Table I. Properties of Saturated Solutions of Magnesium Chloride in *n*-Propanol–Water

Mole Fraction of *n*-Propanol (Salt-Free Basis)	Solubility, Grams of $MgCl_2 \cdot 6H_2O$ 100 Ml. Salt-Free Solvent (25° C.)	Density, Grams/Cm.^{3} (25° C.)	Refractive Index, $n_D^{25°}$
0.000	329.1	1.3343	1.4318[a]
0.074	263.9	1.2987	1.4318
0.138	211.3	1.2649	1.4302
0.265	150.6	1.1998	1.4266
0.360	120.7	1.1586	1.4243
0.491	90.46	1.1046	1.4210
0.577	73.02	1.0692	1.4187
0.685	58.13	1.0339	1.4162
0.762	53.17	1.0144	1.4151
0.821	46.98	0.9967	1.4135
0.922	42.08	0.9779	1.4130
1.000	39.79	0.9692	1.4129

[a] This figure is the refractive index of water (no salt). Because there is no salt in this case, this point does not plot on the same smooth curve as the rest of the data.

The flasks were sealed and thermostated for at least 24 hours and, in some cases, 2 to 3 days in a constant temperature bath (Sargent S-84805) which was maintained at 25 ± 0.01° C. The samples were frequently stirred. Samples of the saturated solutions were carefully withdrawn so as not to remove any of the precipitated salt. Two determinations were made at each concentration, the results being averaged.

Densities were determined by means of Weld-type pycnometer bottles. Refractive indices ($n_D^{25°}$) were determined by a Bausch and Lomb refractometer (BL 7762). All these determinations were conducted isothermally at 25 ± 0.01° C.

The salt solubilities were determined by titrating for the chloride according to Mohr's procedure. The salt is reported as $MgCl_2 \cdot 6H_2O$, since this is the stable form at 25° C. The data obtained are presented in Table I and plotted as smooth curves.

RECEIVED for review May 11, 1964. Accepted November 19, 1964.

Thermodynamic Properties of the Helium-Nitrogen System

DWIGHT B. PFENNING[1] and FRANK B. CANFIELD
School of Chemical Engineering and Material Science, University of Oklahoma, Norman, Okla.

RIKI KOBAYASHI
Department of Chemical Engineering, Rice University, Houston, Tex.

Thermodynamic properties of helium-nitrogen mixtures were calculated for eight compositions at 10° increments from 240° through 560° R. and over the pressure range from 14.7 through 7500 p.s.i.a. These properties included specific volume, enthalpy, entropy, internal energy, fugacity coefficient, Joule-Thomson coefficient, enthalpy of mixing, excess entropy of mixing, and isobaric specific heat. Sets of coefficients of an equation of state are presented for eight compositions.

THERMODYNAMIC properties of gases, as a function of temperature and pressure, can be determined from direct calorimetric measurements, from compressibility data plus ideal-gas specific heat data, or from Joule-Thomson coefficient data plus ideal-gas specific heat data. Joule-Thomson coefficients have been reported for helium-nitrogen mixtures by Roebuck (*18*) from −125° to 250° C. up to 200 atm., and work is in progress at the University of Michigan (*10*) on direct calorimetric measurements. The present paper reports the thermodynamic properties of helium-nitrogen mixtures from 240° to 560° R. at 14.7 to 7500 p.s.i.a. as calculated from compressibility data and ideal-gas specific heat data.

The results presented in this paper will be useful in future attempts to predict the thermodynamic properties of mixtures by the theory of corresponding states. A more immediate and practical application of the results will be in the design of efficient equipment for purifying crude helium.

The thermodynamic properties reported here were calculated by fitting experimental compressibility data to an especially developed equation of state. The least squares fit was performed using an orthogonalization scheme. Compressibility data for the helium-nitrogen system have been reported by many investigators (*3, 8, 9, 13, 14, 16, 20*); however, to restrict the upper temperature to 100° F. and because high pressure data were not available above 100° F., the data from three sources (*3, 8, 13*) were used in evaluating the coefficients of the equation of state.

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[1] Present address: Bell Telephone Laboratories, Murray Hill, N. J.

EQUATION OF STATE

Initially, it was expected that the Benedict-Webb-Rubin equation of state (*5*) would be used to represent the compressibility data, but it soon became evident that this equation would not fit the nitrogen data within twice the estimated experimental error of the data. The modification suggested by Bloomer and Rao (*2*) reduced the RMS error in the compressibility factor from 0.0060 to 0.0033 for a particular set of nitrogen data, but this reduction was not considered sufficient. The final equation used in fitting the compressibility data was:

$$Z = 1 + F_1(T)\rho + F_2(T)\rho^2 + F_3(T)\rho^2 (1 + \gamma\rho^2)e^{-\gamma\rho^2} + B_4\rho^5/RT \qquad (1)$$

$$F_i(T) = A_i + B_i/RT + C_i/RT^3$$

The details concerning the development of this equation are presented by Pfenning (*17*). The RMS error in the compressibility factor for the final equation was 0.0021 for the same set of data as above. The set of data used in this preliminary evaluation differed from the set used in the final evaluation of constants in Equation 1. As a result, the RMS error for pure nitrogen given in Table II, 0.00169, differs from the value given here.

ORTHOGONALIZATION CURVE FITTING

The objective of the curve-fitting scheme was to produce a set of coefficients, d_k, in the equation:

$$f = \sum_{k=1}^{m} d_k f_k$$

such that

$$E_m = \sum_{i=1}^{n} [f_i - \sum_{k=1}^{m} d_k f_k(x_i)]^2$$

was a minimum. The scheme can be divided into two parts. First, a set of orthogonal functions can be constructed from the linearly independent functions f_k using the Schmidt algorithm (*15*). Second, this set of orthogonal functions is used in a Fourier expansion to approximate the function to be fitted. The Fourier expansion has the least squares property and the coefficients, d_k, can be calculated from the Fourier coefficients.

As a result of the calculations, the sums of the squares of the deviations are computed for each value of k from 1 to m. Thus, in order to determine the reduction in the error resulting from the addition of a particular function, f_k, the function can be made the terminal function in the sum,

$$\sum_{k=1}^{m} d_k f_k$$

This method also provides a scheme for controlling the rounding error. Rounding error is not so much a characteristic of the particular method, but is an inherent difficulty in all large scale least squares problems. A process for reorthogonalization (*6*) was used to keep the rounding error under control. When the original functions, f_k, are far from orthogonal, serious rounding error can develop. When this error becomes larger than a prescribed value, a new set of orthogonal functions can be computed from the first orthogonal set. It was found that a maximum of two orthogonalizations were necessary to control the rounding error. A detailed account of the orthogonalization–curve-fitting procedure is given by Pfenning (*17*).

DATA

The data sources of Canfield (*3*), Kramer and Miller (*8*), Miller, Brandt, and Stroud (*13*) were used in this study. The other sources were eliminated in order to restrict the upper temperature to 100° F., and because data at pressures above 100 atm. were not available above 100° F.

Since the results of Canfield constituted the major portion of the data and were given at compositions of 1.000, 0.8768, 0.7523, 0.6041, 0.4456, 0.3006, 0.1578, and 0.0000 mole fraction of helium, the data from the other two sources were constructed at these compositions. For each of the eight compositions, Canfield reported experimental compressibility factors for approximately 25 pressures for each of the six isotherms: 0°, −50°, −90°, −115°, −130°, and −140° C. The corresponding pressure range extended to 500 atm.

The second and third virial coefficients (pure gas and interaction) given by Kramer and Miller permitted calculation of the compressibility factors at 30° C. up to 100 atm. Eleven pressures were selected, and the compressibility factors at each of the compositions were computed.

Miller, Brandt, and Stroud present experimental compressibility factors and a table of compressibility factors smoothed with respect to pressure and composition at 70° F. up to 4000 p.s.i.a. The pure component data used in this study were the experimental values. The mixture data used in this study were selected at eight pressures which corresponded approximately to the pressures at which the experimental data were recorded. The compressibility factors were fitted at each pressure with a third order polynomial as a function of composition at constant pressure and temperature. Once the constants of the polynomials were evaluated, the compressibility factors were computed at the selected compositions.

EVALUATION OF CONSTANTS

A total of 1373 data points were used to evaluate the 11 constants of the equation of state at each of the eight compositions of helium and nitrogen. Since the equation of state contains an exponential term, the coefficient γ was evaluated by making the computation for several values of γ and selecting the value that yielded the minimum RMS error. Table I lists the coefficients that were computed with the curve-fitting scheme at each of the eight compositions. The summary of the errors is presented in Table II which gives the RMS error, average deviation, and the number of data points for each composition. The maximum deviations occurred in nitrogen and nitrogen-rich mixtures. This can be accounted for by the fact that nitrogen is near its critical region for the ranges of temperature and pressure used in this study.

COMPUTATION OF THERMODYNAMIC PROPERTIES

Once the constants in Equation 1 were evaluated for a particular mixture, the computation of the thermodynamic properties as a function of temperature and pressure was carried out by using these constants and the ideal-gas specific heat data for the pure components. The ideal-gas specific heat for helium at constant pressure was taken to be 2.5*R* as given by Keesom (*7*). The specific heat of nitrogen was calculated from the equation by Strobridge (*19*) from the results of Goff and Gratch (*4*),

$$C^*_{PN} = m_1 + m_2 T + m_3 T^2 + m_4 T^3 + m_5 T^4 \qquad (2)$$

where

$$m_1 = 2.9109996 \times 10$$
$$m_2 = -8.0820995 \times 10^{-4}$$
$$m_3 = 8.6142037 \times 10^{-6}$$
$$m_4 = -3.6893228 \times 10^{-8}$$
$$m_5 = 5.6750880 \times 10^{-11}$$

Table I. Coefficients in Equation 1 for Helium, Nitrogen, and Six Helium-Nitrogen Mixtures

These coefficients require that the units for ρ = gram mole/cc., T = ° K., and R = cc. atm./gram mole ° K.

	X_{He} (Mole Fraction Helium)			
	1.000	0.8768	0.7523	0.6041
$A_1 \times 10^{-1}$	0.972057	1.438669	1.827928	2.490412
$B_1 \times 10^{-5}$	0.563683	−0.132340	−0.843268	−2.605482
$C_1 \times 10^{-8}$	−5.588630	−4.559279	−8.617306	−8.626535
$A_2 \times 10^{-2}$	1.648897	1.940421	3.455692	7.005985
$B_2 \times 10^{-6}$	−0.462438	1.195971	0.905408	−1.173606
$C_2 \times 10^{-10}$	1.306920	0.125096	1.060556	3.747064
$A_3 \times 10^{-2}$	−0.260205	−0.055637	−0.435039	−3.626004
$B_3 \times 10^{-6}$	0.076419	−0.514630	−0.653008	4.627467
$C_3 \times 10^{-10}$	0.033986	0.357270	1.028447	−2.916348
$B_4 \times 10^{-10}$	0.567236	1.867400	4.379248	9.093249
$\gamma \times 10^{-3}$	4.00	5.50	6.25	5.00

	X_{He} (Mole Fraction Helium)			
	0.4456	0.3006	0.1578	0.0000
$A_1 \times 10^{-1}$	2.891379	3.418862	3.931421	4.400834
$B_1 \times 10^{-6}$	−0.414032	−0.628594	−0.870711	−1.149074
$C_1 \times 10^{-9}$	−2.066545	−2.994597	−4.189192	−6.104264
$A_2 \times 10^{-3}$	1.039594	1.935755	2.598281	3.075124
$B_2 \times 10^{-7}$	−0.017450	−0.998712	−1.776919	−2.110392
$C_2 \times 10^{-10}$	3.317887	6.556652	4.672255	4.372946
$A_3 \times 10^{-3}$	−0.282771	−0.888726	−1.148098	−0.805274
$B_3 \times 10^{-7}$	−0.065442	0.759829	1.112198	−0.014038
$C_3 \times 10^{-11}$	0.564773	0.971972	2.398543	5.307502
$B_4 \times 10^{-12}$	0.185911	0.444209	0.979728	1.810472
$\gamma \times 10^{-3}$	4.00	3.50	4.00	5.65

Table II. Analysis of Differences between the Experimental Compressibility Factors and Those Calculated from Equation 1

Mole Fraction Helium, X_{He}	RMS Error[a]	Average Deviation[b]	Number of Data Points, n
1.000	0.43×10^{-3}	2.9×10^{-4}	191
0.8768	0.46×10^{-3}	3.1×10^{-4}	164
0.7523	0.59×10^{-3}	3.9×10^{-4}	173
0.6041	0.86×10^{-3}	5.4×10^{-4}	158
0.4456	0.75×10^{-3}	5.1×10^{-4}	170
0.3006	0.89×10^{-3}	5.9×10^{-4}	173
0.1578	1.24×10^{-3}	7.0×10^{-4}	160
0.0000	1.69×10^{-3}	9.1×10^{-4}	184

[a] $\left[\sum_{i=1}^{n} (Z_e - Z_c)_i^2/n\right]^{1/2}$. [b] $\sum_{i=1}^{n} |Z_e - Z_c|_i/n$.

for $C^*_{p_{\mathrm{N}}}$ in joules/gram mole ° K. and T in ° K.

The ideal-gas specific heat for a mixture was then taken to be,

$$C^*_{p_m} = X_{\mathrm{He}}\, C^*_{p_{\mathrm{He}}} + X_{\mathrm{N}}\, C^*_{p_{\mathrm{N}}} \tag{3}$$

The following equations, which were developed from the usual thermodynamic relations, were used in calculating the thermodynamic properties:

$$(H - H^*)_T = P/\rho - RT + Q_1(T)\rho + Q_2(T)\rho^2/2 - Q_3(T)I + B_4\rho^5/5 \tag{4}$$

$$(S_p - S_p^*)_T = R \ln Z - G_1(T)\rho - G_2(T)\rho^2/2 + G_3(T)I \tag{5}$$

$$C_p - C_p^* = T\,K^2/\rho^2\,L - R - J \tag{6}$$

$$H_m = H_R + \int_{T_R}^{T} C_p^*\,\mathrm{d}T + (H - H^*)_T \tag{7}$$

$$S_m = S_R + \int_{T_R}^{T} (C_p^*/T)\,\mathrm{d}T + (S_p - S_p^*)_T - R\ln(P/P_R) - R(X_{\mathrm{He}} \ln X_{\mathrm{He}} + X_{\mathrm{N}} \ln X_{\mathrm{N}}) \tag{8}$$

$$U = H - PV \tag{9}$$

$$C_p = (C_p - C_p^*) + C_p^* \tag{10}$$

$$\mu = (TK/\rho^2\,L - 1/\rho)/C_p \tag{11}$$

$$\ln f/P = (H - H^*)_T/RT - (S_p - S_p^*)_T/R \tag{12}$$

$$H^E = H_m - X_{\mathrm{He}}H_{\mathrm{He}} - X_{\mathrm{N}}H_{\mathrm{N}} \tag{13}$$

$$S^E = S_m - X_{\mathrm{He}}S_{\mathrm{He}} - X_{\mathrm{N}}S_{\mathrm{N}} + R(X_{\mathrm{He}} \ln X_{\mathrm{He}} + X_{\mathrm{N}} \ln X_{\mathrm{N}}) \tag{14}$$

where

$$Q_i(T) = B_i + 3C_i/T^2$$

$$G_i(T) = A_iR - 2C_i/T^3$$

$$I = (\rho^2/2 + 1/\gamma)e^{-\gamma\rho^2} - 1/\gamma$$

$$J = (6C_1\rho + 3C_2\rho^2 - 6C_3I)/T^3$$

$$K = \rho R + G_i(T)\rho^2 + G_2(T)\rho^3 + G_3(T)\rho^3(1 + \gamma\rho^2)e^{-\gamma\rho^2}$$

$$L = RT + 2RT\,F_1(T)\rho + 3RT\,F_2(T)\rho^2 + RT\,F_3(T)\rho^2(3 + 3\gamma\rho^2 - 2\gamma^2\rho^4)e^{-\gamma\rho^2} + 6B_4\rho^5$$

The reference states were selected as H_R = 50 B.t.u./lb. and S_R = 3 B.t.u./lb. ° R. for both helium and nitrogen in the ideal-gaseous state at 1 atm. and 139.311° R. The reference values were chosen so that the enthalpy and entropy values would be positive numbers.

RESULTS AND DISCUSSION

A table of specific volume, enthalpy, entropy, internal energy, fugacity, Joule-Thomson coefficient, enthalpy of mixing, excess entropy of mixing, and isobaric specific heat was computed at 26 pressures from 14.7 to 7500 p.s.i.a. and is available from the American Documentation Institute (*1*). The temperature range for the table extends from

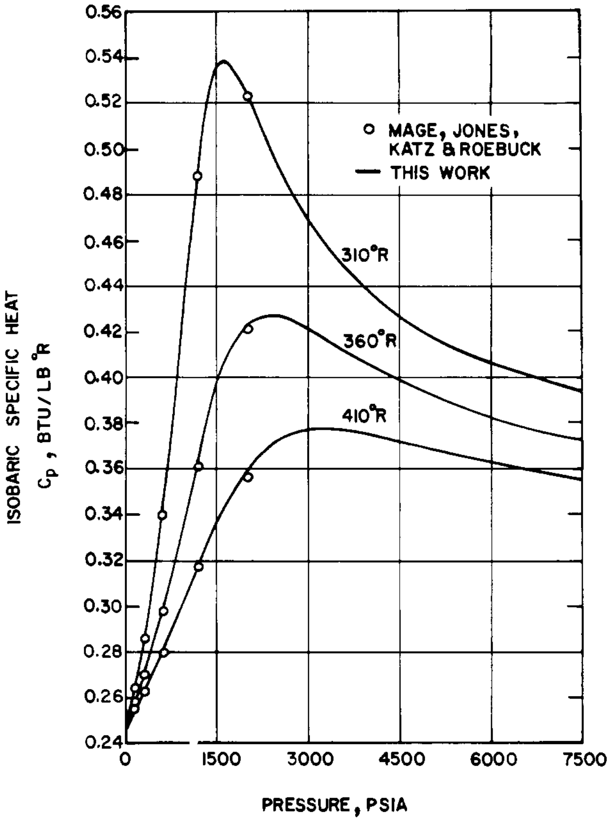

Figure 1. Comparison of C_p for nitrogen

240° to 560° R. in 10° F. increments for each of the eight compositions. A similar table including only specific volume, enthalpy, and entropy is presented by Pfenning (*17*). In the computation of these tables, the experimental data were extrapolated by means of Equation 1 from 4000 to 7500 p.s.i.a. in the interval from 32° to 70° F., from 1500 to 7500 p.s.i.a. in the interval from 70° to 86° F., and from 0 to 7500 p.s.i.a. in the interval from 86° to 100° F.

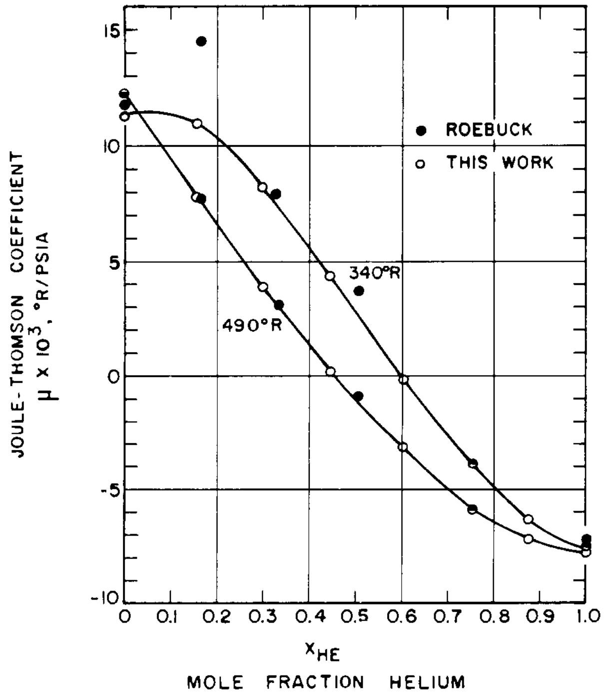

Figure 2. Comparison of Joule-Thomson coefficients at 2650 p.s.i.a.

For convenience in engineering calculations, the results for the extensive properties are given on a per unit mass basis. On the other hand, the compositions of the mixtures are given on a mole fraction basis to emphasize the uniform spacing with respect to composition and to encourage interpolation with respect to mole fraction rather than mass fraction. Consequently, if the results given in any of the above sources are to be further manipulated, care must be taken to assure consistency between mass or mole fraction and a basis per unit mass or per mole, respectively.

The results of Mann (*12*) and Strobridge (*19*) for helium and nitrogen, respectively, were the primary sources used for comparison with the present calculations. Since the reference states for the different investigations do not coincide, a comparison was made on the enthalpy and entropy change with pressure at constant temperature. For both helium and nitrogen, all three sources present enthalpy and entropy at 14.7 and 900 p.s.i.a. at 10° increments from 240° to 540° F. Therefore, it was possible to make exact comparisons in the values of enthalpy at 900 p.s.i.a. minus enthalpy at 14.7 p.s.i.a. for each temperature. A similar comparison was possible for entropy. The average absolute difference between the results of Mann and Strobridge and the present results for the enthalpy change was 5.5% for helium and 1.2% for nitrogen. A similar comparison for the entropy change showed a difference of 0.21% for helium and 0.14% for nitrogen. A direct comparison for specific volume was made at 900 p.s.i.a. for each 10° increment from 240° to 540° R. The average absolute difference amounted to 0.64% for helium and 0.10% for nitrogen. In view of the fact that the equation of state and all of the experimental compressibility data used in this study were different from those used by Mann for helium and by Strobridge for nitrogen, the above comparisons are considered to be quite satisfactory.

The experimental specific heat data of Mage, Jones, Katz, and Roebuck (*11*) permitted the comparison in Figure 1. A maximum deviation of less than 1% was observed between this work and the experimental values presented by Mage and coworkers. In Figure 2, a comparison between the present Joule-Thomson coefficients and those given by Roebuck (*18*) is presented. Except for one point, the maximum deviation was 0.0011° R./p.s.i.a. for the 340° R. isotherm. The maximum deviation for the 490° R. isotherm was 0.0003° R./p.s.i.a.

ACKNOWLEDGMENT

The authors acknowledge the assistance of the Bureau of Mines and the University of Oklahoma Computer Laboratory in carrying out this work. The support of this work by the National Science Foundation under Grants Nos. GP-135 to the University of Oklahoma and G-15360 to Rice University is gratefully acknowledged. This work was also supported by the Helium Research Center, Bureau of Mines, U. S. Department of Interior, Amarillo, Texas.

NOMENCLATURE

A_i = equation of state constant, $i = 1 \rightarrow 3$
B_i = equation of state constant, $i = 1 \rightarrow 4$
C_i = equation of state constant, $i = 1 \rightarrow 3$
C_p = isobaric specific heat
d_k = equation constant, $k = 1 \rightarrow m$
E_m = sum of the squares of the deviations
f = function to be approximated; also fugacity in Equation 12
f_k = linearly independent functions used to approximate f
H = specific enthalpy
m = number of linearly independent functions used to approximate f
n = number of data points
P = absolute pressure

R = gas constant, e.g., 82.0574 cc. atm./gram mole ° K.
RMS = root mean square
S = specific entropy
T = absolute temperature, 0° C. = 273.15° K.
U = specific internal energy
x_i = independent variable
X_i = mole fraction of component i
Z = compressibility factor, $P/\rho RT$

Greek Letters

γ = equation of state constant
μ = Joule-Thomson coefficient
ρ = density

Superscripts

$*$ = ideal-gas state
E = excess function

Subscripts

c = calculated
e = experimental
$_{\mathrm{He}}$ = helium
$_{\mathrm{N}}$ = nitrogen
m = mixture
p = constant pressure
R = reference state
T = constant temperature

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RECEIVED for review May 7, 1964. Accepted October 30, 1964.

Liquid-Vapor Equilibrium and Heats of Vaporization of Allyl Alcohol–Water Mixtures

ROY W. GRABNER and C. W. CLUMP
Lehigh University, Bethlehem, Pa.

Vapor-liquid equilibrium and isobaric heats of vaporization at 760 mm. of Hg pressure are presented for the allyl alcohol–water system. Activity coefficients and heats of vaporization for the allyl alcohol–water system are compared with other three-carbon alcohol–water solutions. Refractive index–concentration data have also been determined for the allyl alcohol–water system.

EXPERIMENTAL DATA on liquid-vapor equilibrium and heats of vaporization are generally scattered through the literature and are sometimes incomplete. Thus it would be useful to have a means of extending the available data to other systems having similar components. The vapor-liquid equilibrium and latent heat of vaporization data presented here are part of a program aimed at supplying pertinent thermodynamic data to reveal the influence of structural changes of alcohol molecules on the phase equilibrium behavior and on the latent heat of vaporization.

An investigation of the literature indicated a few reported vapor-liquid equilibria data for the allyl alcohol–water