

An Interim Analytic Equation of State for Sulfurhexafluoride¹

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An interim analytic equation of state for sulfurhexafluoride is given in the form of a reduced Helmholtz energy function. It represents the thermodynamic properties over the temperature range 222.38 to 525 K for pressures up to 55 MPa. The data selected for determining the linear coefficients of the equation are given, which includes some values predicted using the principle of corresponding states. The method used for the multiproperty fitting is given and, in particular, the functions used for fitting isobaric heat capacities as primary data. Comparisons with values predicted by the equation of state are given for saturation properties, second virial coefficients, densities, and isobaric and isochoric heat capacities. The accuracy of the representation of the equation of state is discussed and, also, the problems arising from inconsistencies between the different data sets. The interim status of this equation of state is due to these inconsistencies.

KEY WORDS: equation of state; saturation properties; sulfurhexafluoride; thermodynamic properties.

1. INTRODUCTION

Sulfurhexafluoride is widely used in the electrical power industry for equipment such as high-voltage circuit breakers and gas-insulated transmission lines and in high-voltage transmitters. As a pseudospherical

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polyatomic molecule it has been the subject of a recent study [1] of the methods of prediction of thermodynamic properties for this class of fluids.

An equation of state was published by Oda et al. [2] in 1983, but a considerable quantity of new data has been reported since then. A new equation of state is presented here, which incorporates the new data and comparisons with it are given.

2. DEVELOPMENT OF THE EQUATION OF STATE

The equation of state used here is expressed in the form of a reduced Helmholtz energy which can be written as

$$\frac{A(\omega, \tau)}{RT} = \alpha^{\text{id}}(\tau) + \ln(\omega/\omega_a) + \alpha(\omega, \tau) \quad (1)$$

where $\omega = \rho/\rho^*$, $\tau = T^*/T$, and ρ^* and T^* are reducing parameters. The reduced density ω_a is that of an arbitrary reference point (P_a, T_a) in the ideal gas where the entropy and enthalpy are taken to be zero. The temperature-dependent part of the ideal gas is represented by $\alpha^{\text{id}}(\tau)$, which can be calculated from the ideal gas isobaric heat capacity by the relationship

$$\alpha^{\text{id}}(\tau) = \iint [(1/\tau^2) - C_p^{\text{id}}(\tau)/(R\tau^2)] d\tau d\tau \quad (2)$$

An equation for the ideal gas isobaric heat capacity, C_p^{id} , is given in Section 4.

The function $\alpha(\omega, \tau)$ represents the real part of the reduced Helmholtz energy and the general functional form chosen as the "bank" of 120 terms is given by

$$\begin{aligned} \alpha^{\text{gen}}(\omega, \tau) = & \sum_{j=1}^8 \sum_{k=1}^6 n_{jk} \omega^j \tau^{(k-1)/2} + e^{-\omega^2} \sum_{j=1}^6 \sum_{k=1}^6 n_{jk} \omega^{2j} \tau^{(k-1)} \\ & + \sum_{j=2}^3 \sum_{k=4}^{21} n_{jk} \omega^{2j} \tau^{(2k+1)} e^{-k\omega^2} \end{aligned} \quad (3)$$

The linear coefficients n_{jk} were determined using SEEQ [3], which is a multiproperty least-squares method where the statistically significant terms are selected from the original bank of terms: the method was first developed by Wagner [4] for fitting vapor pressure curves.

The following sums of weighted squares were minimized simultaneously:

$$S_1 = \sum_{m=1}^{M1} \left[\frac{Z-1}{\omega} - \left(\frac{\partial \alpha}{\partial \omega} \right)_{\tau} \right]_{m}^2 / \sigma_{\text{Res1},m}^2 \quad (4)$$

where Z is the compression factor, $M1$ is the total number of $P\rho T$ data points, and σ_{Res1}^2 is the estimated variance for each data point calculated from the Gaussian error propagation formula.

$$S_2 = \sum_{m=1}^{M2} \left[\rho^* B(\tau) - \left(\frac{\partial \alpha}{\partial \omega} \right)_{\tau, \rho \rightarrow 0} \right]_{m!}^2 / \sigma_{\text{Res2}, m}^2 \quad (5)$$

where B is the second virial coefficient.

$$S_3 = \sum_{m=1}^{M3} \left[\frac{P_\sigma}{RT} - \left(\frac{1}{\rho_1} - \frac{1}{\rho_g} \right) + \ln \left(\frac{\rho_1}{\rho_g} \right) - \{ \alpha(\omega_g, \tau) - \alpha(\omega_1, \tau) \} \right]_{m!}^2 / \sigma_{\text{Res3}, m}^2 \quad (6)$$

where P_σ is the vapor pressure and ρ_1 and ρ_g are the saturated liquid and vapour densities, respectively.

If the equation of state is to be used to calculate derived properties, then it is important that some of those properties are included in the multi-property fit (see Refs. 5 and 6). The only available C_v data are for the critical isochore, in the immediate vicinity of the critical point, and as such are unsuitable for inclusion in an analytic equation of state, but there are a large number of measurements for C_p . These, however, are nonlinear in terms of the coefficients of Eq. (3). In order to incorporate these into the fitting at this stage, they were defined as enthalpy differences as

$$C_p = (\Delta H / \Delta T)_p \quad (7)$$

where ΔH and ΔT are small changes in enthalpy and temperature at constant pressure. For ΔH was substituted $\{H(\omega_2, \tau_2) - H(\omega_1, \tau_1)\}$, where τ_1 and τ_2 are reduced temperatures which correspond to a small finite temperature difference apart (typically 0.01 K) and ω_1 and ω_2 are the reduced densities corresponding to the reduced temperatures τ_1 and τ_2 at the same pressure. The required densities were calculated from a previous fit. If the second derivative of α with respect to τ is taken to be a finite difference of the first derivative, then the weighted sum of squares to be minimized becomes

$$S_4 = \sum_{m=1}^{M4} \left[\frac{C_p - C_p^{\text{id}}}{R} + \frac{\tau_2 \tau_1}{(\tau_2 - \tau_1)} \left\{ \left(\frac{\partial \alpha}{\partial \tau_2} \right)_{\omega_2} - \left(\frac{\partial \alpha}{\partial \tau_1} \right)_{\omega_1} \right\} + \frac{\omega_2 \tau_1}{(\tau_2 - \tau_1)} \left(\frac{\partial \alpha}{\partial \omega_2} \right)_{\tau_2} - \frac{\omega_1 \tau_2}{(\tau_2 - \tau_1)} \left(\frac{\partial \alpha}{\partial \omega_1} \right)_{\tau_1} \right]_{m!}^2 / \sigma_{\text{Res4}, m}^2 \quad (8)$$

The total sum of squares which was minimized was $S_1 + S_2 + S_3 + S_4$.

3. DATA USED IN THE FIT

The data used to fit the equation of state (3) are listed in Table I. The corresponding-states $P\rho T$ values were calculated using PREPROP [19], a prediction package, with methane [20] as the reference fluid. These covered the low-temperature liquid region where there were few experimental data available. The saturated liquid density data of Mears et al. [7] were included as $P\rho T$ points using a vapor pressure equation to calculate the pressures. The two liquid C_p values from Eucken and Schroder [16] were measured at saturation, and again, the relevant pressures were calculated from a vapor pressure equation. The $P_\sigma\rho_l\rho_g T$ data were calculated from a previous fit and were used to include the condition of equality of the Gibbs energies of the two phases at saturation.

The method used to fit the C_p data (see Section 2) is not suitable for the critical region where C_p is changing very rapidly, so the data of Sirota

Table I. Data Used in the Fit

| Source | Data | No. of points used | Temp. range (K) | Pressure range (MPa) |
|---|------|--------------------|-----------------|----------------------|
| <i>PρT</i> | | | | |
| Mears et al. [7] | 1969 | 22 | 232–523 | 1.1–7.9 |
| Ulybin and Zherdev [8] | 1970 | 70 | 233–473 | 0.6–5.5 |
| Ulybin and Zherdev [9] | 1971 | 72 | 243–473 | 0.35–13.3 |
| Watanabe et al. [10] | 1977 | 79 | 273–363 | 1.27–19.6 |
| Likhatskii et al. [11] | 1982 | 11 | 373 | 0.2–1.5 |
| Biswas et al. [12] | 1984 | 143 | 308–332 | 1.8–9.6 |
| Biswas et al. [12] | 1984 | 105 | 333 | 0.12–10.0 |
| Møllerup [13] | 1985 | 125 | 260–340 | 0.02–2.5 |
| Corresponding states [1] | 1987 | 20 | 225–240 | 0.8–5.0 |
| <i>ρ_l</i> | | | | |
| Mears et al. [7] | 1969 | 9 | 232–313 | |
| <i>B</i> | | | | |
| Bellm et al. [14] | 1974 | 10 | 300–550 | |
| Hahn et al. [15] | 1974 | 5 | 200–273 | |
| <i>P_σρ_lρ_gT</i> | | | | |
| Calculated [1] | 1987 | 22 | 222–318 | |
| <i>C_p</i> | | | | |
| Eucken and Schroder [16] | 1938 | 2 | 225, 230 | |
| Sirota et al. [17] | 1979 | 192 | 298–425 | 2.4–20 |
| Bier et al. [18] | 1980 | 42 | 298–473 | 0.1–1.5 |

et al. [17] between 287 and 350 K and 3 and 4.5 MPa were excluded from the fit.

In general, the variances used in Eqs. (4)–(6) and (8) were calculated using the reported experimental errors. When the same procedure was used for the data of Biswas et al. [12] and of Watanabe et al. [10], whose experimental errors were reported to be very much lower than those of all the other data, then the fit to the other data was distorted. So for these two sets of data the variances were arbitrarily increased by a factor of 100.

4. THE EQUATION OF STATE

The complete equation of state is given by Eq. (1), where the equation for the reduced Helmholtz energy of the real fluid contains 18 terms and is given by

$$\alpha(\omega, \tau) = \sum_{i=1}^{18} a_i \omega^j \tau^k e^{-l\omega^2} \quad (9)$$

The coefficients a_i and the exponents j , k , and l are given in Table II, as are the values for the reducing parameters ρ^* and T^* and the value used for the gas constant R .

Table II. Coefficients and Exponents for Eq. (9)^a

| i | a_i | j | k | l |
|-----|---------------------|-----|-----|-----|
| 1 | 0.451605750715 | 1 | 0 | 0 |
| 2 | -2.56622805914 | 1 | 1.5 | 0 |
| 3 | 2.60651992128 | 1 | 2 | 0 |
| 4 | -1.67828092105 | 1 | 2.5 | 0 |
| 5 | 0.212672754716 | 2 | 0.5 | 0 |
| 6 | -1.01753942961 | 2 | 1.5 | 0 |
| 7 | 0.867756445849 | 2 | 2 | 0 |
| 8 | 0.0874385469210 | 3 | 0 | 0 |
| 9 | -0.00263899290314 | 6 | 0.5 | 0 |
| 10 | 0.000301520065174 | 8 | 0 | 0 |
| 11 | 0.0754047705142 | 2 | 0 | 1 |
| 12 | 0.0508199173904 | 2 | 4 | 1 |
| 13 | 0.112137656543 | 4 | 5 | 1 |
| 14 | -0.00714228965831 | 6 | 5 | 1 |
| 15 | 0.0119945259348 | 8 | 5 | 1 |
| 16 | -0.00215984228217 | 10 | 1 | 1 |
| 17 | -0.0601813939956 | 4 | 19 | 2 |
| 18 | 0.00000923253892309 | 4 | 43 | 2 |

^a $\rho^* = 0.00504599 \text{ mol} \cdot \text{cm}^{-3}$; $R = 8.31434 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; $T^* = 318.733 \text{ K}$.

The ideal gas isobaric heat capacity equation is given by

$$\frac{C_p^{\text{id}}}{R} = f_1 + \sum_{i=2}^6 f_i \frac{u_i^2 \exp(u_i)}{[\exp(u_i) - 1]^2} \quad (10)$$

where $u_i = g_i/T$ and the f_i and g_i are given in Table III.

5. COMPARISONS WITH THE DATA

Except where specifically mentioned the comparisons are for the data which were used to fit the equation of state (9). The earlier equation of state by Oda et al. [2] was a good representation of the data then available, but several of the sets of measurements used by them have since been superseded by more accurate data.

5.1. Ideal Gas Isobaric Heat Capacity

The data of Glushko et al. [21] for the temperature range 100–6000 K were fitted to Eq. (10), which represents these data to within $\pm 0.0003\%$.

5.2. Saturation Properties

A comparison of experimental vapor pressures with values calculated from the equation of state (9) by applying the phase equilibrium condition is shown in Fig. 1. None of these were used directly in the fit, but in almost all cases Eq. (9) gives values which are below those of the data. This is discussed further in Section 6. A similar comparison of saturated liquid densities with values calculated from Eq. (9) shows that agreement with the data of Mears et al. [7], which were used, is very good, while that with Watanabe et al. [10], which were not used, is similar, except that the latter deviate more as the critical region is approached.

Table III. Coefficients f_i and g_i Used in Eq. (10)

| Coefficient | Coefficient value | g_i |
|-------------|-------------------|---------|
| f_1 | 3.983 775 678 4 | — |
| f_2 | 2.218 185 101 0 | 1114.38 |
| f_3 | −10.921 337 374 | 925.64 |
| f_4 | 3.310 249 793 9 | 499.26 |
| f_5 | 17.518 967 148 3 | 884.90 |
| f_6 | 2.890 352 380 3 | 1363.93 |

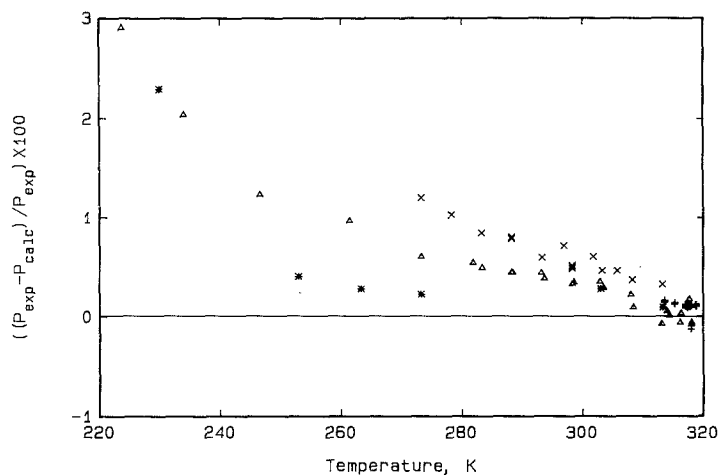


Fig. 1. Comparisons of experimental vapor pressures with the equation of state (9). (*) Mears et al. [7]; (x) Watanabe et al. [10]; (+) Biswas et al. [12]; (Δ) Totskii et al. [22].

5.3. Second Virial Coefficient

The second virial coefficient measurements of Bellm et al. [14] and Hahn et al. [15], both from the same laboratory, show small but systematic deviations from values calculated from Eq. (9) which vary between +2 and $-5 \text{ cm}^3 \cdot \text{mol}^{-1}$.

5.4. $P\rho T$ Data

The data of Mollerup [13], in the gas phase for pressures below about 0.25 MPa, show density deviations from Eq. (9) mostly within $\pm 0.1\%$, which is the reported experimental error. At high pressures the isotherms show systematically different behavior, with the deviations on the 285 K isotherm increasing to +0.26%, while those for the 315 and 340 K isotherms decrease to a maximum of -0.17% . The larger deviations on the 285 and 315 K isotherms occur as the saturation pressure is approached: the 340 K isotherm is supercritical. The Ulybin and Zherdev [9] data cover some of the same region as those of Mollerup, but for the lower temperatures from 243 to 313 K, the density deviations are all negative, with a maximum of -0.6% . The supercritical data of Ulybin and Zherdev [9], between 323 and 473 K, are more evenly scattered within the experimental error of $\pm 0.2\%$. Mears et al [7] data cover some of the same region as those of Mollerup [13] and of Ulybin and Zherdev [9], and

they mostly deviate negatively from Eq. (9), but the maximum is only -0.2% , which is within the experimental error.

The 373 K isotherm has been measured both by Ulybin and Zherdev [9] and by Lithatskii et al. [11] and the density deviations from Eq. (9) are systematically different from each other: those of Likhatskii et al. are mostly positive, with a maximum of 0.16% , while those of Ulybin and Zherdev are mostly negative, with a maximum of -0.17% .

Deviations of Eq. (9) from the isochores of Watanabe et al. [10] are systematic, in general going from negative to positive as the temperature increases. Except for data near to the critical point the deviations are within $\pm 0.2\%$, but this is considerably greater than the experimental error which was given as 0.02% . The data of Ulybin and Zherdev [8] are mostly in the liquid and supercritical region, and their scatter is well within the experimental error of $\pm 0.15\%$.

The largest data set is that of Biswas et al. [12], which covers mostly the near-critical region, but there is also a single supercritical isotherm at 333 K which was used as the reference isotherm for the Burnett measurements. Equation (9) is unable to reproduce this isotherm correctly, as shown in Fig. 2. The density deviations, which show considerable systematic behavior, are mostly positive, with a maximum of 0.2% , whereas the experimental accuracy is reported to be $\pm 0.02\%$. Figure 2 also shows the deviations of other data sets, along the 333 K isotherm, which were used in the fit. The maximum difference of 0.42% between Biswas et

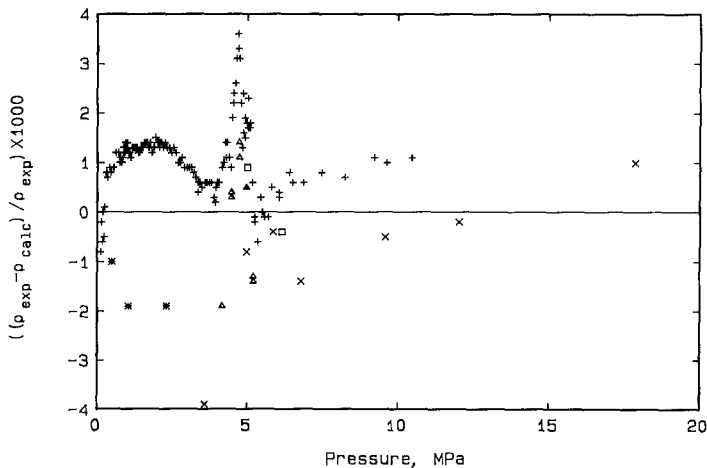


Fig. 2. Comparison of experimental $P\rho T$ data with the equation of state (9), along the 333 K isotherm. (\square) Mears et al. [7]; ($*$) Ulybin and Zherdev [9]; (\times) Watanabe et al. [10]; ($+$) Biswas et al. [12]; (\triangle) Blanke et al. [23].

al. and Watanabe et al. was also noted by Biswas et al.; the estimate of their combined errors is 0.04%. The new measurements by Blanke et al. [23] were received too late to be included in the fit. The isochoric measurements of Biswas et al. [12] outside the critical region show mostly positive deviations from Eq. (9), with a maximum of 0.3%.

The predicted data [1] show similar systematic deviations on each isotherm, going from negative to positive as the pressure increases, but all are within $\pm 0.3\%$, which is much smaller than the estimated accuracy of $\pm 1\%$. The inclusion of these data improved the fit of this region.

The large number of critical-region densities are not well represented by the equation of state, where the deviations in this region may be as large as -21.5% . However, the pressure deviations lie mostly within $\pm 0.11\%$.

5.5. C_p Data

The gas phase measurements of Bier et al. [18] show good precision, well within their experimental error of $\pm 0.2\%$, but the values calculated from Eq. (1) deviate systematically along the isobars, increasing as the temperature increases from a minimum of -0.5% at 298 K to a maximum of 2.2% at 473 K. The gas phase data of Sirota et al. [17] are at higher pressures than those of Bier et al. but cover a similar temperature range. The deviations from the equation of state are fairly evenly scattered between -0.5 and $+2.0\%$. In the liquid region, away from the critical, the deviations lie mostly within $\pm 0.75\%$.

5.6. C_v Data

There are approximately 450 measurements of C_v by Lange [24] along the critical isochore for temperatures extending from the critical temperature up to 324 K. The experimental error was given as $\pm 3.7\%$. These were not used in the fit since their inclusion caused severe distortion of the equation of state not only in the critical region, but also in the low-pressure liquid region. As expected, the equation of state is not able to reproduce these data.

6. CONCLUSIONS

The most notable feature of the comparisons with the data, which are given in Section 5, is the considerable amount of systematic deviation between the different sets. It is very difficult to obtain a good thermodynamic surface when inconsistencies are present. A careful analysis and

selection of the data has not enabled these to be eliminated. It is hoped that the new data by Blanke et al. [23] may help to resolve these difficulties.

The vapor pressure calculated from the equation of state is systematically too small. Since the saturated liquid densities are well represented, this is most probably due to errors caused by extrapolation of the gas densities.

An analytic equation of state can never correctly represent the data very close to the critical point, but for SF₆ the region over which this problem exists is much wider than usual. This may well be due to the inconsistencies between the different data sets. It is recommended that the equation of state should not be used in the region 317.4–323 K and 3.64–4.10 MPa. An analysis of the critical-region data has been made by Sengers et al. [25] in order to fit a scaled equation. The results of this analysis will necessitate the revision of this equation of state.

The limits of the equation of state are from the triple point at 222.38 to 525 K for pressures up to 55 MPa. With the exception of the critical region, the equation represents most of the selected data within their experimental accuracies. The deviations of the equation from the data of Biswas et al. and of Watanabe et al. are larger than their quoted experimental errors by a factor of 10.

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