THE HEAT CAPACITY OF FLUORINATED PROPANE AND BUTANE DERIVATIVES BY DIFFERENTIAL SCANNING CALORIMETRY*

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The constant pressure liquid-phase heat capacities of 21 hydrogen containing fluorinated propane and butane derivatives and one fluorinated ether (CF_3OCF_2H) with boiling points ranging from −34.6° to 76.7°C have been measured to 3% accuracy by differential scanning calorimetry at 40°C. The measurements are needed to help identify alternative refrigerants and blowing agents that do not deplete the stratospheric ozone layer. The DSC method has two significant advantages for this purpose, which are:

(i) only small samples (less than 100 mg) are required, and

(ii) the instruments are available in many laboratories and can be used for the heat capacity measurement of liquids with subambient boiling points without modification or special accessories.

Introduction

The Montreal Protocol [1] and the Clean Air Act of the United States [2] have called for restricting the future production of certain fully halogenated chlorofluorocarbon (CFC) refrigerants, halons, and blowing agents. At present the hydrogen containing compounds (HCFC), HCFC-123 (CCl_2HCF_3) and HFC-134a (CF_3CFH_2) [3], have emerged as substitutes for the refrigerants CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2), respectively. In general the substitutes contain hydrogen which implies a finite atmospheric lifetime and have a low chlorine content which implies a low ozone depletion potential. More recently there have been reassessments of the phaseout schedules for chlorine containing refrigerants and blowing agents [4]. This has motivated the search for "second generation" alternatives for the currently used CFCs.

Our efforts have been concerned with the investigation of fluorinated propane and butane derivatives as second generation CFC alternatives [5]. Evaluating these compounds as CFC alternatives required measurement of their physical properties. For this initial screening process, the liquid-phase heat capacity was estimated as a function of temperature from ideal gas heat capacities and a combination of measured pressure, volume, and temperature (PVT) data and various equations of state [6]. However we desired a measured value of the liquid heat capacity for at least one temperature to check the accuracy of the estimation methods for each compound. We chose differential scanning calorimetry (DSC) [7, 8] for measurement of the liquid-phase heat capacity because of the availability of the instrumentation, the method is convenient for small temperature ranges near the ambient temperature, and only small amounts of sample; i.e., less than 100 mg are required. The DSC method has been used extensively for heat capacity measurements of involatile samples [9], and there are some examples in the literature of heat capacity measurements of volatile liquid samples [10] and liquid samples at temperatures approaching their boiling points [11–13]. However after a search of the literature, we believe this work represents the first successful effort to measure heat capacities of liquids with subambient boiling points near room temperature by DSC methods.

Experimental methods

We employed a Perkin Elmer DSC-4 differential scanning calorimeter with computer controlled temperature scan and output via a 3600 Data Station and Perkin Elmer 660 printer. The calorimeter operated at or above ambient temperature. The samples were contained in 75 μl stainless steel capsules manufactured by Perkin Elmer. The sample was sealed inside the capsule with a press fitted stainless steel cap employing a Viton O-ring seal. The capsules were capable of containing samples at pressures up to 20 atm and the material loss (1 mg/day) was negligible for the experimental time span of the order of 20 min. The greatest dif-

ficulty encountered was the delivery of a liquid sample with a subambient boiling point to the sample capsule. This problem was solved by preparing the samples in a dry cold room. The cold room facilities permitted us to obtain cold room temperatures as low as −35°C. In this environment the samples could be drawn into a microliter syringe which permitted the delivery of precise amounts of sample to the sample capsule. In order to minimize corrections for the presence of vapour, we tried to obtain sample volumes just below the capsule volume so that the dominant portion of sample was liquid. This was relatively easy to accomplish if the liquid density was known. For samples where the liquid density was not measured, estimates of the liquid density [14] were normally satisfactory. Also with some experience, samples with optimal densities could be prepared visually by filling the sample capsule at the cold room temperature (−35°C) to just below the rim of the sample capsule (or about 50 μl). Samples whose overall density was near or exceeded the liquid density at ambient temperatures were inadvertently prepared in this work on several occasions. This resulted in unstable calorimeter output which perhaps was a signal for high sample pressures. However this never resulted in a bursting of the sample capsule.

The calorimeter was calibrated with a 125 mg sapphire disk in the sample compartment using a scan rate of 5 deg/min over the temperature range, 35° to 60°C. For the calibration procedure the calorimeter asymmetry was first obtained with a blank scan in which sample and reference compartments of the calorimeter were empty. The calorimeter scan (35° to 50°C and occasionally 35° to 60°C for samples with boiling points above 15°C) for the samples was performed with the sample capsule in the sample compartment and an empty reference sample capsule on the reference side. The asymmetry of the system for the sample scan was checked by running a scan with the empty sample pan in the sample compartment and the reference sample capsule in the reference compartment. After completing this work we learned that calibration can be improved if performed with a capsule filled with sapphire powder rather than a sapphire disk. However as a check on the accuracy of our procedures, measurements were periodically carried out on CFC-11 and CFC-12 for which accurate heat capacities measured by conventional adiabatic calorimetry are available [15–18]. Our experimental values are within 1.2% of the literature values for CFC-11 and within 3.2% of the literature values for CFC-12 which is consistent with the estimated experimental error of 3%.

Data treatment

The measurement of heat capacity for volatile liquids by the DSC method required sealing the sample in a capsule with both liquid and vapour present. Therefore the calorimeter response for the total heat capacity of the constant volume sample, C, needed to be corrected to the constant pressure heat capacity of the liq-

uid, C_p. The following equations, whose derivations are presented in the Appendix of this paper, were used to calculate these corrections,

$$C_p = C + C_{vap} + C_{\Delta h} + C_\tau + C_\kappa,$$ (1)

$$C_{vap} = F(C - C_{pv}),$$ (2)

$$C_{\Delta h} = -\left[\Delta h - P\frac{\rho_l - \rho_v}{\rho_l \rho_v}\right]\left(\frac{\partial \ln(1+F)}{\partial T}\right)_s$$ (3)

$$C_\tau = \left[P + T\left(\frac{\partial P}{\partial T}\right)_s\right]\left[\frac{\alpha_l}{\rho_l} + F\frac{\alpha_v}{\rho_v}\right]$$ (4)

$$C_\kappa = -P\left(\frac{\partial P}{\partial T}\right)_s\left[\frac{\kappa_l}{\rho_l} + F\frac{\kappa_v}{\rho_v}\right]$$ (5)

In applying the above equations, gram units were used for the heat capacity and the other relevant quantities. The correction, C_{vap}, is for the heat capacity of the vapour C_{pv}, $C_{\Delta h}$ is a correction for the heat of vaporization of the liquid Δh, C_τ is a correction for thermal expansion of liquid and vapour and C_κ is a correction for the compressibility of the liquid and vapour. The corrections C_τ and C_κ must be made because the measurement is made for varying pressure for the liquid and the constant pressure heat capacity of the liquid is desired. The subscript "s" on the partial derivatives indicates that the differentiation is restricted to the liquid-vapour coexistence region. The quantity F is the ratio of the mass of vapour, m_v, to that of liquid m_l i.e.,

$$F = \frac{m_v}{m_l},$$ (6)

and it is calculated from the overall density of the sample using the lever rule relation,

$$F = \frac{\rho_v}{\rho_l}\left(\frac{\rho_l - \rho}{\rho - \rho_v}\right).$$ (7)

The quantity ρ is the overall density of the sample, ρ_v and ρ_l are the vapour and liquid densities, α_v and α_l are the thermal expansion coefficients, κ_v and κ_l are the isothermal compressibilities, T is the absolute temperature, and P is the pressure. Normally air is trapped in the capsule and the pressure P is normally larger than the calculated vapour pressure used to estimate C_τ and C_κ. However the magnitudes of C_τ and C_κ are less than 1% of the heat capacity and the inaccuracies that result from trapped air are negligible. For a complete description of all terms in Eqs (1) to (7) and how they arise, the reader is referred to the Appendix.

The correction unique to this work is the heat of vaporization correction $C_{\Delta h}$. It arises because the relative amounts of liquid and vapour in the capsule vary with temperature and this variation may be either positive or negative depending on the overall density ρ of the sample. If the overall sample densities are too small, $C_{\Delta h}$ is the dominant correction, being as large as 5%. In this work the samples were prepared (see Section II) so that this correction would be less than 1%, which is comparable to sum of the remaining corrections. This is less than our estimated experimental error of 3% and neglecting the corrections would thus be justified. Nevertheless the corrections were applied to ensure that they would be small using the experimental technique herein described for all compounds studied which exhibited a wide range of boiling points. Also it is useful to describe the application of the corrections since they would be essential to achieving the ultimate accuracy obtainable with improved DSC calorimeters equipped with computer averaging equipment [19, 20].

One can calculate the corrections to a sufficient accuracy from a measurement of the boiling point and physical property estimation methods [14]. Since the boiling point is normally measured upon synthesizing a volatile compound, this procedure does not require any additional experimental effort. However our overall research effort required judging these compounds as alternative refrigerants, industrial blowing agents, and solvents, which required as a minimum that we measure the saturated liquid densities, the critical parameters (temperature and density), and vapour pressures up to the boiling point [5]. We have taken advantage of all these data in calculating the corrections from Eqs (1) to (5). The following paragraphs describe these calculations and give necessary modifications if only the boiling point is measured.

The vapour-phase PVT properties needed to calculate the corrections are estimated from the measured critical density and critical temperature using a modified corresponding states method which utilizes Eqs (8) to (10) (14),

$$Z = \frac{P}{\rho R T}, \tag{8}$$

$$Z = Z^{(o)} + \omega Z^{(1)}, \tag{9}$$

$$Z^{(1)} = \frac{Z^{(R)} - Z^{(o)}}{\omega_R}, \tag{10}$$

where ω is the Pitzer acentric factor for the system of interest and ω_R is the same factor for the selected reference fluid, HFC-134a. The quantity $Z^{(o)}$ is the compressibility of a simple fluid which is defined as a function of the reduced variables by the Benedict-Webb-Rubin equations of state with the simple fluid constants of Lee and Kesler [21]. The modified Benedict-Webb-Rubin equation of state with constants obtained by McLinden *et al.* [6] was used to obtain the reference fluid compressibility, $Z^{(R)}$ under the same reduced temperature and density

conditions at which $Z^{(o)}$ was calculated. The acentric factor is calculated from the equations of Lee and Kesler [21],

$$\omega = -\frac{\ln P_c + f^{(o)}(T_{br})}{f^{(1)}(T_{br})}, \tag{11}$$

where P_c is the critical pressure in units of atmospheres,

$$f^{(o)}(T_r) = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln(T_r) + 0.16934 T_r^6, \tag{12}$$

and

$$f^{(1)}(T_r) = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln(T_r) + 0.43577 T_r^6. \tag{13}$$

The quantity T_r $(=T/T_c)$ is the reduced temperature and T_{br} is the reduced boiling point.

The procedure is to calculate $Z^{(o)}$ and $Z^{(1)}$ at the critical point (temperature, density, and pressure in reduced units being unity) and then solving Eqs (11) to (14),

$$Z_c = \frac{P_c}{\rho_o R T_c} = Z_c^{(o)} + \omega Z_c^{(1)}, \tag{14}$$

for the critical pressure and acentric factor using the measured value for the critical density ρ_c and the critical temperature T_c. The subscript c refers to the critical point. The vapour pressure may then be evaluated from Eq. (15) for a reduced temperature T_r,

$$\ln\left(\frac{P}{P_c}\right) = f^{(o)}(T_r) + \omega f^{(1)}(T_r). \tag{15}$$

The vapour pressure and its temperature derivatives, which are needed to calculate the measured heat capacity corrections from Eqs (1) to (5), may then be calculated from Eq. (15). The vapour density and its derivatives are calculated from the equation of state (Eqs (8) to (10)) using the acentric factor calculated from Eqs (11) to (13). The liquid density and its density derivatives are calculated from Eq. (16), an empirical representation of the measured liquid densities [5],

$$\rho_l = A + Bt + Ct^2, \tag{16}$$

where A, B and C are the empirical parameters and t is the centigrade temperature. Normally the liquid compressibility, κ_l was not known. However since the liquid compressibility is a small contribution to a small correction, C_κ, it was neglected; i.e., set equal to zero. The heat of vaporization, Δh is calculated from the heat of vaporization at the boiling point, Δh_b, using Eq. (17) [14, 22, 23],

$$\Delta h = \Delta h_{\mathrm{b}} \left[\frac{1 - T_{\mathrm{r}}}{1 - T_{\mathrm{br}}} \right]^{0.38} . \tag{17}$$

The heat of vaporization at the boiling point is obtained from measurements of the vapour pressure and the Clausius-Clapeyron equation.

If only the boiling point is measured (i.e. no densities are measured) one needs to modify the procedure by estimating the critical parameters (pressure, temperature, and density) from the molecular formulas using group contribution methods (either Ambrose method or Joback modification of Lydersen's method) which are described in Reference [14]. These methods are reasonably accurate if a measured boiling point is available. From these estimates and the measured boiling point, the acentric factor may be calculated from Eq. (11). One can then estimate the vapour density and its derivatives from Eqs (8) to (10) and the vapour pressure and its temperature derivatives from Eq. (15) as before. The liquid density may be estimated as a function of temperature from the Eqs (18) through (21) [14, 24],

$$\frac{V_{\mathrm{l}}}{V^*} = V_{\mathrm{R}}^{(0)} \left[1 - \omega V_{\mathrm{R}}^{(\delta)} \right], \tag{18}$$

$$V_{\mathrm{R}}^{(0)} = 1 - 1.52816(1 - T_{\mathrm{r}})^{\frac{1}{3}} + 1.43907(1 - T_{\mathrm{r}})^{\frac{2}{3}} -$$
$$- 0.81446(1 - T_{\mathrm{r}}) + 0.190454(1 - T_{\mathrm{r}})^{\frac{4}{3}} , \tag{19}$$

$$V_{\mathrm{R}}^{(\delta)} = \frac{[-0.296123 + 0.386914 T_{\mathrm{r}} - 0.0427258 T_{\mathrm{r}}^2 - 0.0480645 T_{\mathrm{r}}^3]}{[T_{\mathrm{r}} - 1.00001]} , \tag{20}$$

$$\rho_{\mathrm{l}} = \frac{M}{V_{\mathrm{l}}} , \tag{21}$$

where the quantity V^* is within 1 to 4% of the critical volume [14] and, for the purposes of calculating corrections for the heat capacity measurements, it may be assumed to be equal to the critical volume. The heat of vaporization at the boiling point is calculated from the boiling point using Riedel's equation [14, 25],

$$\Delta h_{\mathrm{b}} = 1.093 \frac{R T_{\mathrm{c}}}{M} \left[T_{\mathrm{br}} \frac{\ln P_{\mathrm{c}} - 1.013}{0.930 - T_{\mathrm{br}}} \right] . \tag{22}$$

In the above equation M is the molecular weight and P_{c} must be in atmosphere units. For subambient boiling point liquids the boiling point is normally obtained from vapour pressure measurements as a function of temperature, in which case Δh_{b} can be extracted from the vapour pressure measurements rather than from Eq. (22).

Table 1 Measured and calculated quantities used to obtain corrected heat capacities from DSC data on a 79.8 mg sample of CF_3CHFCF_2H at 40°C

Part A Physical properties and level rule quantities

Technique	T_c / °C	ρ_c /	ρ_l (40°C) /	Δh_b /	F	$\frac{\partial \ln(1+F)}{\partial T}$
		kg·m^{-3}		kJ·mol^{-1}		
Measured T_b, T_c, ρ_c, $\rho_l(T)$ and $P(T)$	141.1	579	1340	27.00	0.00428	8.9·10^{-5}
Measured T_b and ρ_l at one temperature	153	593	1342	23.88	0.00409	9.2·10^{-5}
Measured T_b	153	593	1439	23.88	0.00516	12.8·10^{-5}

Part B Calculated corrections and C_p

Technique	C_Δ / J	C_{vap} / J	C_τ / J	C_κ / J	Total Corr	C_p
Measured T_b, T_c, – ρ_c, $\rho_l(T)$ and $P(T)$	−0.0128	0.0018	0.0102	−0.0023	−0.0031	1.310
Measured T_b and ρ_l at one temperature	−0.0101	0.0018	0.0081	−0.0021	−0.0023	1.311
Measured T_b	−0.0139	0.0022	0.0086	−0.0027	−0.0058	1.307

In order to evaluate the various methods for calculating the corrections to the heat capacity measurement, we examined the corrections for a 79.8 mg sample of CF_3CHFCF_2H (T_b=6.5°C) at 40°C in Table 1. Since the sample capsule is 75 µl, this provides an overall sample density, ρ, of 1.06 g/cm^3, which is a very typical value for the sample density. We note in this case that the corrections are less than 0.6% of C_p and the various methods of estimation of the corrections are within 0.3% of C_p. Smaller sample sizes would yield larger corrections. Generally sample sizes that require large corrections (greater than 5%) should be avoided because the corrections assume vapour pressure equilibrium which is probably only partially achieved in a DSC experiment.

Results and discussion

The results for the measurement of C_p for the 22 HFCs and HCFCs which were investigated in this work are given in Table 2 along with their boiling points. Since the calorimeter provided data in the range from 35° to 50°C (in case of higher boiling chemicals the data ranged up to 60°C), we were able to estimate a temperature coefficient of the heat capacity at about 40°C which is also given in

Table 2. At least three samples of each chemical were prepared providing at least three independent measurements. For most of the chemicals six or more DSC measurements were performed. The standard deviations for these measurements were about 1.6%. In order to make a judgement on the absolute accuracy of our measurements, experiments were performed on CFC-11 and CFC-12 for which accurate values of C_p are available [15 to 18].

Table 2 The measured boiling point and liquid-phase heat capacity at 40°C for HFCs and HCFCs which are potential alternatives for currently used refrigerants and blowing agents. The estimates of the temperature coefficients of the heat capacities which are obtained from the DSC measurements are also given.

Compound		T_b /	$\dfrac{dC_p}{dT}$ /	C_p / (40 °C)
ASHRAE [3]	Formula	°C	$J \cdot deg^{-2} \cdot g^{-1}$	$J \cdot deg^{-1} \cdot g^{-1}$
E-125a	CF_3OCF_2H	−34.6	0.0042	1.327
HFC-236ea	CF_3CHFCF_2H	6.5	0.0051	1.304
HFC-245fa	$CF_3CH_2CF_2H$	15.3	0.0034	1.422
HFC-227ea	CF_3CHFCF_3	−18.2	0.0052	1.258
HFC-236fa	$CF_3CH_2CF_3$	−1.1	0.0052	1.371
HCFC-225da	$CF_3CHClCF_2Cl$	50.8	0.0037	1.087
HCFC-226da	$CF_3CHClCF_3$	14.1	0.0052	1.207
C-326d	$c-(CF_2)_3CHCl$	38.1	0.0041	1.158
HCFC-243da	$CF_3CHClCH_2Cl$	76.7	0.0033	1.234
HCFC-226ea	CF_3CHFCF_2Cl	17.1	0.0037	1.205
HCFC-234da	$CF_3CHClCFHCl$	70.1	0.0026	1.176
HCFC-225ba	$CF_3CFClCFHCl$	51.9	0.0024	1.087
HFC-227ca	$CF_3CF_2CF_2H$	−16.3	0.0033	1.254
HFC-245cb	$CF_3CF_2CH_3$	−18.3	0.0055	1.457
HFC-245ca	$HCF_2CF_2CH_2F$	24.96	0.0001	1.454
HFC-236cb	$CF_3CF_2CH_2F$	−1.44	0.0022	1.426
HCFC-235ca	$CF_3CF_2CH_2Cl$	28.1	0.0007	1.275
HFC-254cb	$CF_2HCF_2CH_3$	−0.78	0.0020	1.590
HFC-347ccd	$CF_3(CF_2)_2CH_3$	15.1	0.0041	1.383
HFC-329cca	$CF_3(CF_2)_2CF_2H$	15.1	0.0040	1.223
HFC-338cca	$HCF_2(CF_2)_2CF_2H$	42.5	0.0037	1.333
HFC-338ccb	$CF_3(CF_2)_2CFH_2$	27.8	0.0049	1.342

The literature values for CFC-11 were obtained by conventional calorimetry and have an estimated accuracy of 0.1% [15, 16]. Our average value for CFC-11 at 40°C, 0.887 J/(deg·g), reflects the excellent agreement that was always ob-

tained with the literature value, 0.898 J/(deg·g), for this compound. The reported values for CFC-12 have a somewhat lower estimated accuracy (about 1%) [15, 17, 18] than literature values for CFC-11. Our average value for CFC-12 of 1.049 J/(deg·g) at 40°C is within 3.2% of the literature value, 1.015 J/(deg·g). This agreement is not as good as in the case of CFC-11, but is still consistent with our estimated experimental error of 3%, particularly when the error in the accepted literature value is taken into consideration.

The DSC method has distinct advantages over conventional calorimetry in that it is performed with very small samples (less than 100 mg) and DSC instruments are available in many laboratories and may be used for the measurement of the heat capacity of liquids with subambient boiling points without modification. Its ultimate accuracy for measurement of C_p is perhaps in general not as good as conventional calorimetry. However with improved instrumentation equipped with computer averaging [19, 20], the accuracy of the DSC measurement begins to approach that of conventional calorimeters. With the three compartment modification (sample, reference, and sapphire standard compartments) proposed by Wunderlich [26, 27] the traditional three scan heat capacity measurement can be reduced to a single scan measurement. This would clearly improve the ease with which the heat capacity can be measured and would very likely also improve accuracy by reducing the added error contributions associated with multiple scans.

Appendix

Derivation of equations correcting the calorimeter response to the constant pressure heat capacity

Our derivation for these corrections begins with the following formulas for the total heat capacity, C, measured from the calorimeter response,

$$C = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{1A}$$

$$E = m_v \varepsilon_v + m_l \varepsilon_l \tag{2A}$$

where δQ is the heat absorbed by the sample with a change in temperature δT. The quantity E is the total internal energy (liquid and vapour phases) of the sample, T is the absolute temperature, V is the total volume (liquid and vapour phases), ε_v and ε_l are the specific internal energy of the vapour and liquid phases, respectively, and m_v and m_l are the masses of the vapour and liquid phases, respectively. By expanding Eq. (1A), we obtain

$$C = \varepsilon_v \left(\frac{\partial m_v}{\partial T}\right)_{s,V} + \varepsilon_l \left(\frac{\partial m_l}{\partial T}\right)_{s,V} + m_v \left(\frac{\partial \varepsilon_v}{\partial T}\right)_s + m_l \left(\frac{\partial \varepsilon_l}{\partial T}\right)_s \tag{3A}$$

The constant V condition is not required for the temperature derivatives of ε_v and ε_l because these are intensive variables, which are dependent only on one intensive variable, T, in the coexistence region designated by "s". For constant mass we have,

$$\left(\frac{\partial m_v}{\partial T}\right)_{s,v} = -\left(\frac{\partial m_l}{\partial T}\right)_{s,v} \tag{4A}$$

which implies,

$$C = -[\Delta h - \Delta(PV)]\left(\frac{\partial m_l}{\partial T}\right)_{s,v} + m_v\left(\frac{\partial \varepsilon_v}{\partial T}\right)_s + m_l\left(\frac{\partial \varepsilon_l}{\partial T}\right)_s \tag{5A}$$

where we have used the relation,

$$\varepsilon_l - \varepsilon_v = \Delta h - \Delta(PV) \tag{6A}$$

The quantity, Δh, is the heat of vaporization and,

$$\Delta(PV) = P\left(\frac{1}{\rho_v} - \frac{1}{\rho_l}\right). \tag{7A}$$

The notations ρ_v and ρ_l represent the densities of the liquid and vapour phases, respectively. The following thermodynamic differential relations,

$$\left(\frac{\partial \varepsilon_\alpha}{\partial T}\right)_s = \left(\frac{\partial \varepsilon_\alpha}{\partial T}\right)_P + \left(\frac{\partial \varepsilon_\alpha}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_s, \tag{8A}$$

$$\left(\frac{\partial \varepsilon_\alpha}{\partial T}\right)_P = C_{P_\alpha} - P\left(\frac{\partial V_\alpha}{\partial T}\right)_P, \tag{9A}$$

$$\left(\frac{\partial \varepsilon_\alpha}{\partial P}\right)_T = \left(\frac{\partial h_\alpha}{\partial P}\right)_T - P\left(\frac{\partial V_\alpha}{\partial P}\right)_T - V_\alpha, \tag{10A}$$

$$\left(\frac{\partial h_\alpha}{\partial P}\right)_T = -T\left(\frac{\partial V_\alpha}{\partial T}\right)_P + V_\alpha \tag{11A}$$

may be combined to yield

$$\left(\frac{\partial \varepsilon_\alpha}{\partial T}\right)_s = C_{P_\alpha} - \left[P + T\left(\frac{\partial P}{\partial T}\right)_s\right]\left(\frac{\partial V_\alpha}{\partial T}\right)_P - P\left(\frac{\partial V_\alpha}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_s \tag{12A}$$

where α represents v or l, C_{P_α} is the specific heat capacity at constant pressure of phase α, and h_α is the specific enthalpy of phase α. Equation (12A) may be com-

bined with Eq. (5A) and the result solved for the liquid phase specific heat capacity to yield,

$$C_p = \frac{1}{m_l}(C - m_v C_{pv}) + [\Delta h - \Delta(PV)]\left(\frac{\partial \ln(m_l)}{\partial T}\right)_{s,v} +$$

$$+ \left\{P + T\left(\frac{\partial P}{\partial T}\right)_s\right\}\left\{\left(\frac{\partial V_l}{\partial T}\right)_P + \frac{m_v}{m_l}\left(\frac{\partial V_v}{\partial T}\right)_P\right\} + P\left(\frac{\partial P}{\partial T}\right)_s\left\{\left(\frac{\partial V_l}{\partial P}\right)_T + \frac{m_v}{m_l}\left(\frac{\partial V_v}{\partial P}\right)_T\right\}, \quad (13A)$$

where the subscript "l" on the symbol for the liquid-phase specific heat capacity (C_p) has been dropped.

Equation (13A) is then transformed into a more usable form by rewriting the ratio, m_v / m_l in terms of a lever rule relation which accounts for the constant volume restriction on the sample capsule. We begin with the following relation for the overall density, ρ, of the sample,

$$\rho = \frac{M}{V} = Z_v \rho_v + Z_l \rho_l, \quad (14A)$$

where M ($=m_v + m_l$) is the total mass of the sample, V is the sample volume, and Z_α is the volume fraction of phase α. Equation (14A) can be rewritten in the form of the following lever rule relation.

$$\frac{V_v}{V_l} = \frac{\rho_l - \rho}{\rho - \rho_v}, \quad (15A)$$

where V_α is the volume of phase α. By noting that,

$$\frac{V_v}{V_l} = \frac{m_v \rho_l}{m_l \rho_v}, \quad (16A)$$

it follows that,

$$F = \frac{m_v}{m_l} = \frac{\rho_v}{\rho_l}\left(\frac{\rho_l - \rho}{\rho - \rho_v}\right). \quad (17A)$$

Writing m_l and its derivatives in terms of the lever rule parameter F, we have,

$$m_l = \frac{M}{1 + F}, \quad (18A)$$

$$\left(\frac{\partial \ln(m_l)}{\partial T}\right)_{s,v} = -\left(\frac{\partial \ln(1 + F)}{\partial T}\right)_{s,v}. \quad (19A)$$

From Eqs (17A) and (18A) it follows that the lever rule parameter and its derivatives can be calculated from PVT data in the coexistence region by Eqs (20A) and (21A),

$$1 + F = \frac{\rho}{\rho_l}\left(\frac{\rho_l - \rho_v}{\rho - \rho_v}\right), \tag{20A}$$

$$\left(\frac{\partial \ln(1+F)}{\partial T}\right)_{s,V} = \frac{1}{\rho_l - \rho_v}\left[\frac{\rho_v}{\rho_l}\left(\frac{\partial \rho_l}{\partial T}\right)_s + F\frac{\rho_l}{\rho_v}\left(\frac{\partial \rho_v}{\partial T}\right)_s\right], \tag{21A}$$

where in the differentiation ρ is fixed for fixed V. Combining Eqs (13A) and (17A) to (19A), the final working equations for calculating the liquid–phase heat capacity from DSC data are

$$C_p = C + C_{vap} + C_{\Delta h} + C_\tau + C_\kappa, \tag{22A}$$

$$C_{vap} = F(C - C_{pv}), \tag{23A}$$

$$C_{\Delta h} = -\left[\Delta h - P\frac{\rho_l - \rho_v}{\rho_l \rho_v}\right]\left(\frac{\partial \ln(1+F)}{\partial T}\right)_s, \tag{24A}$$

$$C_\tau = \left[P + T\left(\frac{\partial P}{\partial T}\right)_s\right]\left[\frac{\alpha_l}{\rho_l} + F\frac{\alpha_v}{\rho_v}\right], \tag{25A}$$

$$C_\kappa = -P\left(\frac{\partial P}{\partial T}\right)_s\left[\frac{\kappa_l}{\rho_l} + F\frac{\kappa_v}{\rho_v}\right]. \tag{26A}$$

* * *

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Zusammenfassung — Mittels DSC bei 40°C wurden die Flüssigphasen-Wärmekapazitäten für konstanten Druck von 21 wasserstoffhaltigen fluorierten Propan- und Butanderivaten und von einem fluorierten Ether (CF_3OCF_2H) mit Siedenpunkten zwischen –34.6° und 76.7°C gemessen. Diese Messungen dienen der Suche nach alternativen Kühl- und Treibmitteln, welche die Ozonschicht der Stratosphäre nicht mindern. Für diese Aufgabe hat die DSC-Methode zwei eindeutige Vorteile:

(i) es werden nur geringe Probenmengen benötigt (weniger als 100 mg) und

(ii) die Geräte sind in vielen Laboratorien zugänglich und können ohne Änderungen zur Messung von Wärmekapazitäten von Flüssigkeiten mit Siedepunkten unter Umgebungstemperatur verwendet werden.