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An Equation of State for Isobutane–Isopentane Mixtures with Corrections for Impurities[1]

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A global Helmholtz function accurately representing the thermodynamic properties of isobutane–isopentane mixtures over a wide range of temperatures and pressures has been developed. The Helmholtz function has been used for the generation by computer of tables and charts of properties of interest to designers of power cycles. This Helmholtz function has also been extended to allow for additional components in the mixture, thus enabling the accurate calculation of corrections to the thermodynamic properties when impurities are present in significant amounts.

KEY WORDS: dew-bubble curves; geothermal energy; impurity effects; isobutane; isopentane; mixtures; thermodynamic surface.

1. INTRODUCTION

Interest in the use of hydrocarbon mixtures, particularly isobutane–isopentane mixtures, as working fluids in binary power cycles in the generation of electricity from geothermal energy has prompted a research program to predict more accurately the thermodynamic properties of these mixtures. The Division of Geothermal and Hydropower Technology of the Department of Energy has supported for several years a program of research both to improve the available experimental data base and to correlate these data for the production of tables and charts of use to the designer of power cycles. Interest in the use of mixtures, rather than pure substances, allows the engineer to "tune" the properties of the working fluid to best match the available external conditions and to improve the

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operation of the heat exchanger by adjusting the composition of the mixture. By increasing the accuracy of the prediction of the thermodynamic properties, the engineer is able to design for greater efficiency, since the necessity of "overdesigning" to allow for uncertainties in the predictions is reduced.

Since a highly accurate prediction of the properties of pure isobutane from a correlation done at the NBS [1, 2] was available, it was decided to use this as a reference function for the development of a representation of the Helmholtz function for the mixture. The use of a principal component of the mixture as the reference fluid should lead to a significant improvement in the reliability of property predictions over other more generalized predictive methods.

2. THE ISOBUTANE REFERENCE FUNCTION

For the reference Helmholtz function we have used the global Helmholtz function developed at the NBS and described in earlier publications [1, 2]. The Helmholtz function accurately represents experimental data for pure isobutane over a wide range of temperature (250 to 600 K) and pressure (to 40 MPa). For convenience, this Helmholtz function has been rewritten in dimensionless form [3]. In this paper the reduced, dimensionless properties are represented with a bar over the symbol, and the reduction parameters as a symbol with an asterisk superscript. Thus, we have

$$\begin{aligned} &\text{temperature} \quad \bar{T} = T/T^*, \quad &&\text{where } T^* = 407.84\ \mathrm{K} \\ &\text{pressure} \quad \bar{P} = P/P^*, \quad &&\text{where } P^* = 3.6290\ \mathrm{MPa} \\ &\text{density} \quad \bar{\rho} = \rho/\rho^*, \quad &&\text{where } \rho^* = 3879.6\ \mathrm{mol \cdot m^{-3}} \end{aligned} \tag{1}$$

These reduction parameters are the best estimates of the critical point of isobutane [1, 2, 4]. From these reduction parameters, the reduction parameters for the other thermodynamic properties can be derived:

$$\begin{aligned} A^{**} &= P^*/\rho^* = 935.41\ \mathrm{J \cdot mol^{-1}} \\ S^{**} &= A^{**}/T^* = 2.2936\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \end{aligned} \tag{2}$$

and then, for example,

$$\begin{aligned} &\text{Helmholtz function} \quad &&\bar{A} = A/A^{**} \\ &\text{enthalpy} \quad &&\bar{H} = H/A^{**} \\ &\text{entropy} \quad &&\bar{S} = S/S^{**} \\ &\text{heat capacity at constant } P \quad &&\bar{C}_{\mathrm{p}} = C_{\mathrm{p}}/S^{**} \end{aligned} \tag{3}$$

Also useful is the reduced gas constant:

$$R^{**} = R/S^{**} = 3.6250$$

The Helmholtz function of Refs. 1 and 2 can be rearranged to be written as

$$A(T, \rho) = A_0(T) + A_1(T, \rho) + A_2(T, \rho) + A_3(T, \rho) \tag{4}$$

where A_0 represents the "ideal-gas" portions, $A_1 + A_2$ the "base" function, and A_3 the "residual" function. In dimensionless form this becomes

$$\bar{A}(\bar{T}, \bar{\rho}) = \bar{A}_0(\bar{T}) + \bar{A}_1(\bar{T}, \bar{\rho}) + \bar{A}_2(\bar{T}, \bar{\rho}) + \bar{A}_3(\bar{T}, \bar{\rho}) \tag{5}$$

A detailed description of each of these terms can be found in Ref. 5.

3. THE THERMODYNAMIC SURFACE FOR ISOPENTANE

A Helmholtz function for pure isopentane was constructed from the isobutane reference Helmholtz function using extensions to "simple" corresponding states. If we define the following quantities:

$$f_0 = \bar{T}^c_5/\bar{T}^c_4; \qquad h_0 = \bar{V}^c_5/\bar{V}^c_4 = \bar{\rho}^c_4/\bar{\rho}^c_5; \qquad q_0 = \bar{P}^c_5/\bar{P}^c_4 \tag{6}$$

where the subscripts 4 and 5 refer to isobutane and isopentane, respectively, and the properties of isopentane are made dimensionless by means of the same reference constants as were used for isobutane [see Eq. (1)], the corresponding-states principle says, for all values of ρ and T,

$$\begin{aligned} \bar{Z}_5(\bar{\rho}_5, \bar{T}_5) &= \bar{Z}_4(\bar{\rho}_4 = \bar{\rho}_5 h_0, \bar{T}_4 = \bar{T}_5/f_0) \\ \bar{A}^{\mathrm{cf}}_5(\bar{\rho}_5, \bar{T}_5) &= f_0 \bar{A}_4(\bar{\rho}_4 = \bar{\rho}_5 h_0, \bar{T}_4 = \bar{T}_5/f_0) - R^{**}\bar{T}_5 \ln(h_0) \end{aligned} \tag{7}$$

where Z is the compressibility factor $PV/RT(=\bar{P}\bar{V}/R^{**}\bar{T})$ and $\bar{A}^{\mathrm{cf}}$ is the configurational portion of the Helmholtz function $\bar{A}_{\mathrm{cf}} = \bar{A} - \bar{A}_0$. These relations imply that $f_0 = h_0 q_0$ [6]. The values used for the critical point of isopentane is the current best estimate ($T_c = 460.51$ K, $P_c = 3.371$ MPa, and $\rho_c = 3247.3 \text{ mol} \cdot \text{m}^{-3}$).

Since no two substances obey the principle of corresponding states exactly, we generalize the principle as suggested by Rowlinson and Watson [6] and Leland et al. [7, 8], with two functions $\Phi(\rho, T)$ and $\theta(\rho, T)$ which they have called shape factors. These functions are defined through

$$\begin{aligned} f &= f_0 \theta(\bar{\rho}_4, \bar{T}_4) \\ q &= q_0 \theta(\bar{\rho}_4, \bar{T}_4)/\Phi(\bar{\rho}_4, \bar{T}_4) \end{aligned} \tag{8}$$

so that

$$h = f/q = (\bar{T}^{c}_{5}/\bar{T}^{c}_{4})(\bar{P}^{c}_{4}/\bar{P}^{c}_{5})\ \Phi(\bar{\rho}_4, \bar{T}_4)$$

These functions will be expected to have the following properties: they will be slowly varying functions of T and ρ, and they will be near unity since simple corresponding states is not greatly in disagreement with experiment. They will be constructed so that the use of this f, q, and h in Eq. (6) in place of f_0, q_0 and h_0 will improve the correspondence over that of simple corresponding states.

Our choice for the θ and Φ functions was based on the following considerations:

(a) There exist measurements of the coexisting liquid and vapor densities of isopentane over a range of temperatures taken many years ago by Young [9] and believed to be reasonably good.

(b) Measurements of the vapor pressures of isopentane over a wide range of temperatures have been made at the NBS recently [10].

With little else in the way of experimental data for isopentane available, our choice was to form expressions for θ and Φ that were of relatively simple functional form, did not vary greatly from unity even on extrapolation to very high or very low temperatures, and would map the vapor pressure and coexisting densities onto those of isobutane as closely as possible.

The expressions finally chosen for the shape factors are

$$\begin{aligned} \theta &= 1 + a_1(\bar{\rho} - 1) + a_2(\bar{T} - 1) + a_3(\bar{T} - 1)^2 \\ \Phi &= 1 + a_4(\bar{\rho} - 1) + a_5(\bar{T} - 1) \end{aligned} \tag{9}$$

where

$$a_1 = -0.01, \quad a^2 = 0.0058. \quad a_3 = 0.012, \quad a_4 = -0.065, \quad a_5 = -0.02$$

In Fig. 1, we show these experimental data and their comparisons with predicted values from simple corresponding states and from generalized corresponding states using the shape factors.

4. GENERALIZED CORRESPONDING STATES FOR THE MIXTURE

The above treatment of pure isopentane through corresponding states can be extended to mixtures through the use of what has been called the

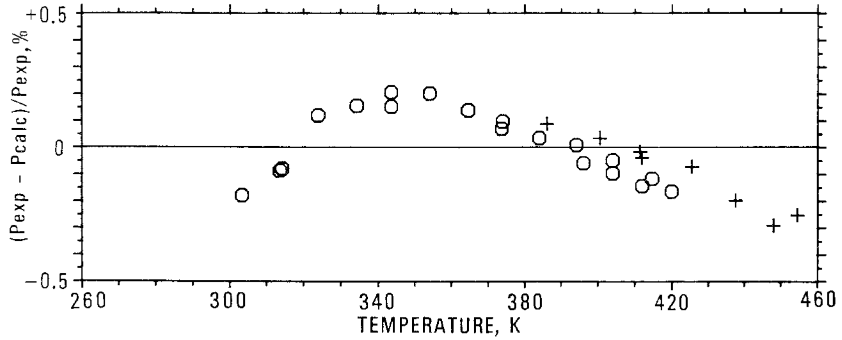

Fig. 1. Vapor pressure of pure isopentane. Differences between measurements at this laboratory and those predicted by the model, in percentages. The two symbols represent two different series of measurements.

"one-fluid" model. In this model the assumption is made that the configurational Helmholtz function for the mixture (less the ideal mixing term) can be represented as the Helmholtz function for a single equivalent substance with the parameters describing this substance to be found. In the following, we use the subscript x to denote properties of a mixture of molar fraction x of isopentane (and $1-x$ of isobutane). The statement of the corresponding states principle would take the form [analogous to Eq. (7)]

$$Z_x(\bar{\rho}_x, \bar{T}_x) = Z_4(\bar{\rho}_4 = \bar{\rho}_x h_x, \bar{T}_4 = \bar{T}_x/f_x)$$

and

$$\bar{A}_x^{\mathrm{cf}}(\bar{\rho}_x, \bar{T}_x) = f_x \bar{A}_4^{\mathrm{cf}}(\bar{\rho}_4 = \bar{\rho}_x h_x, \bar{T}_4 = \bar{T}_x/f_x) - R^{**}\bar{T}_x \ln(h_x)$$

where f_x and h_x are defined by

$$\begin{aligned} f_x &= (\bar{T}_x^{\mathrm{c}}/\bar{T}_4^{\mathrm{c}})[1 + g_\theta(x)\,\theta(\bar{\rho}_4, \bar{T}_4) - 1] \\ h_x &= (\bar{\rho}_4^{\mathrm{c}}/\bar{\rho}_x^{\mathrm{c}})[1 + g_\Phi(x)\,\Phi(\bar{\rho}_4, \bar{T}_4) - 1] \end{aligned} \qquad (10)$$

The $\bar{T}_x^{\mathrm{c}}$ and $\bar{\rho}_x^{\mathrm{c}}$ of Eq. (10) define the path taken by the line of critical points as x varies from 0 (pure isobutane) to 1 (pure isopentane). (This line is referred to as the "pseudocritical" line: the locus of the critical points if the liquid and vapor phases were constrained to have the same concentration. The real critical line is at a slightly higher temperature and is found through a different method.) The $\bar{T}_x^{\mathrm{c}}$ and $\bar{\rho}_x^{\mathrm{c}}$ are functions of the $\bar{T}^{\mathrm{c}}$'s and $\bar{\rho}^{\mathrm{c}}$'s of the pure substances and x and reduce to the $\bar{T}^{\mathrm{c}}$ and $\bar{\rho}^{\mathrm{c}}$ of the pures when $x=0$ or 1. The form of these functions is called the "mixing" rules.

The form we chose (from many that have been proposed) is the "van der Waals" type:

$$\begin{aligned} \bar{V}^{\mathrm{c}}_{x} &= (1-x)^2\,\bar{V}^{\mathrm{c}}_{4} + 2x(1-x)\,\bar{V}^{\mathrm{c}}_{45} + x^2\bar{V}^{\mathrm{c}}_{5} \\ \bar{T}^{\mathrm{c}}_{x} &= (1-x)^2\,\bar{T}^{\mathrm{c}}_{4} + 2x(1-x)\,\bar{T}^{\mathrm{c}}_{45} + x^2\bar{T}^{\mathrm{c}}_{5} \end{aligned} \tag{11}$$

The terms $\bar{V}^{\mathrm{c}}_{45}$ and $\bar{T}^{\mathrm{c}}_{45}$ are defined by the "combining rules":

$$\begin{aligned} \bar{V}^{\mathrm{c}}_{45} &= k[0.5(\bar{V}^{\mathrm{c}}_{4})^{1/3} + 0.5(\bar{V}^{\mathrm{c}}_{5})^{1/3}]^3 \\ \bar{T}^{\mathrm{c}}_{45} &= l[\bar{T}^{\mathrm{c}}_{4}\bar{T}^{\mathrm{c}}_{5}]^{1/2} \end{aligned} \tag{12}$$

The $g_\theta(x)$ and $g_\Phi(x)$ are functions of x which are 0 for $x=0$ and 1 for $x=1$, ensuring that for $x=0$ (pure isobutane), $f_x = h_x = 1$, and for $x=1$ (pure isopentane), f_x and h_x reduce to Eq. (8). The simplest g_θ and g_Φ are $g_\theta = x$ and $g_\Phi = x$ and can be any function for which $g=0$ for $x=0$ and $g=1$ for $x=1$. The coefficients k and l in Eq. (12) are available to be adjusted to adjust the locus of the pseudocritical line (and also the true critical line). Points on the critical line were measured at the NBS at several different compositions [11] and these data were used as a guide for the choice of the k and l. The isobutane reference function predicts a critical temperature about two degrees higher than that measured, and k and l were adjusted so that the predicted critical line will be approximately parallel to the measured one (see Fig. 2).

The predicted coexisting phases were determined by finding solutions to the system of nonlinear equations

$$\begin{aligned} \mu_{4\mathrm{l}}(\rho_{\mathrm{l}}, T, x_{4\mathrm{l}}) &= \mu_{4\mathrm{v}}(\rho_{\mathrm{v}}, T, x_{4\mathrm{v}}) \\ \mu_{5\mathrm{l}}(\rho_{\mathrm{l}}, T, x_{5\mathrm{l}}) &= \mu_{5\mathrm{v}}(\rho_{\mathrm{v}}, T, x_{5\mathrm{v}}) \end{aligned} \tag{13}$$

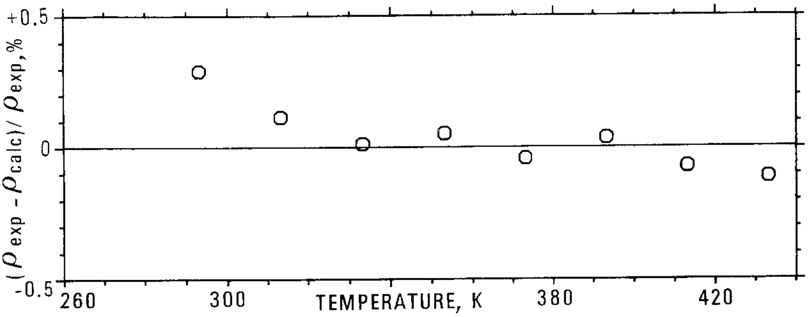

Fig. 2. Differences between saturated liquid densities measured by Young and those predicted by the model, in percentages.

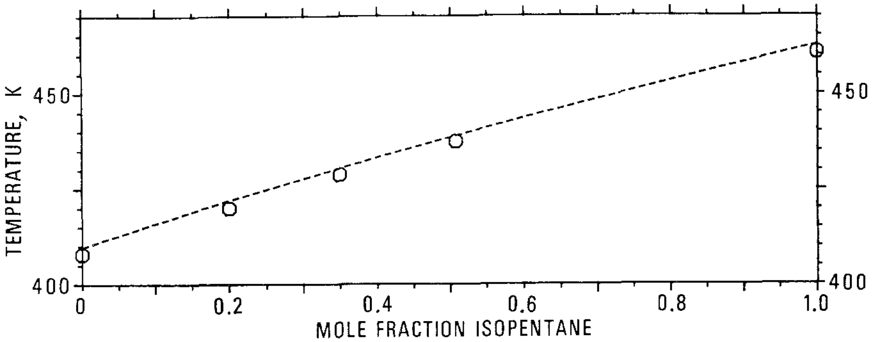

Fig. 3. The critical temperature of isobutane–isopentane mixtures as a function of composition. The measured points are represented by circles and the predicted alues by the dashed line.

where μ represents the chemical potentials of the two components in the two phases (l, liquid; v, vapor). Since $x_{4l} = 1 - x_{5l}$ and $x_{4v} = 1 - x_{5v}$, the solution is completely determined with the specification of any two of the four variables (T, P, x_{5l}, x_{5v}). For the generation of our tables, we specify T or P as desired, and the concentration of either the liquid or the vapor as desired, and with the solution of the system of nonlinear equations, the other two variables are found along with the coexisting densities.

Comparisons of the predicted bubble points and those measured by Morrison [5] are shown in Fig. 3.

5. IMPURITY EFFECTS

Special emphasis is placed in this paper on the estimation of corrections to the predicted values of the thermodynamic properties due to impurities in the components of the mixture. Since a principal area of commercial use of these materials is as a working fluid in power cycles, for which large quantities of materials are required, the cost becomes an important factor. The specifications for commercial grade alkanes allow for up to 5% impurities, principally the other isomers of the purchased material.

In order to make estimations of the impurity effect in a mixture of isobutane and isopentane, we consider the effect of a small concentration of a third substance. Since the major component of the isobutane–isopentane mixtures of commercial interest is the isobutane, we extend the Helmholtz function to describe a mixture of three components, where the third component is *n*-butane. Since the concentration of the *n*-butane is assumed to be small (never more than 5%), we make the following simplifying

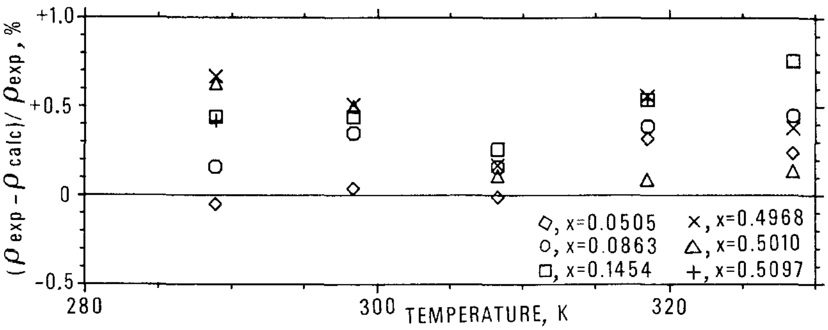

Fig. 4. Density differences in percentages the bubble points of mixtures measured at this laboratory and those predicted by the model.

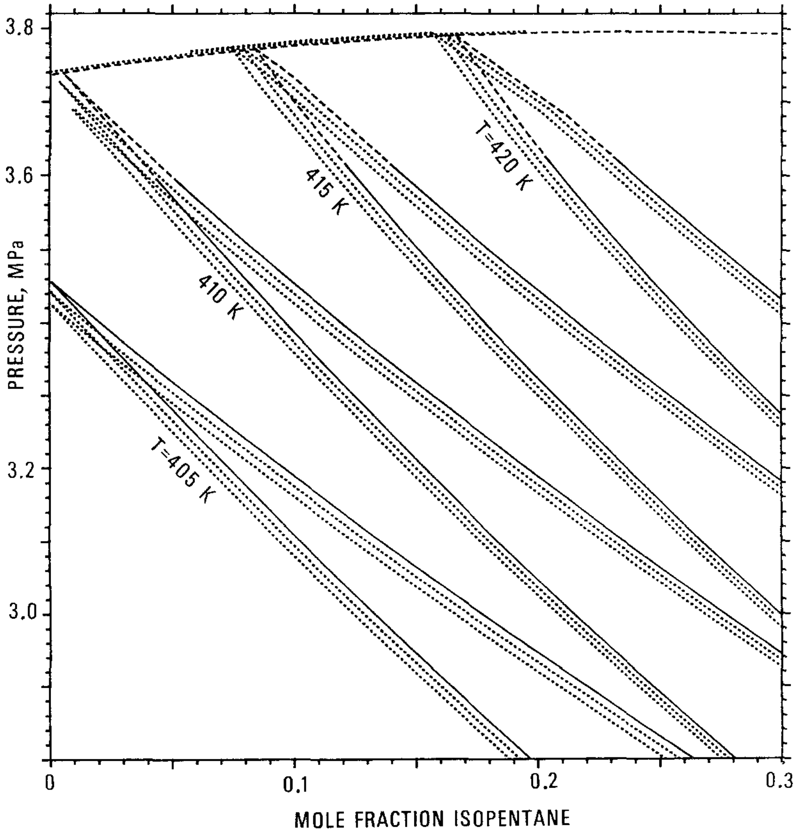

Fig. 5. The dew- and bubble-point pressures of isobutane–isopentane mixtures on isotherms predicted by the model. The dashed line represents presures in the critical region, and the dotted lines represent the same isotherms but where the isobutane contains 2 and 4% of *n*-butane.

assumptions: first, assume the critical line of isobutane–*n*-butane mixtures to be as simple as possible, that is, from the known critical point of *n*-butane (see Table I) to the isobutane critical point as in Eqs. (11) and (12) with $k = l = 1$; and second, assume that the vapor pressures and coexisting densities of *n*-butane need not be as accurately mapped onto isobutane, that is, the θ and Φ of Eqs. (8) both be unity, and that the $g_\theta(x)$ and $g_\Phi(x)$ of Eq. (10) both be equal to x. For the ideal-gas properties of *n*-butane, we use the function constructed by Haynes and Goodwin [12] for use in their computer program for generating the thermodynamic properties of *n*-butane. The extension of the Helmholtz function for the two-component mixture to one for multicomponents is straightforward and follows well-established guidelines [6].

The determination of coexisting phases also follows as an extension to the methods described in Fig. 4, where Eq. (4.5) now becomes a system of three nonlinear equations in three unknowns with the specification of T or P as desired and of the concentrations of all species on the liquid or vapor side as desired. In Fig. 5, the dew and bubble points along isotherms are shown as pressure vs concentration. The solid lines represent the predicted values for mixtures containing only isobutane and isopentane, with the dashed portions of the lines representing values in the critical region. The dotted lines represent the same dew and bubble curve but where the isobutane portion of the mixture contains 2 and 4% *n*-butane.

6. RESULTS

Figures 1 through 4 show comparisons of the values of the experimental measurements used in the adjustments of the various parameters with the values predicted from the mixture Helmholtz function. Figure 1 shows the measured vapor pressures of pure isopentane [10], and Fig. 2 the saturated liquid densities of pure isopentane [9]. These measurements were used for the determination of the parameters in the "shape factors" θ and Φ [Eq. (9)]. Figure 3 shows the measured critical points of the pure isobutane, pure isopentane, and mixtures of several compositions used for the determination of the parameters k and l in the "combining" function (12). Note that the predicted critical line is at about 2K above the measured values at all points. This was intentionally done since the analytic Helmholtz function predicts a critical temperature somewhat higher than the measured value for pure isobutane, and it was considered to be desirable to maintain the proper slope of the critical line rather than the actual values, which are better predicted through the scaling laws [11]. The measured bubble points for several compositions at several temperatures [5] are compared with the predicted values in Fig. 4. These were used in the determination of the functions g_θ and g_Φ of Eq. (10).

In order to estimate the reliability of these predictions we considered the estimated reliability of the isobutane reference function, where the comparisons with the large body of experimental data available show agreement generally to within 0.1 to 0.15% in density over the specified range of validity, and the agreements with the smaller body of data available for pure isopentane within 0.3% for vapor pressures, 0.2% for the saturated liquid densities, and 1.5% for the saturated vapor densities. Also considered were the measurements for mixtures made at this laboratory: an average difference for the bubble-point pressures of about 0.5% and bubble-point densities of about 0.7%. On the basis of these considerations we estimate the uncertainty of predicted vapor pressures to be about 0.3% for pure isopentane, increasing to about 0.8% for the 50% mixture, then decreasing to the stated uncertainties for pure isobutane for low concentrations of isopentane. We expect the range of validity for the surface to be about the same, in reduced units, as that of the isobutane reference function.

7. CONCLUSION

The resulting Helmholtz function describing the thermodynamic surface of the mixture will be a useful tool for the prediction of equilibrium properties for a mixture of importance and interest for geothermal power cycles. Interest is also growing in power recovery from waste heat sources. These mixtures are well suited for power cycles for these uses. The accuracies of these predictions are considerably improved over those of methods of prediction previously available. We provide additional insight into the effects of impurities in the mixture. This mixture Helmholtz function adapts well to evaluation by computer, including the calculation of impurity effects. Computer routines developed in conjunction with this project for the production of charts of properties, a task previously usually done laboriously by hand, are also useful for use for charts of properties for any substance which can be represented with an analytic Helmholtz function.

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