D_v = diffusivity of transferable component, sq. ft./hr.
f_k = friction factor for packed beds, $g_c \dfrac{\Delta P}{\rho u^2} \dfrac{D_p}{L} \dfrac{\epsilon^3}{1-\epsilon}$
g_c = conversion factor, 32.17 lb.$_m$ ft./lb.$_f$ sec.^{2}
G = superficial mass velocity, lb.$_m$/hr. sq. ft.
h = heat transfer coefficient, B.t.u./hr. sq. ft. °F.
j_d = mass transfer factor, $\dfrac{k_g\, p_{gf}}{G/M} \left(\dfrac{\mu}{\rho D_v}\right)^{2/3}_f$
j_h = heat transfer factor, $\dfrac{h}{c_p\, G} \left(\dfrac{C_p \mu}{k}\right)^{2/3}_f$
k = thermal conductivity, B.t.u./hr. ft. °F.
k_g = mass transfer coefficient, lb.-moles/hr. sq. ft. atm.
L = bed height, ft.
M = molecular weight
N_{Re} = modified Reynolds number, D_pG/μ
$N_{Re'}$ = modified Reynolds number, $D_pG/\mu(1-\epsilon)$
P = pressure, atm.
$(\Delta p)_m$ = log-mean partial pressure difference of transferable component, atm.
p_{gf} = partial pressure of nontransferable component, atm.
q = rate of convective heat transfer, B.t.u./hr.
r = rate of mass transfer, lb.-moles/hr.
t = temperature, °F.
$(\Delta t)_m$ = log-mean temperature difference across gas film, °F.
t_{d_1} = temperature of inlet air, °F.
t_{d_2} = temperature of outlet air, °F.
t_s = surface temperature of spheres, °F.
t_w = wet-bulb temperature, °F.
u = superficial velocity, ft./sec.
V = volume of reactor, cu. ft.
ϵ = void fraction of bed
μ = viscosity, lb.$_m$/sec. ft.
ρ = absolute density, lb.$_m$/cu. ft.

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Enthalpy of Nonideal Solutions: *n*-Butanol-Benzene

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This investigation continues the study of the thermodynamic properties of paraffinic alcohols, which exhibit considerable hydrogen bonding, and their nonideal mixtures with nonpolar compounds. This program was started by McCracken and Smith (*8, 9*), who studied the methanol-benzene system, and continued by Storvick (*14, 15*), who investigated the systems of ethanol-benzene and *n*-pentane-benzene.

In this investigation enthalpies of *n*-butanol and binary mixtures of 75, 50, and 25 mole % *n*-butanol in benzene were measured in an adiabatic flow calorimeter at temperatures from 250° to 550°F. and pressures from 20 to 1,000 lb./sq. in. abs. This range of temperature and pressure covered the vapor, liquid, and two-phase regions for all the systems studied. For the mixtures the heat of mixing data supplied by R. V. Mrazek (*10*) were used to refer all mixture enthalpies relative to the pure liquid components. All enthalpy values reported (British thermal units per pound of solution) are based on the reference state of the pure liquid components at 77°F. and their vapor pressure in which state the enthalpy was arbitrarily taken to be zero.

PREVIOUS WORK

Benzene

McCracken (*8*) determined the pressure-enthalpy diagram for benzene over a pressure range of 0 to 1,000 lb./sq. in. abs. and a temperature range of 250° to 500°F. All thermodynamic properties of benzene used in this work for calculations or comparisons were obtained from McCracken's work as preliminary runs made with benzene in the calorimeter were found to agree within experimental error with McCracken's results.

n-Butanol

Shemilt, Esplen, and Mann (*13*) who measured P-V-T properties of pure *n*-butanol from 386° to 580°F. over a pressure range of 100 to 1,000 lb./sq. in. abs. give an excellent summary of the thermodynamic data available in the literature for pure normal butanol. In constructing the pressure-enthalpy diagram for pure normal butanol the vapor pressure and latent heat data of Shemilt et al. were used as their calculated latent heats agreed with the experimental values measured at 450° and 500°F. in this work.

In addition to the data reported from the literature by Shemilt, Ingle and Cady (*4*), while determining molecular weights of butanol vapor near the boiling point, found that as

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the temperature was increased from 242° to 277°F. the molecular weight of the alcohol decreased from about 80 to 76. This decrease was almost linear with temperature. The extrapolated molecular weight at the boiling point was 5.87 higher than the formula weight of 74.12. (Corresponding values of 1.79 for methanol, 2.02 for ethanol, and 3.08 for *n*-propanol were also found.) This difference in molecular weight was attributed to the formation of double or triple molecules in the vapor state (that is association), caused by the strong interaction forces present between the polar molecules. It was also postulated that increasing the temperature could increase the degree of disassociation of the polymolecules and lead to smaller molecular weights at higher temperatures. In preparing the mixtures studied in this investigation the weight of butanol used in making up a mixture of given mole percentage was based upon the formula weight of 74.12.

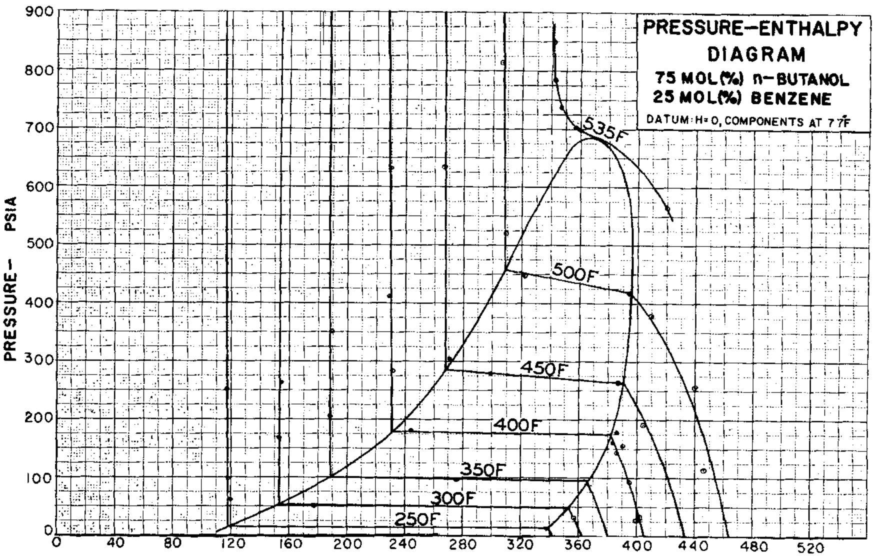

Fig. 2

n-Butanol-Benzene Mixtures

Systems of the type *n*-butanol-benzene exhibit positive deviation from ideal solution behavior. When the pure liquid components both at a given temperature and at total pressure are mixed together, heat must be added to the system in order to maintain that given temperature. This phenomenon is perhaps due to the fact that the alcohol manifests considerable hydrogen bonding (association) with the result that the liquid state is believed to be composed not of single molecules but of clusters of large polymolecules. The addition of nonpolar molecules is postulated to cause these larger molecules to be separated and split up into small polymolecules or even single molecules, destroying the hydrogen bonding. Since energy is necessary to destroy these bonds, heat must be added or a temperature drop would result. The numerical values of the heat of mixing at constant temperature and pressure for *n*-butanol-benzene mixtures given in Table 1 were used to refer the mixture enthalpies relative to the pure component basis. These values were obtained from the data of Mrazek (*10*). His results would support the above postulation, because the heat of mixing increased with benzene concentration.

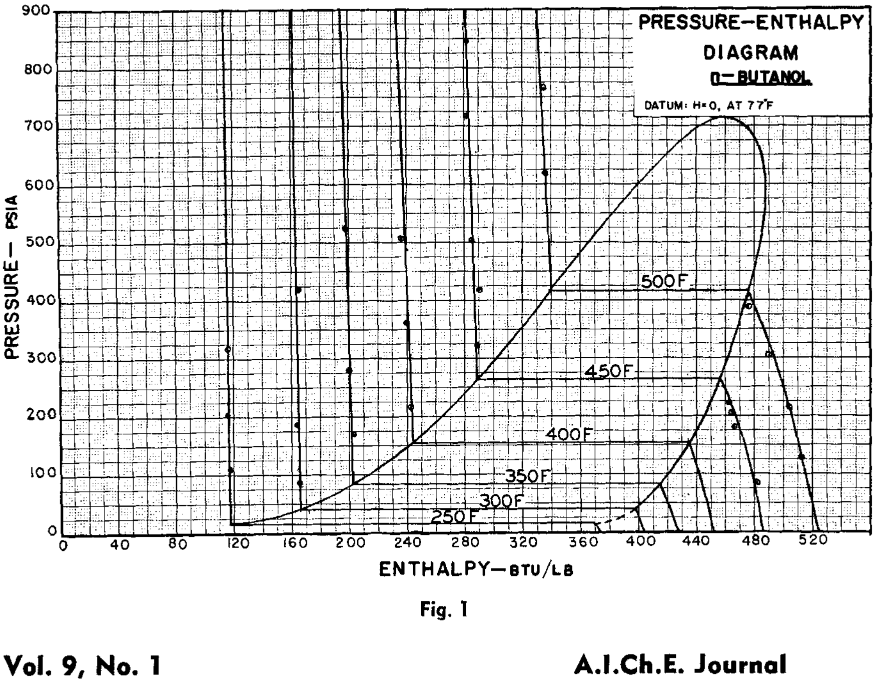

Fig. 1

EXPERIMENTAL

Purity of Chemicals

The *n*-butyl alcohol used in this work was guaranteed to contain 99.8 weight % *n*-butanol. It was not further purified. The benzene used was reagent grade, thiophene free benzene which conformed to American Chemical Society specifications and had a maximum boiling range of 0.5°C. and included a temperature 79.5° to 81.0°C. The Freon 11 used contained not less than 99.99 weight % trichloromonofluoromethane. It had a latent heat of 78.4 B.t.u./lb. at a boiling temperature of 74.6°F.

Throughout this investigation the material in the calorimeter was checked for evidence of thermal degradation with a refractometer and vapor phase chromatograph. No evidence of any change in fluid composition could be detected.

Experimental

The experimental method and procedure for calculating the experimental enthalpy of the mixture relative to the reference state was essentially the same as that used by McCracken (*8*, *9*) and Storvick (*14*, *15*). The original data and all pertinent details are given by Gustafson (*2*) and O'Neill (*11*).

Construction of the Pressure-Enthalpy Diagrams

The most convenient way to operate the equipment was to run at a constant inlet temperature and to vary the pressure for each series of runs. A series of pressures would then represent an isotherm on a pressure-enthalpy diagram. The enthalpy of a mixture at a given temperature and pressure was calculated and the value plotted against pressure for the selected isotherms for each of the mixtures. These experimental values are shown as circles on Figures 1 to 4, the resulting pressure-enthalpy diagrams for the mixtures studied. Tabulated values of the enthalpy of these pure components and mixtures, for the saturated liquid and vapor, and for the superheated liquid and vapor regions are presented in Tables 2 to 11.*

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* Tabular material has been deposited as document 7288 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

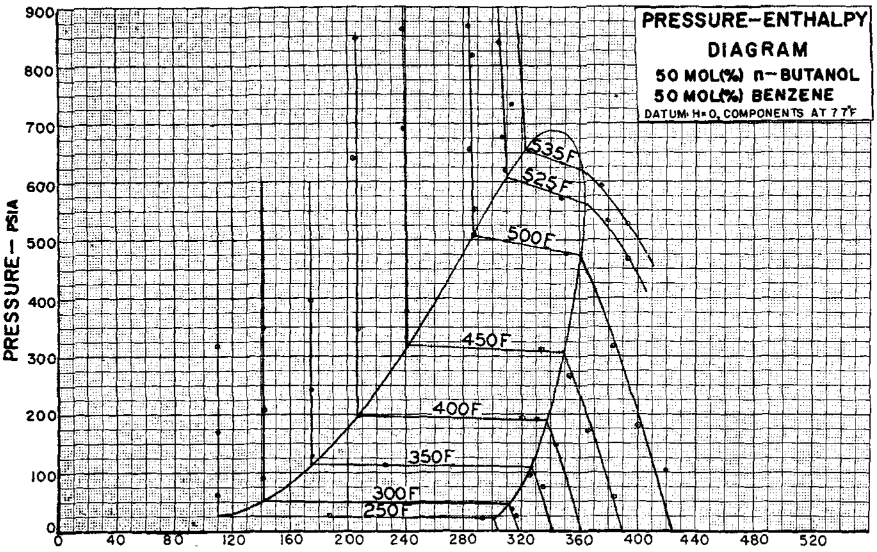

Fig. 3

In constructing the pressure-enthalpy diagram for pure normal butanol, Figure 1, initial smooth curves were drawn by eye through the points of a given isotherm in the liquid and vapor phases. The vapor pressure and latent heat data of Shemilt et al. (*13*) were used in constructing the phase envelope on the diagram in the following way. The liquid enthalpy isotherms were extended to the vapor pressure, and the isotherm was then extended horizontally across an amount equal to the latent heat at that temperature and pressure. Smooth curves in the vapor region were drawn through the experimentally determined points to intersect at the saturated vapor state determined by the liquid enthalpy curves, the latent heats, and the vapor-pressure data. The vapor-phase isotherms were extended to zero pressure. The slopes of the vapor-phase isotherms were found to be identical with those calculated by Shemilt et al. from their experimentally observed P-V-T data.

Cross plots of enthalpy vs. temperature shown in Figure 5* for the liquid at 500 lb./sq. in. abs. and Figure 6* for the vapor phase at zero pressure, along with a plot of latent heat vs. temperature shown in Figure 7*, were made. These were used to check for consistency of results and to slightly readjust the original curves drawn on the pressure-enthalpy diagrams to obtain those shown in Figures 1 to 4.

The pressure-enthalpy diagram for benzene is given by McCracken (*8*).

For the 25, 50, and 75 mole % mixtures of normal butanol in benzene no latent heat or vapor pressure data are available. However data were obtained in the two-phase region in each isotherm for all three mixtures. The pressure enthalpy diagrams for these mixtures, Figures 2 to 4, were constructed in the following way. Straight lines were drawn for the data in the liquid and two-phase region and smooth curves in the vapor-phase region. The intersection of the liquid-phase portion of an isotherm with the two-phase portion determined the bubble point. The intersection of the two-phase region straight line with the vapor-phase curve determined the dew point for the isotherm. The phase envelope was then drawn through the loci for these points. Cross plots of enthalpy vs. temperature for the liquid and vapor phases (Figures 5 and 6) and latent heat vs. temperature (Figure 7) for the mixtures were also drawn and used to smooth the results.

The critical temperature and pressure for the mixtures were estimated on the pressure-enthalpy diagram from the high temperature isotherm data and extrapolations of the latent heats to zero. The method of rectilinear diameters was used to obtain the position of the critical point on the phase envelope. The estimated critical values are given in Table 12. Their estimated maximum uncertainty is ± 4°F. and ± 5 lb./sq. in. abs. Like the systems of methanol-benzene (*8, 9*) and ethanol-benzene (*14, 15*) the estimated critical temperature and pressure of the mixtures were found to lie below those of the pure components. These values were also lower than the pseudocritical constants for the mixtures obtained by the methods of Joffee (*5*) or Kay (*6*).

Precision of Results

The estimated maximum uncertainty in the experimental work, assignable to various causes, are as follows:

Source	Maximum uncertainty in experimental enthalpy, B.t.u./lb.
Temperature measurement	1.0
Pressure measurement	0.5
Freon collection and weighing	0.2-1.0
Sample collection and weighing	1.0-6.0
	2.7-8.5

The high value in the estimated possible uncertainty due to sample collection corresponds to runs with pure *n*-butanol for which the enthalpy of the vapor is relatively high. In all instances care was exercised not to exceed the heat capacity of the calorimeter, a condition which was easily detected.

Referring to Figures 1 to 4, one sees that with only a few exceptions all of the data points lie well within this maximum assignable uncertainty. In the liquid region points are within 1 to 2 B.t.u./lb. of the smooth curve, in the two-phase region points are within 2 to 3 B.t.u./lb., and in the vapor region points are within 3 to 5 B.t.u./lb. The greatest and most frequent experimental deviations were encountered in the vapor state, owing to the relatively small amount of mixture vaporizing a large amount of Freon. Therefore the estimated accuracy of the enthalpy values given in Figures 1 to 4 and in Tables 2 to 11 is ± 1%.

DISCUSSION OF RESULTS

Enthalpy of n-Butanol

The results of this investigation for the enthalpy of pure *n*-butanol may be

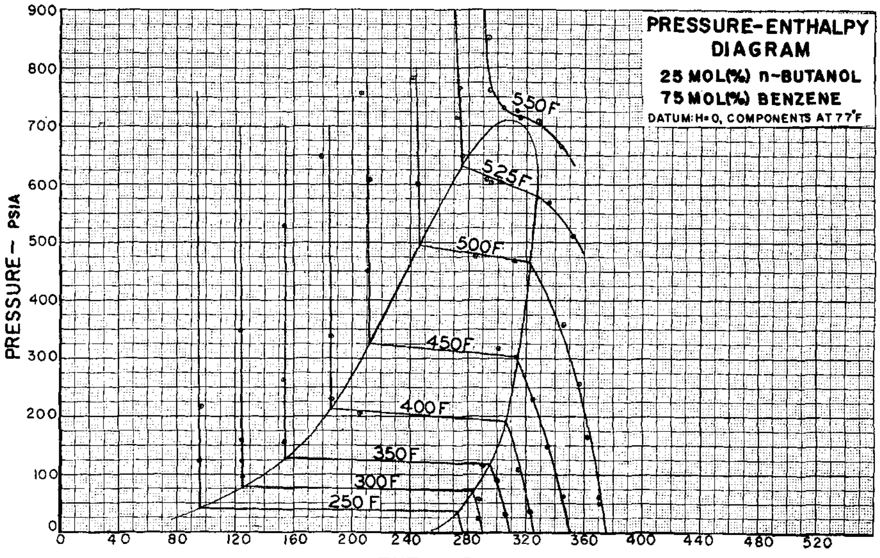

Fig. 4

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* See footnote on page 65.

TABLE 1. HEATS OF MIXING H_m (77°F., 1 ATM.) *n*-BUTANOL-BENZENE*

Mixture	Average molecular weight	H_m, B.t.u./lb.
25 mole % butanol	77.11	6.08
50 mole % butanol	76.12	5.91
75 mole % butanol	75.12	3.37

* Reproduced from the data of Mrazek (*10*).

compared with the calculated results of Shemilt, et al. (*13*), who recently published a pressure-enthalpy diagram for *n*-butanol. The pressure-enthalpy diagram obtained by Shemilt et al., together with the diagram obtained in this investigation, are shown in Figure 8 for comparison. The enthalpy values of the two investigations agree for temperatures below 250°F. However significant differences exist for the higher temperature isotherms. These differences amounted to up to 40 B.t.u./lb. or 13% for the 500°F. isotherm. The reasons for these differences are attributed to the heat capacity equation for the vapor used by Shemilt. Their calculations yielded values which were consistently less than those obtained experimentally in this investigation. As pointed out by Shemilt et al. "the thermodynamic properties reported are in reality over-all apparent values and do not take into account the effect of association between *n*-butanol molecules." Their calculated effect of pressure on the enthalpy of *n*-butanol at a given temperature was found to agree with the experimental results of this investigation. That is the slopes of the isotherms of this investigation conformed with the slopes calculated by Shemilt. In conclusion it is felt that the results of this investigation are more accurate in giving the true enthalpy of normal butanol in the temperature range from 250° to 550°F.

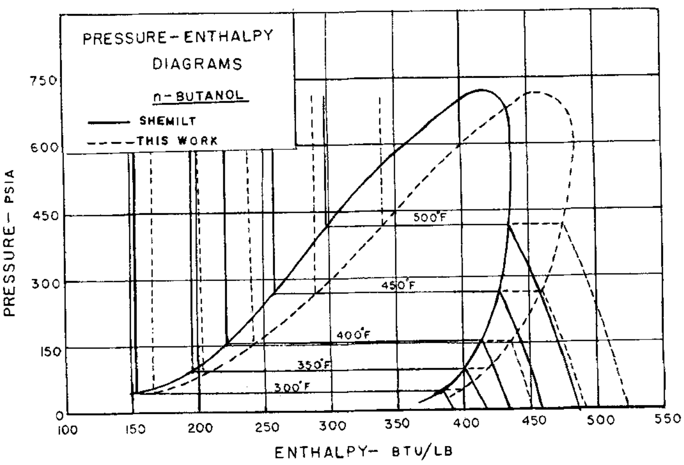

Fig. 8

TABLE 12. ESTIMATED CRITICAL TEMPERATURES AND PRESSURES OF *n*-BUTANOL-BENZENE MIXTURES

Mixtures	T_c, °F.	P_c, lb./sq. in. abs.
Butanol	548.6	714
75% butanol	535	687
50% butanol	537	690
25% butanol	548	710
Benzene	553	716

Effect of Pressure on Enthalpy of n-Butanol

At a constant temperature the enthalpy of the vapor was found to decrease with increasing pressure. Storvick's (*14, 15*) method was found to correlate the experimentally observed effect of pressure on the enthalpy of *n*-butanol vapor within the range of experimental error. Both McCracken (*8, 9*) and Storvick (*14, 15*) attributed the large enthalpy-pressure deviations of the vapor to the association of the gas in the vapor phase for the systems of methanol and ethanol. The work of Ingel and Cady (*4*) and the results of this investigation also indicate that association in the vapor is a logical explanation for the observed large enthalpy deviations. The generalized methods of Hougen and Watson (*3*); Lyderson, Greenkorn, and Hougen (*7*); and Pitzer et al. (*1, 12*) all gave calculated enthalpy decreases which were less than those experimentally observed in the vapor due to pressure.

Enthalpy of Mixtures

There is no data available in the literature for the properties of mixtures of *n*-butanol and benzene with which to make a direct comparison of experimental results. The methods used by McCracken and Storvick for predicting the properties of the mixtures from the known properties of the pure components were found to give predicted enthalpy deviations for the mixtures which were consistently less than the experimentally observed values. This discrepancy was found to increase with increasing pressure at a given temperature and was up to 45% of the observed values at pressures of 400 lb./sq. in. abs. Also the enthalpy of the mixtures could not be accurately calculated from a linear, quadratic, or Lorentz combination of the enthalpies of the pure components at a given temperature and pressure. These methods gave consistently high values for the enthalpy for all three mixtures.

In summary it appears that at the present time no method is available in the literature for predicting the vapor-phase enthalpy of polar-nonpolar mixtures within experimental error. Of those methods presently available the method of Storvick gave the best correlation for the polar alcohols methanol, ethanol, and *n*-butanol and gave results of reasonable accuracy for the mixtures which became increasingly less accurate with increasing pressure.

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