Saturated Liquid Enthalpies of Ethane-*n*-Butane-*n*-Pentane System with Multicomponent Clapeyron Equation

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Enthalpies of the coexisting equilibrium vapor and liquid mixtures of the ethane-*n*-butane-*n*-pentane system are computed at several pressures. Saturated liquid enthalpies are obtained by using a new multicomponent Clapeyron equation with the B-W-R equation of state and the experimental temperature-composition data for the ternary mixture. Saturated vapor enthalpies are calculated by applying the B-W-R equation to the vapor mixture. Ideal gas state enthalpies are used in both vapor and liquid enthalpy calculations.

MULTICOMPONENT CLAPEYRON EQUATION

Equations for the differential heats of vaporization and condensation were recently derived by Tao (*5*) from the unrestricted form of the Gibbs-Duhem. The identical equations were derived by these authors independently, starting from the partial molal free energy expression, as given by Van Ness (*6*)

$$\overline{G}_i = \underline{G} + \left(\frac{\partial \underline{G}}{\partial y_i}\right) - \sum_{j=1}^{n} y_j \left(\frac{\partial \underline{G}}{\partial y_j}\right) \qquad (1)$$

and the required conditions of phase equilibrium; that is

$$\mu_i^V = \mu_i^L, \qquad \text{where } i = 1, 2, \ldots . n$$

to arrive at the following expressions:

$$\left(\frac{dP}{dT}\right)_y = \frac{\underline{H}^L - \sum_1^n x_i\overline{H}_i^V}{T\left[\underline{V}^L - \sum_1^n x_i\overline{V}_i^V\right]} = \frac{\Delta H_c}{T\Delta V_c} \qquad (2)$$

and

$$\left(\frac{dP}{dT}\right)_x = \frac{\underline{H}^V - \sum_1^n y_i\overline{H}_i^L}{T\left[\underline{V}^V - \sum_1^n y_i\overline{V}_i^L\right]} = \frac{\Delta H_V}{T\Delta V_V} \qquad (3)$$

Equations (2) and (3) are the multicomponent Clapeyron Equations. The left-hand sides are the slopes of the dew point and bubble point curves. The numerators of the right-hand terms are the differential heats of condensation and vaporization, respectively.

ENTHALPIES OF COEXISTING EQUILIBRIUM VAPOR AND LIQUID MIXTURES

The enthalpy of a saturated liquid mixture is given in terms of the differential heat of condensation by rearranging Equation (2) as follows:

$$\underline{H}^L = T\left(\frac{dP}{dT}\right)_y \left(\underline{V}^L - \sum_1^n x_i\overline{V}_i^V\right) + \sum_1^n x_i\Delta\overline{H}_i^V + \sum_1^n x_i\underline{H}_i^o \qquad (4)$$

In like manner, the enthalpy of a saturated vapor mixture can be written in terms of the differential heat of vaporization by rearranging Equation (3). The dew point slope and the values of x_i in Equation (4) may be obtained from experimental data, as may the mixture volume of saturated liquid.

The partial volumes and the partial enthalpy differences must be evaluated by an equation of state. These equation of state calculations are more accurate for the vapor phase than they are for the liquid phase. For this reason, Equation (4) was chosen to compute the enthalpies of saturated liquid mixtures rather than the companion equation by using the differential heat of vaporization. The application of Equation (4) to a bubble point liquid mixture gives, as a by-product, the enthalpy of the coexisting equilibrium vapor mixture.

Values of the dew point curve derivative can be obtained from experimental data if these data give the dew point curves for constant composition vapor mixtures by fitting the data to a proper vapor pressure equation. Such data are usually available for binaries but are very rarely available for multicomponent systems.

Dew point calculations, made with a vapor-liquid, *K*-value prediction method (*2*), can be a source of pressure-temperature values at constant vapor composition from which the derivative can be obtained. In applying this technique to several binary mixtures, we found that the values of $(dP/dT)_y$ were in agreement with values obtained from experimental dew point curves, even though the calculated dew points did not agree with the observed. In other words, the calculated dew point curve was parallel to the experimental dew point curve but displaced from it.

Values of $\overline{V}_i^V$ and $\Delta\overline{H}_i^V$ were formulated in terms of the B-W-R (*1*) equation of state and applied with the reduced constants of the generalized form (*3*). The expression for $\Delta\overline{H}_i^V$ has appeared previously (*4*).

APPLICATION TO A TERNARY

The above method has been applied to the ethane-*n*-butane-*n*-pentane mixture, for which pressure-temperature composition data are available (*7*). The enthalpy calculations were made for three isotherms at each of four pressures, and the results are given in Table 1, along with *P-T-x-y* data.

TABLE 1. ENTHALPIES OF COEXISTING EQUILIBRIUM VAPOR AND LIQUID FOR ETHANE-*n*-BUTANE-*n*-PENTANE SYSTEM

$H = 0$ at $P = 0$ and $T = 0°R$.

Pressure, lb./sq.in.abs.	Temp., °F.	y_i, Saturated vapor, mole fraction		x_i, Saturated liquid, mole fraction		Enthalpies, B.t.u./lb. mole		
		C_2	C_4	C_2	C_4	H^V	H^L	$(H^V - H^L)_{P,T}$
500	200	0.777	0.067	0.370	0.126	7,055	3,636	3,419
		0.735	0.141	0.354	0.259	7,108	3,578	3,530
		0.684	0.228	0.333	0.400	7,167	3,607	3,560
		0.630	0.324	0.312	0.550	7,221	3,606	3,615
500	250	0.599	0.116	0.253	0.149	9,040	5,675	3,365
		0.527	0.243	0.225	0.310	9,141	5,725	3,416
		0.454	0.382	0.196	0.482	9,217	5,708	3,509
		0.377	0.536	0.168	0.665	9,272	5,632	3,640
500	300	0.371	0.171	0.152	0.170	11,641	8,118	3,523
		0.278	0.360	0.118	0.353	11,722	8,139	3,583
		0.173	0.570	0.077	0.554	11,766	8,265	3,501
		0.052	0.811	0.026	0.779	11,653	8,587	3,066
600	200	0.800	0.058	0.446	0.111	6,683	4,179	2,504
		0.763	0.124	0.432	0.227	6,709	4,094	2,615
		0.720	0.200	0.414	0.352	6,735	4,088	2,664
		0.670	0.286	0.393	0.486	6,751	4,099	2,652
600	250	0.639	0.101	0.323	0.135	8,520	6,110	2,410
		0.576	0.211	0.296	0.281	8,575	6,160	2,415
		0.513	0.333	0.269	0.439	8,603	6,130	2,473
		0.444	0.471	0.242	0.609	8,605	6,035	2,670
600	300	0.444	0.143	0.219	0.156	10,852	8,254	2,598
		0.374	0.301	0.192	0.323	10,876	8,084	2,792
		0.283	0.484	0.156	0.506	10,878	8,175	2,703
		0.181	0.684	0.121	0.704	10,752	8,794	1,958
700	200	0.817	0.052	0.524	0.095	6,324	4,707	1,617
		0.782	0.110	0.511	0.196	6,328	4,659	1,669
		0.744	0.177	0.496	0.302	6,320	4,591	1,729
		0.704	0.252	0.480	0.416	6,298	4,507	1,791
700	250	0.661	0.090	0.390	0.122	8,065	6,777	1,288
		0.607	0.187	0.369	0.252	8,069	6,720	1,349
		0.556	0.293	0.348	0.391	8,051	6,540	1,511
		0.490	0.424	0.320	0.544	7,990	6,507	1,483
700	300	0.482	0.128	0.279	0.144	10,225	8,899	1,326
		0.423	0.269	0.261	0.296	10,209	8,669	1,540
		0.322	0.440	0.228	0.463	10,072	9,016	1,056
800	200	0.823	0.046	0.603	0.079	5,956	5,101	855
		0.791	0.102	0.590	0.164	5,924	5,047	867
800	250	0.673	0.081	0.458	0.108	7,615	7,147	468
		0.623	0.172	0.442	0.223	7,566	6,993	573
800	300	0.481	0.121	0.332	0.134	9,607	9,290	317

Saturated vapor enthalpies were calculated directly via a B-W-R expression for the enthalpy of the mixture. Saturated liquid enthalpies were found via Equation (4). Also included in Table 1 are the enthalpy differences at constant P and T for coexisting vapor and liquid.

CONCLUSION

Enthalpies of the coexisting equilibrium vapor and liquid mixtures have been computed for the ethane-*n*-butane-*n*-pentane by using experimental *P-T-x-y* data, a dew point calculation method, an equation of state and a multicomponent Clapeyron equation.

This method should be better than the direct calculation of the saturated liquid mixture enthalpy via an equation of state, that is, by not using the multicomponent Clapeyron equation. One reason for this improvement is that the equations of state are more reliable for the vapor phase than they are for the liquid phase.

NOTATION

$\underline{G}$ = $\Sigma\, z_i \overline{G}_i$ = molal free energy of mixture
$\overline{G}_i$ = partial molal Gibbs free energy of i
$\underline{H}$ = $\Sigma\, z_i \overline{H}_i$ = molal enthalpy of mixture
$\overline{H}_i$ = partial molal enthalpy of i
$\underline{H_i^o}$ = molal enthalpy of component i in ideal gas state
$\underline{V}$ = $\Sigma\, z_i \overline{V}_i$ = molal volume of mixture
$\overline{V}_i$ = partial molal volume of component i
x_i = mole fraction of component i in liquid
y_i = mole fraction of component i in vapor
z_i = mole fraction of component i in system, liquid or vapor
μ_i = chemical potential of i
i, j, n = components
L = vapor phase
V = liquid phase

LITERATURE CITED

1. Benedict, M., G. B. Webb, and L. C. Rubin, *J. Chem. Phys*, 8, 334 (1940).
2. Chao, K. C., and J. D. Seader, *AIChE J.*, 7, 598 (1961).
3. Edmister, W. C., J. Vairogs, and A. J. Klekers, *ibid.*, **14**, 479-482 (1968).
4. Papadopoulos, A., R. L. Pigford, and Leo Friend, *Chem. Eng. Progr. Symposium Ser. No. 7*, **49**, 119-130 (1953).
5. Tao, L. C., *AIChE J.*, to be published.
6. Van Ness, H. C., "Classical Thermodynamics of Non-Electrolyte Solutions," MacMillan, New York (1964).
7. Vinod, S. M., and George Thodos, *J. Chem. Eng. Data*, 7, 169 (1962).

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