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The enthalpy of acetone

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Measurements of the specific enthalpy increment of acetone are reported; 206 measurements cover the range 373.2 to 623.2 K at pressures from 0.1 to 11.9 MPa. The overall accuracy is 0.6 per cent. The specific enthalpy of the saturated liquid and of the saturated vapour and the enthalpy of vaporization are derived from the measurements. Comparison with cubic equations of state shows that the Patel–Teja equation is the best of those tested.

1. Introduction

Compression measurements on acetone vapour have been made by Anderson, Kudchadker, and Eubank(1) in the range 298.2 to 423.2 K at pressures up to saturation. Keller and Stiel(2) have made similar measurements in the range 508.2 to 538.2 K at pressures from 9.6 to 30.3 MPa. Both groups report problems with the decomposition of acetone at temperatures above 420 K. In a (p, V, T) apparatus where the vapour may be confined for many hours, even a slow rate of decomposition may result in the accumulation of significant amounts of impurity. Condensation reactions form substances which may coat the walls and greatly increase the errors due to adsorption. In a flow-calorimetric apparatus the residence time in the hot zone may be only a few minutes and the extent of decomposition may be negligible. Flow calorimetric experiments are, of course, free from adsorption errors. Pennington and Kobe(3) used a flow calorimeter to measure the vapour-phase heat capacity of acetone up to 439.2 K and 0.17 MPa. They also measured the enthalpy of vaporization up to 345.0 K. Wormald(4) used a flow calorimeter to measure the isothermal enthalpy-pressure coefficient of acetone in the range 313.2 to 373.2 K at pressures up to 80 kPa. Eubank and Smith(5) used a boil-off calorimeter to make the only previous direct measurements of the specific enthalpy increment of acetone. Their 67 measurements cover the range 394.7 to 532.8 K at pressures up to 6.7 MPa with an overall accuracy of around 4 per cent. We now report 206 measurements of the specific enthalpy increment of acetone in the range 373.2 to 623.2 K at pressures up to 11.9 MPa with an overall accuracy of better than 0.6 per cent.

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2. Experimental

The flow calorimeter and details of the experimental technique were the same as previously described.(6) The calorimeter was tested using steam and the results were compared with the 1984 NBS/NRC steam tables.(7) The mean deviation of 90 measurements of the specific enthalpy of steam from tabulated values was -0.03 per cent, and the standard deviation was 0.43 per cent. Flow-rate fluctuation due to uneven vaporization of water in the flash boiler were the largest source of random error. The low molar volume and high enthalpy of vaporization made it difficult to flash-vaporize water smoothly. No such problems were experienced with acetone, and the random error is less than for water.

Acetone of 99.8 moles per cent purity was dried with anhydrous potassium carbonate and doubly distilled, first and last fractions being rejected. The density of the purified material was $784.55\ \text{kg}\cdot\text{m}^{-3}$ at 298.15 K (literature:(8) $784.40\ \text{kg}\cdot\text{m}^{-3}$). Analysis using g.l.c. showed the material to be not less than 99.9 moles per cent $(CH_3)_2CO$. Freshly dried and distilled acetone was used for every run; the material was not recycled without repurification. After pumping acetone at a flow rate of approximately $0.3\ \text{g}\cdot\text{s}^{-1}$ through the apparatus for 1 h to obtain a steady state, measurements were taken over a 0.5 h period and averaged. The maximum temperature at which measurements were made was 623.2 K. At temperatures above 523.2 K liquid emerging from the calorimeter had a slight yellow coloration. Samples were analysed by g.l.c. and the density was measured.

3. Calculation of results

When a steady state had been reached a stream of acetone vapour at pressure p and temperature T_1 entered the water-cooled heat-exchange calorimeter and emerged as liquid at temperature T_2 at the same pressure. Heat lost by the acetone was gained by the cooling water. Measurement of the water flow rate and temperature rise allowed calculation of the quantity $\Delta h'$ where

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

The specific enthalpy increment Δh relative to 298.15 K and the saturation pressure p_s was calculated from the equation:

$$\Delta h = \Delta h' + \int_{298.15\ \text{K}}^{T_2} c_p(p, T)\mathrm{d}T + \int_{p_s}^{p} v(1-\alpha T)\mathrm{d}p, \tag{2}$$

where c_p is the specific heat capacity of acetone,(9) v is the specific volume, and α is the isobaric expansivity at 298.15 K.(9) When the calorimeter was correctly adjusted T_2 was close to 298.15 K, the c_p integral was small, and the pressure dependence could be neglected. Correction for heat leaks, for the rate at which kinetic energy entered the calorimeter, and a small (0.02 per cent) correction for the presence of dissolved air in the acetone pumped into the calorimeter were made as previously described.(6) Systematic errors were the same as for the measurements on n-hexane, and were estimated to be no greater than 0.2 per cent. The biggest source of random error arose from fluctuations in the operation of the metering pump supplying the acetone. Under most conditions the random error was around 0.3 per cent. Close to the critical temperature and pressure small fluctuations in flow rate caused large changes in the density of the fluid in the calorimeter, and the random error on some of the measurements was around 1 per cent.

4. The effect of decomposition products

Decomposition of the acetone was greatest at 623.2 K. From the flow rate, the volume of the hot zone and the specific volume of acetone calculated using the Patel–Teja(10) equation of state, the residence time in the hot zone for a run at 623.2 K and 10.49 MPa was found to be 500 s. Analysis by g.l.c. showed that the acetone contained 0.01 mole per cent of methanol, 0.17 mole per cent of diacetone alcohol, 0.78 mole per cent of mesityl oxide, and 0.05 mole per cent of phorone, a total of 1.01 moles per cent of impurity. For runs at lower pressures the residence time in the calorimeter was shorter and smaller amounts of impurity were detected. Above 573.2 K it was found that the amount of mesityl oxide formed was about twice as much as all other impurities. At 573.2 K and 10.28 MPa the amount of mesityl oxide was 0.07 mole per cent and the total impurity was 0.1 mole per cent. At 473.2 K and 10.58 MPa the acetone contained 0.08 mole per cent of phorone and 0.02 mole per cent of mesityl oxide, again a total of 0.1 mole per cent.

An estimate of the effect of impurities on the measured specific enthalpy increment was made assuming that under all conditions the whole of the impurity was mesityl oxide. Critical constants for mesityl oxide estimated by the method of Lydersen(11) are $T_c = 605$ K and $p_c = 4.95$ MPa. Pitzer's acentric factor ω obtained from the vapour pressure is 0.456. The residual molar enthalpy was calculated using the Patel–Teja(10) equation of state. The molar enthalpy relative to 298.15 K and the saturation pressure was calculated using the enthalpy of vaporization estimated by the method of Riedel(12) and the ideal-gas heat capacity estimated by the method of Rihani and Doriaswami.(13) The molar enthalpy $H_m(x)$ of the mixture is given by

$$H_m(x) = H_m^E + xH_m(A) + (1-x)H_m(B), \qquad (3)$$

where $H_m(A)$ is the molar enthalpy of acetone and $H_m(B)$ is the molar enthalpy of mesityl oxide. H_m^E was calculated using the Patel–Teja equation of state. For worst-case conditions: 623.2 K and 10.49 MPa, the measured specific enthalpy increment was $947.2\ \mathrm{kJ \cdot kg^{-1}}$. Correction for the 1.01 moles per cent impurity gave $944.3\ \mathrm{kJ \cdot kg^{-1}}$ for the specific enthalpy increment of pure acetone, a difference of only 0.3 per cent. At 573 K and 10.28 MPa the difference was less than 0.1 per cent, and at lower temperatures, even in the liquid phase where the residence time in the hot zone was approximately 1500 s, the difference was always less than 0.1 per cent. The isotherm for which the measurements are likely to be most sensitive to impurity is that at 510.2 K, 2.1 K above T_c. However even for runs at close to p_c (4.70 MPa), where H_m^E is largest, the uncertainty due to impurity was calculated to be less than 0.1 per cent. The overall accuracy of the 206 measurements is estimated to be 0.6 per cent.

5. Comparison with other work

Results of 206 measurements of the enthalpy of acetone are listed in table 1 and shown in figure 1. The upper boundary of the two-phase region was located using the vapour-pressure measurements of Ambrose, Sprake, and Townsend.(14) The intersection of the vertical lines drawn across the two-phase region with the isotherms drawn through the measurements made on liquid acetone fixed the lower boundary. Enthalpy increments for saturated liquid and gaseous acetone, and specific enthalpies of vaporization $\Delta_{\text{vap}}h$ are listed in table 2. The maximum uncertainty in $\Delta_{\text{vap}}h$ is estimated to be 2 $\text{kJ}\cdot\text{kg}^{-1}$. At temperatures up to 345.0 K Pennington and Kobe(3) measured $\Delta_{\text{vap}}h$ directly. These measurements and those listed in table 2 were fitted to the Watson equation:(15)

$$\Delta_{\text{vap}}h(T) = \Delta_{\text{vap}}h(T_{\text{b}})\{(1-T/T_{\text{c}})(1-T/T_{\text{b}})^{-1}\}^{n}. \tag{4}$$

Using $T_{\text{b}} = 329.4$ K, $T_{\text{c}} = 508.1$ K, $\Delta_{\text{vap}}h(T_{\text{b}}) = 501.7\ \text{kJ}\cdot\text{kg}^{-1}$ the best value of n was found to be 0.3915. Values of $\Delta_{\text{vap}}h^{\text{c}}$ calculated using the Watson equation are listed in table 2. Comparison of the experimental values of $\Delta_{\text{vap}}h$ with the Watson equation is made in figure 2. The standard deviation of the points from the curve is 0.3 per cent.

Ideal-gas enthalpies computed from spectroscopic quantities by Chao and Zwolinski(16) were adjusted to the reference state ($T = 298.15$ K, $p = p_{\text{s}}$) using the isothermal enthalpy-pressure coefficient equation of Wormald(4) and $\Delta_{\text{vap}}h(298.15\ \text{K}, p_{\text{s}})$ from TRC(8) tables. The curve shown in figure 3 was calculated from a quadratic equation fitted to these points. Extrapolation of Eubank and Smith's enthalpy increments to zero pressure yields points which are on average 3 per cent higher than the curve, whereas extrapolation of the table 1 measurements yields ideal-gas enthalpies which are 0.5 per cent higher, well within the combined uncertainty of the measurements and the computed ideal-gas enthalpies.

6. Comparison with cubic equations of state

While it is not expected that cubic equations of state will fit the (p, V, T) or (H, p, T) surface of a polar fluid with anything other than moderate accuracy, the use of cubic equations to fit mixture properties makes it desirable to know which of the modern equations best fits the properties of acetone. We have examined the equations of Soave,(17) Gibbons and Laughton,(18) Peng and Robinson,(19) and Patel and Teja.(10) Soave(17) modified the Redlich–Kwong equation introducing the Pitzer acentric factor ω into the attractive-energy term. While the equation is an improvement over the RK equation predicted liquid densities are poor. Gibbons and Laughton(18) modified the Soave equation and improved the fit to vapour pressures by introducing two substance-dependent parameters. The fit to liquid densities is not improved. Peng and Robinson(19) improved the fit to liquid densities by modifying the form of the attractive-energy term. The improvement is due to the lowering of the calculated critical compression factor Z_{c}' from 0.3333 for the Soave equation to 0.3074, which is close to that for hydrocarbons and many polar fluids.

TABLE 1. Measurements of the specific enthalpy increment Δh of acetone. The enthalpy increment Δh was calculated using equation (2) as described in the text. $\Delta h = 0$ for liquid acetone at 298.15 K and saturation pressure

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}
373.2	0.10	644.9	0.20	635.1	0.46	165.8	1.24	168.6	7.09	169.3
	0.10	639.4	0.32	630.0	0.50	169.3	2.19	168.2	10.75	172.2
	0.16	641.8	0.33	626.5	0.78	169.7	4.30	168.9		
398.2	0.10	682.8	0.23	677.4	0.41	667.3	0.60	654.8	2.09	229.2
	0.10	683.7	0.29	669.8	0.50	657.3	0.85	224.8	4.20	232.1
	0.20	681.7	0.34	673.5	0.59	657.1	1.45	226.1	7.16	229 9
423.2	0.10	726.7	0.40	713.6	0.99	683.6	1.25	304.1	4.32	292.9
	0.17	726.6	0.69	699.6	1.10	668.4	1.27	293.9	7.22	288.4
	0.31	714.8	0.80	693.6	1.14	644.2	1.82	295.1	10.95	295.5
448.2	0.10	766.4	0.74	745.4	1.53	713.8	2.22	365.0	4.53	363.6
	0.26	762.6	1.01	731.0	1.78	696.7	3.28	364.8	7.19	358.5
	0.45	757.4	1.33	725.5						
473.2	0.10	813.3	1.22	774.7	2.36	729.3	3.15	441.9	5.67	433.8
	0.29	806.4	1.47	768.7	2.62	717.3	3.82	438.9	7.15	430.8
	0.56	800.9	1.72	754.7	2.96	436.3	4.57	436.0	10.58	423.5
	0.84	791.2	2.24	737.4	3.00	437.7				
490.2	0.10	843.5	0.76	829.9	2.72	757.8	3.87	490.2	5.35	483.1
	0.10	849.0	1.55	804.5	3.36	728.5	4.30	498.0	7.01	467.9
	0.29	840.7	2.09	782.5	3.67	517.7	4.58	484.6	10.74	473.8
498.2	0.10	854.4	1.68	816.0	3.28	752.7	4.20	542.6	4.42	538.0
	0.16	847.4	2.03	804.0	3.77	727.1	4.27	553.4	4.88	524.1
	0.44	847.1	2.47	790.0	3.97	711.7	4.31	525.6	5.72	518.1
	0.66	843.4	2.79	778.1	4.09	528.8	4.32	524.6	7.26	498.4
	1.23	827.5								
505.2	3.49	769.4	4.58	571.3	5.29	545.9	5.81	541.1	8.53	527.4
	3.90	747.4	4.80	564.5	5.33	545.5	6.22	541.0	10.57	511.7
	4.24	723.3	4.91	559.5	5.57	544.4	7.30	529.4	11.19	522.9
	4.38	718.3	4.94	556.2						
510.2	0.10	882.5	2.50	818.2	4.84	678.1	5.08	592.7	6.33	552.6
	0.36	874.8	3.20	790.7	4.90	676.7	5.36	577.9	7.09	546.5
	0.86	863.0	3.73	770.0	4.92	643.3	5.58	571.8	9.26	536.6
	1.35	846.6	4.35	734.5	4.93	664.8	6.00	568.1	11.11	538.5
	1.79	837.5	4.69	705.7	5.05	647.8				
523.2	0.10	910.4	2.42	850.1	4.62	771.3	6.01	646.8	7.59	593.2
	0.57	898.4	3.18	830.9	5.25	728.6	6.39	630.3	10.02	583.3
	1.75	872.4	3.87	807.5	5.80	676.2	6.68	616.2		
548.2	0.10	959.4	2.45	910.8	4.57	852.0	6.83	767.7	11.04	682.0
	0.77	938.0	3.18	898.5	5.30	832.1	7.68	725.7		
	1.59	927.4	3.86	874.8	6.21	790.7	9.32	686.7		
573.2	0.10	1011.3	2.88	964.9	5.66	892.7	8.62	798.4	11.94	761.5
	1.65	980.4	4.40	923.6	7.19	847.0	10.28	769.7		
598.2	0.10	1066.6	3.27	1008.8	5.79	966.7	8.58	914.5	11.79	842.7
	1.81	1024.9	4.64	989.1	7.28	931.9	10.05	867.2		
623.2	0.10	1119.5	3.05	1072.1	5.91	1018.5	9.14	961.5	11.75	923.0
	1.70	1090.5	4.48	1044.2	7.58	991.5	10.49	947.2		

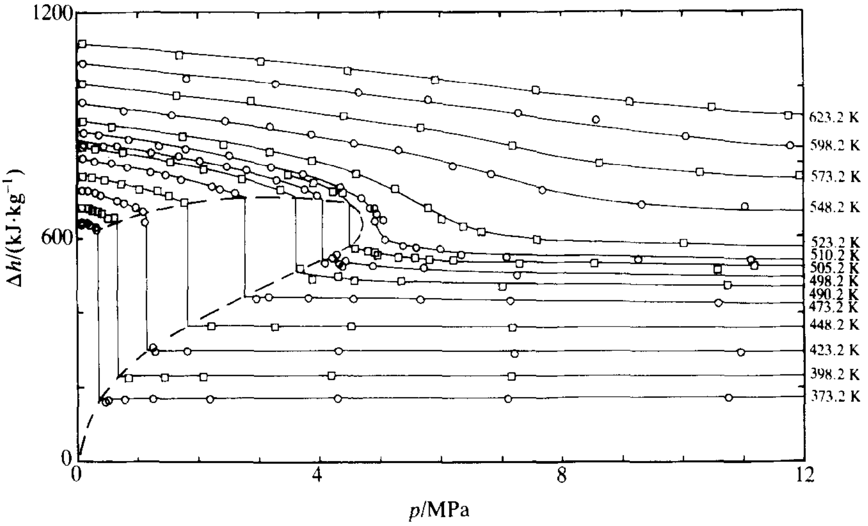

FIGURE 1. The specific enthalpy increment Δh of acetone plotted against pressure. Points on alternate isotherms are marked with circles and squares for clarity.

The Peng–Robinson equation fits the thermodynamic properties of many non-polar and weakly polar fluids better than most three-parameter cubic equations. Patel and Teja[10] modified the Peng–Robinson equation by adding a parameter c which allows Z'_c to be varied to optimize the fit to liquid densities for a wide range of fluids, including polar and long chain molecules. The equation is

$$p = RT/(V-b)-a(T)/\{V(V+b)+c(V-b)\}, \tag{5}$$

where

$$a(T) = a_c\{1+F(1-T_r^{1/2})\}^2. \tag{6}$$

The parameters a_c, b, and c can be calculated from criticality conditions which yield

$$\Omega_c = 1-3Z'_c, \tag{7}$$

TABLE 2. The specific enthalpy of vaporization $\Delta_{vap}h$ of acetone. The specific enthalpies of the saturated vapour $\Delta h(\mathrm{g})$ and saturated liquid $\Delta h(\mathrm{l})$ were obtained from the measurements listed in table 1 as described in the text. $\Delta_{vap}h^c$ was calculated from equation (4)

T/K	$\Delta h(\mathrm{g})$/$\mathrm{kJ\cdot kg^{-1}}$	$\Delta h(\mathrm{l})$/$\mathrm{kJ\cdot kg^{-1}}$	$\Delta_{vap}h$/$\mathrm{kJ\cdot kg^{-1}}$	$\Delta_{vap}h^c$/$\mathrm{kJ\cdot kg^{-1}}$
373.2	619.0	169.0	450.0	449.4
398.2	644.0	230.0	414.0	414.8
423.2	668.0	294.0	374.0	374.9
448.2	692.5	364.5	328.0	327.0
473.2	706.5	442.5	264.0	264.7
490.2	708.5	508.0	200.5	203.8
498.2	701.0	542.0	159.0	161.6
505.2	680.0	580.0	100.0	99.9

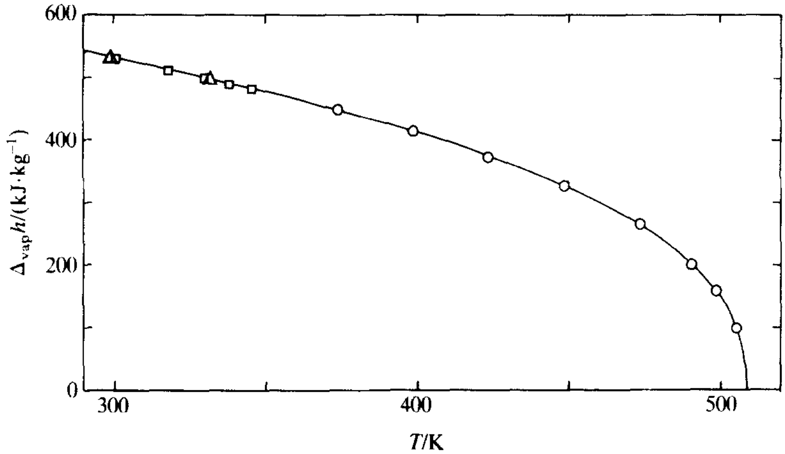

FIGURE 2. The specific enthalpy of vaporization $\Delta_{\rm vap}h$ of acetone. □, reference 3; △, reference 8; ○, table 2; ———, calculated using equation (3).

$$c = \Omega_c RT_c/p_c, \tag{8}$$

$$\Omega_a = 3Z_c'^2 + 3(1-2Z_c')\Omega_b + \Omega_b^2 + 1 - 3Z_c', \tag{9}$$

and

$$a_c = \Omega_a R^2 T_c^2/p_c. \tag{10}$$

Ω_b is the smallest positive root of

$$\Omega_b^3 + (2-3Z_c')\Omega_b^2 + 3Z_b'^2\Omega_b - Z_c'^3 = 0, \tag{11}$$

and

$$b = \Omega_b RT_c/p_c. \tag{12}$$

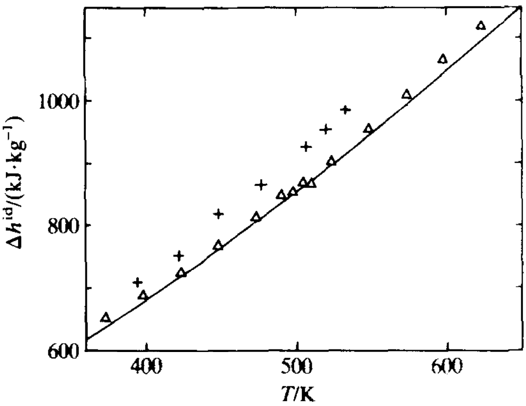

FIGURE 3. The specific enthalpy $\Delta h^{\rm id}$ of the ideal gas for acetone. △, Obtained by extrapolating the measurements listed in table 1 to $p = 0$; +, obtained by extrapolating the measurements of Eubank and Smith(5) to $p = 0$; ———, calculated from a quadratic equation fitted to ideal-gas enthalpies obtained from spectroscopic measurements.(16)

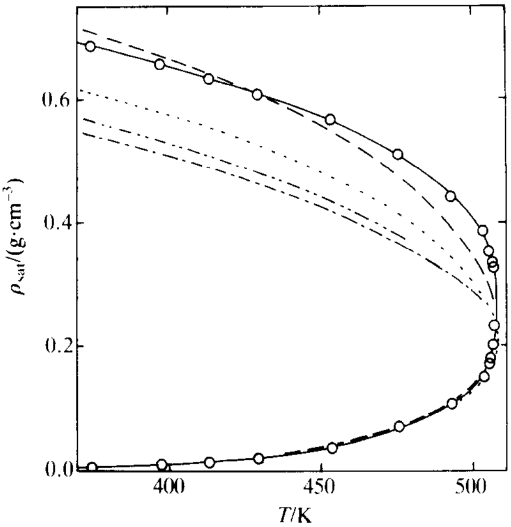

FIGURE 4. Comparison of saturated liquid and vapour densities for acetone with equations of state. ○, Measurements of Campbell and Chatterjee;(20) ———, best line through the reference 20 measurements; — — —, calculated using the Patel–Teja(10) equation of state; . . . ., calculated using the Peng–Robinson(19) equation of state; —·—·—, calculated using the Gibbons–Laughton(18) equation of state; —··—··, calculated using the Soave(17) equation of state.

Parameter F is adjusted to fit the vapour pressure. Parameter c allows the compression factor to be varied to optimize the fit to the saturated liquid density. If $c = b$ the equation reduces to the Peng–Robinson form, and if $c = 0$ it reduces to the Soave form. The residual enthalpy $(H - H^{\mathrm{id}})$ is given by

$$(H - H^{\mathrm{id}}) = pV - RT - (a - T\mathrm{d}a/\mathrm{d}T)(1/2N)\ln\{(V+Q)(V+M)^{-1}\}, \qquad (13)$$

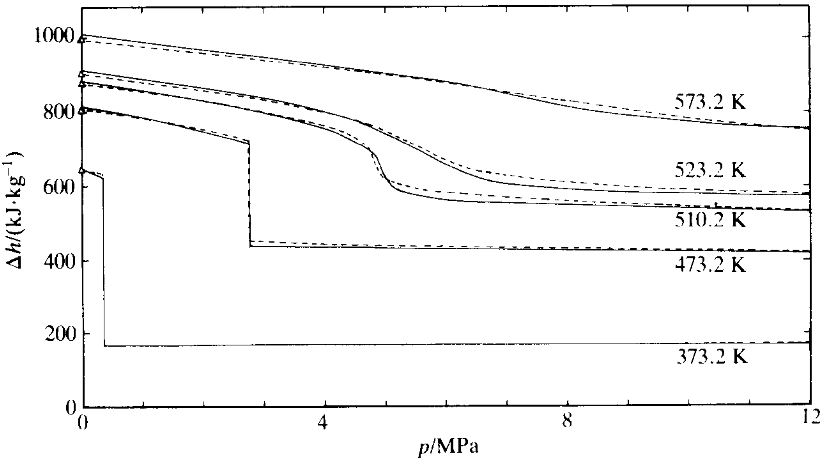

FIGURE 5. Comparison of the specific enthalpy of acetone with the Patel–Teja equation. ———, Best curves through the table 1 measurements; — — —, calculated using the Patel–Teja equation;(10) △, ideal-gas enthalpies obtained from spectroscopic measurements.(16)

where

$$N = \{bc+0.25(b+c)^2\}^{1/2}, \tag{14}$$

$$M = 0.5(b+c)-N, \tag{15}$$

$$Q = 0.5(b+c)+N. \tag{16}$$

To test the four equations of state we compared the fit to our enthalpy measurements and to the saturated liquid and vapour densities of Campbell and Chatterjee.(20) It was at once clear that density measurements provided a much better test than enthalpies. Comparison with saturated liquid and vapour densities is made in figure 4. All four equations fit the vapour-density measurements to within 1 or 2 per cent. The Patel–Teja equation gives the best fit to saturated liquid densities and is clearly the best of the four. Second best is the equation of Peng and Robinson. The equation of Gibbons and Laughton gives the best fit to vapour densities but the fit to liquid densities is similar to that for the Soave equation.

Comparison of best curves through the table 1 measurements with the Patel–Teja equation is made in figure 5. Ideal-gas enthalpies were taken from reference 16. The equation fits the measured enthalpy increments to within 2 to 3 per cent except in the critical region where the fit is to within 5 per cent.

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