$R$ = 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

$\gamma$ = equation of state constant
$\mu$ = Joule-Thomson coefficient
$\rho$ = 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.

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

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**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 system (*4, 5, 10*), but data for isobaric latent heats of vaporization for various compositions of allyl alcohol were not found.

## EXPERIMENTAL

**Materials.** Commercial grade allyl alcohol having impurities primarily of water, diallyl ether, and isopropyl alcohol was purified by distillation. All of the impurities form low boiling azeotropes with allyl alcohol and should be removable by distillation. A small laboratory fractionating column was charged with the commercial grade alcohol and operated at total reflux until a constant condensate temperature was maintained. Twenty-milliliter samples of condensate were periodically removed until no temperature change was noticed after withdrawal of the condensate sample. A heart cut was taken from the remaining liquid. The normal boiling point of the purified allyl alcohol was 96.92° C., and the refractive index at 25° C. was 1.4127. These values compare with 96.94° C. and 1.4134, respectively, as reported in the literature (*10*).

Distilled water was used directly without additional purification.

**Analysis.** The equilibrium liquid and condensed vapor samples were analyzed by methods which were dependent on the composition of the samples. Alcohol concentrations up to 0.40 mole fraction were analyzed by refractive index measurement. A tabulation of refractive index as a function of concentration at 31.1° C. is given in Table I. Refractive index readings could be read to 0.0005 mole fraction at low alcohol concentrations and to 0.0015 mole fraction at higher concentrations. Above 0.40 mole fraction allyl alcohol, the refractive index did not change sufficiently with composition to permit accurate analysis. At these higher alcohol concentrations, the samples were analyzed for water content by titration with Karl Fischer Reagent using a dead stop end point detection (*7*). This method gave concentrations to 0.0005 mole fraction water.

**Apparatus and Procedure.** The experimental apparatus used to measure simultaneously liquid-vapor equilibrium and isobaric heats of vaporization has been previously described (*1*). The apparatus was adaptable to the present needs without any major modifications.

**Results.** Vapor and liquid compositions, equilibrium temperatures, and activity coefficients at one atmosphere for the allyl alcohol-water system are presented in Table II. Activity coefficients were calculated from the defining equations:

$$\gamma_1 = y_1\pi / x_1 P_1 \text{ and } \gamma_2 = y_2\pi / P_2 x_2$$

These equations assume that the vapors form an ideal solution, and the ratio of the fugacity of the pure component in the vapor phase to the liquid phase equals the ratio of the total pressure $\pi$, to the pure component vapor pressure, at the equilibrium temperature. Vapor pressure used in calculating the activity coefficients were obtained by interpolating International Critical Table values for water and an average value calculated from the vapor pressure equations of Shell Chemical (*10*) and Hands and Norman (*4*) for allyl alcohol.

The liquid-vapor equilibrium data are plotted as a temperature-composition diagram in Figure 1, where the data from this investigation are compared with other works (*4, 5, 10*). These data were correlated using the van Laar equation. This equation was used with constants of $A$ = 0.439 and $B$ = 0.964 to recalculate temperature-composition equilibrium values to smooth the data, shown in Figure 1 as the solid curve. The solid line through the saturated

Table I. Refractive Indices of Mixtures of Allyl Alcohol–Water at 31.1°C.

| Mole Fraction, Allyl Alcohol | Refractive Index | Mole Fraction, Allyl Alcohol | Refractive Index |
|---|---|---|---|
| 0.0071 | 1.3338 | 0.2151 | 1.3771 |
| 0.0428 | 1.3441 | 0.2264 | 1.3781 |
| 0.0533 | 1.3470 | 0.2352 | 1.3794 |
| 0.0714 | 1.3530 | 0.2437 | 1.3803 |
| 0.0929 | 1.3575 | 0.2584 | 1.3816 |
| 0.1015 | 1.3603 | 0.2798 | 1.3824 |
| 0.1235 | 1.3636 | 0.2851 | 1.3837 |
| 0.1361 | 1.3664 | 0.2978 | 1.3850 |
| 0.1484 | 1.3683 | 0.3087 | 1.3869 |
| 0.1637 | 1.3705 | 0.3288 | 1.3874 |
| 0.1800 | 1.3728 | 0.3574 | 1.3898 |
| 0.1882 | 1.3739 | 0.3786 | 1.3909 |
| 0.1914 | 1.3743 | 0.3979 | 1.3919 |
| 0.1989 | 1.3749 | 0.4327 | 1.3939 |

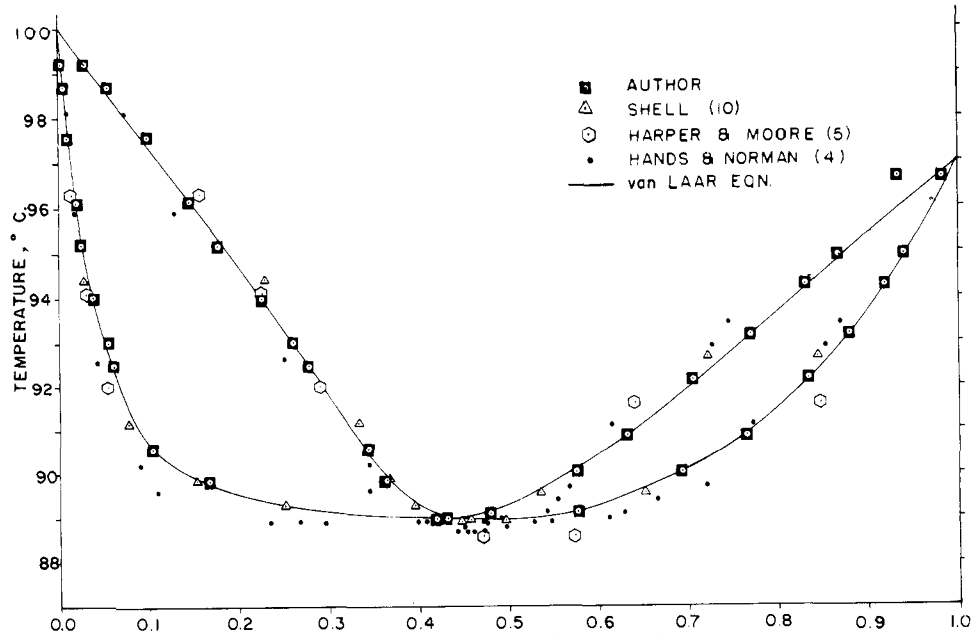

Figure 1. Temperature-composition diagram for the allyl alcohol–water system

Table II. Vapor-Liquid Equilibrium Data for Allyl Alcohol–Water at One Atmosphere Pressure

| Temp., °C. | Mole Fraction, Allyl Alcohol | | Activity Coefficient | |
|---|---|---|---|---|
| | Liquid | Vapor | Water, $\gamma_1$ | Allyl alcohol, $\gamma_2$ |
| 100.00 | 0.0000 | 0.0000 | 1.000 | ... |
| 99.18 | 0.0025 | 0.0309 | 1.001 | 11.379 |
| 98.68 | 0.0049 | 0.0554 | 0.995 | 10.598 |
| 97.54 | 0.0113 | 0.0994 | 1.002 | 8.593 |
| 96.14 | 0.0193 | 0.1446 | 1.004 | 7.715 |
| 95.18 | 0.0267 | 0.1780 | 1.006 | 7.102 |
| 94.04 | 0.0397 | 0.2260 | 1.002 | 6.330 |
| 93.06 | 0.0556 | 0.2634 | 1.007 | 5.474 |
| 92.48 | 0.0622 | 0.2793 | 1.012 | 5.291 |
| 90.58 | 0.1058 | 0.3456 | 1.036 | 4.140 |
| 89.96 | 0.1680 | 0.3658 | 1.109 | 2.837 |
| 89.14 | 0.4216 | 0.4336 | 1.472 | 1.385 |
| 89.06 | 0.5517 | 0.4750 | 1.757 | 1.158 |
| 90.04 | 0.6921 | 0.5747 | 1.994 | 1.074 |
| 90.88 | 0.7658 | 0.6338 | 2.189 | 1.038 |
| 92.18 | 0.8340 | 0.7058 | 2.363 | 1.010 |
| 93.16 | 0.8813 | 0.7690 | 2.498 | 1.002 |
| 94.96 | 0.9402 | 0.8696 | 2.632 | 0.995 |
| 96.58 | 0.9824 | 0.9596 | 2.599 | 0.989 |

liquid and saturated vapor data of this work deviates from the data of other investigators by a maximum of 0.8° C. and 0.9° C., respectively. However, the data of Harper and Moore were obtained at a pressure of 752 mm. of Hg, and Hands and Norman obtained their data at pressures of approximately one atmosphere, and then applied correction to the saturation temperatures only.

A thermodynamic check on the consistency of the liquid-vapor equilibrium data of this work was made using the criterion of Redlich and Kister (*9*). The positive and negative areas of the curves, representing the ratio of activity coefficients as a function of mole fraction allyl alcohol in the liquid phase, differed by about 2%. This is sufficiently good agreement. Although the Redlich-Kister criterion is valid only at constant temperature, the temperature range of 11° C. encountered in this system is small enough to consider the requirement of isothermal conditions nearly valid.

The experimental heats of vaporization for allyl alcohol-water are tabulated as a function of composition in Table III. There are no available data with which to make a comparison.

Figure 2 shows the activity coefficient–composition relationship for the three-carbon alcohol–water systems. Figure 3 shows the heats of vaporization for the same systems.

Table III. Heats of Vaporization, Allyl Alcohol–Water at One Atmosphere Pressure

| Mole Fraction, Allyl Alcohol | Heat of Vaporization, $\Delta H^v$ (Cal./G.) | Mole Fraction, Allyl Alcohol | Heat of Vaporization, $\Delta H^v$ (Cal./G.) |
|---|---|---|---|
| 0.0000 | 539.03 | 0.3658 | 291.23 |
| 0.0000 | 540.69 | 0.4336 | 266.38 |
| 0.0309 | 523.09 | 0.4750 | 252.54 |
| 0.0554 | 491.47 | 0.5747 | 232.26 |
| 0.0994 | 445.34 | 0.6338 | 218.06 |
| 0.1446 | 415.44 | 0.7058 | 200.90 |
| 0.1780 | 391.83 | 0.7690 | 194.14 |
| 0.2260 | 363.88 | 0.8303 | 186.45 |
| 0.2634 | 333.62 | 0.8696 | 183.05 |
| 0.2793 | 333.39 | 0.9596 | 169.54 |
| 0.3456 | 295.90 | | |

The comparison of the activity coefficients for the alcohol solutions at equilibrium are directly related to changes in structure and molecular arrangement. These changes in molecular structure result in changes in the intermolecular forces, and hence influence the magnitude of the deviations of the solution from ideal behavior. Thus, the introduction of a double bond in a normal alcohol molecule is characterized by a significant decrease in the deviations from ideal solution behavior as compared with the normal alcohol-water solution. A branched alcohol, however, shows only a slight decrease in the deviations from ideal behavior. It might be argued that since these three-carbon alcohol-water systems do not exhibit identical temperature-composition behavior, the differences in activity coefficients is attributable to temperature effects on activity coefficients. This temperature dependency of the activity coefficient is given by

$$\left[\frac{\partial \ln\gamma_i}{\partial T}\right]_{\pi,\, x_i} = \frac{H_i - \bar{H}_i}{RT^2}$$

In these alcohol-water systems only a 15° C. temperature is encountered, so that a large enthalpy difference would be necessary to account for the difference in activity coefficients. Since the largest temperature differences are at the dilute water concentrations, one would not expect large

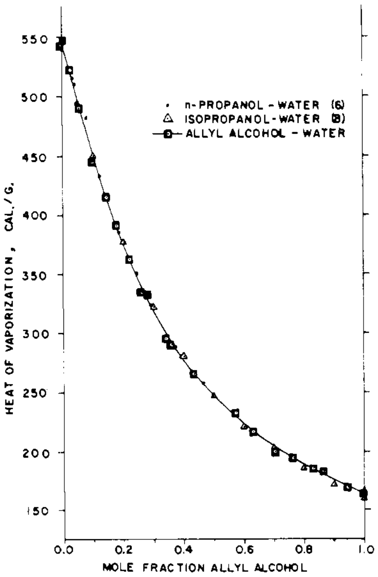

Figure 2. Activity coefficient–composition relationship for three-carbon alcohol–water systems

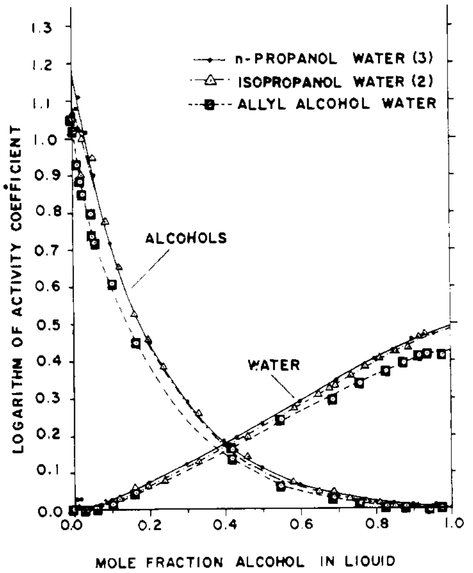

Figure 3. Heats of vaporization–composition relationship for three-carbon alcohol–water systems

enthalpy differences in this region. Therefore, the differences in activity coefficients must be attributed to the change in intermolecular forces, resulting from changes in molecular structure.

Figure 3 shows the heats of vaporization-composition relationship for the three-carbon alcohol-water systems. The heat of vaporization for the various alcohol solutions shows only slight deviation with molecular structure. Thus, the intermolecular forces appear to be of less significance with respect to this parameter than in solution behavior.

Therefore, the influence of molecular structure of components in a binary system is reflected primarily in the properties of the liquid phase through changes in intermolecular forces.

## ACKNOWLEDGMENT

The support of the National Science Foundation through its Grant 14297 is appreciated.

## NOMENCLATURE

$H_i$ = molar enthalpy of pure component $i$
$\bar{H}_i$ = partial molar enthalpy of component $i$
$P_i$ = vapor pressure of pure component $i$
$R$ = gas constant
$T$ = ° Kelvin
$\gamma$ = activity coefficient
$\pi$ = total pressure
$x_i$ = mole fraction component $i$ in liquid phase
$y_i$ = mole fraction component $i$ in vapor phase

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RECEIVED for review June 22, 1964. Accepted September 17, 1964.

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# Constitution Diagram for the PbTe–Sb System

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**The constitution diagram of the quasi-binary system PbTe-Sb has been determined by thermal analysis, metallographic, and x-ray procedures. A eutectic is formed at 89.5 ± 0.1 wt. % Sb and 601.0° C. The solid solubility of Sb in PbTe is less than 0.1 wt. % and that of PbTe in Sb is less thán 0.5%.**

EXPLORATORY STUDIES of the ternary system tellurium antimony-lead, by x-ray analysis and microscopic examination, revealed that the PbTe phase and antimony probably formed a true quasi-binary section. This isopleth was investigated by thermal analysis, x-ray, and microscopic examination.

## EXPERIMENTAL

**Materials.** The lead, tellurium (American Smelting and Refining Co.), and the antimony (Bunker Hill Co.) each had a purity of 99.99+% by spectrographic analysis.

**Procedure.** All alloys were prepared by weighing the desired amount of each element on an analytical balance in a quartz tube, which was then evacuated, sealed off, and placed in a muffle furnace controlled at a temperature at least 50° above the melting point of the composition under study. During the 20 tó 30 minutes that the alloy was held at temperature, it was vigorously shaken to ensure homogenization. The alloy weights used varied between 40 and 80 grams each, depending on the specific gravity of the alloy. After being cooled in air, the alloys were transferred to mullite (aluminum silicate) crucibles to take the thermal data.

Heating and cooling curves were recorded with the alloys under a protective atmosphere of nitrogen as the temperature was changed at a controlled rate of 2 to 4° C. per minute by a motorized variable transformer. During each cooling run, the molten alloy was stirred by a mullite rod rotated at constant speed by a Cenco variable-speed stirrer until the freezing metal stopped the motion. The temperature of the alloys was measured with a calibrated chromel-alumel thermocouple, which was protected from the molten liquid and centered in the alloy by a thin-walled mullite tube. Since the electromotive force produced by the chromel-alumel thermocouple was often greater than the range of the Honeywell Extended Range Recorder used for charting the e.m.f., an external precision potentiometer was used as an auxiliary. Critical points were checked with a Leeds and Northrup K-2 precision potentiometer.

The samples for metallographic examination were polished by conventional techniques. Etching was carried

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