Specific Enthalpy Increments for Butan-1-ol at Temperatures from 423.2 to 623.2 K and Pressures to 10.2 MPa

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Measurements of specific enthalpy increments for butan-1-ol are reported. A counter-current water-cooled flow calorimeter was used to measure 109 enthalpy increments over the temperature range of 423.2 to 623.2 K at pressures from 0.1 to 10.2 MPa. Extrapolation of the gas phase measurements to zero pressure gave values in close agreement with pure-component ideal-gas enthalpies calculated by extrapolation of data on the lower alcohols. Values of the specific enthalpy of vaporization derived from the measurements are in agreement with other work and are well fitted by a modification of the Watson equation. A method for the calculation of the two-phase enthalpy-pressure envelope is described.

KEY WORDS: enthalpy increments; ideal gas enthalpies; butan-1-ol; flow calorimeter.

1. INTRODUCTION

A counter-current water-cooled heat-exchange flow calorimeter for the measurement of enthalpy increments at temperatures up to 700 K and pressures up to 15 MPa has been described [1]. The calorimeter operates by pumping liquid or liquid mixture from a reservoir at atmospheric pressure through a flash vaporizer at a controlled temperature and pressure and allowing the hot vapor to condense in a water cooled heat exchanger. The cooling water was supplied at a temperature of about 275 K, and the flow rate was adjusted so that the condensate leaving the calorimeter

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was at a temperature close to 298.15 K, the reference state temperature. Enthalpy increments were calculated from the flow rate of the cooling water, the flow rate of the fluid, and the temperatures of the incoming and outflowing water and fluid. The calorimeter was tested by making 90 measurements of enthalpy increments for steam over the range of temperature 423.2 to 623.2 K at pressures up to 10.3 MPa. These agreed with steam tables to within $\pm 0.5\%$. The calorimeter has been used previously to measure specific enthalpy increments for n-hexane [1], methanol [2], ethanol [3], propan-1-ol [4], propan-2-ol [5], propanone [6], benzene [7], and molar enthalpy increments for the equimolar mixtures (propanone + n-hexane) [8,9], (propanone + benzene) [10], (methanol + water) [11], and (ethanol + water) [12]. Specific enthalpy increments for butan-1-ol are now reported.

Table I. Specific Enthalpy Increments $\Delta h/(\text{kJ}\cdot\text{kg}^{-1})$ for Butan-1-ol Measured Relative to the Saturation Pressure p_s of the Liquid at the Standard Temperature 298.15 K

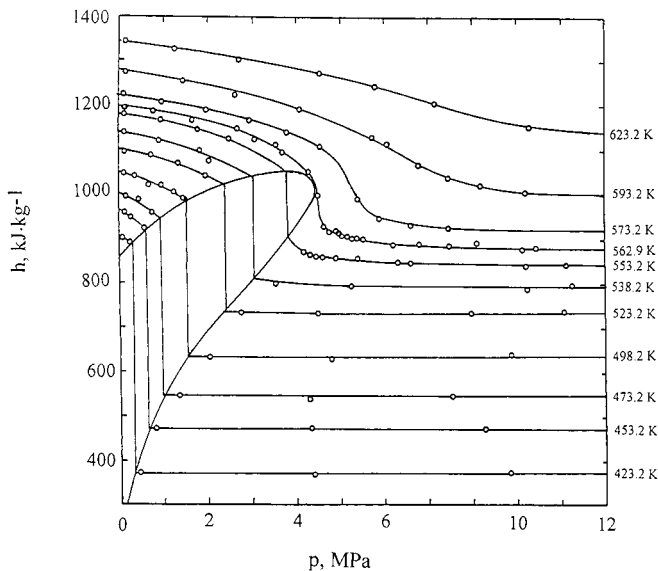| T (K)	p (MPa)	Δh (kJ·kg⁻¹)	p (MPa)	Δh (kJ·kg⁻¹)	p (MPa)	Δh (kJ·kg⁻¹)	p (MPa)	Δh (kJ·kg⁻¹)	p (MPa)	Δh (kJ·kg⁻¹)
423.2	0.10	905	0.25	893	0.46	372	4.45	371	8.85	375
453.2	0.11	960	0.57	925	4.36	477				
	0.25	949	0.72	475	8.25	473				
473.2	0.17	998	0.74	959	4.32	543				
	0.49	989	1.33	548	7.50	549				
498.2	0.15	1050	0.66	1025	1.27	1005	2.03	635	8.85	640
	0.35	1042	0.93	1026	1.44	994	4.81	630		
523.2	0.14	1097	1.35	1072	2.78	734	7.89	736		
	0.74	1087	1.94	1040	4.47	735	10.1	740		
538.2	0.15	1141	1.85	1100	3.52	802	9.22	792		
	0.92	1123	2.56	1075	5.25	797	10.2	799		
553.2	0.14	1183	2.52	1127	4.32	868	4.98	861	6.63	849
	0.94	1169	3.65	1054	4.48	863	5.45	857	9.19	843
	1.81	1145	4.20	875	4.61	862	6.28	851	10.1	845
562.9	0.14	1194	3.55	1113	4.74	920	5.29	905	6.86	893
	0.73	1190	3.67	1097	4.90	923	5.51	906	7.47	892
	1.65	1168	4.32	1052	4.98	917	5.51	905	8.12	895
	2.62	1150	4.52	1000	5.02	913	5.54	905	9.09	881
	3.05	1126	4.65	932	5.17	910	6.22	891	9.42	886
573.2	0.12	1226	1.97	1188	3.81	1139	5.38	988	6.57	935
	0.99	1209	2.94	1167	4.55	1109	5.93	951	7.47	927
593.2	0.14	1275	2.62	1227	5.70	1131	6.83	1067	8.18	1024
	1.44	1256	4.13	1198	6.06	1114	7.44	1042	9.21	1010
623.2	0.16	1347	2.68	1305	5.83	1248	9.29	1157		
	1.24	1328	4.55	1276	7.15	1209				

Fig. 1.   Specific enthalpy increments Δh for butan-1-ol plotted as a function of the pressure p. ○, Table I.

2. EXPERIMENTAL

Enthalpy increments were measured with the counter-current heat-exchange calorimetric apparatus described previously [1]. The mole percent purity of the butan-1-ol was 99.6, and it was used as supplied. Analysis by gas-liquid chromatography showed the principal impurities to be di-*n*-butyl ether (0.15 %) 2 methyl propan-1-ol (0.15 %) and water (0.1 %). The alcohol was pumped at a rate of approximately $0.17 \, \text{g} \cdot \text{s}^{-1}$ through the apparatus. It was usually possible to adjust the flow rate of the cooling water so that the temperature of the alcohol leaving the calorimeter differed by little more than 2 or 3 K from the standard state temperature 298.15 K. At the temperatures $T = 593.2 \, \text{K}$ and $T = 623.2 \, \text{K}$ the fluid leaving the apparatus was analyzed by g.l.c. to check for possible decomposition, but no evidence of this was found. Enthalpy increments measured over the temperature range $T = (423.2 \text{ to } 623.2) \, \text{K}$ at pressures from $p = (0.1 \text{ to } 10.2) \, \text{MPa}$, and calculated as described below, are listed in Table I and plotted against pressure in Fig. 1.

3. CALCULATION OF ENTHALPY INCREMENTS

At the pressure p of the experiment a stream of butan-1-ol vapor at a high temperature T_1 enters the water-cooled heat-exchange calorimeter and

emerges as liquid at a temperature T_2 which is close to 298.15 K, and at the same pressure. Energy lost by the butan-1-ol is gained by the cooling water. Measurement of the water flow rate and temperature rise allows the calculation of the quantity $\Delta h'$ where

$$\Delta h' = h(p, T_1) - h(p, T_2) \tag{1}$$

The desired quantity is the difference Δh between the specific enthalpy of the alcohol at (p, T_1) and the standard state conditions 298.15 K and the saturation pressure p_s at this temperature.

$$\Delta h = h(p, T_1) - h(p_s, 298.15 \text{ K}) \tag{2}$$

Δh can be calculated from $\Delta h'$ by the addition of two terms;

$$\Delta h = \Delta h' + \int_{298 \text{ K}}^{T_2} c_p(p, T)\, dT + \int_{p_s}^{p} v(1 - \alpha T)\, dp \tag{3}$$

where $c_{p,m}$ is the specific heat capacity of the alcohol, v is the specific volume, and α is the isobaric expansivity at 298.15 K calculated from density measurements listed in Ref. 13. The cooling water flow rate was adjusted until T_2 was close to 298.15 K so that the c_p integral was small and the pressure and temperature dependence of c_p could be neglected. Small corrections for heat leaks and for the rate at which kinetic energy enters the calorimeter when the pressure is low were made as previously described [1]. Systematic errors in the measurements are estimated to be no greater than $\pm 0.3 \text{ kJ} \cdot \text{kg}^{-1}$. Random errors arose mainly from fluctuations in the operation of the metering pump supplying the alcohol and were estimated to be $\pm 2 \text{ kJ} \cdot \text{kg}^{-1}$. In the near-critical region, small fluctuations in the flow rate of the alcohol, and in the pressure and temperature, produced larger than usual fluctuations in the measured enthalpy increments. The random error in this region was therefore larger, but was estimated to be no more than $\pm 6 \text{ kJ} \cdot \text{kg}^{-1}$.

4. THE GASEOUS REGION AT LOW PRESSURES

An important test of the accuracy of the measurements is to extrapolate them to zero pressure and to make comparisons with ideal gas enthalpies obtained from spectroscopic measurements or gas phase heat capacities. Wilhoit and Zwolinsky [13] note that three sets of ideal-gas thermodynamic functions for butan-1-ol have been published. Dyatkina [14] and Chermin [15] calculated ideal gas properties from statistical mechanics, and Green [16] used an incremental method based on the

extrapolation of trends found in the first three normal alcohols. This method sums the contribution due to the hydroxyl end group and increments due to the number of methylene groups in the molecule, so that values for butan-1-ol were obtained by adding a methylene increment to the value for propan-1-ol. Because of large uncertainties in the vibrational frequencies and barriers to internal rotation, Wilhoit and Zwolinsky preferred to recommend the ideal-gas heat capacities and enthalpies obtained by Green [16] rather than statistical mechanical values. To make comparisons with our measurements which are based on a standard state of $T = 298.15$ K, it was necessary first to adjust these enthalpies to a scale on which the ideal-gas enthalpy is zero at 298.15 K, and secondly, to add the enthalpy of vaporization of butan-1-ol at this temperature.

Wilhoit and Zwolinsky [13] list several values of the enthalpy of vaporization of butan-1-ol. Counsell et al. [17] made calorimetric measurements at 356.40, 372.62, and 390.88 K which they extrapolated to 298.15 K and obtained the value 710.5 kJ·kg^{-1}. Calorimetric measurements made at 298.15 K by Wadso [18] yielded 706 kJ·kg^{-1}. Majer et al. [19] have more recently measured enthalpies of vaporization of isomeric butanols and have reviewed the literature values. They recommend the value 706.3 kJ·kg^{-1}, which is almost the same as the value 707 kJ·kg^{-1} recommended by the Thermodynamics Research Center [20], and this is the value we have chosen. With these adjustments the ideal-gas enthalpy increments are given by the equation

$$\{h^{ig}(T) - h^{ig}(298.15 \text{ K})\}/\text{kJ·kg}^{-1}$$
$$= 367.1 + 0.6122(T/\text{K}) + 1.5471 \times 10^{-3}(T/\text{K})^2 \qquad (4)$$

Equation (4) is valid over the range 298.15 to 650 K.

Measurements of the heat capacity of butan-1-ol vapor have been made by Counsell et al. [17] at the temperatures 398.15, 413.15, 433.15, and 453.15 K, and at the pressures 25.3, 50.7, and 101.3 kPa. The heat capacities at each temperature were fitted with cubic equations in powers of the pressure, and extrapolation to zero pressure was made. The zero-pressure molar heat capacities were then fitted with the equation

$$C_p^0/(\text{J·mol·K}^{-1}) = -3.263 + 0.43053(T/\text{K}) - 1.9079 \times 10^{-4}(T/\text{K})^2 \qquad (5)$$

It is informative to compare the enthalpy increment obtained by integration of Eq. (5) over the temperature range 398.15 to 453.15 K, with the increment for this same temperature range calculated from Eq. (4). Equation (5) gives 107.9 kJ·kg^{-1}, and Eq. (4) gives 106.1 kJ·kg^{-1}, a difference of 1.7%. Inspection of the calorimetric measurements suggests that most of this
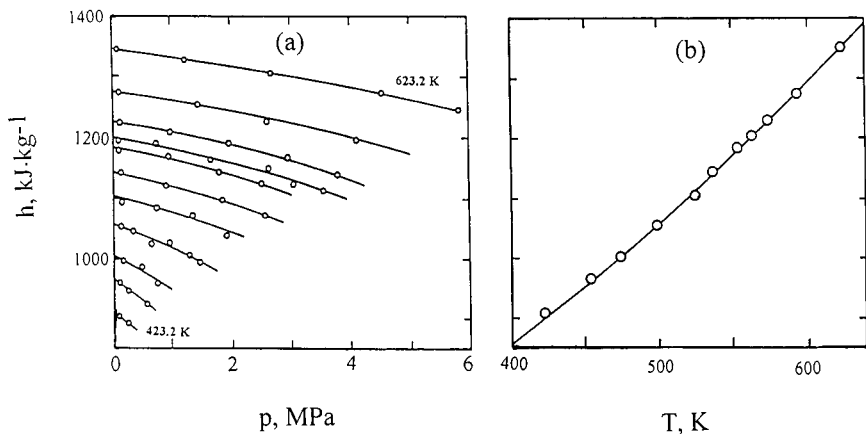
Fig. 2. (a) Specific enthalpy increments Δh for butan-1-ol at low pressures plotted as a function of pressure p, showing the extrapolation to zero pressure. $\bigcirc$, Table I. (b) Zero pressure values of the specific enthalpy of butan-1-ol obtained from Fig. 1 shown plotted against temperature. The curve was fitted to ideal gas enthalpies calculated by Green [16] using an incremental method, as described in the text.

difference could arise from the uncertainty in the extrapolation to zero pressure, which could be as much as 2%. The above comparison is of course not affected by the value chosen for the enthalpy of vaporization.

Figure 2a shows gas phase enthalpies at pressures below 6 MPa extrapolated to zero pressure. Except for the measurements at 423.2 K, where only two gas phase measurements were made, the extrapolation to zero pressure was done by fitting the measurements with quadratic equations. The zero pressure intercepts are listed in Table II and shown in Fig. 2b where they are compared with Eq. (4). The standard deviation

Table II. Ideal-Gas Enthalpies h^{ig} for Butan-1-ol Obtained by Extrapolating to Zero Pressure the Table I Measurements at Pressures Below 4 MPa, as Described in the Text[a]

T (K)	h^{ig} (kJ · kg^{-1})	T (K)	h^{ig} (kJ · kg^{-1})	T (K)	h^{ig} (kJ · kg^{-1})	T (K)	h^{ig} (kJ · kg^{-1})
423.2	(913)	498.2	1053	553.2	1186	593.2	1278
453.2	(969)	523.2	1096	562.9	1196	623.2	1348
473.2	989	538.2	1143	573.2	1227		

[a] The values of 913 kJ · kg^{-1} at 423.2 K, and 969 kJ · kg^{-1} at 453.2 K, are estimated to be 1.6 percent too large, and we recommend that the smaller values 898 and 953 kJ · kg^{-1} should be used. These are consistent with enthalpy increments derived from measurements of the heat capacity of butan-1-ol vapor as described in the text.

Table III. Specific Enthalpies h(liq) and h(gas) at the Saturation Temperature T and Pressure p_s, the Specific Enthalpy of Vaporization Δh(vap), and the Uncertainty $\delta \Delta h$(vap) in this Quantity, for Butan-1-ol[a]

T (K)	p_s (MPa)	h(liq) (kJ·kg^{-1})	h(gas) (kJ·kg^{-1})	Δh(vap) (kJ·kg^{-1})	$\delta \Delta h$ (kJ·kg^{-1})
298.15	0.0002			707	2
390.82	0.1013			584	2
423.2	0.281	375	890	515	10
453.2	0.613	470	925	455	15
473.2	0.960	545	945	400	15
498.2	1.568	634	985	351	15
523.2	2.412	735	1015	280	15
538.2	3.056	797	1030	233	25
553.2	3.827	890	1050	160	25

[a] The values at 298.15 K and the normal boiling temperature 390.82 K were obtained from the literature, all other values were obtained from the Table I measurements.

of the zero pressure increments from values calculated from Eq. (4) is 7.4 kJ·kg^{-1} and the mean deviation is 0.92 kJ·kg^{-1}. If the zero pressure increments are fitted with a quadratic equation in powers of the temperature and the enthalpy increment between 398.15 and 453.15 K is calculated, the value obtained is 94.3 kJ·kg^{-1}, and this is quite inconsistent with the values 107.9 or 106.1 kJ·kg^{-1} calculated above. Figure 2b shows that the points at the two lowest temperatures 423.2 and 453.2 K are above the curve calculated from Eq. (4). At these temperatures, particularly at 423.2 K, the pressure range is small, and the extrapolation to zero pressure is more uncertain than at higher temperatures. If both points are reduced by 1.6%, and a quadratic equation is again fitted, the calculated enthalpy increment between the temperatures 398.15 and 453.15 K is 106.9 kJ·kg^{-1}, in good agreement with the two values calculated above. This suggests that the zero pressure enthalpy increments obtained at 423.2 and 453.2 K are indeed too large by 1.6%. In Table II the ideal gas enthalpies obtained from the Table I measurements are listed, but the footnote to this table gives values at 423.2 and 453.2 K, reduced by 1.6% which we believe to be better. This 1.6% reduction is permissable because it is within the bounds of experimental error at these two temperatures.

5. ENTHALPIES OF VAPORIZATION

The seven isotherms at temperatures between 423.2 and 553.2 K start at low pressures in the gas phase region, they intersect the upper part of

the two-phase boundary at the dew-point pressure, cross the two-phase region, intersect the lower part of the boundary at the bubble-point pressure, and continue to higher pressures in the liquid phase. The vertical lines which cross the two-phase region are at the saturation pressure of the alcohol. Saturation pressures were calculated from the equation

$$\ln(p/p^\circ) = a(1 + bT) + c/T + d \ln T \tag{6}$$

where p° is standard atmospheric pressure, T is the kelvin temperature, $a = 415.86$, $b = 1.48904 \times 10^{-4}$, $c = -21400$, and $d = -64.537$. With these coefficients Eq. (6) fits the vapor pressures of butan-1-ol measured by Ambrose et al. [21] from 419.34 K up to the critical point ($T_c = 563.0$ K, $p_c = 4.427$ MPa) to within $\pm 0.2\%$, which is adequate for our purposes. The difference between the specific enthalpies of the saturated vapor $\Delta h(g)$ and the saturated liquid $\Delta h(l)$) is the specific enthalpy of vaporization Δh_{vap}, and all three quantities are listed in Table III.

Enthalpies of vaporization for butan-1-ol have been reviewed by Wilhoit et al. [13], and more recently Majer et al. [19] have reviewed the enthalpies of vaporization of all the isomeric butanols. At the normal boiling temperature $T_b = 390.82$ K Majer et al. recommend the value $\Delta h_{vap}(T_b) = (584 \pm 2)$ kJ · kg^{-1}. To compare the enthalpies of vaporization derived from our measurements and listed in Table III with other work, we need to fit our data and the literature values with an appropriate equation. The Watson [22] equation is inadequate for this purpose, Vine and Wormald [3] found that this equation was a poor fit to the enthalpies of vaporization for ethanol, and they suggested the equation

$$\Delta_{vap} h(T) = \Delta_{vap} h(T_b)\{ax + (1 - a) x^m\}^n \tag{7}$$

where

$$x = (1 - T/T_c)(1 - T_b/T_c)^{-1} \tag{8}$$

and a, n, and m are adjustable parameters. When $a = 1$ the equation reduces to that of Watson [22]. The equation was tested by fitting 30 values of the enthalpy of vaporization of water from T_b to T_c obtained from steam tables [23]. The best fit parameters for water are $a = 1.1286$, $m = 2.9508$, and $n = 0.3967$. These fit the data with a standard deviation of ± 4 kJ · kg^{-1}, whereas the standard deviation obtained with the Watson equation was ± 26 kJ · kg^{-1}.

To obtain an equation which best fits the specific enthalpy of vaporization of butan-1-ol over a wide range of temperature, we fitted the Table III values to Eq. (7) together with the measurements reviewed by
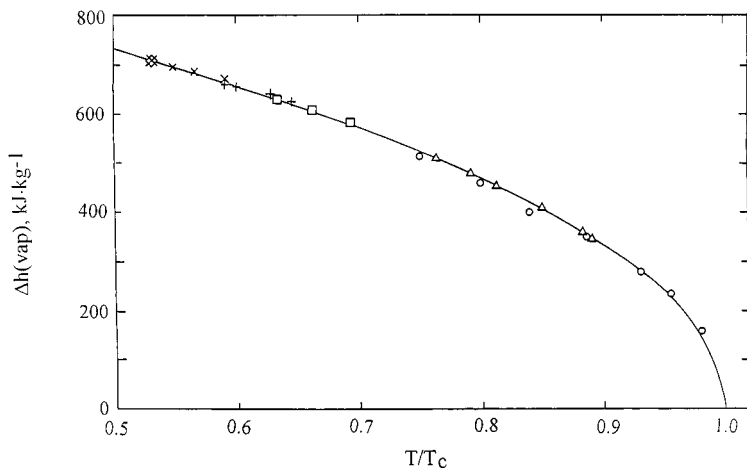
Fig. 3. Specific enthalpies of vaporization of butan-1-ol plotted as a function of the reduced temperature T/T_c. $\bigcirc$, Table III, derived from the Table I measurements. $\square$, Counsell et al. [17], $\diamondsuit$, Wadso [18], $\times$, Polak et al. [24], $\triangle$, Radsoz and Lydersen [25], +, Svoboda et al. [26]. The curve was calculated from Eq. (7).

Majer et al. The data selected were the measurements of Wadso [18], Polak et al. [24], Counsell et al. [17], Radosz et al. [25], and Svoboda et al. [26]. The parameter m in Eq. (7) was set at $m = 3$. The best fit parameters are $\Delta h_{vap}(T_b) = 576.5 \text{ kJ} \cdot \text{kg}^{-1}$, $a = 0.99582$, and $n = 0.4865$, and the standard deviation of the fit was $\sigma = 7 \text{ kJ} \cdot \text{kg}^{-1}$. The $\Delta h_{vap}(T)$ curve for butan-1-ol is shown plotted against reduced temperature in Fig. 3, which shows the enthalpies of evaporation obtained from our measurements to be in satisfactory agreement with other work.

6. CONSTRUCTING THE TWO-PHASE BOUNDARY

To construct the two-phase boundary on the enthalpy pressure diagram shown in Fig. 1, it is convenient first of all to fit the specific enthalpies of vaporization with an equation in which the argument is a function of reduced pressure p_r rather than reduced temperature T_r. Equation (7) is again of suitable form, and it was soon established that the parameter $m = 1.5$ was a good choice.

$$\Delta h_{vap}(p) = \Delta h_{vap}(p^\circ)(ay + (1-a) \ y^{1.5})^n \tag{9}$$

where y is given by

$$y = \{\ln(p/P_c)\}/\{\ln(p^\circ/P_c)\} \tag{10}$$

The specific enthalpy of vaporization $\Delta h_{vap}(p^{\circ})$ at the standard pressure $p^{\circ} = 0.101325$ MPa is, of course, the same quantity as $\Delta h_{vap}(T_b)$. As before, $\Delta h_{vap}(p^{\circ})$ was treated as an adjustable parameter. Least squares optimization gave $\Delta h_{vap}(p^{\circ}) = 578.7$ kJ·kg^{-1}, $a = 1.6558$, and $n = 0.4770$. With these parameters Eq. (9) fits the vaporization enthalpies listed in Table III with a standard deviation of $\sigma = 7$ kJ·kg^{-1}, which is as good as the fit obtained using Eq. (7). This is adequate for our purposes, and the curve is almost indistinguishable from that shown in Fig. 3.

To construct the two-phase envelope we first simplified Fig. 1 by subtracting ideal-gas enthalpies calculated from Eq. (4) from the measurements listed in Table I and so obtained residual enthalpy increments

$$\Delta h^{res} = \Delta h(p) - \Delta h^{ig} \tag{11}$$

Residual enthalpy increments were then plotted against reduced pressure p_r as shown in Fig. 4. The use of reduced pressure facilitates comparison with similar diagrams for other fluids. The two-phase envelope is now more symmetric than before. The midpoint of each of the seven vertical sections, which are the enthalpies of vaporization, was marked, and a curve through these midpoints was drawn and extrapolated to $p/P_c = 1$. In this way a
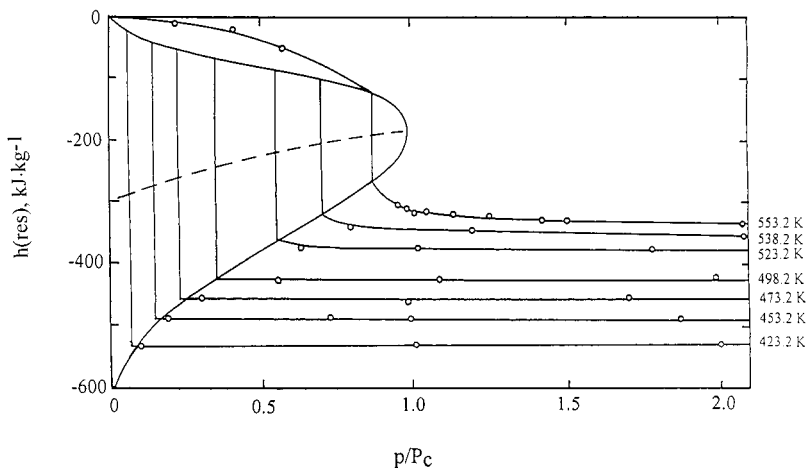
Fig. 4. Residual specific enthalpy increments for butan-1-ol plotted against reduced pressure p/P_c. The length of the vertical lines is a measure of the specific enthalpy of vaporization. The broken curve is the locus of the midpoints of the vertical lines, and was calculated from Eq. (13) as described in the text. The curve intersects the two-phase boundary at the critical point residual enthalpy $h_c = 182$ kJ·kg^{-1}. $\bigcirc$, calculated from Table I measurements. For clarity, only one gas-phase isotherm, at $T = 553.2$ K, is shown.

value of the residual enthalpy h_c at the critical point was obtained, and found to be $h_c = (182 \pm 10) \text{ kJ} \cdot \text{kg}^{-1}$. At the pressure $p^\circ = 0.101325 \text{ MPa}$, which is a reduced pressure of $p_r = 0.023$, the enthalpy of vaporization recommended by Majer et al. [19] is $(584 \pm 2) \text{ kJ} \cdot \text{kg}^{-1}$. At this pressure the residual enthalpy of the liquid at the bubble-point pressure is the sum of two terms, the residual enthalpy of the gas and the specific enthalpy of vaporization of the liquid.

$$\Delta h_{\text{res}} = \int_0^{p^\circ} (\partial h/\partial p)_T \, dp + \Delta h_{\text{vap}} \tag{12}$$

Here $(\partial h/\partial p)_T$ can be calculated from the isothermal Joule–Thomson coefficient $\phi = B - T(dB/dT)$ of the vapor at the normal boiling temperature 390.82 K divided by the molar mass. The integration is carried out from $p = 0$ to $p = p^\circ$. Second virial coefficients for normal alcohols can be estimated from the correlation of Tsonopoulos et al. [27], and differentiation with respect to temperature yields values of ϕ. For butan-1-ol at 390.82 K the value of ϕ was found to be $-6080 \text{ cm}^3 \cdot \text{mol}^{-1}$, and the value of the integral in Eq. (12) was calculated to be $8 \text{ kJ} \cdot \text{kg}^{-1}$. The uncertainty on this figure is about $\pm 1 \text{ kJ} \cdot \text{kg}^{-1}$. The specific enthalpy of vaporization at 390.82 K is $(584 \pm 2) \text{ kJ} \cdot \text{kg}^{-1}$. The midpoint at $292 \text{ kJ} \cdot \text{kg}^{-1}$ of a vertical line drawn on the figure corresponding to an enthalpy of vaporization of $584 \text{ kJ} \cdot \text{kg}^{-1}$ fixes the low pressure limit of the midpoint curve. As required by Eq. (12) this midpoint is plotted in Fig. 4 at $(292 + 8) \text{ kJ} \cdot \text{kg}^{-1}$ and at $p^\circ/P_c = 0.023$, which is almost zero reduced pressure.

An analysis of similar measurements on propan-1-ol [4] and propan-2-ol [5] showed that the locus of the midpoints of the two-phase region residual enthalpies for each of these fluids can be fitted to within experimental error by an equation of the form

$$h_{\text{mid}} = \{0.5\Delta h_{\text{vap}}(p^\circ) - h_c\}(1 - p_r)^z \tag{13}$$

where

$$z = 1 + s\{\ln(p_r - 1)\} \tag{14}$$

When the adjustable parameter $s = 0$, the equation generates a linear midpoint line similar to the rectilinear diameter law for coexisting liquid and gas densities. At the midpoints of the two-phase region, liquid and gas residual enthalpies for butan-1-ol can be fitted by a linear function only down to $p_r = 0.4$; to fit the midpoints at lower reduced pressures requires a function which is not far from linear at $p_r > 0.4$ and which changes more

quickly as p_r approaches zero. The logarithmic functionality given by Eq. (14) fulfills this requirement. The best value of the parameter s was found to be $s = 0.5$, the same as for propan-1-ol [4] and propan-2-ol [5]. Finally at each value of p_r the midpoint residual enthalpy was calculated from Eqs. (13) and (14), the dew point enthalpy $h(\text{gas})$ was obtained by subtracting one half of the enthalpy of vaporization calculated from Eq. (7), and the bubble point enthalpy $h(\text{liq})$ was calculated by adding the same amount.

To calculate the two-phase envelope shown in Fig. 1, it is only necessary to add ideal-gas enthalpies calculated from Eq. (4). As the ordinate in Fig. 1 is pressure rather than temperature, it is convenient to generate an equation which expresses the saturation temperature T_{sat} as a function of the pressure. The saturation temperature of butan-1-ol, obtained by fitting vapor pressure measurements as a function of $\ln(p/p^\circ)$, is given by the equation

$$T_{\text{sat}}/\text{K} = 390.91 + 29.01\{\ln(p/p^\circ)\} + 2.2516\{\ln(p/p^\circ)\}^{2.5} \qquad (15)$$

The alternative procedure is to iteratively solve Eq. (5) to yield values of T_{sat} at each chosen pressure, but it is less convenient. Ideal gas enthalpies can now be calculated at temperatures T_{sat}, and the transformation of the two-phase envelope shown in Fig. 4 back to that shown in Fig. 1 is straightforward. Values of the midpoint curve $h_{\text{mid}}(1)$ shown in Fig. 1 were calculated from values of $h_{\text{mid}}(4)$ shown in Fig. 4 from the equation

$$h_{\text{mid}}(1) = h^{\text{ig}} - h_c - h_{\text{mid}}(4) \qquad (16)$$

where h^{ig} was calculated from Eq. (4), and $h_{\text{mid}}(4)$ was calculated from Eq. (13). Addition or subtraction of one half of the enthalpy of vaporization calculated from Eq. (9) generates the two-phase envelope shown in Fig. 1. It can be seen from Fig. 4, though not from Fig. 1, that the calculated loop does not perfectly fit the liquid phase saturation residual enthalpies at the temperatures 423.2, 453.2, and 473.2 K, but the difference is no larger than the uncertainty of the measurements.

The 25 measurements at 562.9 K are as close to the critical temperature ($T_c = 563.0 \pm 0.2$ K) as we could get. As the purity of our material was 0.996 mole fraction, the principal impurities being di-n-butyl ether and 2 methylpropan-1-ol, the critical temperature of the butanol we were using could easily differ from that of pure butan-1-ol by 1 K. We note that the ideal-gas enthalpies obtained by extrapolating our measurements to zero pressure as shown in Fig. 2 are in good agreement with those obtained by Green's extrapolation from measurements on lower alcohols. Evidently this

quantity is not sensitive to the slight impurity of our material. Close to the critical pressure ($p_c = 4.427$ MPa), the isenthalp at 562.9 K shown in Fig. 1 is almost vertical, and the accuracy of the measurements in this region depends crucially on good pressure control. The nearest to p_c we could get were measurements at 4.32 and 4.52 MPa. It is difficult to know what the shape of the isenthalp should be in the near-critical region; we can only comment that the measurements do not look unreasonable.

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