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THE EQUATION OF STATE OF ISOBUTANE: AN INTERIM ASSESSMENT

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Introduction

The design and preliminary costing of a binary geothermal energy plant is an involved process requiring the combined use of a number of correlations in an overall model for the plant's operation [S1977a]. Some correlations relate component sizing to the operating parameters of temperature and pressure. Others then relate component sizing to cost of their manufacture. The basic operating temperature of a plant is determined by the temperature of the operating well. Pressures and heat exchanger temperature differences then depend in part on the properties of the working fluid. The properties of the working fluid can therefore play an important role in the plant design and costing. This must lead one to conclude that fluid properties must be known within reasonable accuracy limits for proper design and costing of potential plants.

The exact limits of uncertainties in fluid properties data which can be tolerated in a design are not easy to assess. Thermodynamics provides an extensive framework which connects the caloric and mechanical properties of a fluid through the thermodynamic relations. It is generally necessary, in applying these relations to specific design problems, to perform mathematical manipulations on measured fluid properties to produce data of the kind needed in the designs. These manipulations can involve differentiation, integration (or combinations of the two) as well as statistical fits of measured fluid property data to mathematical forms. In such manipulations the original errors of measurement are combined and transformed, often in non-linear ways, so as to affect the design under conditions removed from those of the original property measurements. This kind of propagation of the errors of measurement can be difficult, if not impossible, to trace. One can, however, be sure that, as a general rule, the original errors will become magnified in these transformation processes. It is therefore essential that fluid properties data be known with much better accuracy than the uncertainty in the plant design from all other causes. An assessment of the effect of errors in data measurement on a plant design can be made through computer modelling. Errors of various kinds can be superimposed on models of the measured fluid properties data and the effect of these errors in a design observed. An attempt at this was made by Starling et al. [S1977a]. Slightly different versions of the same model for isobutane properties were used to illustrate data uncertainty. This made it difficult to specify the precise nature of the errors being introduced and hence the exact way in which design sensitivity to error was being probed could not be determined. A more detailed analysis in which errors are inserted directly has shown that certain kinds of errors can indeed have a drastic effect on heat exchanger design and even design feasibility [K1978]. In what follows we shall assume that the properties of the working fluid must be known to perhaps an order of magnitude better than the overall plant design uncertainty.

Isobutane is being widely considered as a prime candidate, either as a pure fluid or as part of a fluid mixture, for the working fluid in geothermal binary cycles. Although measurements of its properties exist, there is considerable disagreement among the different sets of measurements. Furthermore, these measurements have been made over relatively limited regions of temperature and pressure. This combination of problems has made it difficult to produce an overall correlation of the properties of isobutane which might be used with a reasonable degree of confidence. In fact, the two major recent correlations of the properties of isobutane [S1977b-D1973] differ from each other by a considerable and unacceptable amount.

The combination of the potential importance of geothermal energy in the national energy picture, the certain need to develop binary geothermal cycles, the potential choice of isobutane as a working fluid, the disagreement among published property measurements for isobutane and the differences between the major correlations of its properties led to the establishment of this project. The project has been aimed at carrying out a careful and accurate assessment of the data situation for isobutane and at the development of an accurate set of data sufficient in extent to produce a correlation which might be used with confidence in plant design computer programs. The project program has been designed to make maximum use of existing information. Measurements have been made under conditions which have been carefully selected to test the accuracy of published data with special emphasis on those conditions for which there are major discrepancies among literature values. The first phase of the effort was to be the production of new data taken under such conditions as to allow for direct comparison with the best published data. This was to be followed immediately by an assessment of the need for more extensive measurements. This assessment would be expected to depend very strongly on the relationship between our new measurements and the data published by each of the earlier researchers. This was to lead to additional measurements as required which in turn would be followed by a new correlation.

It was agreed that the areas of immediate need for assessment were the vapor pressure, critical region and vapor and gas isotherms. This first part of the program has essentially been completed and the results are contained herein. We have chosen to present these results as an informal report to sponsor at this time despite the fact that additional data reduction and an important recalibration are still necessary. We have done this in order to make our results available to interested parties so that they can contribute to the decision process for establishing the need for additional measurements. A paper will be submitted for publication in the near future.

In what follows there will be separate discussions of our measurements of vapor pressure and vapor isotherms and of our correlation of the properties in the critical region. There is also a rather preliminary comparison of some of the published correlations. Our results have now made such a comparison of correlations somewhat academic, however. Our work has shown that the vapor phase and vapor pressure data of Sage and Lacey [S1938, M1940] need to be omitted from any future correlation. The large differences between our results and theirs leads us to expect major revisions will be needed in those existing correlations which included their data. Hence a detailed study of those correlations at this time would not appear to be very useful.

Our work, although carried out over a rather limited set of conditions, has already clarified the data situation considerably. We have been able to correlate the data in the critical region thereby reducing the pressure for new measurements. We have replaced the vapor pressure data by new and accurate data, thereby removing a major source of confusion in the isobutane literature. We have shown that, below the critical point, the data of Connolly [C1962] are probably sufficiently accurate to preclude redoing while the vapor pressure and vapor pressure data of Sage et al. are not sufficiently accurate to be considered in any correlation.

In the following, each of the areas of work is described separately in some detail and acknowledgements of assistance are included where appropriate.

The Critical Region of Isobutane

There is a detailed set of critical-region PVT data in the temperature range 134.60 to 135.15°C for isobutane reported by Beattie, Edwards and Marple [B1949]. In addition, there is a block of supercritical PVT data by the same authors [B1950] in the range of 150 to 300°C. We report here a fit of the critical-region PVT data plus part of the 150°C isotherm to a simple scaled equation of state called the Linear Model [S1969 a,b]. The Linear Model is formulated in terms of parametric variables, which are obtained by a transformation of the physical variables temperature and density. The variables, adjustable and fixed parameters, transformation equations and parametric functions are defined in Tables 1 and 2.

In fitting this model to the isobutane data, a transcendental parameter transformation plus a non-linear least-squares fit have to be effected. For the parameter transformation we use a procedure that was recently documented by Moldover [M1978]. The non-linear fitting routine is that developed by Bevington [B1969]. For the standard deviations of the measured variables P,ρ,T we estimated

$$\begin{aligned} \sigma_p &= 10^{-4}\ \text{MPa} \\ \sigma_T &= 0.005\ \text{K} \qquad\qquad (1) \\ \sigma_\rho &= 0.001\ \text{mol/dm}^3. \end{aligned}$$

The best fit we obtained had a reduced chi-square of 0.97 which is quite satisfactory. The deviations of the experimental points from the fitted surface are shown in Figs. 1 and 2. The best values for the parameters obtained are listed in Table 3. In Table 4, we compare our values of the critical parameters with those obtained by Beattie from the same data set. The most striking result is the very considerable lowering of the critical temperature, namely almost 0.3 K below that reported by Beattie [B1949]. Part of the reason is the known phenomenon that spline-drawn coexistence curves are usually not sufficiently flat; the one sketched by Beattie et al. is almost parabolic instead of roughly cubic, which leads to an overestimate of T_c. It is, however, also possible that the slope of the two-phase isotherms, caused by impurity, is interpreted by our model as the finite compressibility of the one-phase region. Our model is quite determined about this large decrease in the estimate of T_c; when we omit the 150°C isotherm, T_c drops by (.268±0.012) K instead of (.278±009) K below Beattie's estimate, which is obviously the same within error.

We conclude that barring impurity effects, the Beattie data are consistent with a simple scaled equation to within estimated errors of 10^{-4} MPa in pressure, 0.005 K in temperature and 0.001 mol/dm^3 in density; Beattie's critical constants, however, require major adjustments.

Vapor pressure of Isobutane

There are five sets of vapor pressure data for isobutane above 0°C reported in the literature, those of Seibert and Burrell [S1915], Dana et al. [D1926], Sage and Lacey [S1938], Beattie et al. [B1949] and Connolly [C1962]. Four of these data sets are intercompared in Fig. 3, the data set of Seibert and Burrell is too far off to be shown in this figure.

It is clear that even the four data sets plotted scatter widely. At the lower temperatures, they span a range of more than 0.1 bar on a total pressure of only a few bars. This unsatisfactory state of the data was our motivation in remeasuring the vapor pressure curve.

We have made our measurements on a "Research Grade" sample of isobutane claimed to be 99.98% pure. We will discuss the impurity content and the estimated impurity effects in a separate section of this report.

We have made the vapor pressure measurements in our Burnett apparatus, a detailed description of which was published elsewhere [W1971]. In order to perform vapor measurements on a substance with elevated critical temperature, such as isobutane, we had to make a number of modifications. Our supply containers were placed above the gas handling system and the supply was always tapped from the liquid phase which, in general, was purer than the vapor. In order to inject the fluid, at room temperature, into the sample cell at elevated temperatures, a volume pump was used so that the liquid pressure could be raised sufficiently for transfer, and injected in well-determined amounts. We began by using a 1 cc sample from the injector at room temperature, and added fluid, as needed, at elevated temperatures so as to maintain a two-phase situation. In all cases, we measured near the vapor side of the phase boundary. In several instances, we measured the vapor pressure with two different amounts of fluid. In general, the vapor pressure did not vary by more than 10^{-4} MPa. Only at 25°C, the pressure of two samples of, resp.,1 and 5 cm^3 of liquid differed by 3×10^{-4} MPa.

The results of our vapor pressure measurements are summarized in Table 5. We stress that our temperature values are preliminary; our thermometer was calibrated several years ago, and a check of its icepoint is needed before the temperature readings can be definitively assessed. Such a check, however, can not be made before all the measurements are completed. We have fitted our vapor pressure curve with a scaled form that has proven very useful in other fluids [L1972, H1977]:

$$\frac{P}{P_c} = 1 + A_1 \Delta T^* + A^- |\Delta T^*|^{2-\theta} + A_2(\Delta T^*)^2 + A_3(\Delta T^*)^3 \qquad (2)$$

Here $\Delta T^* = (T-T_c)/T_c$. For the parameters P_c, T_c, we used the values obtained from our best fit to Beattie's PVT data (Table 3). Our data are fitted by Eqn. (2) to within a few millibars. The coefficients of the fit are listed in Table 6. The deviations from the curve are listed in Table 5 and pictured in Fig. 3. We feel that the scatter of the data reflects the variability due to impurity effects in samples of varying liquid-to-vapor ratios. The scatter of our data is far less than that of the earlier data in the literature. At the higher temperatures, our data show rough agreement with those of Beattie, Connolly and Dana. At the temperatures below 60°C, however, our data follow a course of their own and do not agree with any data reported previously. It is our conviction that differences between authors are primarily due to differences in sample composition. We have therefore worked out a model for small impurity effects in isobutane, and present this in the next section.

Impurity effects in Isobutane

The principal uncertainty in our measurements of the equation of state of isobutane is sample purity. Our approach has been to obtain the best sample commercially available, to monitor sample composition before and after the measurements, to develop a model for estimating the effect of impurities known to be present, and to check our estimates by measuring the vapor pressure at various fill densities. This approach permits us to assign realistic error estimates to the vapor pressures we report.

A. Sample composition

We have used Philips Petroleum samples. For preliminary work we have used the instrument grade, claimed to be 99.5% pure. For the definitive measurements we used research grade, claimed to be at least 99.9% pure.

For monitoring the sample composition we used a gas chromatograph provided with a gas sampling valve. We used prepared standard mixtures containing known proportions of lower hydrocarbons for calibration of the gas chromatograph trace. Our measurements are qualitative only and we estimate our compositions to be accurate to perhaps 20%.

The impurities found in our isobutane supply are listed in Table 7. In no case were we able to distinguish the n-butane peak. Although the two butane peaks, *when present in comparable amounts,* separate easily in our column, in actual samples the n-butane peak is swamped by the large isobutane tail.

In our experiments, samples are always taken from the liquid phase for measurement. When samples are analyzed after the measurements, varying compositions are found, probably due to fractionation in the gas handling system. Typical impurity compositions would be 300 ppm propane and 30 ppm N_2.

B. Model for estimation of impurity effects.

We have used a simple model first developed by Keesom [K1901] to estimate impurity effects. The model is based on the assumption that isobutane and slightly impure isobutane obey a principle of corresponding states. A binary mixture of composition x will have pseudocritical parameters that are slightly different from the critical parameters of the pure host

$$\begin{aligned} T_{cx} &= T_c(1 + \alpha x) \\ P_{cx} &= P_x(1 + \beta x) \\ V_{cx} &= V_c(1 + \{\alpha - \beta\}x) \end{aligned} \qquad (3)$$

The mixture parameters α,β are estimated from the critical parameters of the pure components 1 and 2.

$$\begin{aligned} \alpha &= \sqrt{\left(\frac{T_{c2}}{T_{c1}}\right)^3 \frac{P_{c1}}{P_{c2}}} - \frac{1}{2}\frac{T_{c2}}{T_{c1}}\frac{P_{c1}}{P_{c2}} - \frac{1}{2} \\ \beta &= \sqrt{\left(\frac{T_{c2}}{T_{c1}}\right)^3 \frac{P_{c1}}{P_{c2}}} - \frac{3}{2}\frac{T_{c2}}{T_{c1}}\frac{P_{c1}}{P_{c2}} + \frac{1}{2} \end{aligned} \qquad (4)$$

Here 1 is the host, 2 the impurity. Keesom developed these estimates on the basis of the so-called Clausius equation of state, a modification of Van der Waals's. (The values assumed for the interaction parameters are, as is usual in any mixture model, the weakest link).

The impurity effect on the vapor pressure is obtained by expanding, for small x, the conditions for 2-phase equilibrium in a mixture. Define a parameter k as follows

$$k = [\alpha \frac{T}{P} \frac{dP_\sigma}{dT} - \beta][Z_V - Z_L] \qquad (5)$$

Here P_σ is the vapor pressure of the pure host, Z_V, Z_L the compressibility factors PV/RT of the vapor and liquid of the pure host. In our calculations, we have accepted values for P_σ, Z_V, Z_L, $\frac{dP_\sigma}{dT}$ from the correlation by Das et al. [D1973]. Then, the dew point pressure P_d of the impure system of overall concentration x is given by

$$\frac{(P_d - P_\sigma)}{P_\sigma x} = \frac{1-e^k}{Z_V - Z_L} \qquad (6)$$

Likewise, the bubble-point pressure P_b is given by

$$\frac{P_b - P_\sigma}{P_\sigma\, x} = \frac{e^{-k}-1}{Z_V - Z_L} \qquad (7)$$

For a mixture of overall composition x, with a fraction, b, of molecules in the liquid phase, the vapor pressure P is given by

$$\frac{P - P_\sigma}{P_\sigma\, x} = \frac{1-e^k}{be^k+(1-b)} \quad \frac{1}{Z_V - Z_L} \qquad (8)$$

C. Results.

We have used the model to calculate the effect of one percent of a known impurity on the vapor pressure of isobutane. We have done the calculations at three temperatures, namely 300, 350 and 400 K. We have considered four different impurities, namely nitrogen, ethane, propane and n-butane. We have calculated the impurity effect at four liquid-vapor ratios, namely dew point, 1 cc of liquid on 50 cc total, critical density and bubble point. The results of our calculations are summarized in Table 8. In Table 9, we estimate the effect on our measurements due to the known impurity concentrations in our experiment. The known impurities contribute small amounts, not exceeding 10^{-3} MPa (0.01 bar) to the vapor pressure, amounts that increase in absolute, but decrease in relative magnitude as the temperature increases.

The large differences between our own and the preceding data sets (Fig. 3) can not be explained by impurity in our sample. The departure of Connolly's data from our own has the general appearance that a volatile impurity in Connolly's data would take. The departure of Beattie's data from ours, however, cannot be explained solely by a large amount of n-butane present in Beattie's data, even though such an impurity would escape Beattie's way of checking for impurities.

PV isotherms for isobutane vapor

We have measured two isotherms in the vapor phase of isobutane. One isotherm was measured at 104.444°C (220°F) at which temperature PV data were available from two sources, namely Connolly [C1962] and Sage and Lacey [S1938]. Another isotherm was measured at 121.11°C (250°F) at which temperature Connolly had measured the PV relation [C1962]. At each temperature, three series of three or four Burnett expansions were performed. The pressures were measured on a Ruska gas-lubricated piston gage which had been calibrated at the National Bureau of Standards. For the cell constant, we assumed the values previously determined by expansions using helium [W1979]. The data were analyzed using a nonlinear least-squares formulation of the Burnett problem based on a density virial expansion [W1973]. The results are given in Tables 10 and 11. Note that the significance of the virial coefficients deteriorate rapidly with order with the fourth having no significant figures. The numbers contained in Table 10 are nevertheless essential to the reproduction of the experimental data and, because of the statistical correlation between the virials listed, all figures presented *must be used.* This is true despite the fact that some of these have no significance for "stand alone" virial coefficients.

Adsorption is generally a problem in these kinds of measurements on the vapor side below the critical temperature. We checked for the presence of adsorption by using the cell constant as a free parameter. The values we obtained this way agreed with our previous helium results to ± 1 part in 20,000, with the values obtained for density and compressibility factor in the cases of fixed N and free N, respectively, agreeing with each other to 1 part in 5000 over the entire range of the vapor isotherm thereby indicating that the effect of adsorption is negligible.

We have not yet estimated the effect of impurities on the vapor isotherms. Previous work for ethylene using our model [H1978] indicates that those effects are relatively small.

Our results are compared with those of Connolly and of Sage and Lacey in Fig. 4. The compressibility factors, compared at the same density, agree with those of Connolly, at 104.44°C and at 121.11°C, to within 0.002 in Z. The difference with Sage and Lacey, at 104.44°C, is very large, of the order of 0.01 in Z. Thus, our data confirm those of Connolly but put those of Sage and Lacey into serious question.

Some Comparisons Among Published Correlations

There have been a number of correlations of the properties of isobutane published. We have selected three correlations for intercomparison on the basis of their availability, because of their extent and since the properties of isobutane were of major importance to the correlator in each case. Each correlation used a version of the Benedict, Webb, Rubin (BWR) equation for the pressures as a function of the density. For several reasons this could not be expected to result in identical correlations. First of all, where there is extensive disagreement among data sets, as there is for isobutane, a correlation can be expected to be extremely sensitive to the data selection process. Secondly, there are significant differences among the particular versions of the BWR equation used. Finally, one author was also interested in a generalized version of the BWR equation which would be simultaneously applicable to a number of hydrocarbons. An indication of the differences to be expected can be had from the differences between two similar versions produced by the same group [S1977b, S1977c]. While the differences are sufficiently small so as not to affect an overall plant design [S1977a] they are nevertheless significant.

Table 12 contains comparisons between the vapor pressures predicted by the correlations and the measurements of Waxman and Davis reported herein. It should be noted that Das et al. and Starling et al. [S1977b] are much closer to the new values of Waxman and Davis reported herein than are Starling et al. of [S1977c]. The former pair of correlations differ from each other by an excessive amount, however, with each differing from Waxman and Davis in a systematic manner.

Table 13 contains a comparison between the two correlations of the compressibility factor for the saturated volume. The differences between the two correlations are certainly excessive.

Table 14 contains comparisons of the second virial coefficients of the two correlations. It also contains experimental values taken from Table 10 and from the literature. Here, the results of Starling et al. are much superior to those of Das et al.

Table 15 shows a comparison between the data of Waxman and Davis and the correlation of Starling et al. [S1977b] for T = 104.44°C. The former have been extrapolated to the vicinity of the saturation boundary. Differences are systematic and increase with the increasing effects of non-idealities, approaching 5% near saturation. The extrapolation of the data of Waxman and Davis can be expected to contribute negligible error since the contribution of each term in the virial series to the compressibility factor is almost an order of magnitude less than that of the preceding term, becoming approximately 1% for the fourth virial. The relationship between the correlation of Starling et al. [S1977b] and the data of Waxman and Davis at 121.11 is very nearly identical with Table 15.

It is clear, even from the rather cursory comparison carried out here, that the correlations are in rather violent disagreement and that neither is adequate for the task of predicting the properties of isobutane for use in plant design models. Wherever one or the other correlation is moderately close to experiment in any particular region of pressure and temperature can only be due to fortuitous circumstances since each correlation leans heavily on inaccurate data. This belief is reinforced by the overall large differences between the correlations. It will obviously be essential for a new correlation to be developed once an adequate set of data has been produced.

Conclusion

This report contains a partial assessment of the equation-of-state data and the existing correlations for isobutane. We have reached the following conclusions:

(a) vapor pressure

Below 60°C our data disagree with all other data in the literature by amounts of the order of 0.007 MPa (1 p.s.i.) for vapor pressures that are all below 1 MPa. We have shown that the known impurities in our sample cannot have caused the discrepancies with the earlier data. Above 60°C, our data agree modestly, to within 0.005 MPa, with those of Beattie, on vapor pressure going up to 3 MPa.

(b) vapor phase

Our PV measurements at 104.44 and 121.11 C confirm the virial data of Connolly to 0.002 in Z. Our results at 104.44°C depart strongly from the data of Sage and Lacey, by as much as 0.01 in Z.

(c) critical region

We were able to correlate the critical-region data plus the 150°C isotherm of Beattie et al. with a scaled equation that has proven very useful in other fluids. The principal result of the fit is a considerable decrease of the critical temperature from the value reported by Beattie.

We feel that this strong decrease may be due in part to small impurity effect; the main reason, however, lies in the fact that the coexistence curve is much flatter than Beattie had assumed. We are of the opinion that there is a good chance that Beattie's data in the supercritical region are sound.

(d) correlations

With existing large discrepancies between data sets, it is to be expected that the results of correlations depend heavily on the data sets chosen and the weights assigned. We have indeed found that there are large discrepancies between the correlation of Das et al. and that of Starling, running as high as 10% in Z in the vapor phase near the phase boundary even reasonably far from critical.

Assessment of further work

From our point of view, the following work will be required as a minimum in order to establish the equation of state of isobutane.

(a) A check of Beattie's supercritical data at at least one temperature.

(b) Further spot checks of Sage and Lacey's data.

(c) Spot checks of the saturated liquid densities and of some densities in the liquid phase.

(d) A recalibration of our thermometers.

We realize that there may be a need for caloric data to supplement the equation of state data in regions of technical interest. We suggest that this need be assessed by the interested parties. Independent of the outcome, the following work will be unavoidable.

(e) After the new data are obtained, the thermodynamic behavior of isobutane will have to be reformulated, with close interaction between the experimenters, correlators and users of the data.

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Table 1

Definition of reduced variables

Critical-point constants	3 adjustable parameters
pressure	P_c
volume	V_c
density	$\rho_c = 1/V_c$
temperature	T_c, K

Reduced quantities

pressure	$P^* = P/P_c$
temperature	$\Delta T^* = (T-T_c)/T_c$
density	$\Delta\rho^* = (\rho-\rho_c)/\rho_c$

Table 2

Definition of parameters

Critical exponents $\alpha, \beta, \gamma, \delta$

coexistence-curve exponent $\beta = .355$

critical-isotherm exponent $\delta = 4.32$

$\gamma = \beta(\delta-1) \qquad \alpha = 2-\beta(\delta+1)$

Linear-Model parameters a, k, b^2

three constants: a, k, b^2

a, k are adjustable

b^2 is calculated from $b^2 = \dfrac{(\delta-3)}{(\delta-1)(1-2\beta)}$

Parametric variables r, θ

two parameters r, θ for each data point

They are calculated from the transformation

$$\Delta T^* = r(1-b^2\theta^2)$$

$$\Delta\rho^* = r^\beta k\theta$$

Free energy function $f(\theta)$

$$f(\theta) = f_o + f_2\theta^2 + f_4\theta^4$$

$$f_o = -\frac{\beta(\delta-3) - b^2\alpha\gamma}{2b^4(2-\alpha)\,(1-\alpha)\alpha}$$

$$f_2 = \frac{\beta(\delta-3) - b^2\alpha(1-2\beta)}{2b^2(1-\alpha)\alpha}$$

$$f_4 = -(1-2\beta)/2\alpha$$

Pressure

$$P^* = -A_o^*(T^*) + P^*_{anom}$$

$$P^*_{anom} = r^{\beta\delta}\, a\theta(1-\theta^2) + r^{2-\alpha}\, ak\{\theta^2(1-\theta^2) - f(\theta)\} \qquad \text{(1-phase)}$$

$$P^*_{anom} = -r^{2-\alpha}\, ak\, f(1) \qquad \text{(2-phase)}$$

Analytic Background

$$A_o^*(T^*) = -1 + A_1^*(\Delta T^*) + A_2^*(\Delta T^*)^2 + A_3^*(\Delta T^*)^3$$

$A_1^* \ldots A_3^*$ are adjustable

Table 3

Linear-Model parameters for the critical region of isobutane

Critical-point constants

$P_c = (3.6306 \pm 0.0006)$ MPa

$\rho_c = (3.906 \pm 0.002)$ mol/dm^3

$T_c = (407.851 \pm 0.009)$ K

Critical exponents (fixed)

$\alpha = 0.100$

$\beta = 0.355$

$\gamma = 1.19$

$\delta = 4.352$

Linear-model constants

$a = 20.787 \pm 0.16$

$k_0 = 1.44096 \pm 0.009$

$b^2 = 1.3909$ (fixed)

Analytic background

$A_1^* = 7.1318 \pm 0.04$

$A_2^* = - 198.12 \pm 43$

$A_3^* = 4722 \pm 1100$

Table 4

Critical Parameters of Isobutane obtained from
data of Refs [B1949,B1950]

	as reported in [B1949]	From fit to scaled equation
P_c	(3.648±0.005) MPa	(3.6306±0.0006) MPa
ρ_c	3.80 mol/dm^3	(3.906±0.002) mol/dm^3
T_c	(134.98±0.05)°C	(134.701±0.009) °C

Table 5

Vapor pressure of ~99.98% pure sample of isobutane.

Preliminary temperature values prior to thermometer calibration.

Temperature, °C	Pressure, MPa	$P_{exp}-P_{calc}$ (10^{-4} MPa)
25.000	0.3500	-2
30.000	0.4043	+2
35.000	0.4641	+1
40.000	0.5304	+1
45.000	0.6032	-3
50.000	0.6836	-3
55.000	0.7725	+5
60.000	0.8683	-1
60.000	0.8676	-5
70.000	1.0867	+1
80.000	1.3432	+3
90.000	1.6408	-2
100.000	1.9855	-1
110.000	2.3819	+1
120.000	2.8361	-1
125.000	3.0879	0

Table 6

Fit to vapor pressures of isobutane

$$\frac{P-P_c}{P_c} = A_1\,\Delta T^* + A^-\,|\Delta T^*|^{2-\theta} + A_2\,(\Delta T^*)^2 + A_3\,(\Delta T^*)^3$$

$\Delta T^* = (T-T_c)/T_c$

$$\left.\begin{array}{ll} P_c & = 3.6306 \text{ MPa} \\ T_c & == 407.851 \text{ K} \\ \theta & = 0.11 \end{array}\right\} \quad \text{fixed}$$

$A_1 = 6.818526 \pm 0.006$

$A^- = 22.01824 \pm 0.58$

$A_2 = -10.73853 \pm 0.71$

$A_3 = 6.8431 \pm 0.22$

Table 7

Impurities in Isobutane, in ppm

	Instrument grade	Research grade		After Measurements, representative
Claim	99.5%	99.9% minimum 99.98% typical		
	liquid	liquid	vapor	
nitrogen		~10	2000	30
ethane	7000			
propane	1000	70	500	300
water (?)			2000	
n-butane (estimated from claimed overall impurity)	<5000	<1000		<1000

Table 8

Estimated vapor pressure increase in 10^{-4} MPa (millibars)
due to 1% of impurity in isobutane

	N_2	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$
300K, P_σ = .3704 MPa				
dewpoint	41	36	23	-14
1 cm^3 of liquid	83	64	33	-12
critical density	657	200	50	-10
bubble point	1134	229	51	-10
350K, P_σ = 1.2605 MPa				
dewpoint	166	130	76	-37
1 cm^3 of liquid	210	155	114	-35
critical density	1104	385	125	-31
bubble point	2353	473	133	-31
400K, P_σ = 3.193 MPa				
dewpoint	695	426	210	-78
1 cm^3 of liquid	719	435	212	-78
critical density	1230	587	242	-75
bubble point	1874	694	259	-73

Table 9

Estimated pressure error, in 10^{-4} MPa

(millibars), due to known impurities in our isobutane sample.

		30 ppm nitrogen	300 ppm propane	1000 ppm n-butane
300K	dew point	0	1	-1
	1 cm^3 of liquid	0	1	-1
	critical density	2	2	-1
	bubble point	3	2	-1
350K	dew point	1	2	-4
	1 cm^3 of liquid	1	3	-4
	critical density	3	4	-3
	bubble point	7	4	-3
400K	dew point	2	6	-8
	1 cm^3 of liquid	2	6	-8
	critical density	4	7	-7
	bubble point	6	8	-7

Table 10

Virials of isobutane at 104.444 and 121.111°C

	104.444°C	121.111°C
B, cm^3/mol	$-378.3436 \pm 1.$	$-344.4418 \pm .3$
C, cm^6/mol	$40043.55 \pm 3000.$	$36436.58 \pm 500.$
D, cm^9/mol	$(-5.66 \pm 2.5)x10^6$	$(-2.01 \pm 2.)x10^5$

Table 11

Compressibility factor of isobutane vapor

	ρ, mol/dm^3	$Z = PV/RT$
104.444°C	0.1	0.96256
	0.2	0.92589
	0.3	0.88995
	0.4	0.85471
	0.5	0.82013
	0.6	0.78619
	0.7	0.75284
121.111°C	0.1	0.96592
	0.2	0.93257
	0.3	0.89994
	0.4	0.86804
	0.5	0.83686
	0.6	0.80641
	0.7	0.77668
	0.8	0.74766
	0.9	0.71937
	1.0	0.69179
	1.1	0.66493
	1.2	0.63879
	1.3	0.61336

Table 12

Comparisons of vapor pressure[d] correlations

T°C	Waxman et al.[c]	Starling et al.[f]	Das et al.[e]	Starling et al.[b]
30	.4043	.4078 (0.9)	0.3999 (-1.1)[a]	.3880 (-4.0)
40	.5304	.5350 (0.9)	0.5246 (-1.1)	.5093 (-4.0)
50	.6836	.6893 (0.8)	0.6727 (-1.6)	
60	.8683	.8740 (0.7)	0.8583 (-1.2)	
70	1.0867	1.0926 (0.5)	1.0742 (-1.2)	
80	1.3432	1.3484 (0.4)	1.3154 (-2.1)	
90	1.6408	1.6458 (0.3)	1.6229 (-1.1)	
100	1.9855	1.9890 (0.2)	1.9650 (-1.0)	1.9005 (-4.3)

[a] numbers in parentheses are percent deviation from Waxman et al.[c]

[b] This refers to [S1977c]

[c] This work

[d] Pressure in MPa

[e] This refers to [D1973]

[f] This refers to a private communication from Starling based on his use of the equations of [S1977b]

Table 13

Comparison of correlations of saturated vapor compressibility factors

T°K	Starling et al.	Das et al.	$(\Delta Z/Z)100.$
270	.9512	.9386	1.3
280	.9375	.9228	1.6
300	.9035	.8842	2.2
320	.8597	.8360	2.8
340	.8046	.7767	3.6
360	.7350	.7032	4.5
380	.6436	.6074	6.0
390	.5839	.5441	7.3
400	.5043	.4564	10.5
406	.4308	.3657	17.8
408	.3846	.3069	25.3

Table 14

Comparisons of second virial coefficients

	104.444°C	121.111°C
This work	-378.34	-344.44
Connolly	-374.0	-341.1
Das et al.	-393.9	-353.4
Starling et al. [S1977b]	-368.1	-335.6

Table 15

Comparison of the compressibility factor predicted by Starling et al. and the data of Waxman and Davis for T = 104.44°C

P (atm)	$Z_{Starling}$	Z_{Waxman}	% Dev.
1.	.98802	.98768	.03
2.	.97582	.97513	.07
3.	.96339	.96233	.11
4.	.95072	.94927	.15
5.	.93779	.93593	.20
6.	.92458	.92227	.25
7.	.91108	.90828	.31
8.	.89725	.89392	.37
9.	.88307	.87916	.44
10.	.86851	.86396	.53
11.	.85353	.84825	.62
12.	.83810	.83198	.74
13.	.82215	.81508	.87
14.	.80563	.79745	1.03
15.	.78847	.77897	1.22
16.	.77058	.75949	1.46
17.	.75184	.73878	1.77
21.	.66461	.63502*	4.66

* extrapolated value

Figure Captions

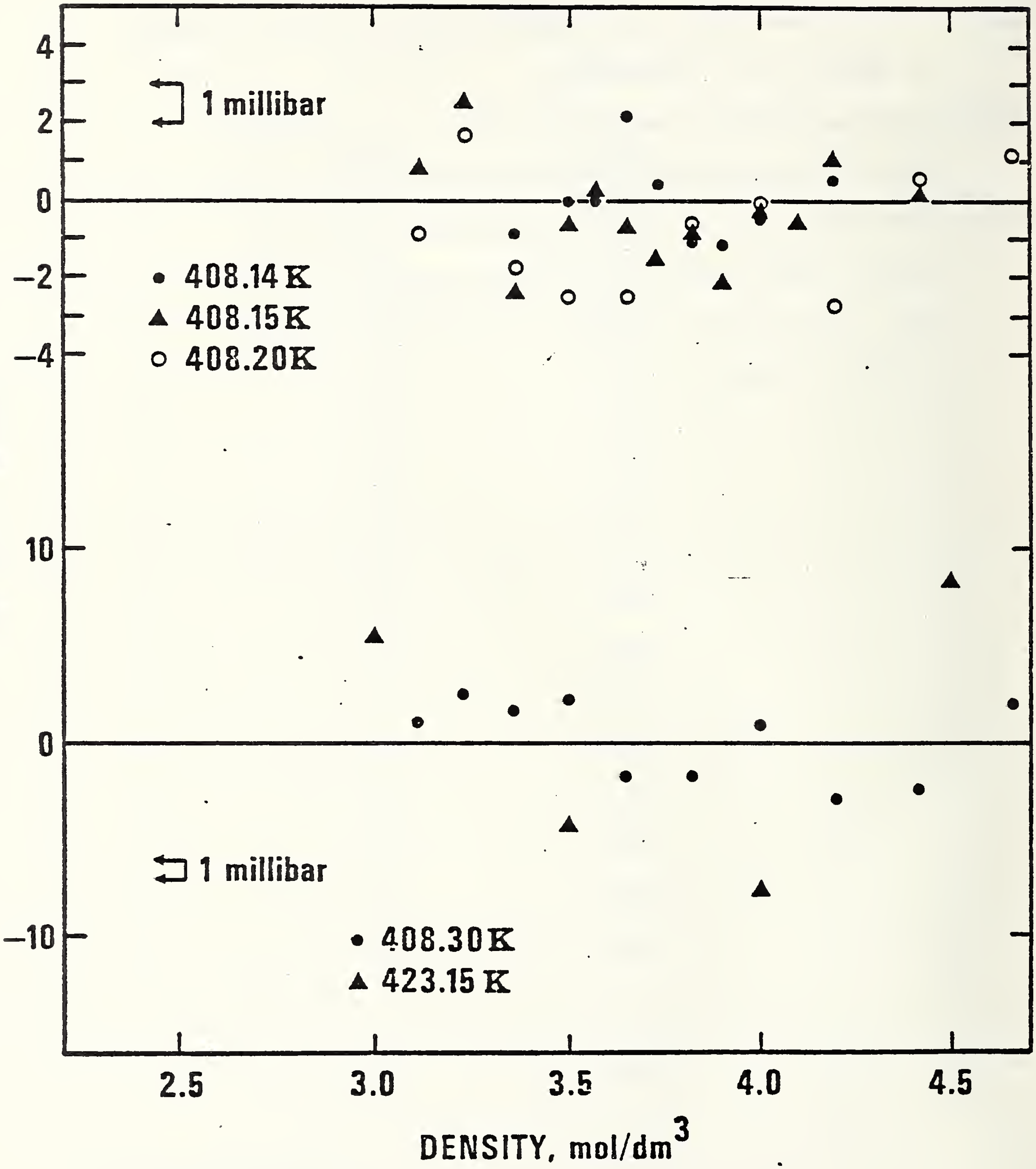
Figure 1. Fit of Linear Model scaled equation to critical-region isotherms of Beattie et al. [B1949].

Figure 2. Fit of Linear Model scaled equation to critical-region isotherms of Beattie et al. [B1949,1950].

Figure 3. Intercomparisons of vapor pressure data in the literature. Base line is scaled equation fitted to our vapor pressures.

Figure 4. Intercomparisons of the PVT measurements of Sage et al. [M1940, S1938], Connolly [C1962] and the results of this work. The base line is based on calculations using the virials of Table 10.

Figure 1.



4
2
0
−2
−4
10
0
−10
1 millibar
1 millibar
● 408.14 K
▲ 408.15 K
○ 408.20 K
● 408.30 K
▲ 423.15 K
ΔP, (10⁻⁴ MPa)
2.5
3.0
3.5
4.0
4.5
DENSITY, mol/dm³

Figure 2.

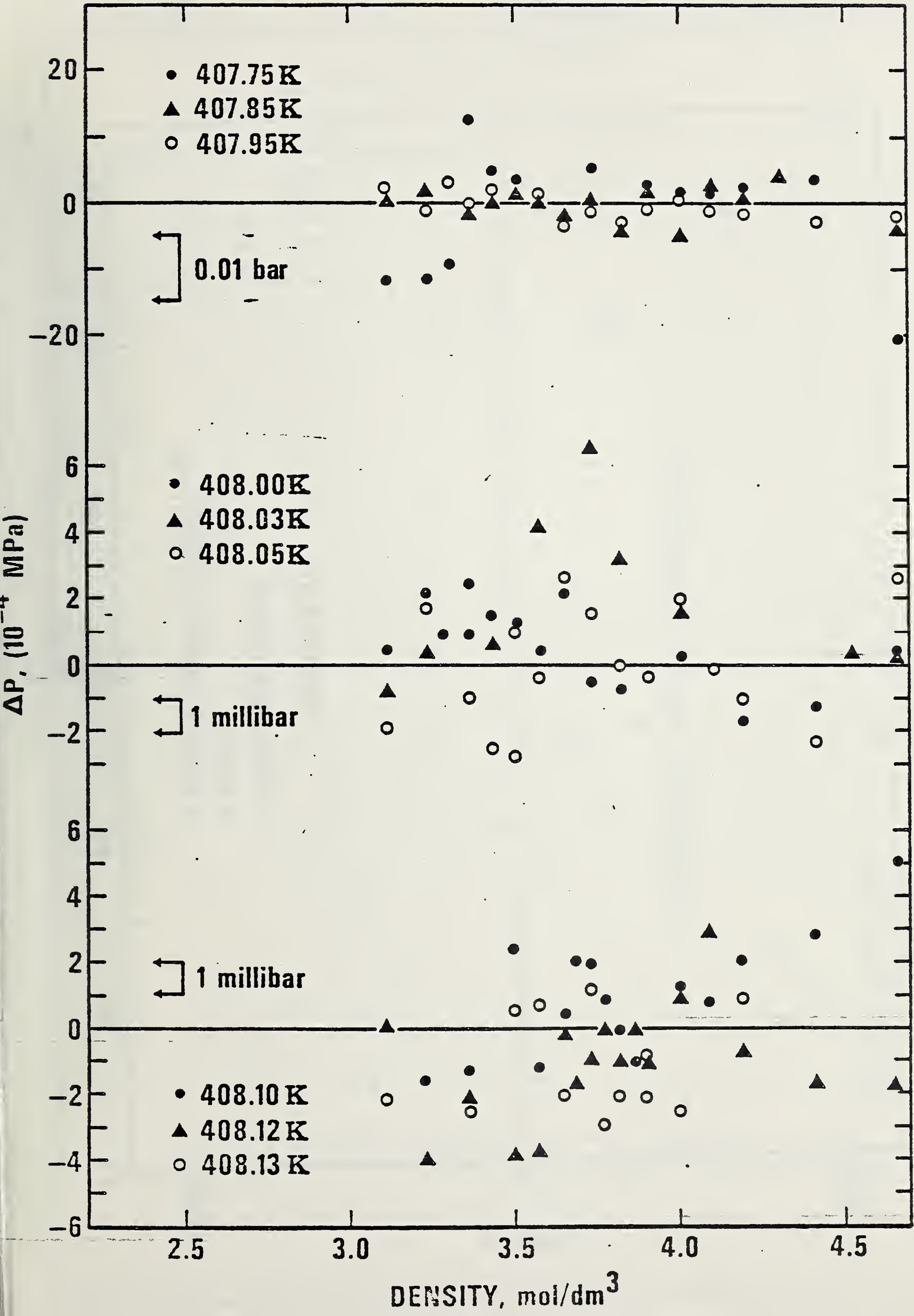

● 407.75 K
▲ 407.85 K
○ 407.95 K
0.01 bar
● 408.00 K
▲ 408.03 K
○ 408.05 K
1 millibar
1 millibar
● 408.10 K
▲ 408.12 K
○ 408.13 K
20
0
−20
6
4
2
0
−2
6
4
2
0
−2
−4
−6
ΔP, (10⁻⁴ MPa)
2.5
3.0
3.5
4.0
4.5
DENSITY, mol/dm³

Figure 3.

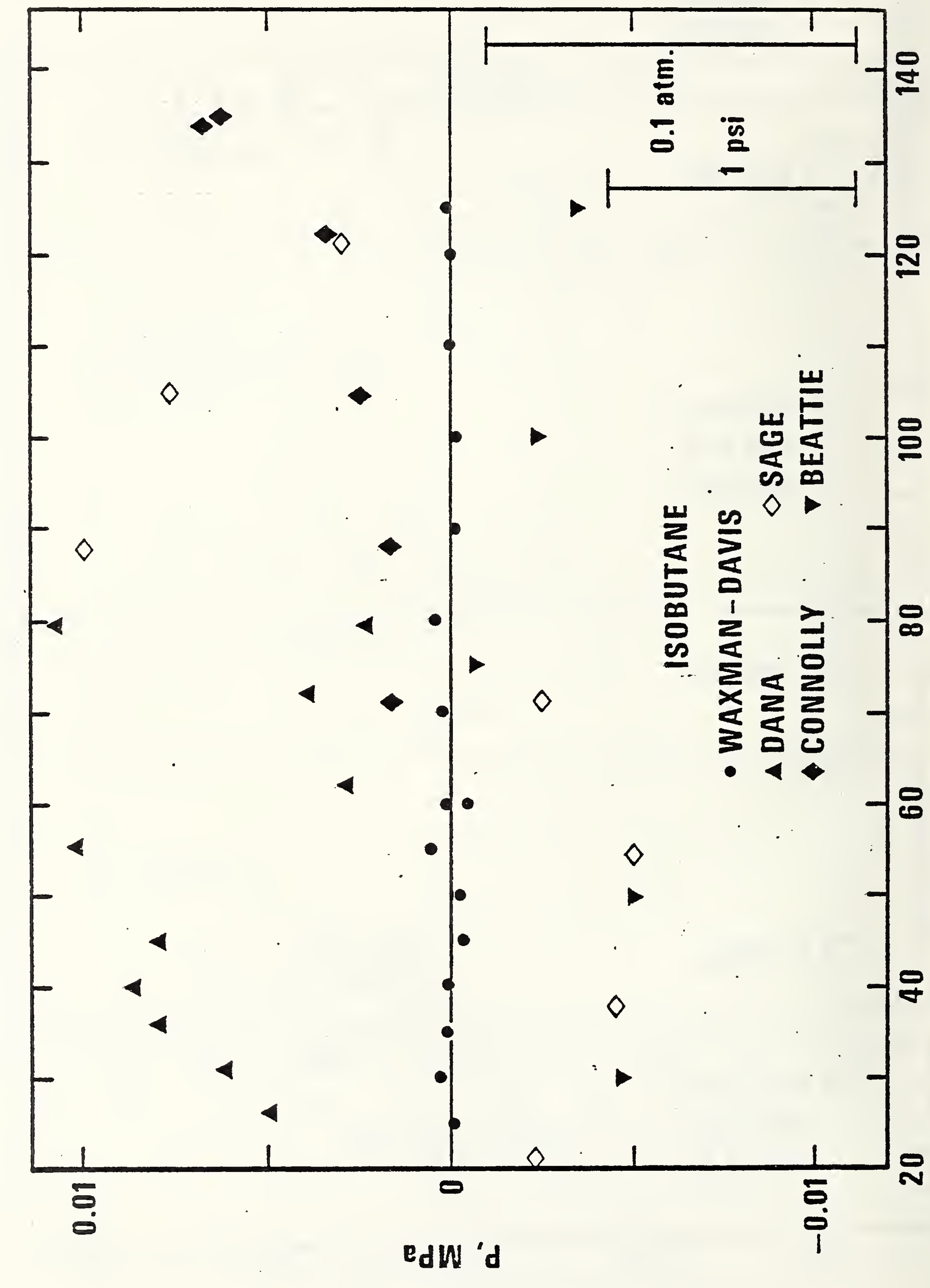
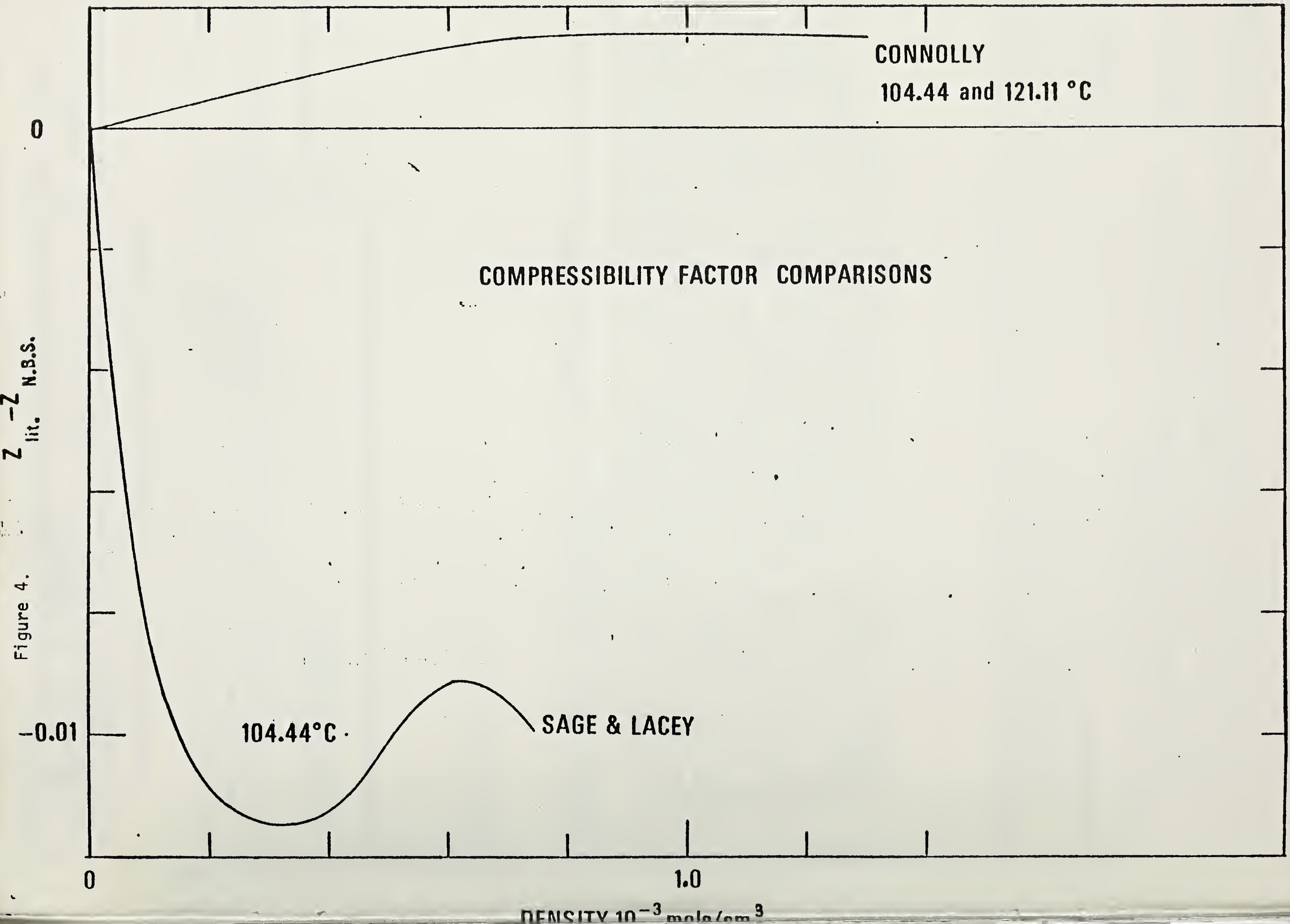

0.01
0
-0.01
P, MPa
20
40
60
80
100
120
140
T,C
ISOBUTANE
• WAXMAN-DAVIS
▲ DANA
◆ CONNOLLY
◇ SAGE
▼ BEATTIE
0.1 atm.
1 psi

Figure 4.


COMPRESSIBILITY FACTOR COMPARISONS
CONNOLLY
104.44 and 121.11 °C
104.44°C
SAGE & LACEY
$Z_{lit.} - Z_{N.B.S.}$
0
-0.01
0
1.0
DENSITY 10^{-3} mole/cm^3

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New and very accurate measurements of the vapor pressure and two PVT isotherms of isobutane below critical are presented. The vapor pressure data have been correlated to within parts per 10,000 using a scaled vapor pressure equation. The Beattie data in the critical region has been correlated using a scaling law approach. This required a shift in the critical temperature of 0.3 K from that published by Beattie. The significance of this shift in an overall correlation is not yet clear. The two PV isotherms are compared with literature data and the results of Sage and Lacy shown to be inaccurate. Those of Connolly appear to be sufficiently accurate for including in future correlations. Two correlations of Starling et al. and that of Das et al. are intercompared and are compared with these new results. As might be expected, these correlations, being based on inaccurate data, are not of sufficient accuracy for use as representations of the properties of isobutane. A program is presented for the completion of a correlation of the properties of isobutane to engineering accuracy.

12. KEY WORDS (*Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons*)

Critical region; density; equation of state; geothermal; isobutane; thermodynamic; vapor pressure.

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