Thermodynamic Properties of Liquid Carbon Tetrafluoride

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Available thermodynamic data on CF_4 have been collected and their reliability examined. They have been used to calculate the values of the following properties: (1) the enthalpy of vaporization of the liquid from the triple point (89.56 K) to 220 K; (2) the configurational internal energy of the liquid and gas at the saturation vapor pressure, and the adiabatic compressibility of the liquid over the same range; (3) the coefficient of expansion of the liquid from the triple point to 190 K; (4) the ratio C_P/C_V, the heat capacity at constant volume, the thermal pressure coefficient, and the isothermal compressibility of the liquid from 90 K to the normal boiling point (145.16 K).

Introduction

We have measured in recent years the primary thermodynamic excess properties—G^E, H^E, and V^E—of a number of binary mixtures of liquefied gases. The experimental results have been used to test modern theories of liquid mixtures, and in particular the perturbation theory developed by Gubbins and co-workers. For such a theory to be successful it is essential that the intermolecular potential of each one of the pure components be known as accurately as possible. Powles, Gubbins, and collaborators in their study of hydrogen chloride (*1*) indicated the reasons that a knowledge of the configurational internal energy of the liquid as a function of temperature is useful in improving the intermolecular potential function, and stressed the need for such data. Results of this kind have recently become available for hydrogen chloride from high-pressure $P-V-T$ measurements (*2*).

As calculations concerning the system HCl + CF_4 are now in progress (*3*) with the object of comparing experiment and theory for this system, and since we have already measured in this (Oxford) laboratory the vapor pressure (*4*) and the density (*5*) of liquid carbon tetrafluoride over wide temperature ranges, it seemed worthwhile to calculate the internal configurational energy of CF_4 along the saturation line and the values of some other derived thermodynamic quantities. For this purpose one needs, of course, other information, and we shall briefly comment on the available data and on the methods actually used in the calculations.

Calculations

The internal configurational energy of a pure liquid U^*_l at temperature T and the saturation pressure P_s is the difference between the internal energy of the liquid and that of a perfect gas at the same temperature:

$$U^*_l(T,P_s) = U_l(T,P_s) - U_{pg}(T,P_s) = U_l(T,P_s) - U_{pg}(T,0) \quad (1)$$

where the subscript pg refers to the perfect gas.

When one assumes that the vapor in equilibrium with the liquid follows the virial equation of state

$$PV_g/RT = 1 + B'P + C'P^2 + \ldots \quad (2)$$

where

$$B' = B/RT \qquad C' = (C - B^2)/(RT)^2 \quad (3)$$

and so forth, and B, C, ... are the second, third, ... (volume) virial coefficients, U^*_l is then given by the expression

$$U^*_l(T,P_s) = -\Delta H_v + RT - V_lP_s + (B - B_1)(P_s - BP_s^2/RT) + (2C - C_1)[P_s^2/(2RT)] \quad (4)$$

neglecting all the virial coefficients after the third. In this equation

$$B_1 = T(dB/dT) \qquad C_1 = T(dC/dT) \quad (5)$$

ΔH_v is the enthalpy of vaporization, and V_l is the molar volume of the saturated liquid.

Therefore, to carry out the calculation of U^*_l, one should have, at least, values of V_l and of the virial coefficients B and C (and their temperature coefficients), and reliable values of ΔH_v. One source of these is an appropriate vapor-pressure equation such as the Wagner equation

$$\ln P_s = \ln P_c + (A_1\tau + A_2\tau^{1.5} + A_3\tau^3 + A_4\tau^6)/T_R \quad (6)$$

where $\tau = (1 - T_R)$, and P_c and T_R are the critical pressure and the reduced temperature, respectively. Ambrose (*6*) has demonstrated that this equation applies over a wide temperature range, and in fact the widest possible one spanning the triple point to the critical temperature. In the fitting of our experimental values of P_s to eq 6 to obtain the parameters A_i (*4*), the constraints discussed in Ambrose's paper (*6*) were adopted, so that values of ΔH_v derived from the Clausius–Clapeyron equation

$$dP_s/dT = \Delta H_v/[T(V_g - V_l)] \quad (7)$$

should conform closely to experiment over a large temperature interval. An accurate calorimetric value of ΔH_v at the normal boiling point of CF_4 was obtained by Smith and Pace (*7*), and it is important to note that the value of ΔH_v at the same temperature obtained from eq 7 and the Wagner equation for CF_4 agrees virtually exactly with the calorimetric value.

Experimental second virial coefficients B of carbon tetrafluoride given by Lange and Stein (*8*) (from −70 to 95 °C) and by Douslin et al. (*9*) (from 0 to 350 °C) were fitted by orthogonal polynomials to an expression of the type

$$B/V_c = \sum_i a_i T_R^i \quad (8)$$

up to the fourth degree (the standard deviation being $\sigma(B) = \pm 0.1$ cm^3 mol^{-1}). Its use on extrapolation to lower temperatures should give reasonably reliable values of B, as experience with other substances has shown (*10*).

As for the third virial coefficient C, the equation proposed by Chueh and Prausnitz (*11*) was used. An estimate of parameter d in this expression was obtained by using experimental values of C (*8*, *9*) in a plot of C/V_c^2 as a function of T_R and com-

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Table I. Thermodynamic Properties of Liquid and Gaseous Carbon Tetrafluoride[a]

T, K	P_s, kPa	$-B$, cm^3 mol^{-1}	C, cm^6 mol^{-2}	V_l, cm^3 mol^{-1}	V_g, dm^3 mol^{-1}	ΔH_v, kJ mol^{-1}	$-U^{\pm}_l$, kJ mol^{-1}	$-U^{\pm}_g$, kJ mol^{-1}	obsd
89.56	0.109	718		46.727	6830.7	14.260	13.515	0.000	triple point
90	0.120	714		46.782	6235.0	14.200	13.452	0.000	
100	0.777	643		48.023	1069.4	13.746	12.916	0.001	
110	3.416	578		49.294	267.15	13.296	12.386	0.002	
120	11.316	520		50.656	87.646	12.878	11.895	0.008	
130	30.379	467		52.141	35.106	12.468	11.423	0.020	
140	69.520	420		53.770	16.312	12.043	10.958	0.045	
145.16	101.360	398		54.676	11.495	11.810	10.715	0.065	normal boiling point
150	140.622	378		55.571	8.473	11.580	10.485	0.089	
160	258.150	339	−1768	57.596	4.789	11.061	10.003	0.162	
170	438.670	305	+4395	59.937	2.883	10.465	9.498	0.268	
180	700.435	275	7608	62.748	1.817	9.780	8.977	0.416	
190	1063.240	248	9139	66.257	1.183	8.991	8.438	0.611	
200	1548.702	224	9705	70.18	0.783	8.073	7.869	0.860	
210	2181.271	202	9733	76.10	0.522	7.015	7.301	1.167	
220	2990.970	183	9472	85.05	0.341	5.711	6.653	1.540	
227.5[b]	3742[b]	170	9175	(140)[c]	(0.140)[c]	(0)			critical point

[a] With the exception of the virial coefficients B and C, which are independent of pressure, all of the properties listed refer to saturation conditions. [b] From ref *13*. [c] From ref *14*.

paring the trend shown by this plot with that for other substances (*11*). In this manner a figure of $d = 1.0$ was obtained for CF_4. The Chueh and Prausnitz expression was then used to estimate C values down to 160 K, at which temperature the calculated values start to become negative, and therefore the method is no longer reliable. The neglect of the third virial coefficient below 160 K should not give rise to any serious error in the derived quantities since the pressures involved never exceed 0.2 MPa.

From this information the internal configurational energy of the saturated vapor $U^{\ddagger}_g$ can also be derived from the expression

$$U^{\ddagger}_g(T,P_s) = -|B_1(P_s - BP_s^2/RT) + C_1(2P_2^2/RT)| \quad (9)$$

For pressures above 2 MPa, the inclusion of terms involving the fourth virial coefficient D in eq 4 and 9 did in no case change the calculated values of $U^{\ddagger}_l$ and $U^{\ddagger}_g$ by more than ~1%. D was obtained from a linear extrapolation of the experimental values given by Douslin et al. (*9*).

The molar volumes of the liquid V_l were derived from the experimental work of Terry et al. (*5*). A small correction was applied to their values, since these are now recognized to embody a systematic error and as a result to be 0.4% too high (*10*). Outside the temperature range to which their expression applies, estimates of V_l were made by using the law of the rectilinear diameter with parameters given in their paper and values of V_g calculated as explained above.

Since experimental results are also available for the velocity of sound, u, in liquid carbon tetrafluoride (*12*), we have calculated the mechanical coefficients for this substance. The procedure adopted was much the same as that indicated by Blagoi et al. (*12*). First, the velocity of sound was used to estimate the adiabatic compressibility κ_S

$$\kappa_S = V_l/(Mu^2) \quad (10)$$

where M is the mass of unit amount of substance, and also the quantity γ

$$\gamma = 1 + T\alpha_p^2u^2/C_p \simeq 1 + T\alpha_\sigma^2u^2/C_\sigma \quad (11)$$

where the subscript σ refers to saturation conditions. Values of the expansion coefficient α_σ

$$\alpha_\sigma = (1/N_l)(\partial V_l/\partial T)_\sigma \quad (12)$$

were derived from the (corrected) expression of Terry et al., while those of the saturation heat capacity C_σ were taken from the accurate calorimetric work of Smith and Pace (*7*). From these values of κ_S and γ, the isothermal compressibility κ_T

$$\kappa_T = -(1/V_l)(\partial V_l/\partial P)_T \quad (13)$$

could be obtained, since

$$\kappa_T = \gamma\kappa_S \quad (14)$$

κ_T was in turn used to estimate the isobaric expansion coefficient α_P through the relationship

$$\alpha_P = \alpha_\sigma + \kappa_T\gamma_\sigma \quad (15)$$

where γ_σ is the temperature coefficient of the vapor pressure

$$\gamma_\sigma = (\partial P/\partial T)_\sigma \quad (16)$$

taken from our own work (*4*). Next, the heat capacity of the liquid at constant pressure C_P was estimated from the expression

$$C_P = C_\sigma + TV_l\alpha_P\gamma_\sigma \quad (17)$$

In the temperature range over which reliable values of C_σ for CF_4 are available (90 to ~145 K), the pressures involved are always low, and therefore C_P does not differ significantly from C_σ, nor α_P from α_σ. No iteration is then necessary to refine the first set of values obtained from the calculations outlined above. Finally, the heat capacity of the liquid at constant volume C_V was estimated from

$$C_P = \gamma C_V \quad (18)$$

and the thermal pressure coefficient γ_V was obtained from

$$\gamma_V = \alpha_P/\kappa_T \quad (19)$$

Results and Discussion

The results of the calculations outlined above are shown in Tables I and II.

It would clearly be helpful if an assessment could be made of the reliability of at least some of the values in these tables. As far as the second virial coefficients are concerned, such an assessment should obviously be made at lower temperatures for which the correctness of the extrapolations that we have made (from experimental B values in the range from ~200 to ~320 K) could perhaps be questioned. The method proposed by Curtiss and Hirschfelder (*15*) to estimate B from a combination of the Clausius–Clapeyron and the virial equation of state (truncated after the second term) seems to be a reasonable choice for comparison. By using this, one arrives at a value

Table II. Mechanical, Adiabatic, and Thermal Coefficients of Saturated Liquid Carbon Tetrafluoride

T, K	$10^3\alpha_\sigma$, K^{-1}	$10^3\alpha_P$, K^{-1}	$10^3\kappa_S$, MPa^{-1}	$10^3\kappa_T$, MPa^{-1}	γ_σ, kPa K^{-1}	γ_V, MPa K^{-1}	γ	C_P, J mol^{-1} K^{-1}	C_V, J mol^{-1} K^{-1}
89.56	2.70		0.44		0.0233				
90	2.69	2.69	0.44	0.83	0.0253	3.24	1.882	78.0	41.5
100	2.59	2.59	0.51	0.93	0.1285	2.78	1.819	77.1	42.4
110	2.65	2.65	0.60	1.09	0.4525	2.43	1.824	77.2	42.3
120	2.80	2.80	0.71	1.33	1.225	2.11	1.871	77.4	41.4
130	2.98	2.98	0.85	1.62	2.736	1.84	1.906	78.2	41.0
140	3.18	3.19	1.05	2.01	5.291	1.59	1.913	79.5	41.5
145.16	3.30	3.32	1.17	2.25	7.112	1.48	1.921	80.3	41.8
150	3.42		1.32		9.171				
160	3.76		1.67		14.611				
170	4.25		2.17		21.797				
180	4.97		2.93		30.885				
190	5.98		4.21		42.034				
200			6.45		55.462				
210			11.61		71.541				
220			27.40		91.106				
227.5					111.275				

for B at 89.56 K—the triple-point temperature T_{tr} of CF_4—which is only 3% in excess of that obtained from eq 8. Moreover, at the normal boiling-point temperature (T_b = 145.16 K) the deviation between the values of B arrived at by the two methods is even less (*4*): 0.5%. It is well-known that the method of Curtiss and Hirschfelder relies on the accuracy of the vapor-pressure equation since the B coefficients derived in this manner strongly depend on dP/dT. The agreement obtained in the present case can thus perhaps be simultaneously regarded as supporting our vapor-pressure equation, and hence giving confidence in the calculated γ_σ values.

The expression of Chueh and Prausnitz with d = 1.0 reproduces the experimental values of C at both −70 and 0 °C within the experimental uncertainty quoted by Lange and Stein (*8*). The values of V_g, the molar volume of the gaseous phase, listed in Table I should therefore be reasonably accurate.

We measured the molar volume of liquid carbon tetrafluoride (*10*) at the triple-point temperatures of hydrogen chloride (T_{tr} = 158.95 K) and hexafluoroethane (T_{tr} = 173.11 K) in a pyknometer which had been calibrated at 158.95 and 182.32 K (the triple-point temperature of nitrous oxide) by using a highly purified sample of ethane and the density results of Haynes and Hiza (*16*). At both temperatures our results were 0.4% lower than those obtained from the work of Terry et al. (*5*). A discrepancy of almost the same magnitude has been found for several substances (*17*). Accordingly, allowance was made for this, so that the values of V_l reported in Table I (and hence those of α_σ) should be of adequate quality for our main purposes.

To judge the quality of the ΔH_v values listed in Table I is perhaps difficult. Although carbon tetrafluoride is an important substance in industry, and otherwise, as far as we are aware only one measurement of sufficient accuracy appears to have been reported for its enthalpy of vaporization. This is that by Smith and Pace (*7*), whose reported value at the normal boiling point is $\Delta H_{v,b}$ = 11814 ± 5 J mol^{-1}. Use of the Clausius–Clapeyron equation and our vapor-pressure equation gives 11 810 J mol^{-1}, which is virtually the same figure, as already mentioned. We have also tried to assess the quality of the estimated ΔH_v at the triple-point temperature of CF_4 (89.56 K) by using it in an evaluation from vapor-pressure data of the enthalpy of fusion ΔH_f. Several authors (*7*, *18*, *19*) have reported experimental values of ~0.70 kJ mol^{-1} for this quantity. Simon et al. (*20*) estimated the enthalpy of sublimation of carbon tetrafluoride at its own triple-point temperature as ΔH_{sb} = 14.73 kJ mol^{-1}, from their measured vapor pressure of the solid. The difference between this value and ours (ΔH_v(89.56 K) = 14.26 kJ mol^{-1}) gives ΔH_f = 0.47 kJ mol^{-1}, which can be regarded as being in reasonable agreement with the experimental value, especially if one takes into account that the ΔH_f so calculated is only ~3% of the terms from whose difference it was obtained. One further test on our reported $\Delta H_v(T_{tr})$ is by using the thermodynamic relationship

$$(\partial \Delta H_v/\partial T)_P \approx C_{P,g} - C_{P,l} \qquad (20)$$

From the experimental $\Delta H_{v,b}$ and the $C_{P,l}$ from ref 7, and by assuming the perfect-gas heat capacity for gaseous CF_4 in the range from T_{tr} to T_b, one obtains $\Delta H_v(T_{tr})$ = 14.76 kJ mol^{-1}. This is only ~3% higher than the figure reported in Table I.

Since the quantities involved in the calculation of U^*_l and U^*_g all seem reasonably trustworthy, one should expect the same for the calculated values of both configurational internal energies.

In view of the particular behavior of substances in the critical region, no attempt was made to extend the calculations to the critical temperature. However, it is interesting to note that the values calculated from eq 4 and 9 for U^*_l and U^*_g at T_c = 227.5 K are −1.75 and −1.87 kJ mol^{-1}, respectively, in good agreement with each other.

Little can be said about the remaining quantities listed in Table II. The agreement with values calculated by Biagoi et al. (*12*) is variable. While the differences remain within their quoted uncertainties for C_V and γ, the agreement is poor for κ_T and κ_S. Since the same values of the velocity of sound, u, were used in both the Russian work and in ours, the difference between the two sets of κ_S values can only be assigned to the possible use of rather poor estimates of V_l by Biagoi and coworkers, especially at the lower temperatures for which comparison with our figures could be made. (The difference between the two sets of κ_S values at 140, 120, and 100 K is respectively 0, 20, and 40% of their reported κ_S figures).

Finally, our listed values for the expansion coefficients may be compared with α = (2.59 ± 0.04) × 10^{-3} K^{-1} for T from 94 to 107 K, as extracted from the work of Croll and Scott (*21*).

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Measurement of the Electrical Conductivites of Molten $NaNO_3$–KNO_3–$NaNO_2$ and Molten LiF–NaF–KF by Displacing the Positions of Electrodes

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In order to obtain the true electrical conductance of solution in the ac bridge method, it is necessary to eliminate both the frequency effect resulting from circuitry and that of the metal/salt interfacial impedance. In this study we devised the apparatus of electrical conductances so that the interfacial impedance could be neglected by subtracting the measured resistances between two positions of electrodes which were moved through a capillary cell by using a micrometer. With this method it has been found that the same solution resistance could be obtained at any frequency without extrapolating infinitely the measured resistance against the reciprocal of frequency. The experiments were carried out for molten $NaNO_3$, KNO_3, heat transfer salt (HTS) (a mixture of molten $NaNO_3$–KNO_3–$NaNO_2$, 7:44:49 mol %), and FLINAK (a mixture of molten LiF–NaF–KF ternary eutectic, 46.5:11.5:42.0 mol %).

Introduction

For the measurement of electrical conductivity of molten salts, two different types of conductance cells have been used: the capillary cell and the immersion cell. In general, molten salts except covalent compound like the mercuric halides have higher specific conductivities than those of aqueous electrolytes. When one takes into account that the resistance value of the immersion cell (1 ~ 10 Ω) is low as compared with that of the capillary cell (500 ~ 1500 Ω), polarization effects at the surface of the electrodes of the immersion cell will make accurate measurement of resistance values practically impossible. For accurate measurement of resistance, the ac conductance bridge techniques with high cell constants are readily applicable as compared with the immersion cell.

The measured resistance in the ac bridge technique also contains the frequency effects resulting from circuitry and the electrode impedance resulting from polarization effects at the electrodes, which depend on the frequency of the applied alternating voltage. If the former effects are neglected, one can consider that the measured resistance, R_m, and the resistance associated with the electrode/solution interface, R_z, depend on the frequency of the applied current.

$$R_m = R_s + R_z \quad (1)$$

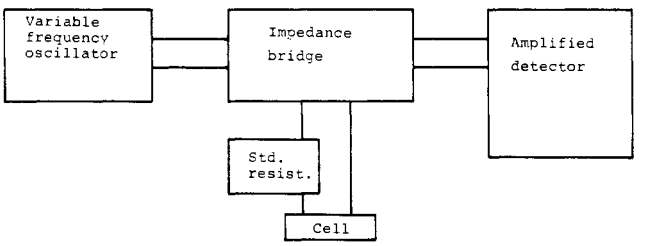

Figure 1. Experimental assembly for electrical conductivity.

R_z must be either corrected or eliminated experimentally so that R_m represents the true resistance of the solution.

In the measurements of molten salts, a value of R_m is generally extrapolated to infinite frequency with $f^{-1/2}$ or f^{-1}, where R_z is assumed to be zero. However, it has been reported that, in molten nitrates (*1*) and chlorides and fluorides (*2*), R_m is nonlinear in $f^{-1/2}$ or f^{-1}, with resistance approaching a nearly constant value at high frequencies. Although the effects of the metal/salt interfacial impedance have been studied by some investigators (*3*, *4*), the phenomena at the interface are too complicated to clarify. This polarization effect appears to lead to the error of specific conductivity of molten salts, especially fluoride melts which exhibit high ionic conductivity. The purpose of the present work is to eliminate the polarization impedance.

We devised an apparatus of electrical conductivities so that two electrodes could be moved through a capillary cell by using a micrometer. The difference of measured resistances between two arbitrarily chose electrode positions shows the true solution resistance of a melt, R_s, since the polarization impedance could be considered to have the same value at any position and be neglected by subtracting.

In order to check this method, the specific conductivities of a 1.0 demal KCl solution and of molten $NaNO_3$ and KNO_3 were measured. Then, those of heat transfer salt and FLINAK were measured since they are stable over a relatively wide range of temperatures and, to our knowledge, there are no available data for FLINAK. With this method we found that the same solution resistance, R_s, could be obtained at any frequency and that it was not necessary to extrapolate the measured resistance with respect to frequency.

Experimental Section

Figure 1 shows a schematic outline of the bridge circuit ap-

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