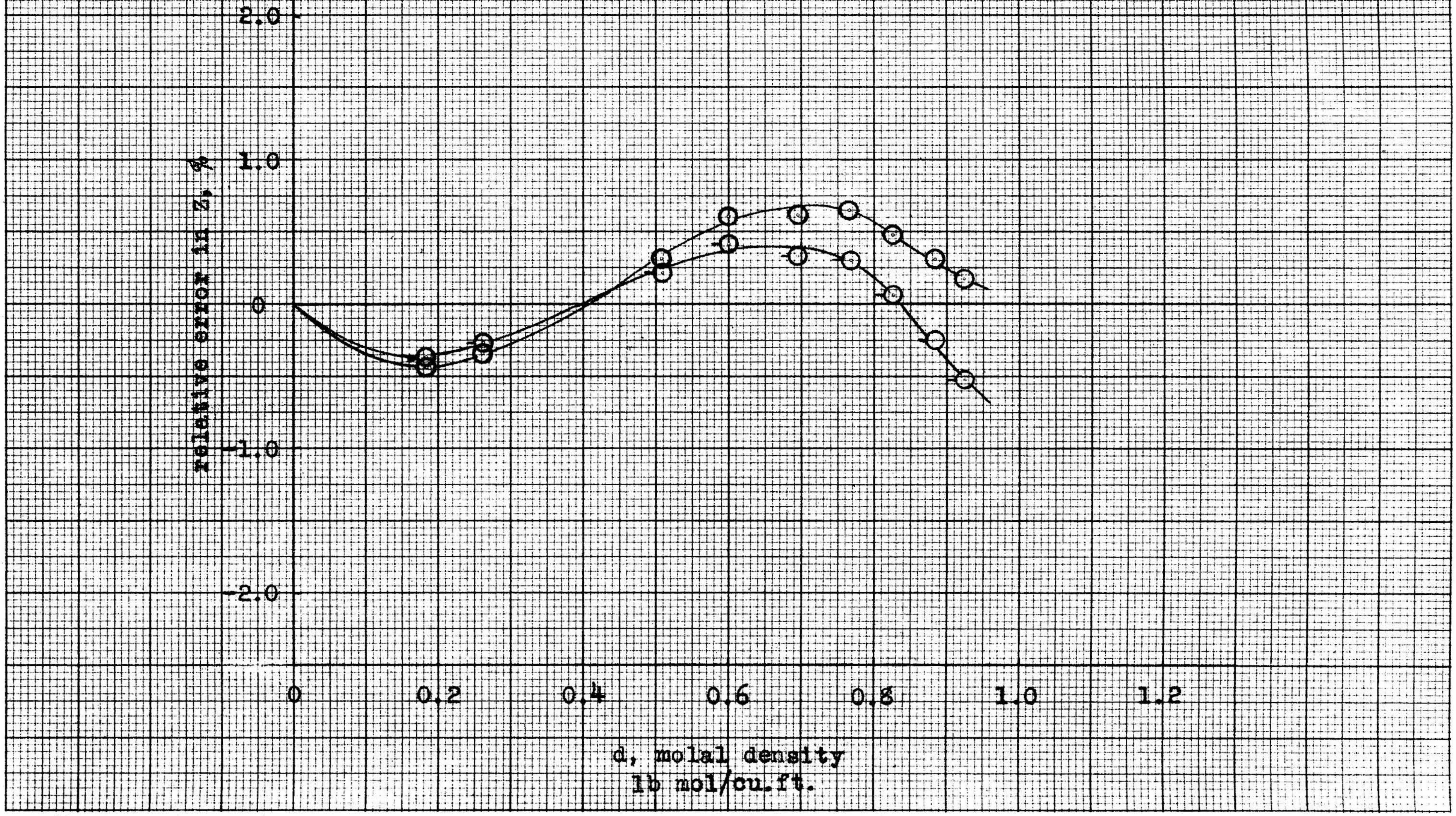


FIGURE 18

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
Methane at 340 °F.

FIGURE 19

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
Methane at 400 °F.

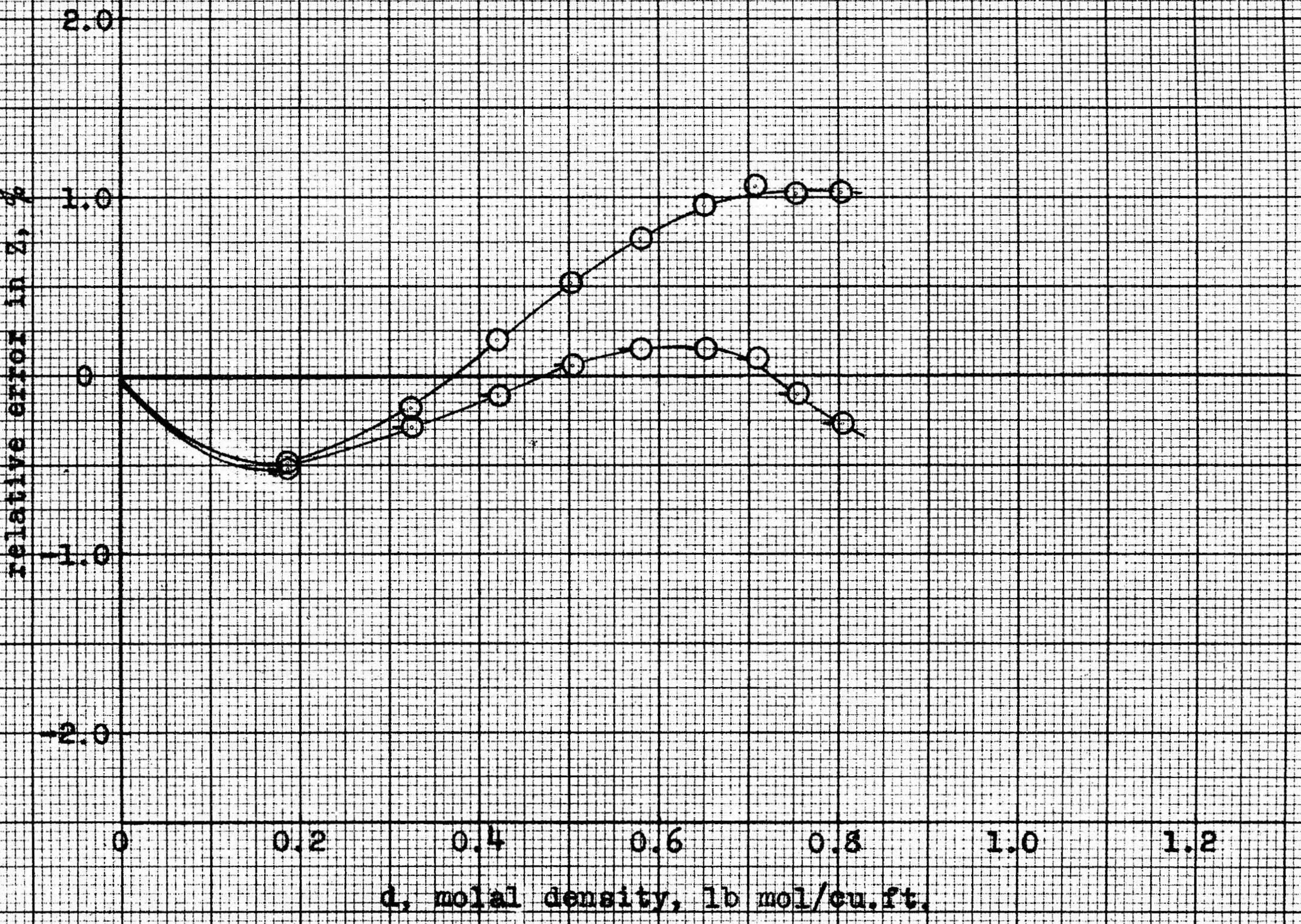
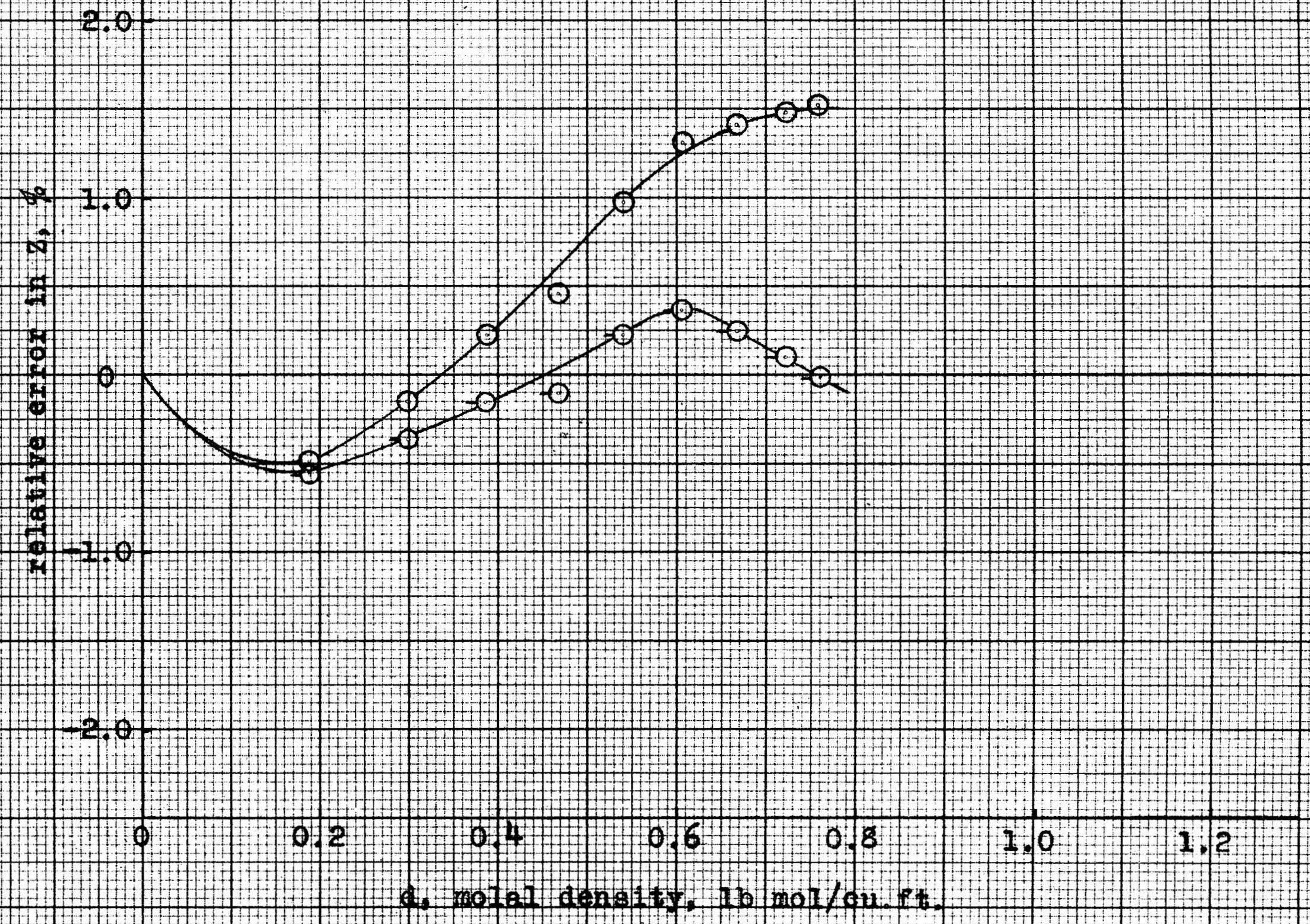


FIGURE 20

RELATIVE ERROR IN Z vs MOLAL DENSITY
for
Methane at 460 °F.



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