

# Ideal Gas Thermodynamic Properties of Sulphur Heterocyclic Compounds

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The available structural parameters, fundamental frequencies and enthalpies of formation for thiirane, thiirene, thietane, 2H-thiete, 1,2-dithiete, tetrahydrothiophene, 2,3-dihydrothiophene, 2,5-dihydrothiophene, thiophene, 1,2-dithiolane, 1,3-dithiolane, 1,2,4-trithiolane, tetrahydro-2H-thiopyran, 5,6-dihydro-2H-thiopyran, 1,3-dithiane, 1,4-dithiane, 1,4-dithiin, 1,3,5-trithiane, thiepane and 1,3,5,7-tetrathiocane were critically evaluated and recommended values were selected. Molecular constants and enthalpies of formation for some of the molecules were estimated, as experimental values for these compounds are not available. Using the rigid-rotor harmonic-oscillator approximation, this information was used to calculate the chemical thermodynamic functions,  $C_p^\circ$ ,  $S^\circ$ ,  $-(G^\circ - H_0^\circ)/T$ ,  $H^\circ - H_0^\circ$ , and the properties of formation,  $\Delta_f H^\circ$ ,  $\Delta_f G^\circ$ ,  $\log K_f^\circ$ , to 1500 K in the ideal gas state at a pressure of 1 bar. The contributions to the thermodynamic properties of compounds having inversion motion (thietane, 2,3- and 2,5-dihydrothiophene) or pseudo-rotation (tetrahydrothiophene) have been computed by employing a partition function formed by the summation of the inversional or pseudo-rotational energy levels. These energy levels have been calculated by solving the wave equation using appropriate potential functions. The calculated values of the thermodynamic functions are compared with those reported in other works. Comparison with experimental data, where such are available, is also presented. The thermodynamic properties for twelve of the compounds are reported for the first time. ©1995 American Institute of Physics and American Chemical Society.

Key words: ideal thermodynamic properties; molecular structure; sulphur heterocyclic compounds; vibrational frequencies.

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## 1. Introduction

As an extension of our studies of the thermodynamic properties of monocyclic hydrocarbons<sup>1</sup> and heterocyclic compounds,<sup>2,3</sup> the calculation of the ideal gas thermodynamic properties of 20 monocyclic three-, four-, five-, six-, seven- and eight-membered sulphur compounds is carried out in this report. For eight of these molecules, the thermodynamic properties have been reported previously. Recently, more complete and reliable information has become available on the structure and vibrational assignments and this information permits us to make more precise calculations of the thermodynamic functions of some molecules and to calculate the thermodynamic properties of others for the first time.

The available data on vibrational frequencies, structural parameters and enthalpies of formation have been critically examined and the most reliable values have been selected. The molecular constants and enthalpies of formation for some compounds were estimated in the present work, as the experimental values for these molecules are not available, are incomplete, or unreliable. The selected molecular constants are given in Tables 1, 2.

Based on the selected values of the molecular constants, the ideal gas thermodynamic functions (heat capacity  $C_p^\circ$ , entropy  $S^\circ$ , Gibbs energy  $-(G^\circ - H^\circ)/T$ , and enthalpy  $H^\circ - H^\circ$ ) were calculated by the standard statistical mechanical method using a rigid-rotor harmonic-oscillator approximation. The enthalpy of formation  $\Delta_f H^\circ(298.15 K)$ , if any, was taken from the data of Pedley *et al.*,<sup>4</sup> otherwise its value was estimated in the present work using the incremental method, a variant of the group additivity approach to calculations of  $\Delta_f H^\circ$ . The accepted enthalpy of formation,  $\Delta_f H^\circ(298.15 K)$  and the

calculated thermodynamic functions have been used to calculate the enthalpies of formation  $\Delta_f H^\circ(T)$ , the Gibbs energies of formation  $\Delta_f G^\circ(T)$ , and the logarithm of the equilibrium constant of formation  $\log K_f^\circ$ , by the usual thermodynamic formulae. The last three properties are for formation from C(cr, graphite),  $H_2(g)$ , S(cr, 0–393 K), S(liq, 393–718 K), and  $S_2(g)$ , 718–1500 K). The procedures for calculation of the thermodynamic properties are similar to those used in Ref. 5. The fundamental physical constants and thermodynamic properties of the elements in their reference states used in the calculations were also taken from Ref. 5. The chemical thermodynamic property values for selected temperatures up to 1500 K for a pressure of 1 bar are given in Tables 3–22.

The inversion motion contributions to the thermodynamic properties for thietane, 2,3- and 2,5-dihydrothiophene were calculated by use of the potential function of type  $V(x) = ax^4 + bx^2$ . These potential functions are based on experimentally observed transitions and barrier heights of the inversion mode for the respective molecules. The contributions due to inversion were obtained by the summation over the energy levels calculated from the potential functions.

The pseudo-rotational contributions to the thermodynamic properties of tetrahydrothiophene were obtained by direct summation over the energy levels, calculated with the potential function of type  $V(\varphi) = 0.5 [V_2(1 - \cos 2\varphi) + V_4(1 - \cos 4\varphi)]$ .

Chiral conformations ( $C_1$ ,  $C_2$ ,  $D_2$  symmetry) exist as equimolar mixtures of two enantiomeric forms. The contribution to the thermodynamic properties of two optical isomers is obtained by adding the entropy of mixing  $S_{mix}^\circ = R \ln 2$  to  $S^\circ$  and  $-(G^\circ - H^\circ)/T$ , which is equivalent to assuming the effective symmetry number  $\sigma_{eff} = \sigma/n$ , where  $\sigma$  is the symmetry number,  $n = 2$  is the number of optical isomers. For this reason, Table 1 shows the number of optical isomers together with other molecular constants.

Uncertainties in the calculated thermodynamic properties (Table 23) were obtained by taking into account the inaccuracy of the selected molecular structural and spectroscopic data and inaccuracy due to deviation from the rigid-rotor harmonic-oscillator model. The procedure for the approximate evaluation of these uncertainties was described previously.<sup>5</sup> Uncertainties in the adopted enthalpies of formation (Table 23) were taken from the data of Pedley *et al.*,<sup>4</sup> or were estimated in the present work.

Comparisons of the calculated and experimental entropy and heat capacity values are given in Tables 24 and 25, respectively. The data from references using the same source of primary data are given in the same column.

## 2. Thiirane

The molecular structure of thiirane has been investigated by microwave spectroscopy<sup>6-8</sup> and *ab initio* calculations.<sup>9-14</sup> The structural parameters obtained from microwave studies are in good agreement with those calculated by *ab initio* methods. The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants<sup>7</sup> of Okiye *et al.*

The IR and Raman spectra of thiirane have been the subject of a number of investigations;<sup>15-21</sup> and there have been a number of normal coordinate analyses<sup>11,15-25</sup> and semiempirical and *ab initio* calculations.<sup>11,12,14,26</sup>

The only uncertainties are about the assignment of two lowest  $A_2$  modes. Fundamentals presented in Table 2 are those obtained by Allen *et al.*<sup>11</sup> from IR spectra of gaseous thiirane and Raman spectra of the liquid (except for the unobserved modes  $\nu_6 - \nu_8$  and  $\nu_{12}$ ). The values of  $\nu_6$  and  $\nu_{12}$  were taken from the IR spectrum observed by Hirokawa *et al.*;<sup>20</sup> these values are in good agreement with those obtained in experimental and theoretical works. For  $\nu_7$ , the value obtained from Raman spectroscopy<sup>19</sup> was accepted. This value agrees with other experimental data<sup>17,21</sup> and it is confirmed by normal coordinate analyses<sup>11,12,25</sup> and a scaled *ab initio* calculation.<sup>12</sup> The  $\nu_8$  frequency was selected according to experimental data<sup>11,17-19</sup> and calculated values.<sup>11,12,25</sup>

The enthalpy of formation for thiirane (Table 3) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for thiirane are given in Table 3. The calculated values of  $S^\circ(T)$  and  $C_p^\circ(T)$  are in good agreement with values obtained in most reliable calculations<sup>16,27,28</sup> (Tables 24, 25). Due to the discrepancy in the molecular constants used, the discrepancies with two other calculations<sup>22,29</sup> amount to 6 and 7  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $S^\circ(1000\text{ K})$  and 2 and 6  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $C_p^\circ(500\text{ K})$ .

### 3. Thiirene

There are no experimental data on the rotational constants or the molecular structure of thiirene. The geometrical structure of thiirene was calculated by semiempirical<sup>30</sup> and *ab initio*<sup>11,12,31-36</sup> methods. The product of the principal moments of inertia (Table 1) was calculated using the estimated structural parameters:  $r(\text{C}-\text{S}) = 1.85 \pm 0.05 \text{ \AA}$ ,  $r(\text{C}=\text{C}) = 1.28 \pm 0.03 \text{ \AA}$ ,  $r(\text{C}-\text{H}) = 1.07 \pm 0.02 \text{ \AA}$ ,  $\angle \text{H}-\text{C}=\text{C} = 152 \pm 5^\circ$ . These values are close to those obtained from *ab initio* calculations.<sup>11,12,34</sup>

This unstable molecule has been synthesized only in solid matrices at liquid helium temperatures and has been identified by its IR spectrum which is, however, as yet incompletely characterized. Experimental IR spectra have been reported for thiirene and several of its isotopic derivatives by two groups.<sup>37-39</sup> and 40-42. Although the two groups agree on most features of the spectra there are some differences. Vibrational frequencies  $\nu_1, \nu_2, \nu_4, \nu_6 - \nu_8$  given in Table 2 were assigned by Safarik *et al.*<sup>42</sup> with the aid of normal coordinate calculation. Later, their assignment was confirmed by *ab initio* calculations with a scaling procedure.<sup>11,12</sup> The values of  $\nu_3, \nu_5$  and  $\nu_9$  were estimated on the basis of the most exact theoretical calculations,<sup>11,12,42</sup> their uncertainties are estimated to be about  $50 \text{ cm}^{-1}$ .

There are no experimental data on the enthalpy of formation of thiirene. Only the value estimated by semiempirical calculation is known ( $205 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>30</sup> In this work, the value of  $\Delta_f H^\circ(298.15\text{ K})$  (Table 4) was estimated by comparison of known values of  $\Delta_f H^\circ(298.15\text{ K})$  for cyclopropane ( $53.3 \text{ kJ}\cdot\text{mol}^{-1}$ ), cyclopropene ( $277.1 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> and thiirane ( $82.0$

$\text{kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> assuming that the difference between  $\Delta_f H^\circ(298.15\text{ K})$  values for thiirane and thiirene is approximately the same as the difference between  $\Delta_f H^\circ(298.15\text{ K})$  values for cyclopropane and cyclopropene.

The ideal gas thermodynamic properties for thiirene given in Table 4 are reported for the first time. No experimental data are available for comparison.

### 4. Thietane

According to the microwave studies of rotational spectra,<sup>43,44</sup> the far-infrared measurements,<sup>45-47</sup> the low frequency Raman spectra studies,<sup>48,49</sup> the investigation of the infrared spectra in the  $\text{CH}_2$  scissoring region<sup>50</sup> and the electron diffraction data,<sup>51,52</sup> the ring-puckering vibration of thietane follows a double minimum potential function with a central barrier of  $274 \text{ cm}^{-1}$ . The high barrier ensures that thietane in its ground state is puckered; the equilibrium dihedral angle has been claimed to be  $26-30^\circ$  from experimental data,<sup>44,50-52</sup>; about  $35^\circ$  from semiempirical<sup>53</sup> and  $13-20^\circ$  from *ab initio*<sup>9,14,54</sup> calculations. The product of the principal moments of inertia for the puckered configuration ( $C_s$  symmetry) given in Table 1 was calculated using the rotational constants determined from microwave study.<sup>44,55</sup> It should be noted, although the puckering configuration belongs to the  $C_s$  symmetry point group, the appropriate non-rigid molecular group is  $C_{2v}$  which corresponds to the planar configuration at the barrier top.

Some assignments of the vibrational spectra of thietane are known.<sup>54,56-58</sup> The fundamental frequencies listed in Table 2 were taken from the reliable interpretation of the vibrational spectra by Shaw *et al.*<sup>54</sup> These authors investigated the IR spectra in the vapor phase and in the liquid phase, Raman spectra in the liquid phase for thietane and four deuterated isotopomers and confirmed their vibrational assignments by scaled *ab initio* calculation.

The thermodynamic-property contributions due to inversion of the thietane ring were obtained by direct summation over the energy levels calculated with the potential function determined by Harris *et al.*<sup>44</sup> from microwave intensity measurements. The potential function for inversion is  $V(x) = (5.05 \cdot 10^{-5} x^4 - 23.5 \cdot 10^3 x^2) \text{ cm}^{-1}$  (where  $x$  ( $\text{\AA}$ ) is the ring-puckering coordinate) with a barrier height of  $274 \text{ cm}^{-1}$  and a reduced mass of  $104.6 \text{ a.u.}$

The enthalpy of formation for thietane (Table 5) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for thietane are given in Table 5. The calculated values of  $S^\circ(298.15\text{ K})$ ,  $S^\circ(327.53\text{ K})$  and  $C_p^\circ(377.20\text{ K})$  coincide with the calorimetric values (Tables 24, 25) within the uncertainties of the experimental values. The calculated values of  $S^\circ(T)$  and  $C_p^\circ(T)$  are in good agreement with the statistical calculation of Scott *et al.*<sup>56</sup> El-Sabban and Scott<sup>58</sup> used the approximate formula to estimate a few levels higher than those reported by Harris *et al.*<sup>44</sup> Due to this approximation and to the discrepancy in the vibrational frequencies used, the discrepancies with  $S^\circ(1000\text{ K})$  and  $C_p^\circ(1000\text{ K})$  values calculated by El-Sabban and Scott<sup>58</sup> amount to 3 and  $7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively (Tables 24, 25).

## 5. 2H-Thiete

A planar equilibrium structure of the four-membered ring of 2H-thiete has been established from the microwave spectra of 2H-thiete and nine isotopically substituted species.<sup>59</sup> The results of *ab initio* calculations<sup>60,61</sup> are in agreement with the experimental evidence. The rotational constants determined by Rodler and Bauder<sup>59</sup> were used to calculate the product of the three principal moments of inertia (Table 1).

There has been no experimental study of 2H-thiete's vibrational spectrum. However, vibrational frequencies have been determined by Yu *et al.*<sup>61</sup> using scaled quantum mechanical calculation and the probable reliability of the frequency prediction has been estimated to be  $\pm 30 \text{ cm}^{-1}$ . These frequencies are presented in Table 2, except for  $\nu_{18}$ . The value of the lowest out-of-plane deformation mode  $\nu_{18}$ , given in Table 2, was determined from microwave investigation.<sup>59</sup>

There are no experimental data on the enthalpy of formation of 2H-thiete. Its value was estimated in the present work (Table 6) by comparison of known values of  $\Delta_f H^\circ$  (298.15 K) for related compounds. We believe that in passing from thietane ( $\Delta_f H^\circ(298.15 \text{ K}) = 60.6 \text{ kJ}\cdot\text{mol}^{-1}$ ) to 2H-thiete the change in  $\Delta_f H^\circ(298.15 \text{ K})$  values might be expected to be approximately the same as in passing from cyclobutane ( $28.4 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> to cyclobutene ( $156.7 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup>, or in passing from tetrahydrothiophene ( $-34.1 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> to 2,3-dihydrothiophene ( $90.7 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup>.

The ideal gas thermodynamic properties for 2H-thiete are presented in Table 6. These values are reported for the first time and there are no experimental data for comparison.

## 6. 1,2-Dithiete

All rotational constants of 1,2-dithiete have been obtained from its microwave spectrum.<sup>62</sup> However, the experimental information was not sufficient to determine the molecular structure without assumptions. To estimate the molecular structure of 1,2-dithiete Rodler and Bauder<sup>62</sup> transferred some structural parameters from the structurally related four-membered ring molecules. A molecular structure proposed is compatible with *ab initio* calculations.<sup>61,63-67</sup>

The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants by Rodler and Bauder.<sup>62</sup>

Eight frequencies of 1,2-dithiete were assigned by Diehl *et al.*<sup>68</sup> from low-temperature matrix IR spectrum. For the identification of the absorption bands the corresponding vibrational frequencies and IR intensities were calculated quantum chemically by taking electron correlation into account. Vibrational frequencies  $\nu_2$ - $\nu_5$ ,  $\nu_8$  and  $\nu_{10}$ - $\nu_{12}$  given in Table 2 are those observed experimentally by Diehl *et al.*<sup>68</sup> and are in excellent agreement with their calculated (scaled) frequencies. For unobserved frequencies  $\nu_1$ ,  $\nu_6$ ,  $\nu_7$  and  $\nu_9$ , the values obtained by Goddard<sup>66</sup> from *ab initio* calculation are presented in Table 2; their uncertainties are estimated to be about  $50 \text{ cm}^{-1}$ .

There are no experimental data on the enthalpy of formation of 1,2-dithiete. Only the value estimated by semiempirical calculation is known ( $176 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>69</sup> In this work the

value of  $\Delta_f H^\circ(298.15 \text{ K})$  (Table 7) was estimated by comparison of known values of  $\Delta_f H^\circ$  for related four-membered (cyclobutane, cyclobutene, thietane) and aliphatic (ethylmethyl sulphide, dimethyl disulphide) compounds (the  $\Delta_f H^\circ(298.15 \text{ K})$  values for the above compounds were taken from Ref. 4):

$$\begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 96.0 \end{array} = \begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 60.6 \end{array} + \begin{array}{c} \text{CH}_3\text{-S-S-CH}_3 \\ \leftarrow \\ (-24.2) \end{array} - \begin{array}{c} \text{CH}_3\text{-S-CH}_2\text{-CH}_3 \\ \leftarrow \\ (-59.6) \end{array} \quad (1)$$

$$\begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 224.3 \end{array} = \begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 96.0 \end{array} + \begin{array}{c} \square \\ \leftarrow \\ 156.7 \end{array} - \begin{array}{c} \square \\ \leftarrow \\ 28.4 \end{array} \quad (2)$$

The value of  $\Delta_f H^\circ(298.15 \text{ K}) = 224.3 \text{ kJ}\cdot\text{mol}^{-1}$  estimated using Eqs. (1) and (2) is consistent with values estimated from Eqs. (3) and (4):

$$\begin{array}{c} \square_{\text{S}}^{\text{O}} \\ \leftarrow \\ 111.5 \end{array} = \begin{array}{c} \square_{\text{O}}^{\text{O}} \\ \leftarrow \\ 10 \end{array} + \begin{array}{c} \text{CH}_3\text{-S-S-CH}_3 \\ \leftarrow \\ (-24.2) \end{array} - \begin{array}{c} \text{CH}_3\text{-O-O-CH}_3 \\ \leftarrow \\ (-125.7) \end{array} \quad (3)$$

est., Ref. 2  
↓  
using eqn(2)

$$\begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 239.8 \end{array}$$

$$\begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 225.4 \end{array} = \begin{array}{c} \square_{\text{S}}^{\text{S}} \\ \leftarrow \\ 190 \end{array} + \begin{array}{c} \text{CH}_3\text{-S-S-CH}_3 \\ \leftarrow \\ (-24.2) \end{array} - \begin{array}{c} \text{CH}_3\text{-S-CH}_2\text{-CH}_3 \\ \leftarrow \\ (-59.6) \end{array} \quad (4)$$

est., this work

Although Eqs. (3) and (4) include estimated values of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,2-dioxetane and 2H-thiete, they demonstrate the inner conformity of our estimations for oxygen and sulphur heterocyclic compounds.

The ideal gas thermodynamic properties for 1,2-dithiete presented in Table 7 are reported for the first time. No experimental data are available for comparison.

## 7. Tetrahydrothiophene

The far-infrared spectra of tetrahydrothiophene<sup>70-72</sup> were interpreted by assuming that the molecule was undergoing a hindered pseudo-rotation. According to microwave,<sup>73-76</sup> electron diffraction<sup>77</sup> and theoretical studies,<sup>78</sup> tetrahydrothiophene exists in the twisted ( $C_2$ ) conformation in its ground state. In the present work, it is assumed that tetrahydrothiophene has a non-planar twist ground-state conformation ( $C_2$  symmetry) and that the molecule undergoes hindered pseudo-rotation through its planar configuration ( $C_{2v}$  symmetry). The

product of the principal moments of inertia given in Table 1 was calculated using the reported three ground-state rotational constants.<sup>75</sup>

The complete vibrational assignments of tetrahydrothiophene have been reported from the analysis of IR spectra of all three physical states and the Raman spectra of the liquid and solid.<sup>76,79,80</sup> Fundamentals presented in Table 2 are those obtained by Durig *et al.*<sup>76</sup> from Raman spectra of the solid except for  $\nu_{17}$ . The value of twist fundamental ( $\nu_{17}$ ) was taken from far-infrared data.<sup>72</sup>

The thermodynamic-property contributions due to restricted pseudo-rotation of the tetrahydrothiophene ring were obtained by direct summation over the energy levels calculated with the potential function of  $V(\varphi) = 0.5 [-774.3(1 - \cos 2\varphi) + 167.3(1 - \cos 4\varphi)] \text{ cm}^{-1}$ , where  $\varphi$  is the angle of pseudo-rotation, as reported by Smithson and Wieser.<sup>72</sup> This potential function and a pseudo-rotation constant  $B = 2.35 \text{ cm}^{-1}$  were employed to generate pseudo-rotation energy levels for the calculation of the pseudo-rotational contributions.

The enthalpy of formation for tetrahydrothiophene (Table 8) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for tetrahydrothiophene are given in Table 8. The calculated values of  $S^\circ(T)$  are in good agreement with calorimetric data<sup>81</sup> and with other available calculations<sup>27,28,58,71,81,82</sup> (Table 24). The calculated values of  $C_p^\circ(T)$  are  $0.9\text{--}1.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  more than those obtained from calorimetric measurements<sup>81</sup> and from the other statistical calculations (Table 25). However, we believe that these discrepancies are within uncertainties of the experimental values of  $C_p^\circ(T)$ . The coincidence of the experimental  $C_p^\circ(T)$  values with those calculated previously was achieved by fitting the empirical parameters in formula for approximate calculation of pseudo-rotation contributions.

## 8. 2,3-Dihydrothiophene

The ring-puckering vibration in 2,3-dihydrothiophene has been studied in the infrared (as difference bands between the CH stretching and ring-puckering vibrations),<sup>83</sup> in the far-infrared,<sup>84</sup> in the Raman<sup>85</sup> and in the microwave region.<sup>84,86</sup> All of these studies indicate that the ring has a non-planar equilibrium conformation. The ring-puckering vibration is described by a double minimum potential function. The product of the principal moments of inertia for the non-planar conformation ( $C_1$  symmetry) of 2,3-dihydrothiophene given in Table 1 was calculated using the rotational constants determined from microwave study.<sup>84</sup>

The vibrational spectrum of 2,3-dihydrothiophene was not investigated either experimentally or theoretically. In this work vibrational frequencies of 2,3-dihydrothiophene (Table 2) were calculated using 24 force constants transferred from tetrahydrothiophene, thiophene and 2,5-dihydrothiophene. Normal coordinate calculations were carried out for the above three molecules using their fundamental frequencies from Table 2. The average uncertainty of the calculated vibrational frequencies is estimated to be about  $50 \text{ cm}^{-1}$ .

The thermodynamic-property contributions due to inversion of the 2,3-dihydrothiophene ring were obtained by direct summation over the energy levels calculated with the

potential function. Several investigations of the double minimum ring-puckering potential function of 2,3-dihydrothiophene have been reported.<sup>83-85</sup> The potential function determined by Durig *et al.*<sup>84</sup> from far-infrared investigation was used in this work. The potential function for inversion is  $V(x) = (6.50 \cdot 10^5 x^4 - 2.92 \cdot 10^4 x^2) \text{ cm}^{-1}$  (where  $x$  ( $\text{\AA}$ ) is the ring-puckering coordinate) with a barrier height of  $328 \text{ cm}^{-1}$  and with a reduced mass of 117 a.u.

The enthalpy of formation for 2,3-dihydrothiophene (Table 9) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for 2,3-dihydrothiophene presented in Table 9 are reported for the first time. No experimental data are available for comparison.

## 9. 2,5-Dihydrothiophene

The ring-puckering motion of 2,5-dihydrothiophene has been studied by infrared,<sup>83</sup> far-infrared<sup>87,88</sup> and microwave spectroscopy.<sup>86,89</sup> All of these studies have confirmed that 2,5-dihydrothiophene has a planar equilibrium configuration ( $C_{2v}$  symmetry) and a single minimum ring-puckering potential function. The product of the principal moments of inertia for the planar conformation of 2,5-dihydrothiophene given in Table 1 was calculated using the rotational constants determined from microwave study.<sup>89</sup>

Green and Harvey<sup>90</sup> have reported the vibrational assignment for 2,5-dihydrothiophene from the IR measurements in gaseous and liquid states and from the Raman study in the liquid state. Their assignment is listed in Table 2.

The thermodynamic-property contributions due to ring-puckering of the 2,5-dihydrothiophene were obtained by direct summation over the energy levels calculated with the potential function determined by Green and Harvey<sup>87</sup> from far-infrared spectrum. The potential function for ring-puckering vibration is  $V(x) = (4.66 \cdot 10^2 x^4 + 1.66 \cdot 10^4 x^2) \text{ cm}^{-1}$  (where  $x$  ( $\text{\AA}$ ) is the ring-puckering coordinate) with a reduced mass of 166.3 a.u.

The enthalpy of formation for 2,5-dihydrothiophene (Table 10) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for 2,5-dihydrothiophene are given in Table 10. No experimental data are available for comparison. The calculated values of  $S^\circ(T)$  and  $C_p^\circ(T)$  are in good agreement with those calculated by Rehman and Lee<sup>82</sup> (Table 24, 25).

## 10. Thiophene

Information on structural parameters and rotational constants of thiophene has been obtained from microwave studies,<sup>74,91,92</sup> electron diffraction data<sup>93,94</sup> and theoretical calculations.<sup>36,95,96</sup>

The product of the principal moments of inertia for the planar conformation ( $C_{2v}$  symmetry) given in Table 1 was calculated using the rotational constants determined from microwave study.<sup>91</sup>

The vibrational spectra of thiophene have been investigated by many authors<sup>26,97-110</sup> and complete vibrational assignments have been reported. The fundamental frequencies used in our calculations (Table 2) are those by Rico *et al.*<sup>98</sup> These authors

observed the vibrational frequencies for thiophene and its deuterated derivatives from IR spectra of liquid and gaseous phases and the Raman spectrum of the liquid; their vibrational assignment has been confirmed by vibrational analysis.<sup>99,105,106,110</sup>

The enthalpy of formation for thiophene (Table 11) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for thiophene are given in Table 11. The calculated values of  $S^\circ(T)$  and  $C_p^\circ(T)$  agree well with the calorimetric values<sup>97</sup> and with those obtained in other statistical calculations<sup>27,28,58,82,97,98,102,111</sup> (Tables 24, 25).

## 11. 1,2-Dithiolane

There are no experimental data on the rotational constants or the molecular structure of 1,2-dithiolane. The available theoretical calculations<sup>36,112,113</sup> do not give the reliable values of the structural parameters for this molecule, especially for the dihedral angle  $\tau(S-S)$ . The twist conformation of  $C_2$  symmetry was accepted for 1,2-dithiolane in this work by analogy with 1,2-dioxolane.<sup>2</sup> The product of the principal moments of inertia given in Table 1 was calculated using the estimated structural parameters:  $r(C-S) = 1.82 \pm 0.02 \text{ \AA}$ ,  $r(C-C) = 1.54 \pm 0.02 \text{ \AA}$ ,  $r(S-S) = 2.04 \pm 0.03 \text{ \AA}$ ,  $r(C-H) = 1.09 \pm 0.02 \text{ \AA}$ ,  $\angle C-S-S = 94 \pm 5^\circ$ ,  $\angle C-C-S = 107 \pm 5^\circ$ ,  $\angle C-C-C = 111.2^\circ$ ,  $\angle C-C-H = \angle S-C-H = 110 \pm 2^\circ$ ,  $\tau(S-S) = 35 \pm 5^\circ$ ,  $\tau(C-S) = 33.3^\circ$ ,  $\tau(C-C) = 15.1^\circ$ . These values are based on comparison with related compounds (tetrahydrothiophene, 1,2,4-trithiolane and five-membered oxygen heterocyclic compounds).

Experimental or theoretical data on vibrational spectrum of 1,2-dithiolane are unknown. In this work, the vibrational frequencies of 1,2-dithiolane (Table 2) have been calculated using 20 force constants transferred from tetrahydrothiophene and 1,2,4-trithiolane. Normal coordinate calculations were carried out for tetrahydrothiophene and 1,2,4-trithiolane using vibrational assignments from Table 2. An average uncertainty of the calculated vibrational frequencies of 1,2-dithiolane is believed to be about  $50 \text{ cm}^{-1}$ .

There are no experimental data on the enthalpy of formation for 1,2-dithiolane, but its value was calculated by a semiempirical method ( $53 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>36</sup> In this work, the value of  $\Delta_f H^\circ(298.15 \text{ K})$  (Table 12) was estimated by comparison of known values of  $\Delta_f H^\circ(298.15 \text{ K})$  for tetrahydrothiophene ( $-34.1 \text{ kJ}\cdot\text{mol}^{-1}$ ),<sup>4</sup> ethylmethyl sulphide ( $-59.6 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> and dimethyl disulphide ( $-24.2 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> assuming that the difference between  $\Delta_f H^\circ(298.15 \text{ K})$  values for 1,2-dithiolane and tetrahydrothiophene is approximately the same as the difference between  $\Delta_f H^\circ(298.15 \text{ K})$  values for dimethyl disulphide and ethylmethyl sulphide.

The ideal gas thermodynamic properties for 1,2-dithiolane are given in Table 12. No experimental or theoretical data are available for comparison.

## 12. 1,3-Dithiolane

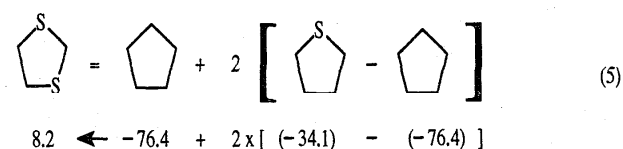
The nuclear magnetic resonance investigations suggest that the 1,3-dithiolane ring assumes preferentially a  $C_2$  half-chair

conformation.<sup>114,115</sup> According to molecular mechanics calculation<sup>116</sup> 1,3-dithiolane is a restricted pseudo-rotator and two half-chair forms ( $C_2$  and  $C_1$  symmetry) have nearly the same energy. In the present work, the half-chair conformation of  $C_2$  symmetry was accepted for 1,3-dithiolane by analogy with 1,3-dioxolane. The product of the principal moments of inertia given in Table 1 was calculated using the estimated structural parameters:  $r(C-S) = 1.82 \pm 0.02 \text{ \AA}$ ,  $r(C-C) = 1.54 \pm 0.02 \text{ \AA}$ ,  $r(C-H) = 1.09 \pm 0.02 \text{ \AA}$ ,  $\angle S-C-C = 106 \pm 5^\circ$ ,  $\angle S-C-S = 109.4^\circ$ ,  $\angle C-S-C = 97.4^\circ$ ,  $\angle C-C-H = \angle S-C-H = 110 \pm 2^\circ$ ,  $\tau(S-C-C-S) = 52 \pm 5^\circ$ ,  $\tau(C-S-C-S) = 12.7^\circ$ ,  $\tau(C-C-S-C) = 39.6^\circ$ . These values are based on comparison with related compounds (tetrahydrothiophene, 1,2,4-trithiolane and five-membered oxygen heterocyclic compounds). The adopted value of torsional angle  $\tau(S-C-C-S)$  was obtained by Irtacabal and Liotard<sup>116</sup> from molecular mechanics calculations.

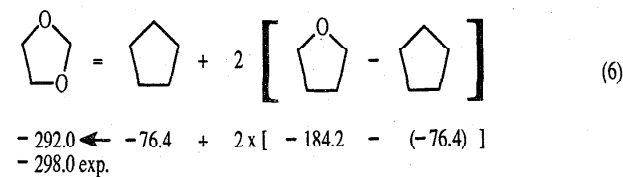
By analogy with 1,3-dioxolane,<sup>2</sup> one can expect that the molecule 1,3-dithiolane undergoes hindered pseudo-rotation. Unfortunately, there is no information about the potential energy function and the pseudo-rotational contributions to the thermodynamic functions could not be estimated correctly. The low-frequency ring vibrational mode ( $\nu_{27}$ ) estimated in this work (see below) approximates the pseudo-rotational motion of 1,3-dithiolane ring.

Experimental or theoretical data on the vibrational spectrum of 1,3-dithiolane are unknown. In this work, the vibrational frequencies of 1,3-dithiolane (Table 2) have been calculated using 19 force constants transferred from tetrahydrothiophene and 1,3-dithiane. Normal coordinate calculations were carried out for tetrahydrothiophene and 1,3-dithiane using vibrational assignments from Table 2. An average uncertainty of the calculated vibrational frequencies of 1,3-dithiolane is believed to be about  $50 \text{ cm}^{-1}$ . The large uncertainty takes place for torsional force constant  $\tau(S-C)$  estimated in this work. But we believe that such a low value of ring-puckering mode  $\nu_{27}$  is conditioned by low barrier to pseudo-rotation in 1,3-dithiolane.

There are no experimental or theoretical data on the enthalpy of formation for 1,3-dithiolane. In this work, the value of  $\Delta_f H^\circ(298.15 \text{ K})$  (Table 13) was estimated by comparison of known values of  $\Delta_f H^\circ(298.15 \text{ K})$  for cyclopentane and tetrahydrothiophene (the  $\Delta_f H^\circ(298.15 \text{ K})$  values for these compounds were taken from Ref. 4):



The same approach for 1,3-dioxolane



leads to a value in reasonably good agreement with the experiment.

The ideal gas thermodynamic properties for 1,3-dithiolane are given in Table 13. No experimental or theoretical data are available for comparison.

### 13. 1,2,4-Trithiolane

The twist half-chair conformation with  $C_2$  symmetry has been determined from the microwave spectra of eight isotopic species of 1,2,4-trithiolane.<sup>117</sup> Analysis of the vibrational spectra and photoelectron data<sup>118,119</sup> and molecular mechanics calculations<sup>120</sup> showed also that the preferential form of 1,2,4-trithiolane in the vapor phase was the half-chair ( $C_2$ ). The product of the principal moments of inertia given in Table 1 was calculated using the rotational constants determined from microwave data.<sup>117</sup>

There is no complete vibrational assignment for 1,2,4-trithiolane. Guimon *et al.*<sup>119</sup> investigated IR and Raman spectra of 1,2,4-trithiolane in the liquid phase and assigned some of the vibrational modes. Vibrational frequencies  $\nu_1$ – $\nu_{20}$  given in Table 2 have been calculated using 16 force constants estimated by comparison of the force constants of tetrahydrothiophene, tetrahydrofuran and 1,2,4-trioxolane molecules. For low-frequency ring vibrational mode, the value estimated from microwave data<sup>117</sup> is given in Table 2.

There are no experimental or theoretical data on the enthalpy of formation for 1,2,4-trithiolane. In this work, the value of  $\Delta_f H^\circ(298.15\text{ K})$  (Table 14) was estimated assuming that the difference between  $\Delta_f H^\circ(298.15\text{ K})$  for 1,2,4-trithiolane and 1,2-dithiolane ( $0\text{ kJ}\cdot\text{mol}^{-1}$ ) is approximately the same as the difference between  $\Delta_f H^\circ(298.15\text{ K})$  values for tetrahydrothiophene ( $-34.1\text{ kJ}\cdot\text{mol}^{-1}$ ) and cyclopentane ( $-76.4\text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>4</sup>

The ideal gas thermodynamic properties for 1,2,4-trithiolane are presented in Table 14. No experimental or theoretical data are available for comparison.

### 14. Tetrahydro-2H-thiopyran

From the microwave spectroscopic investigation<sup>121</sup> the chair conformation ( $C_2$  symmetry) was deduced for tetrahydro-2H-thiopyran, but the rotational constants proved insufficient to uniquely specify the molecular conformation. The molecular structure of tetrahydro-2H-thiopyran has been determined by gas-phase electron diffraction.<sup>122</sup> The electron diffraction data are consistent with a chair conformation of the molecule. Molecular mechanics calculations also indicated the chair form to be the most stable.<sup>122</sup> The product of the principal moments of inertia for the chair conformation of tetrahydro-2H-thiopyran (Table 1) was calculated using the rotational constants of Kitchin *et al.*<sup>121</sup>

To obtain the agreement between the calculated and observed values of the heat capacity, another stable conformation, the twisted form ( $C_1$  symmetry) with relative energy of  $1300\text{ cm}^{-1}$ , was considered together with the basic stable chair form in the present work. Relative energy of the twisted form was obtained by Schultz *et al.*<sup>122</sup> from molecular mechanics calculation.

Vibrational spectra of tetrahydro-2H-thiopyran in different phase states were investigated by several authors.<sup>123–127</sup> All of these studies have been presented partial vibrational assignments, except for the study of Vedal *et al.*<sup>127</sup> The fundamental frequencies used in this work (Table 2) were taken from the investigation of Vedal *et al.*<sup>127</sup> These authors observed the vibrational frequencies from IR and Raman spectra for the vapor, liquid and solid states and carried out a normal coordinate analysis to confirm the vibrational assignment.

The enthalpy of formation for tetrahydro-2H-thiopyran (Table 15) was taken from the data of Pedley *et al.*<sup>4</sup>

The ideal gas thermodynamic properties for tetrahydro-2H-thiopyran are given in Table 15. The discrepancy between the calculated and experimental heat capacity values amounts to  $\sim 2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (Table 25), but we believe this discrepancy is within uncertainties of the experimental and calculated values. The coincidence of the experimental  $C_p^\circ(T)$  values with those calculated by other authors<sup>27,28,58,128</sup> (Table 25) was achieved by adjusting some of the unobserved molecular constants. We feel no necessity to improve some more the agreement with the calorimetric data because of the uncertainties of the experimental  $C_p^\circ(T)$  values. Besides the discrepancy in the vibrational frequencies and the product of the principal moments of inertia, the effects of chair-boat tautomerism and of anharmonicity were considered in previous works<sup>27,28,58,128</sup> using approximate methods. The marked differences between their and our calculated thermodynamic functions take place at high temperatures and make up  $7\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $S^\circ(1000\text{ K})$  and  $19\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $C_p^\circ(1000\text{ K})$ . In spite of good agreement of the experimental  $S^\circ(T)$  and  $C_p^\circ(T)$  values with those calculated in previous works,<sup>27,28,58,128</sup> it is impossible to consider the thermodynamic functions calculated in these works as more reliable than ours because the molecular constants used at that time were not specified. Vedal *et al.*<sup>127</sup> used the same vibrational frequencies as in this work; due to the discrepancy in the principal moments of inertia used and due to the neglect of twisted form, the discrepancies in  $S^\circ$  and  $C_p^\circ$  values amount to 2 and  $5\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at 500 K.

### 15. 5,6-Dihydro-2H-thiopyran

From the far-infrared spectrum for the out-of-plane ring-bending and the ring-twisting vibrations, Tecklenburg *et al.*<sup>129</sup> have calculated the potential energy surface for 5,6-dihydro-2H-thiopyran. The minimum energy on the potential surface corresponds to the half-chair conformation with a twisting angle of  $37.8^\circ$ . This result is compared to molecular mechanics calculation.<sup>129</sup>

The product of the principal moments of inertia given in Table 1 was calculated for half-chair conformation ( $C_1$  symmetry) using the estimated structural parameters:  $r(\text{C}-\text{S}) = 1.81 \pm 0.02\text{ \AA}$ ,  $r(\text{C}-\text{C}) = 1.52 \pm 0.02\text{ \AA}$ ,  $r(=\text{C}-\text{C}) = 1.50 \pm 0.02\text{ \AA}$ ,  $r(\text{C}=\text{C}) = 1.34 \pm 0.02\text{ \AA}$ ,  $r(\text{C}-\text{H}) = 1.09 \pm 0.02\text{ \AA}$ ,  $r(=\text{C}-\text{H}) = 1.08 \pm 0.02\text{ \AA}$ ,  $\angle \text{C}=\text{C}-\text{C} = 122 \pm 2^\circ$ ,  $\angle \text{C}-\text{C}-\text{C} = 113 \pm 2^\circ$ ,  $\angle \text{C}-\text{S}-\text{C} = 89 \pm 5^\circ$ ,  $\angle \text{C}-\text{C}-\text{H} = 110 \pm 5^\circ$ ,  $\angle =\text{C}-\text{C}-\text{H} \approx 120 \pm 5^\circ$ ,  $\tau(\text{C}-\text{S}) = 39.4^\circ$ .

Only the two lowest out-of-plane ring-deformation modes were assigned from far-infrared spectra of 5,6-dihydro-2H-thiopyran<sup>129</sup> and these values are accepted in Table 2. The

other fundamental frequencies (Table 2) were calculated in this work using 22 force constants transferred from tetrahydro-2H-thiopyran and cyclohexene. Average uncertainty of calculated vibrational frequencies is believed to be about  $50 \text{ cm}^{-1}$ .

There are no experimental or theoretical data on the enthalpy of formation for 5,6-dihydro-2H-thiopyran. In this work the value of  $\Delta_f H^\circ(298.15 \text{ K})$  (Table 16) was estimated by comparison of known values of  $\Delta_f H^\circ(298.15 \text{ K})$  for related compounds. We believe that in passing from 5,6-dihydro-2H-thiopyran to tetrahydro-2H-thiopyran ( $\Delta_f H^\circ(298.15 \text{ K}) = -63.5 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> the change in  $\Delta_f H^\circ(298.15 \text{ K})$  values might be expected approximately the same as in passing from cyclohexene ( $-5.0 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> to cyclohexane ( $-123.4 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> or from 2,5-dihydrothiophene ( $86.9 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> to tetrahydrothiophene ( $-34.1 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup>.

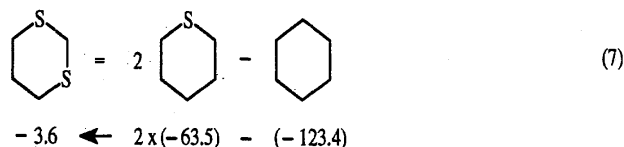
The ideal gas thermodynamic properties for 5,6-dihydro-2H-thiopyran are given in Table 16. No experimental or theoretical data are known for comparison.

### 16. 1,3-Dithiane

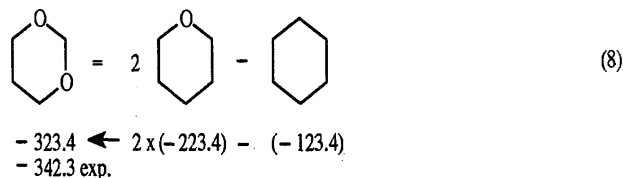
A gas-phase electron diffraction study,<sup>130</sup> microwave data<sup>131</sup> and dipole moments investigation<sup>132</sup> provided the evidence that the chair conformation is the most stable form of 1,3-dithiane. The product of the principal moments of inertia for the chair conformer ( $C_2$  symmetry) given in Table 1 was calculated using the rotational constants determined from microwave data.<sup>131</sup>

The partial assignments of vibrational frequencies for 1,3-dithiane were obtained from IR and Raman spectra of the liquids and solids.<sup>126,133</sup> To confirm these assignments and to estimate unobserved frequencies, a normal coordinate analysis was carried out in this work. The initial values of force constants were transferred from tetrahydro-2H-thiopyran molecule. The vibrational frequencies calculated in this work (Table 2) agree satisfactory with those assigned from vibrational spectra, except for lowest ring-deformation frequency of  $80 \text{ cm}^{-1}$ .<sup>133</sup> The value of  $167 \text{ cm}^{-1}$  is obtained for this frequency in the present work and it is close to the lowest frequency in 1,4-dithiane.<sup>126,134</sup> The average uncertainty of calculated fundamentals of 1,3-dithiane is estimated to be about  $50 \text{ cm}^{-1}$ .

There are no experimental or theoretical data on the enthalpy of formation of 1,3-dithiane. The Eq. (7) was used to estimate the value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,3-dithiane (the data on the enthalpy of formation of related compounds were taken from Ref. 4):



The same approach for 1,3-dioxane



results in a somewhat a overestimated value. It is necessary to use the factor 2.085 in place of 2.0 in Eq. (8) to obtain the agreement with experiment. The use of factor 2.085 in Eq. (7) gives the value of  $-9.0 \text{ kJ}\cdot\text{mol}^{-1}$  for enthalpy of formation of 1,3-dithiane. The accepted value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,3-dithiane (Table 17) is based on this estimate.

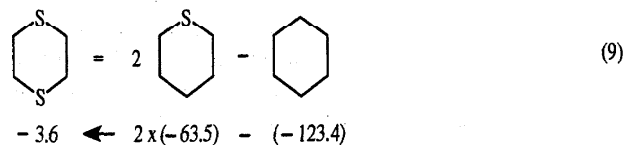
The ideal gas thermodynamic properties for 1,3-dithiane are given in Table 17. No experimental or theoretical data are known for comparison.

### 17. 1,4-Dithiane

It was determined from X-ray investigation,<sup>135</sup> that crystals of 1,4-dithiane have chair configuration ( $C_{2h}$  symmetry). This structure was confirmed by *ab initio* calculation.<sup>136</sup> The product of the principal moments of inertia given in Table 1 was calculated using the estimated structural parameters:  $r(\text{C}-\text{S}) = 1.81 \pm 0.02 \text{ \AA}$ ,  $r(\text{C}-\text{C}) = 1.53 \pm 0.02 \text{ \AA}$ ,  $r(\text{C}-\text{H}) = 1.11 \pm 0.02 \text{ \AA}$ ,  $\angle \text{C}-\text{S}-\text{C} = 99 \pm 2^\circ$ ,  $\angle \text{S}-\text{C}-\text{C} = 113 \pm 5^\circ$ ,  $\angle \text{S}-\text{C}-\text{H} = \angle \text{C}-\text{C}-\text{H} = 110 \pm 2^\circ$ ,  $\tau(\text{C}-\text{S}) = 60.2^\circ$ ,  $\tau(\text{C}-\text{C}) = 68.6^\circ$ . These values are based on data.<sup>135,136</sup>

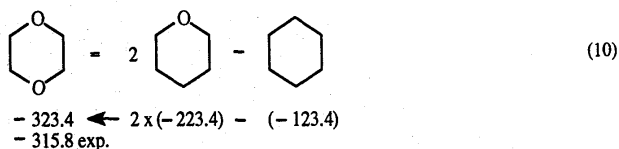
The vibrational spectra of 1,4-dithiane have been studied by several researches.<sup>126,134,137-139</sup> Fundamentals presented in Table 2 are those obtained by Ellestad *et al.*<sup>134</sup> These authors have investigated the IR spectra in the vapor, liquid and solid phases and Raman spectra of liquids and solids, and have carried out a normal coordinate calculation to confirm their vibrational assignment.

There are no experimental or theoretical data on the enthalpy of formation of 1,4-dithiane. Eq. (9) was used to estimate the value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,4-dithiane (the data on the enthalpy of formation of related compounds were taken from Ref. 4):





The same approach for 1,4-dioxane



leads to a slightly underestimated value. To obtain agreement with experiment it is necessary to use the factor 1.966 instead of 2.0 in Eq. (10). The use of factor 1.966 in Eq. (9) gives the value of  $-1.4 \text{ kJ}\cdot\text{mol}^{-1}$  for enthalpy of formation of 1,4-dithiane. The recommended value of  $\Delta_f H^\circ$  (298.15 K) for 1,4-dithiane (Table 18) is based on this estimate.

The ideal gas thermodynamic properties for 1,4-dithiane are given in Table 18. The calculated values of thermodynamic functions are in good agreement with those obtained by Ellestad *et al.*,<sup>134</sup> as nearly the same molecular constants were used in both calculations. No experimental data are available for comparison.

### 18. 1,4-Dithiin

According to X-ray diffraction studies<sup>140,141</sup> the 1,4-dithiin ring is, in the solid state, nonplanar with a dihedral angle of about  $137^\circ$  between the two SCCS planes. This result is consistent with the dipole moment measurements<sup>142</sup> in the solution state. However, experimental studies<sup>143-145</sup> of the ultraviolet photoelectron spectrum and NMR proton coupling constants in a nematic phase were unable to choose between a boat, planar or rapidly inverting structure. Conflicting results have also been obtained in theoretical studies, both at semiempirical and at different basis set *ab initio* levels,<sup>36,96,146-153</sup> although most of the results predict the boat-like form to be slightly favored over the planar one. It was suggested in this work that, in the gas phase, the 1,4-dithiin molecule is very flexible, with the boat form ( $C_{2v}$  symmetry) being the minimum in energy. The product of the principal moments of inertia given in Table 1 was calculated using the estimated structural parameters:  $r(\text{C}-\text{S}) = 1.78 \pm 0.03 \text{ \AA}$ ,  $r(\text{C}=\text{C}) = 1.34 \pm 0.03 \text{ \AA}$ ,  $r(\text{C}-\text{H}) = 1.08 \pm 0.02 \text{ \AA}$ ,  $\angle \text{C}-\text{S}-\text{C} = 100 \pm 2^\circ$ ,  $\angle \text{C}-\text{C}-\text{S} = 125.4^\circ$ ,  $\angle \text{C}-\text{C}-\text{H} = 122 \pm 5^\circ$ ,  $\angle \text{S}-\text{C}-\text{H} = 112.6^\circ$ ,  $\varphi = 140 \pm 40^\circ$  (the angle between the two SCCS planes).

Vibrational spectrum of 1,4-dithiin was investigated neither experimentally nor theoretically. In this work vibrational frequencies (Table 2) have been calculated using 13 force constants transferred from thiophene and 2,5-dihydrothiophene. Simple valence force fields for these molecules have been determined using vibrational frequencies from Table 2. The average uncertainty of calculated vibrational frequencies is estimated to be about  $50 \text{ cm}^{-1}$ . The calculated frequency  $\nu_{19}$  ( $B_1$ ) proved to be quite insensitive to the torsional force constants: the varying of torsional force constants in quite a wide range changes the value of lowest frequency  $\nu_{19}$  ( $B_1$ ) only by a few  $\text{cm}^{-1}$ . We believe that such a low value of this mode means that the molecule can easily oscillate between two non-planar boat forms via the planar one.

There are no experimental or theoretical data on the enthalpy of formation of 1,4-dithiin and its value was estimated in present work (Table 19) by analogy with 1,4-dioxin<sup>3</sup> assuming that in passing from 1,4-dithiane ( $\Delta_f H^\circ(298.15 \text{ K}) = 0 \text{ kJ}\cdot\text{mol}^{-1}$ ) to 1,4-dithiin, the change in  $\Delta_f H^\circ(298.15 \text{ K})$  values may be expected to be nearly the same as in passing from tetrahydrothiophene ( $-34.1 \text{ kJ}\cdot\text{mol}^{-1}$ )<sup>4</sup> to thiophene ( $114.9 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>4</sup> This estimation is rather rough but it falls in-between results obtained from other difference equations including cyclohexene and cyclohexane.

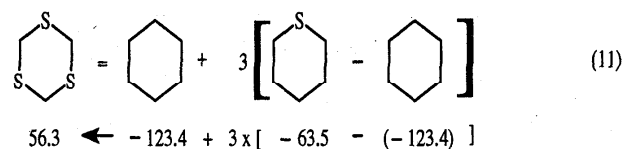
The ideal gas thermodynamic properties for 1,4-dithiin are given in Table 19. No experimental or calculated data are available for comparison.

### 19. 1,3,5-Trithiane

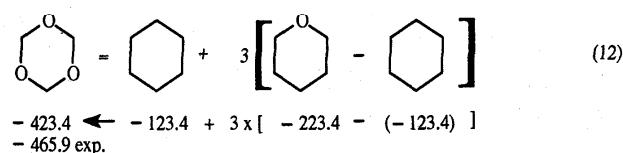
Electron diffraction investigations<sup>154,155</sup> as well as X-ray crystallography<sup>156,157</sup> and microwave spectroscopy<sup>158</sup> showed that in both the gas and solid phase 1,3,5-trithiane had the chair conformation ( $C_{3v}$  symmetry). From microwave data,<sup>158</sup> the rotational constant  $B_0$  was determined only and the product of the principal moments of inertia for chair conformation of 1,3,5-trithiane (Table 1) was calculated using the structural parameters obtained from electron diffraction study.<sup>155</sup>

Vibrational spectra of 1,3,5-trithiane were studied by various workers.<sup>139,159-164</sup> The marked difference (from 80 to 279  $\text{cm}^{-1}$ ) exists for the assignment of the lowest ring bending vibration  $\nu_{20}(E)$ . Vibrational frequencies listed in Table 2 were obtained by Asai and Noda<sup>162</sup> from IR data for the solid phase; their assignment was confirmed by normal coordinate analysis. For the frequency  $\nu_{20}(E)$  unobserved experimentally, the value calculated by Asai and Noda<sup>162</sup> was accepted. This value agrees with the estimation of  $\nu_{20}$  from relative intensity measurements in microwave spectrum.<sup>158</sup>

There are no experimental or theoretical data on the enthalpy of formation of 1,3,5-trithiane. Eq. (11) was used to estimate the value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,3,5-trithiane (the data on the enthalpy of formation of related compounds were taken from ref. 4):



The same approach for 1,3,5-trioxane



leads to the overestimated value. To obtain agreement with experiment it is necessary to use the factor 3.425 in place of

3.0 in Eq. (12). The use of factor 3.425 in Eq. (11) gives the value of  $81.8 \text{ kJ}\cdot\text{mol}^{-1}$  for enthalpy of formation of 1,3,5-trithiane. The recommended value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,3,5-trithiane (Table 20) is based on this estimate.

The ideal gas thermodynamic properties for 1,3,5-trithiane are given in Table 20. No experimental or theoretical data are available for comparison.

## 20. Thiepane

There are no experimental or theoretical data on molecular structure and vibrational spectrum of thiepane. By analogy with oxepane,<sup>3</sup> the mixture of two asymmetric twist-chair conformations ( $C_2$  symmetry) of equal energy was taken into account in the present work. The product of the principal moments of inertia given in Table 1 was calculated using the estimated structural parameters:  $r(\text{C-S}) = 1.81 \pm 0.03 \text{ \AA}$ ,  $r(\text{C-C}) = 1.53 \pm 0.02 \text{ \AA}$ ,  $r(\text{C-H}) = 1.10 \pm 0.02 \text{ \AA}$ ,  $\angle \text{C}_7\text{-S}_1\text{-C}_2 = 100 \pm 5^\circ$ ,  $\angle \text{C}_3\text{-C}_4\text{-C}_5 = \angle \text{C}_4\text{-C}_5\text{-C}_6 = \angle \text{C}_5\text{-C}_6\text{-C}_7 = \angle \text{C}_6\text{-C}_7\text{-S}_1 = 113 \pm 5^\circ$ ,  $\angle \text{S}_1\text{-C}_2\text{-C}_3 = 112.5^\circ$ ,  $\angle \text{C}_2\text{-C}_3\text{-C}_4 = 110.9^\circ$ ,  $\angle \text{C-C-H} = \angle \text{S-C-H} = 109 \pm 3^\circ$ ,  $\tau(\text{S}_1\text{-C}_2) = 96.9^\circ$ ,  $\tau(\text{C}_2\text{-C}_3) = 78.4^\circ$ ,  $\tau(\text{C}_3\text{-C}_4) = 53.5^\circ$ ,  $\tau(\text{C}_4\text{-C}_5) = 82 \pm 5^\circ$ ,  $\tau(\text{C}_5\text{-C}_6) = 102 \pm 5^\circ$ ,  $\tau(\text{C}_6\text{-C}_7) = 34 \pm 5^\circ$ ,  $\tau(\text{C}_7\text{-S}_1) = 43 \pm 5^\circ$ . These values are based on comparison with structural parameters of tetrahydro-2H thiopyran and oxepane.

Fundamental frequencies presented in Table 2 were estimated in this work by normal coordinate calculations using force constants transferred from tetrahydro-2H-thiopyran, tetrahydro-2H-pyran and oxepane. Simple valence force fields for these molecules were preliminary determined using vibrational frequencies from ref. 3 and Table 2. Average uncertainty of calculated vibrational frequencies of thiepane is believed to be about  $50 \text{ cm}^{-1}$ .

The enthalpy of formation for thiepane (Table 21) was taken from the data of Pedley *et al.*<sup>4</sup>

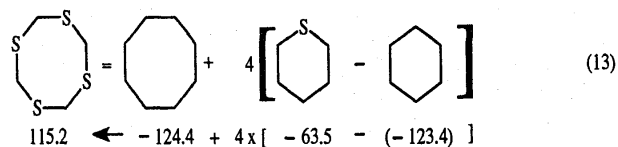
The ideal gas thermodynamic properties for thiepane are given in Table 21. No experimental data are available for comparison. The values of thermodynamic functions estimated by approximate comparative methods are presented in two reference books.<sup>27,28</sup> These functions were obtained by comparison of known data for thiacycloalkanes and cycloalkanes. The agreement between these and our values of  $S^\circ(T)$  and  $C_p^\circ(T)$  (Tables 24, 25) could be considered as satisfactory for temperatures below 500 K: the discrepancies do not exceed  $2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $S^\circ(T)$  and  $8\text{-}10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $C_p^\circ(T)$ . For references 28 and 27, respectively the discrepancies at 1000 K amount to 10 and  $18 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $S^\circ$  and 21 and  $35 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $C_p^\circ$ . It is difficult to compare statistically calculated values (Table 21) with values obtained by comparative method<sup>27,28</sup> but the statistical method is usually believed to be more accurate.

## 21. 1,3,5,7-Tetrathiocane

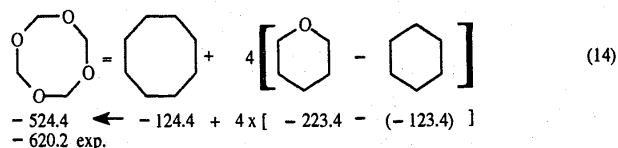
From X-ray investigation<sup>165,166</sup> the boat-chair conformation was found for solid 1,3,5,7-tetrathiocane. It was verified by IR and Raman spectra that 1,3,5,7-tetrathiocane has the boat-chair structure in the solution and in the solid state.<sup>164,167,168</sup> The product of the principal moments of inertia for boat-chair conformation ( $C_2$  symmetry) presented in Table 1 was calculated using the structural parameters estimated on the basis of X-ray data.<sup>165,166</sup>

Vibrational spectra of the liquid and solid 1,3,5,7-tetrathiocane were investigated.<sup>164,167,168</sup> Nash *et al.*<sup>164</sup> assigned most of the fundamentals (except for C-H stretching modes,  $\nu_1\text{-}\nu_8$ , and two lowest ring-deformation modes,  $\nu_{41}$  and  $\nu_{42}$ ) on the basis of normal coordinate calculations. These frequencies are given in Table 2. The values of  $\nu_1\text{-}\nu_8$  (Table 2) were taken from data of Torres and Brioux de Mandirola<sup>168</sup> and ring-deformation modes  $\nu_{41}$  and  $\nu_{42}$  were estimated in this work by comparison of the ring-deformation frequencies for molecules 1,3,5-trioxane, 1,3,5-trithiane and 1,3,5,7-tetrathiocane.

There are no experimental or theoretical data on the enthalpy of formation of 1,3,5,7-tetrathiocane, and its value was estimated using Eq. (13) (the enthalpy of formation values for related compounds were taken from ref. 4):



The same approach for 1,3,5,7-tetraoxocane



leads to the overestimated value. To obtain agreement with experiment it is necessary to use the factor 4.958 in place of 4.0 in Eq. (14). The use of factor 4.958 in Eq. (13) gives the value of  $172.6 \text{ kJ}\cdot\text{mol}^{-1}$  for the enthalpy of formation of 1,3,5,7-tetrathiocane. The adopted value of  $\Delta_f H^\circ(298.15 \text{ K})$  for 1,3,5,7-tetrathiocane is based on this estimate. The ideal gas thermodynamic properties for 1,3,5,7-tetrathiocane are given in Table 22. No experimental or theoretical data are available for comparison.

TABLE 1. Symmetry groups and products of three principal moments of inertia for sulphur heterocyclic compounds in their ground electronic state<sup>a</sup>






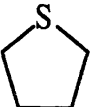

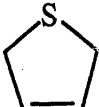

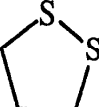

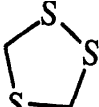
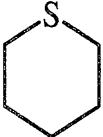
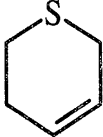
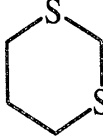
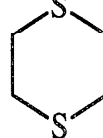
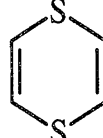
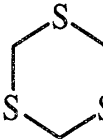
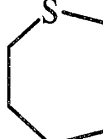
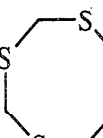
Molecule		Name	CAS Registry No.	Point group	Symmetry number, $\sigma$	Number of optical isomers, $n$	$I_A I_B I_C \cdot 10^{117}$ $\text{g}^3 \cdot \text{cm}^6$
$\text{C}_2\text{H}_4\text{S}$		thiirane	420-12-2	$C_{2v}$	2	1	309.6
$\text{C}_2\text{H}_2\text{S}$		thiirene	157-20-0	$C_{2v}$	2	1	189
$\text{C}_3\text{H}_6\text{S}$		thietane	287-27-4	$C_s$	2 <sup>b</sup>	1	1973
$\text{C}_3\text{H}_4\text{S}$		2H-thiete	503-31-1	$C_s$	1	1	1340
$\text{C}_2\text{H}_2\text{S}_2$		1,2-dithiete	7092-01-5	$C_{2v}$	2	1	3356
$\text{C}_4\text{H}_6\text{S}$		tetrahydrothiophene	110-01-0	$C_2$	2	1 <sup>c</sup>	8013
$\text{C}_4\text{H}_6\text{S}$		2,3-dihydrothiophene	1120-59-8	$C_1$	1	1 <sup>c</sup>	6194
		2,5-dihydrothiophene	1708-32-3	$C_{2v}$	2	1	6447
$\text{C}_4\text{H}_4\text{S}$		thiophene	110-02-1	$C_{2v}$	2	1	4192
$\text{C}_3\text{H}_6\text{S}_2$		1,2-dithiolane	557-22-2	$C_2$	2	2	17040
		1,3-dithiolane	4829-04-3	$C_2$	2	2	17740
$\text{C}_2\text{H}_4\text{S}_3$		1,2,4-trithiolane	289-16-7	$C_2$	2	2	34514

TABLE 1. Symmetry groups and products of three principal moments of inertia for sulphur heterocyclic compounds in their ground electronic state<sup>a</sup>

Molecule	Name	CAS Registry No.	Point group	Symmetry number, $\sigma$	Number of optical isomers, $n$	$I_A I_B I_C \cdot 10^{17}$ $\text{g}^3 \cdot \text{cm}^6$
$\text{C}_5\text{H}_{10}\text{S}$	 tetrahydro-2H-thiopyran	1613-51-0	$C_s$	1	1	25721
$\text{C}_5\text{H}_8\text{S}$	 5,6-dihydro-2H-thiopyran	40697-99-2	$C_1$	1	2	18500
$\text{C}_4\text{H}_8\text{S}_2$	 1,3-dithiane	505-23-7	$C_s$	1	1	51236
	 1,4-dithiane	505-29-3	$C_{2v}$	2	1	51450
$\text{C}_4\text{H}_6\text{S}_2$	 1,4-dithiin	290-79-9	$C_{2v}$	2	1	38410
$\text{C}_3\text{H}_6\text{S}_3$	 1,3,5-trithiane	291-21-4	$C_{3v}$	3	1	101770
$\text{C}_6\text{H}_{12}\text{S}$	 thiepane	4753-80-4	$C_1$	1	2	61490
$\text{C}_4\text{H}_8\text{S}_4$	 1,3,5,7-tetrathiocane	2373-00-4	$C_s$	1	1	692330

<sup>a</sup>Ground state statistical weight is equal to 1.

<sup>b</sup>Although thietane has the non-planar conformation of  $C_s$  symmetry for which  $\sigma = 1$  and  $n = 1$ , the symmetry number  $\sigma = 2$  is given in the Table due to the fact that the molecule is undergoing the inversion through its planar form ( $C_{2v}$  symmetry,  $\sigma = 2$ ,  $n = 1$ ).

<sup>c</sup>Although tetrahydrothiophene and 2,3-dihydrothiophene have the non-planar structure of  $C_2$  and  $C_1$  symmetry, respectively, for which  $n = 2$ , the number of optical isomers  $n = 1$  is given in the Table due to the fact that tetrahydrothiophene is undergoing restricted pseudo-rotation through its planar configuration ( $C_{2v}$  symmetry,  $\sigma = 2$ ,  $n = 1$ ) and 2,3-dihydrothiophene is undergoing the inversion through its planar form ( $C_s$  symmetry,  $\sigma = 1$ ,  $n = 1$ ).

<sup>d</sup>Other stable conformers were also taken into account for tetrahydro-2H-thiopyran and thiepane (point group, symmetry number ( $\sigma$ ), number of optical isomers ( $n$ ) and relative energy ( $T$ ) are listed below for each conformer):

$C_1$ ,  $\sigma = 1$ ,  $n = 2$ ,  $T = 1300 \text{ cm}^{-1}$  (tetrahydro-2H-thiopyran);

$C_1$ ,  $\sigma = 1$ ,  $n = 2$ ,  $T = 0 \text{ cm}^{-1}$  (thiepane).

TABLE 2. Vibrational frequencies for the reference molecules

Molecule	Frequencies (cm <sup>-1</sup> )
C <sub>2</sub> H <sub>4</sub> S thiirane	A <sub>1</sub> : 3014, 1457, 1110, 1024, 627 A <sub>2</sub> : 3088, 1175, 895 B <sub>1</sub> : 3013, 1436, 1051, 660 B <sub>2</sub> : 3088, 945, 824
C <sub>2</sub> H <sub>2</sub> S thiirene	A <sub>1</sub> : 3208, 1660, 900, 657 A <sub>2</sub> : 700 B <sub>1</sub> : 563 B <sub>2</sub> : 3167, 911, 500
C <sub>3</sub> H <sub>6</sub> S thietane	A': 2994, 2972, 2946, 2903, 1470, 1452, 1224, 1183, 975, 933, 845, 700, 529,— <sup>a</sup> A'': 2994, 2950, 1454, 1281, 1229, 1165, 1011, 986, 823, 677
C <sub>3</sub> H <sub>4</sub> S 2H-thiete	A': 3095, 3055, 2939, 1611, 1453, 1275, 1189, 1071, 944, 819, 685, 602 A'': 2992, 1069, 939, 901, 688, 325
C <sub>2</sub> H <sub>2</sub> S <sub>2</sub> 1,2-dithiote	A <sub>1</sub> : 3115, 1501, 1049, 798, 494 A <sub>2</sub> : 970, 421 B <sub>1</sub> : 637 B <sub>2</sub> : 3088, 1215, 791, 566
C <sub>4</sub> H <sub>8</sub> S tetrahydrothiophene	A: 2971, 2946, 2922, 2862, 1464, 1441, 1321, 1276, 1213, 1131, 1023, 888, 829, 822, 678, 472, 290 B: 2962, 2952, 2940, 2932, 1459, 1451, 1305, 1263, 1196, 1125, 1061, 1037, 958, 684, 516,— <sup>a</sup>
C <sub>4</sub> H <sub>6</sub> S 2,3-dihydrothiophene	A: 3066, 3063, 2957, 2939, 2880, 2863, 1543, 1463, 1407, 1283, 1255, 1197, 1173, 1125, 1091, 1077, 1029, 973, 928, 887, 781, 761, 687, 594, 513, 393,— <sup>a</sup>
C <sub>4</sub> H <sub>6</sub> S 2,5-dihydrothiophene	A <sub>1</sub> : 3065, 2936, 1647, 1451, 1273, 1119, 953, 716, 506 A <sub>2</sub> : 2903, 1112, 894, 641, 383 B <sub>1</sub> : 3065, 2866, 1451, 1343, 1227, 961, 824, 665 B <sub>2</sub> : 2936, 1114, 893, 669,— <sup>a</sup>
C <sub>4</sub> H <sub>4</sub> S thiophene	A <sub>1</sub> : 3126, 3098, 1409, 1360, 1083, 1036, 839, 608 A <sub>2</sub> : 898, 683, 565 B <sub>1</sub> : 3125, 3098, 1507, 1256, 1085, 872, 751 B <sub>2</sub> : 867, 712, 452
C <sub>3</sub> H <sub>6</sub> S <sub>2</sub> 1,2-dithiolane	A: 2962, 2910, 2907, 1457, 1443, 1334, 1268, 1173, 1068, 844, 810, 640, 326, 191 B: 2967, 2959, 2909, 1454, 1363, 1324, 1278, 1090, 954, 812, 674, 374, 210
C <sub>3</sub> H <sub>6</sub> S <sub>2</sub> 1,3-dithiolane	A: 2977, 2902, 2897, 1500, 1475, 1325, 1297, 1236, 1079, 994, 912, 715, 408, 243, B: 2973, 2967, 2895, 1494, 1368, 1277, 1234, 967, 899, 807, 612, 440, 36
C <sub>2</sub> H <sub>4</sub> S <sub>3</sub> 1,2,4-trithiolane	A: 2976, 2898, 1414, 1360, 1168, 1024, 862, 801, 578, 434, 211 B: 2976, 2894, 1355, 1327, 1173, 948, 809, 710, 378, 82
C <sub>5</sub> H <sub>10</sub> S tetrahydro-2H-thiopyran	A': 2948, 2929, 2929, 2904, 2878, 2849, 1451, 1440, 1426, 1348, 1299, 1237, 1215, 1061, 965, 897, 826, 813, 656, 504, 359, 344, 194 A'': 2948, 2929, 2892, 2878, 1433, 1405, 1338, 1313, 1269, 1259, 1141, 1090, 1013, 929, 905, 791, 688, 398, 242
C <sub>5</sub> H <sub>8</sub> S 5,6-dihydro-2H-thiopyran	A: 3060, 3058, 2951, 2927, 2925, 2877, 2876, 2852, 1636, 1551, 1452, 1449, 1374, 1352, 1296, 1276, 1258, 1205, 1189, 1171, 1150, 1043, 1013, 1003, 933, 907, 865, 831, 802, 721, 627, 448, 376, 335, 236, 139
C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> 1,3-dithiane	A': 2958, 2900, 2900, 2860, 2838, 2818, 1426, 1387, 1285, 1210, 1175, 1009, 887, 815, 792, 679, 636, 470, 336, 315, 217 A'': 2940, 2824, 1432, 1417, 1272, 1244, 1180, 1152, 1090, 1010, 921, 748, 672, 312, 167
C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> 1,4-dithiane	A <sub>g</sub> : 2936, 2905, 1404, 1297, 1206, 999, 944, 628, 333, 277 A <sub>u</sub> : 2955, 2919, 1408, 1275, 1152, 994, 894, 669, 253 B <sub>g</sub> : 2944, 2905, 1410, 1206, 1110, 821, 694, 374 B <sub>u</sub> : 2955, 2919, 1418, 1283, 1156, 904, 653, 480, 169
C <sub>4</sub> H <sub>4</sub> S <sub>2</sub> 1,4-dithiin	A <sub>1</sub> : 3111, 1525, 1246, 893, 520, 355, 125 A <sub>2</sub> : 3110, 1363, 1082, 935, 691 B <sub>1</sub> : 3113, 1388, 1099, 936, 785, 283, 28 B <sub>2</sub> : 3108, 1516, 1270, 803, 602
C <sub>3</sub> H <sub>6</sub> S <sub>3</sub> 1,3,5-trithiane	A <sub>1</sub> : 2953, 2892, 1376, 908, 654, 405, 282 A <sub>2</sub> : 1225, 1180, 753 E: 2953, 2892, 1400, 1218, 1172, 795, 738, 664, 308, 142
C <sub>6</sub> H <sub>12</sub> S thiopane	A: 2948, 2945, 2943, 2942, 2941, 2940, 2876, 2875, 2874, 2874, 2872, 2869, 1485, 1476, 1445, 1436, 1432, 1426, 1351, 1344, 1336, 1318, 1314, 1291, 1280, 1253, 1168, 1160, 1149, 1148, 1043, 1015, 989, 966, 923, 909, 859, 815, 807, 782, 725, 682, 640, 482, 434, 343, 293, 274, 269, 144, 127
C <sub>4</sub> H <sub>8</sub> S <sub>4</sub> 1,3,5,7-tetrathiocane	2955, 2950, 2935, 2912, 2902, 2902, 2885, 2878, 1379, 1374, 1367, 1360, 1234, 1226, 1212, 1207, 1174, 1156, 1138, 1137, 874, 854, 814, 804, 729, 717, 715, 708, 670, 644, 631, 614, 378, 348, 332, 270, 242, 237, 184, 149, 90, 60

<sup>a</sup>The ring-puckering frequency is not given in the Table because the contribution derived for the inversion motion (thietane, 2,3- and 2,5-dihydrothiophene) or for the restricted pseudo-rotation (tetrahydrothiophene) has been obtained by direct summation over the energy levels.

TABLE 3. Ideal gas thermodynamic properties for thiirane,  $C_2H_4S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	94.048	94.048	$\infty$
100	33.411	212.621	179.347	3.327	90.565	90.891	-47.476
200	39.472	237.036	202.621	6.883	86.436	92.757	-24.225
298.15	53.315	255.238	216.993	11.403	82.000	96.808	-16.960
300	53.603	255.569	217.230	11.502	81.917	96.897	-16.871
400	68.628	273.085	229.019	17.627	75.692	102.599	-13.398
500	81.300	289.811	239.520	25.146	70.772	109.894	-11.480
600	91.481	305.567	249.229	33.803	66.870	118.105	-10.282
700	99.770	320.312	258.342	43.379	63.724	126.900	-9.469
800	106.690	334.099	266.960	53.712	4.227	128.902	-8.416
900	112.575	347.014	275.145	64.682	3.352	144.544	-8.359
1000	117.635	359.144	282.944	76.199	2.746	160.267	-8.371
1100	122.009	370.566	290.396	88.187	2.363	176.037	-8.359
1200	125.802	381.348	297.530	100.582	2.166	191.838	-8.350
1300	129.099	391.551	304.374	113.331	2.127	207.643	-8.343
1400	131.970	401.226	310.949	126.387	2.226	223.453	-8.337
1500	134.475	410.418	317.277	139.712	2.434	239.240	-8.331

TABLE 4. Ideal gas thermodynamic properties for thiirene,  $C_2H_2S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	303.079	303.079	$\infty$
100	33.847	210.211	176.878	3.333	302.601	293.095	-153.095
200	42.956	235.935	200.451	7.097	301.373	284.032	-74.181
298.15	54.730	255.338	215.408	11.905	300.000	275.816	-48.321
300	54.929	255.678	215.655	12.007	299.973	275.665	-47.997
400	64.108	272.810	227.850	17.984	296.506	267.838	-34.976
500	70.697	287.862	238.379	24.742	293.749	260.978	-27.264
600	75.610	301.205	247.759	32.068	291.444	254.651	-22.169
700	79.492	313.163	256.263	39.830	289.421	248.680	-18.556
800	82.710	323.994	264.063	47.944	230.660	235.782	-15.395
900	85.459	333.898	271.280	56.356	230.199	236.452	-13.723
1000	87.844	343.028	278.004	65.024	229.748	237.172	-12.388
1100	89.929	351.501	284.305	73.915	229.308	237.934	-11.298
1200	91.757	359.406	290.238	83.001	228.880	238.738	-10.392
1300	93.361	366.815	295.847	92.259	228.471	239.573	-9.626
1400	94.771	373.786	301.167	101.667	228.084	240.446	-8.971
1500	96.011	380.368	306.230	111.207	227.717	241.334	-8.404

TABLE 5. Ideal gas thermodynamic properties for thietane,  $C_3H_6S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	79.937	79.937	$\infty$
100	39.660	232.460	196.561	3.590	73.656	82.165	-42.918
200	49.013	262.192	222.541	7.930	67.289	93.078	-24.309
298.15	68.334	285.143	239.410	13.635	60.600	107.165	-18.775
300	68.746	285.566	239.693	13.762	60.475	107.451	-18.709
400	90.815	308.395	254.019	21.750	52.170	124.141	-16.211
500	110.232	330.810	267.147	31.832	45.558	142.906	-14.929
600	126.278	352.373	279.569	43.683	40.362	162.892	-14.181
700	139.545	372.867	291.446	56.994	36.264	183.646	-13.704
800	150.679	392.248	302.846	71.522	-23.893	197.727	-12.910
900	160.134	410.556	313.807	87.075	-25.189	225.516	-13.088
1000	168.222	427.858	324.355	103.503	-26.018	253.419	-13.237
1100	175.171	444.225	334.515	120.681	-26.460	281.385	-13.362
1200	181.157	459.730	344.310	138.504	-26.580	309.381	-13.467
1300	186.325	474.439	353.759	156.885	-26.431	337.369	-13.555
1400	190.799	488.415	362.882	175.747	-26.046	365.345	-13.631
1500	194.682	501.715	371.698	195.025	-25.476	393.274	-13.695

TABLE 6. Ideal gas thermodynamic properties for 2H-thiete, C<sub>3</sub>H<sub>4</sub>S, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	201.703	201.703	∞
100	35.192	227.197	193.551	3.365	198.195	197.159	-102.984
200	46.574	254.500	217.662	7.368	194.186	197.631	-51.615
298.15	64.635	276.367	233.429	12.802	190.000	200.220	-35.077
300	64.990	276.768	233.695	12.922	189.922	200.281	-34.872
400	83.106	298.007	247.136	20.348	183.960	204.402	-26.692
500	98.045	318.220	259.351	29.434	179.276	210.052	-21.944
600	109.931	337.187	270.761	39.855	175.578	216.575	-18.854
700	119.519	354.877	281.529	51.344	172.596	223.649	-16.689
800	127.435	371.370	291.740	63.704	113.224	223.910	-14.620
900	134.088	386.774	301.453	76.789	112.435	237.798	-13.801
1000	139.744	401.203	310.715	90.488	111.881	251.760	-13.150
1100	144.584	414.754	319.563	104.711	111.522	265.765	-12.620
1200	148.746	427.518	328.033	119.382	111.328	279.798	-12.179
1300	152.336	439.569	336.153	134.441	111.276	293.836	-11.806
1400	155.444	450.975	343.951	149.833	111.355	307.881	-11.487
1500	158.143	461.794	351.450	165.516	111.538	321.905	-11.210

TABLE 7. Ideal gas thermodynamic properties for 1,2-dithiete, C<sub>2</sub>H<sub>2</sub>S<sub>2</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	231.613	231.613	∞
100	34.579	227.792	194.338	3.345	230.458	220.448	-115.149
200	47.323	255.115	218.311	7.361	227.840	211.395	-55.210
298.15	62.859	276.954	234.089	12.780	225.000	203.932	-35.728
300	63.131	277.343	234.355	12.897	224.947	203.800	-35.484
400	76.105	297.365	247.647	19.887	218.028	197.304	-25.765
500	85.822	315.445	259.429	28.008	212.705	192.721	-20.133
600	93.089	331.765	270.148	36.970	208.453	189.144	-16.466
700	98.697	346.554	280.024	46.571	204.922	186.210	-13.895
800	103.180	360.036	289.195	56.672	88.027	169.340	-11.057
900	106.865	372.408	297.763	67.180	87.823	179.522	-10.419
1000	109.951	383.832	305.806	78.025	87.694	189.720	-9.910
1100	112.567	394.437	313.387	89.155	87.623	199.922	-9.493
1200	114.802	404.330	320.558	100.526	87.589	210.134	-9.147
1300	116.723	413.597	327.362	112.105	87.602	220.342	-8.853
1400	118.382	422.309	333.836	123.862	87.644	230.559	-8.602
1500	119.821	430.527	340.011	135.774	87.713	240.749	-8.384

TABLE 8. Ideal gas thermodynamic properties for tetrahydrothiophene, C<sub>4</sub>H<sub>8</sub>S, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	-8.301	-8.301	∞
100	43.812	242.976	205.499	3.748	-17.485	0.140	-0.073
200	64.101	278.871	233.666	9.041	-25.920	21.031	-5.493
298.15	92.550	309.627	253.634	16.694	-34.100	45.838	-8.031
300	93.112	310.202	253.981	16.866	-34.250	46.330	-8.067
400	122.367	341.066	271.903	27.665	-43.687	74.404	-9.716
500	147.442	371.154	288.763	41.195	-51.106	104.795	-10.948
600	168.042	399.918	304.913	57.003	-56.833	136.548	-11.887
700	185.089	427.142	320.448	74.686	-61.246	169.139	-12.621
800	199.430	452.819	335.405	93.931	-121.541	195.088	-12.738
900	211.642	477.033	349.810	114.501	-122.823	234.752	-13.624
1000	222.110	499.887	363.685	136.202	-123.513	274.526	-14.340
1100	231.115	521.489	377.058	158.874	-123.711	314.340	-14.927
1200	238.880	541.940	389.954	182.383	-123.496	354.160	-15.416
1300	245.592	561.332	402.398	206.615	-122.940	393.938	-15.828
1400	251.407	579.751	414.414	231.472	-122.079	433.671	-16.180
1500	256.460	597.272	426.025	256.871	-120.979	473.323	-16.482

TABLE 9. Ideal gas thermodynamic properties for 2,3-dihydrothiophene,  $C_4H_6S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	109.781	109.781	$\infty$
100	40.674	244.634	208.801	3.583	103.431	110.818	-57.884
200	55.966	276.923	235.286	8.328	97.142	120.601	-31.497
298.15	79.782	303.530	253.402	14.945	90.700	133.494	-23.387
300	80.267	304.026	253.712	15.094	90.581	133.757	-23.289
400	105.718	330.658	269.626	24.413	82.569	149.138	-19.475
500	127.572	356.675	284.450	36.112	76.243	166.516	-17.396
600	145.349	381.562	298.579	49.789	71.313	185.062	-16.111
700	159.856	405.093	312.132	65.073	67.439	204.336	-15.248
800	171.890	427.249	325.151	81.679	7.458	216.906	-14.162
900	182.013	448.096	337.665	99.388	6.289	243.163	-14.113
1000	190.608	467.729	349.699	118.030	5.545	269.527	-14.078
1100	197.948	486.249	361.279	137.468	5.152	295.946	-14.053
1200	204.240	503.750	372.429	157.585	5.052	322.390	-14.033
1300	209.655	520.317	383.174	178.287	5.200	348.826	-14.016
1400	214.329	536.030	393.535	199.492	5.572	375.250	-14.001
1500	218.376	550.958	403.537	221.131	6.121	401.629	-13.986

TABLE 10. Ideal gas thermodynamic properties for 2,5-dihydrothiophene,  $C_4H_6S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	105.454	105.454	$\infty$
100	41.505	236.477	199.099	3.738	99.259	107.461	-56.131
200	57.813	269.375	226.495	8.576	93.063	118.032	-30.826
298.15	83.306	297.089	245.196	15.472	86.900	131.615	-23.058
300	83.806	297.606	245.517	15.626	86.786	131.888	-22.963
400	109.417	325.303	262.014	25.316	79.145	147.856	-19.308
500	130.866	352.106	277.372	37.368	73.172	165.730	-17.313
600	148.192	377.553	291.968	51.351	68.548	184.703	-16.080
700	162.328	401.494	305.923	66.900	64.939	204.355	-15.249
800	174.079	423.960	319.288	83.737	5.190	217.268	-14.186
900	183.988	445.052	332.102	101.654	4.229	243.842	-14.152
1000	192.417	464.885	344.399	120.485	3.673	270.499	-14.129
1100	199.626	483.571	356.210	140.097	3.454	297.194	-14.112
1200	205.812	501.213	367.566	160.377	3.517	323.900	-14.099
1300	211.137	517.902	378.493	181.231	3.817	350.582	-14.086
1400	215.731	533.722	389.022	202.580	4.333	377.242	-14.075
1500	219.706	548.744	399.173	224.357	5.020	403.848	-14.063

TABLE 11. Ideal gas thermodynamic properties for thiophene,  $C_4H_4S$ , at 1 bar

$T$ K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	127.177	127.177	$\infty$
100	34.165	227.769	194.388	3.338	123.581	122.582	-64.029
200	48.743	254.902	218.228	7.335	119.238	123.219	-32.181
298.15	72.816	278.773	234.226	13.282	114.900	126.114	-22.094
300	73.275	279.225	234.502	13.417	114.821	126.181	-21.970
400	96.137	303.539	248.730	21.923	108.902	130.633	-17.059
500	114.274	327.027	262.060	32.483	104.361	136.590	-14.269
600	128.247	349.151	274.752	44.639	100.837	143.388	-12.483
700	139.208	369.775	286.872	58.033	98.011	150.708	-11.246
800	148.055	388.961	298.448	72.411	38.755	151.196	-9.872
900	155.369	406.835	309.510	87.593	38.034	165.298	-9.594
1000	161.518	423.532	320.086	103.446	37.504	179.471	-9.374
1100	166.743	439.178	330.209	119.866	37.132	193.685	-9.197
1200	171.216	453.883	339.909	136.769	36.895	207.930	-9.051
1300	175.065	467.744	349.214	154.088	36.782	222.183	-8.927
1400	178.391	480.842	358.153	171.765	36.789	236.450	-8.822
1500	181.278	493.251	366.749	189.752	36.895	250.699	-8.730



TABLE 12. Ideal gas thermodynamic properties for 1,2-dithiolane,  $C_3H_6S_2$ , at 1 bar

T K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	20.868	20.868	$\infty$
100	44.913	246.642	209.950	3.669	13.977	22.322	-11.660
200	64.413	283.739	238.081	9.132	7.091	33.301	-8.697
298.15	86.530	313.474	258.089	16.513	0.000	47.679	-8.353
300	86.970	314.011	258.432	16.674	-0.134	47.971	-8.352
400	110.315	342.264	275.887	26.551	-11.013	65.175	-8.511
500	130.949	369.160	291.875	38.643	-19.545	85.206	-8.901
600	148.167	394.606	306.897	52.625	-26.192	106.817	-9.299
700	162.462	418.553	321.155	68.179	-31.396	129.410	-9.657
800	174.444	441.052	334.751	85.041	-149.337	138.264	-9.028
900	184.581	462.200	347.749	103.006	-150.061	174.268	-10.114
1000	193.209	482.106	360.199	121.907	-150.272	210.321	-10.986
1100	200.584	500.876	372.143	141.606	-150.063	246.369	-11.699
1200	206.908	518.607	383.617	161.989	-149.513	282.390	-12.292
1300	212.346	535.389	394.652	182.958	-148.676	318.344	-12.791
1400	217.038	551.301	405.278	204.433	-147.598	354.237	-13.217
1500	221.100	566.417	415.521	226.345	-146.329	390.024	-13.582

TABLE 13. Ideal gas thermodynamic properties for 1,3-dithiolane,  $C_3H_6S_2$ , at 1 bar

T K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	30.716	30.716	$\infty$
100	46.220	257.622	216.862	4.076	24.231	31.478	-16.442
200	62.718	294.328	247.001	9.465	17.272	41.364	-10.803
298.15	84.660	323.327	267.431	16.665	10.000	54.741	-9.590
300	85.102	323.852	267.777	16.823	9.863	55.015	-9.579
400	108.652	351.593	285.288	26.522	-1.194	71.263	-9.306
500	129.534	378.146	301.225	38.460	-9.879	90.379	-9.442
600	146.978	403.354	316.166	52.313	-16.656	111.104	-9.672
700	161.466	427.133	330.337	67.757	-21.969	132.831	-9.912
800	173.607	449.509	343.849	84.528	-140.002	140.833	-9.195
900	183.872	470.566	356.771	102.416	-140.803	175.996	-10.214
1000	192.605	490.404	369.152	121.252	-141.080	211.217	-11.033
1100	200.065	509.120	381.034	140.895	-140.927	246.437	-11.702
1200	206.459	526.809	392.451	161.229	-140.425	281.636	-12.259
1300	211.954	543.557	403.436	182.157	-139.630	316.772	-12.728
1400	216.694	559.442	414.017	203.595	-138.589	351.849	-13.127
1500	220.795	574.536	424.220	225.474	-137.352	386.823	-13.470

TABLE 14. Ideal gas thermodynamic properties for 1,2,4-trithiolane,  $C_2H_4S_3$ , at 1 bar

T K	$C_p^\circ$	$S^\circ$ $J \cdot K^{-1} \cdot mol^{-1}$	$-(G^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$\Delta_f H^\circ$ $kJ \cdot mol^{-1}$	$\Delta_f G^\circ$	$\log K_f^\circ$
0	0.000	0.000	0.000	0.000	55.603	55.603	$\infty$
100	46.644	256.480	217.276	3.920	51.335	49.783	-26.004
200	63.934	293.850	246.799	9.410	45.856	50.276	-13.131
298.15	84.084	323.098	267.201	16.666	40.000	53.696	-9.407
300	84.465	323.619	267.547	16.822	39.890	53.779	-9.364
400	103.835	350.640	284.988	26.261	28.051	59.467	-7.765
500	119.826	375.594	300.647	37.473	18.967	68.354	-7.141
600	132.581	398.612	315.082	50.118	11.886	78.933	-6.872
700	142.855	419.848	328.552	63.907	6.257	90.566	-6.758
800	151.294	439.492	341.207	78.628	-169.091	81.318	-5.309
900	158.336	457.730	353.153	94.119	-169.125	112.632	-6.537
1000	164.275	474.729	364.471	110.258	-168.819	143.927	-7.518
1100	169.320	490.629	375.225	126.945	-168.243	175.169	-8.318
1200	173.625	505.551	385.470	144.098	-167.462	206.359	-8.982
1300	177.316	519.598	395.252	161.649	-166.498	237.467	-9.541
1400	180.493	532.858	404.612	179.544	-165.402	268.511	-10.018
1500	183.237	545.406	413.584	197.733	-164.199	299.440	-10.427

TABLE 15. Ideal gas thermodynamic properties for tetrahydro-2H-thiopyran, C<sub>5</sub>H<sub>10</sub>S, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	-29.954	-29.954	∞
100	45.160	247.473	211.027	3.645	-42.302	-14.960	7.814
200	73.630	287.140	239.496	9.529	-53.167	16.629	-4.343
298.15	109.722	323.026	261.084	18.468	-63.500	53.117	-9.306
300	110.457	323.707	261.469	18.672	-63.688	53.835	-9.373
400	149.748	360.916	281.666	31.700	-74.839	94.500	-12.340
500	184.389	398.169	301.251	48.459	-83.284	137.835	-14.399
600	212.786	434.387	320.442	68.367	-89.399	182.679	-15.903
700	235.850	468.981	339.212	90.838	-93.711	228.382	-17.042
800	254.808	501.751	357.500	115.401	-153.542	267.405	-17.459
900	270.611	532.703	375.264	141.695	-154.103	320.068	-18.576
1000	283.929	561.923	392.483	169.440	-153.883	372.749	-19.470
1100	295.239	589.530	409.153	198.414	-153.029	425.373	-20.199
1200	304.899	615.644	425.283	228.433	-151.655	477.902	-20.802
1300	313.187	640.384	440.886	259.348	-149.860	530.288	-21.307
1400	320.329	663.862	455.981	291.033	-147.691	582.533	-21.734
1500	326.507	686.178	470.590	323.382	-145.232	634.599	-22.098

TABLE 16. Ideal gas thermodynamic properties for 5,6-dihydro-2H-thiopyran, C<sub>5</sub>H<sub>8</sub>S, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	80.873	80.873	∞
100	46.091	253.324	215.857	3.747	71.626	88.311	-46.128
200	69.299	292.107	244.741	9.473	63.297	108.218	-28.263
298.15	98.774	325.077	265.798	17.674	55.000	132.043	-23.133
300	99.372	325.690	266.165	17.857	54.845	132.517	-23.073
400	131.309	358.695	285.178	29.407	45.121	159.663	-20.850
500	159.639	391.127	303.140	43.993	37.427	189.200	-19.765
600	183.271	422.389	320.429	61.176	31.515	220.146	-19.165
700	202.866	452.158	337.139	80.513	27.007	251.953	-18.801
800	219.263	480.349	353.295	101.643	-33.305	277.128	-18.094
900	233.113	506.996	368.906	124.281	-34.548	316.015	-18.341
1000	244.885	532.183	383.987	148.197	-35.153	355.006	-18.543
1100	254.935	556.007	398.552	173.201	-35.230	394.027	-18.711
1200	263.545	578.568	412.622	199.136	-34.863	433.041	-18.850
1300	270.944	599.962	426.217	225.869	-34.127	471.999	-18.965
1400	277.323	620.281	439.359	253.290	-33.058	510.898	-19.062
1500	282.843	639.607	452.070	281.305	-31.724	549.699	-19.142

TABLE 17. Ideal gas thermodynamic properties for 1,3-dithiane, C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	17.639	17.639	∞
100	48.447	254.102	216.417	3.768	7.787	25.553	-13.347
200	77.713	296.497	246.241	10.051	-1.300	46.857	-12.238
298.15	110.431	333.535	268.928	19.263	-10.000	72.371	-12.679
300	111.061	334.220	269.328	19.468	-10.159	72.877	-12.689
400	143.533	370.710	290.136	32.230	-22.097	101.901	-13.307
500	171.029	405.794	309.787	48.004	-31.201	133.958	-13.994
600	193.426	439.026	328.585	66.265	-38.058	167.677	-14.597
700	211.800	470.268	346.618	86.555	-43.212	202.389	-15.102
800	227.115	499.579	363.925	108.523	-160.903	223.341	-14.582
900	240.036	527.096	380.543	131.898	-161.219	271.403	-15.752
1000	251.016	552.970	396.505	156.466	-160.898	319.461	-16.687
1100	260.390	577.346	411.848	182.048	-160.055	367.456	-17.449
1200	268.419	600.356	426.607	208.499	-158.789	415.363	-18.080
1300	275.317	622.121	440.817	235.694	-157.169	463.138	-18.609
1400	281.263	642.747	454.510	263.531	-155.249	510.792	-19.058
1500	286.405	662.331	467.718	291.920	-153.094	558.276	-19.441

TABLE 18. Ideal gas thermodynamic properties for 1,4-dithiane, C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	27.850	27.850	∞
100	47.428	247.780	210.507	3.727	17.956	36.354	-18.989
200	76.919	289.514	239.933	9.916	8.775	58.329	-15.234
298.15	109.653	326.245	262.343	19.052	0.000	84.544	-14.812
300	110.282	326.925	262.739	19.256	-0.161	85.064	-14.811
400	142.733	363.187	283.341	31.939	-12.178	114.830	-14.995
500	170.217	398.092	302.828	47.632	-21.362	147.648	-15.424
600	192.570	431.172	321.489	65.810	-28.302	182.145	-15.857
700	210.880	462.277	339.403	86.011	-33.545	217.650	-16.241
800	226.137	491.462	356.606	107.885	-151.331	239.407	-15.631
900	239.019	518.861	373.128	131.160	-151.747	288.287	-16.732
1000	249.987	544.627	389.003	155.625	-151.529	337.174	-17.612
1100	259.370	568.905	404.265	181.105	-150.789	386.008	-18.330
1200	267.425	591.827	418.949	207.454	-149.623	434.764	-18.925
1300	274.361	613.513	433.089	234.552	-148.101	483.396	-19.423
1400	280.351	634.070	446.717	262.295	-146.274	531.913	-19.846
1500	285.542	653.594	459.863	290.596	-144.207	580.269	-20.206

 TABLE 19. Ideal gas thermodynamic properties for 1,4-dithiin, C<sub>4</sub>H<sub>6</sub>S<sub>2</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	161.477	161.477	∞
100	52.057	262.364	218.488	4.388	158.241	155.036	-80.982
200	70.628	303.815	251.449	10.473	154.345	153.274	-40.031
298.15	93.033	336.136	274.115	18.491	150.000	153.672	-26.922
300	93.462	336.712	274.500	18.664	149.917	153.692	-26.760
400	115.361	366.670	293.845	29.130	141.493	155.737	-20.337
500	133.593	394.445	311.223	41.611	134.943	160.042	-16.719
600	148.123	420.137	327.263	55.724	129.795	165.574	-14.414
700	159.749	443.875	342.248	71.139	125.641	171.873	-12.825
800	169.222	465.845	356.342	87.603	8.352	164.310	-10.728
900	177.080	486.244	369.656	104.930	7.935	183.836	-10.669
1000	183.685	505.253	382.276	122.977	7.745	203.395	-10.624
1100	189.289	523.030	394.273	141.633	7.739	222.958	-10.587
1200	194.076	539.711	405.705	160.808	7.883	242.520	-10.556
1300	198.185	555.412	416.623	180.426	8.169	262.057	-10.529
1400	201.729	570.232	427.070	200.426	8.579	281.580	-10.506
1500	204.799	584.257	437.086	220.756	9.094	301.046	-10.483

 TABLE 20. Ideal gas thermodynamic properties for 1,3,5-trithiane, C<sub>3</sub>H<sub>6</sub>S<sub>3</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	101.639	101.639	∞
100	52.662	253.101	213.133	3.997	94.387	103.340	-53.979
200	81.467	298.322	244.898	10.685	87.085	115.109	-30.063
298.15	111.289	336.433	268.847	20.151	80.000	130.394	-22.844
300	111.834	337.123	269.266	20.357	79.870	130.703	-22.757
400	138.919	373.125	290.783	32.937	67.229	148.839	-19.436
500	160.727	406.562	310.639	47.962	57.702	170.330	-17.794
600	177.983	437.451	329.235	64.930	50.457	193.579	-16.852
700	191.904	465.969	346.758	83.448	44.870	217.889	-16.259
800	203.403	492.368	363.330	103.230	-130.271	221.301	-14.449
900	213.064	516.899	379.046	124.067	-129.963	265.242	-15.394
1000	221.264	539.783	393.989	145.795	-129.203	309.119	-16.147
1100	228.266	561.209	408.227	168.280	-128.077	352.892	-16.757
1200	234.270	581.335	421.823	191.415	-126.666	396.561	-17.262
1300	239.434	600.296	434.829	215.106	-125.006	440.090	-17.683
1400	243.893	618.207	447.294	239.278	-123.151	483.501	-18.039
1500	247.754	635.168	459.259	263.865	-121.142	526.742	-18.343

TABLE 21. Ideal gas thermodynamic properties for thiepane, C<sub>6</sub>H<sub>12</sub>S, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	-26.458	-26.458	∞
100	55.736	270.964	229.979	4.098	-41.413	-6.252	3.266
200	90.329	320.012	263.158	11.371	-53.911	33.809	-8.830
298.15	131.305	363.493	289.058	22.193	-65.800	79.425	-13.915
300	132.126	364.308	289.520	22.437	-66.018	80.319	-13.985
400	175.800	408.364	313.725	37.856	-78.721	130.826	-17.084
500	214.521	451.870	337.021	57.424	-88.611	184.382	-19.262
600	246.963	493.940	359.693	80.548	-95.999	239.725	-20.870
700	274.042	534.104	381.764	106.638	-101.379	296.123	-22.097
800	296.857	572.229	403.210	135.215	-102.052	345.978	-22.590
900	316.239	608.343	424.015	165.895	-103.229	409.566	-23.770
1000	332.791	642.542	444.173	198.369	-103.415	473.229	-24.719
1100	346.970	674.942	463.692	232.375	-102.779	536.866	-25.493
1200	359.146	705.668	482.588	267.696	-101.454	600.422	-26.135
1300	369.630	734.839	500.880	304.148	-100.566	663.829	-26.673
1400	378.681	762.571	518.590	341.574	-100.173	727.086	-27.128
1500	386.520	788.971	535.742	379.843	-100.385	790.144	-27.515

TABLE 22. Ideal gas thermodynamic properties for 1,3,5,7-tetrathiocane, C<sub>4</sub>H<sub>8</sub>S<sub>4</sub>, at 1 bar

T K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup> J·K <sup>-1</sup> ·mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup>	Δ <sub>f</sub> H <sup>o</sup> kJ·mol <sup>-1</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub> <sup>o</sup>
0	0.000	0.000	0.000	0.000	198.022	198.022	∞
100	72.807	290.915	240.889	5.003	188.026	204.619	-106.880
200	114.896	354.413	282.397	14.403	178.773	224.808	-58.713
298.15	155.625	407.954	315.055	27.698	170.000	249.304	-43.676
300	156.360	408.919	315.631	27.986	169.841	249.791	-43.492
400	192.631	459.040	345.301	45.496	153.722	277.919	-36.292
500	221.586	505.265	372.735	66.265	141.755	310.335	-32.420
600	244.396	547.761	398.415	89.608	132.814	344.947	-30.030
700	262.761	586.862	422.581	114.997	126.063	380.856	-28.419
800	277.920	622.969	445.402	142.054	-106.778	388.802	-25.386
900	290.655	656.459	467.015	170.500	-105.704	450.702	-26.158
1000	301.464	687.657	487.537	200.121	-104.039	512.443	-26.767
1100	310.696	716.834	507.070	230.741	-101.899	573.982	-27.256
1200	318.611	744.217	525.703	262.216	-99.388	635.323	-27.655
1300	325.422	769.995	543.513	294.426	-96.554	696.427	-27.982
1400	331.301	794.331	560.568	327.269	-93.467	757.325	-28.256
1500	336.393	817.367	576.927	360.660	-90.180	817.952	-28.483

TABLE 23. The uncertainties in the calculated thermodynamic functions ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and adopted enthalpies of formation ( $\text{kJ}\cdot\text{mol}^{-1}$ )

Molecule	Uncertainties in $-(G^\circ - H^\circ)/T$		Uncertainties in $C_p^\circ$		Uncertainties in $\Delta_f H^\circ$ (298.15 K)	
	298.15 K	1000 K	298.15 K	1000 K		
$\text{C}_2\text{H}_4\text{S}$	thiirane	0.5	2.0	1.5	5.0	1.3
$\text{C}_2\text{H}_2\text{S}$	thiirene	1.5	4.0	2.0	4.5	50.0
$\text{C}_3\text{H}_6\text{S}$	thietane	2.0	3.0	2.5	5.0	1.4
$\text{C}_3\text{H}_4\text{S}$	2H-thiete	3.0	5.0	4.0	6.0	50.0
$\text{C}_2\text{H}_2\text{S}_2$	1,2-dithiete	2.0	3.5	2.5	5.5	50.0
$\text{C}_4\text{H}_8\text{S}$	tetrahydrothiophene	2.0	3.5	3.0	5.0	1.3
$\text{C}_4\text{H}_6\text{S}$	2,3-dihydrothiophene	3.0	5.5	4.0	6.5	1.3
	2,5-dihydrothiophene	2.5	4.0	3.5	5.5	1.2
$\text{C}_4\text{H}_4\text{S}$	thiophene	1.0	3.0	2.5	7.0	1.0
$\text{C}_3\text{H}_6\text{S}_2$	1,2-dithiolane	4.0	6.0	5.0	9.0	50.0
	1,3-dithiolane	4.0	6.0	5.0	9.0	50.0
$\text{C}_2\text{H}_4\text{S}_3$	1,2,4-trithiolane	5.0	7.0	6.0	10.0	50.0
$\text{C}_5\text{H}_{10}\text{S}$	tetrahydro-2H-thiopyran	2.5	6.0	4.0	13.0	1.0
$\text{C}_5\text{H}_8\text{S}$	5,6-dihydro-2H-thiopyran	4.0	8.0	5.5	14.0	50.0
$\text{C}_4\text{H}_8\text{S}_2$	1,3-dithiane	3.5	6.5	4.5	13.5	50.0
	1,4-dithiane	3.0	6.0	3.5	11.0	50.0
$\text{C}_4\text{H}_4\text{S}_2$	1,4-dithiin	4.0	7.0	5.0	14.0	75.0
$\text{C}_3\text{H}_6\text{S}_3$	1,3,5-trithiane	3.0	5.0	4.0	10.0	50.0
$\text{C}_6\text{H}_{12}\text{S}$	thiepane	5.0	9.0	7.5	16.0	2.1
$\text{C}_4\text{H}_8\text{S}_4$	1,3,5,7-tetrathiocane	7.0	11.0	10.0	17.0	50.0

TABLE 24. Comparison of experimental<sup>a</sup> entropies with calculated values ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

$S^\circ(T)$						
$\text{C}_2\text{H}_4\text{S}$ thiirane						
T, K	Refs.16,27	Ref.22	Ref.29	Ref.28		This work
298.15	255.4		259.2	255.2		255.2
300		256.5				255.6
500	290.2	293.5	295.9	289.8		289.8
1000	359.8	365.1	366.0	359.1		359.1
1500				410.4		410.4
$\text{C}_3\text{H}_6\text{S}$ thietane						
T, K	Ref.56	Refs.27,56	Refs.28,58			This work
298.15	$285.3 \pm 1.0$	285.2	285.2			285.1
327.53	$291.9 \pm 1.0$	292.0	292.0			291.9
500		331.3	331.4			330.8
1000		429.3	431.1			427.9
$\text{C}_4\text{H}_8\text{S}$ tetrahydrothiophene						
T, K	Ref.81	Refs.27,58,81	Ref.71	Ref.82	Ref.28	This work
298.15		309.5	309.8	309.3	310.0	309.6
349.86	$325.3 \pm 0.8$	325.2	325.7	325.1		325.6
370.16	$331.6 \pm 0.8$	331.4	331.9	331.2		331.9
394.28	$338.7 \pm 0.8$	338.8	339.2	338.6		339.3
500		370.3	370.6	370.1	370.9	371.2
1000		498.8		498.6	499.5	499.9
1500				595.9		597.3

TABLE 24. Comparison of experimental<sup>a</sup> entropies with calculated values ( $J \cdot K^{-1} \cdot mol^{-1}$ ) — Continued

$S^\circ(T)$									
C <sub>4</sub> H <sub>6</sub> S 2,5-dihydrothiophene									
<i>T, K</i>	<i>Ref.82</i>								<i>This work</i>
298.15	297.0								297.1
500	352.0								352.1
1000	464.7								464.9
1500	548.5								548.8
C <sub>4</sub> H <sub>4</sub> S thiophene									
<i>T, K</i>	<i>Ref.97</i>	<i>Ref.97</i>	<i>Refs.27,111</i>	<i>Ref.98</i>	<i>Ref.102</i>	<i>Ref.58</i>	<i>Ref.82</i>	<i>Ref.28</i>	<i>This work</i>
298.15		278.8	279.0	278.7	278.5	278.7	278.6	278.8	278.8
318.52	283.9±0.8	283.8		283.7	283.5	283.7	283.5		283.7
336.24	288.3±0.8	288.1		288.0	287.8	288.0	287.8		288.1
357.32	293.2±0.8	293.2		293.1	292.9	293.2	293.0		293.2
500		326.8	327.3	327.0	326.4	327.1	326.8	327.0	327.0
1000		422.8	425.3	423.4	422.3	424.8	423.2	423.5	423.5
1500		492.5			491.8		492.9	493.2	493.2
C <sub>5</sub> H <sub>10</sub> S tetrahydro-2H-thiopyran									
<i>T, K</i>	<i>Ref.128</i>	<i>Refs.27,128</i>	<i>Refs.28,58</i>	<i>Ref.127</i>					<i>This work</i>
298.15		323.4	323.3						323.0
300				322.9					323.7
351.44	342.8±0.8	342.8	342.8						342.8
500		398.4	398.3	395.9					398.2
1000		569.3	569.1						561.9
C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> 1,4-dithiane									
<i>T, K</i>	<i>Ref.134</i>								<i>This work</i>
300	326.7								326.9
500	397.9								398.1
C <sub>6</sub> H <sub>12</sub> S thiepane									
<i>T, K</i>	<i>Ref.27</i>	<i>Ref.28</i>							<i>This work</i>
298.15	362.0	362.5							363.5
500	450.5	452.2							451.9
1000	661.1	653.0							642.5

<sup>a</sup>Experimental values of  $S^\circ(T)$  are italic.

TABLE 25. Comparison of experimental<sup>a</sup> heat capacities with calculated values ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )

$C_p^\circ$									
<b>C<sub>2</sub>H<sub>4</sub>S thirane</b>									
T, K	Refs.16,27	Ref.22	Ref.29	Ref.28					This work
298.15	53.7		55.3	53.3					53.3
300		58.2							53.6
500	81.8	87.7	83.4	81.3					81.3
1000	118.0	119.7	118.5	117.7					117.6
1500				134.5					134.5
<b>C<sub>3</sub>H<sub>6</sub>S thietane</b>									
T, K	Ref.56	Refs.27,56	Refs.28,58						This work
298.15		69.3	68.6						68.3
377.20	86.6	86.8	86.6						85.9
500		111.1	112.0						110.2
1000		170.2	175.2						168.2
<b>C<sub>4</sub>H<sub>8</sub>S tetrahydrothiophene</b>									
T, K	Ref.81	Refs.27,58,81	Ref.82	Ref.28					This work
298.15		90.9	90.8	90.9					92.6
378.25	115.0	115.0	114.9						116.3
402.20	121.8	121.8	121.7						123.0
449.20	134.4	134.3	134.3						135.3
487.20	143.5	143.6	143.6						144.5
500		146.6	146.5	146.6					147.4
1000		222.3	222.2	222.5					222.1
1500			255.7						256.5
<b>C<sub>4</sub>H<sub>6</sub>S 2,5-dihydrothiophene</b>									
T, K	Ref.82								This work
298.15	83.2								83.3
500	130.5								130.9
1000	192.8								192.4
1500	218.6								219.7
<b>C<sub>4</sub>H<sub>4</sub>S thiophene</b>									
T, K	Ref.97	Ref.97	Refs.27,111	Ref.98	Ref.102	Ref.58	Ref.82	Ref.28	1 This work
298.15		72.5	72.9	72.8	72.2	72.8	72.7	72.7	72.8
344.0	83.9	83.3		83.9	83.0	83.9	83.8		83.9
371.2	90.2	89.4		90.0	89.1	90.2	90.0		90.0
402.3	96.9	95.9		96.6	95.6	96.9	96.6		96.6
436.2	103.6	102.4		103.3	102.1	103.6	103.2		103.3
471.2	109.9	108.6		109.5	108.4	110.0	109.4		109.5
500		113.4	114.9	114.3	113.1	114.8	114.1	114.2	114.3
1000		161.3	165.4	161.5	161.0	164.0	161.6	161.5	161.5
1500		181.3			180.9		180.9	181.3	181.3

TABLE 25. Comparison of experimental<sup>a</sup> heat capacities with calculated values ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) — Continued

$C_p^\circ$					
<b><math>\text{C}_5\text{H}_{10}\text{S}</math> tetrahydro-2H-thiopyran</b>					
<i>T</i> , K	Ref.128	Refs.27,128	Refs.28,58	Ref.127	This work
298.1		108.2	108.2		109.7
300				109.2	110.5
399.2	<i>149.1</i>	149.1	149.1		149.5
423.2	<i>158.5</i>	158.6	158.6		158.3
453.2	<i>170.3</i>	170.1	170.2		169.0
483.2	<i>181.2</i>	181.2	181.2		179.0
500		187.2	187.2	179.4	184.4
1000		302.7	303.1		283.9
<b><math>\text{C}_4\text{H}_8\text{S}_2</math> 1,4-dithiane</b>					
<i>T</i> , K	Ref.134				This work
300	110.3				110.3
500	170.2				170.2
<b><math>\text{C}_6\text{H}_{12}\text{S}</math> thiepane</b>					
<i>T</i> , K	Ref.27	Ref.134			This work
298.1	124.6	130.8			131.3
500	225.9	222.1			214.5
1000	368.2	353.3			332.8

<sup>a</sup>Experimental values of  $C_p^\circ(T)$  are italic.



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