Vapor−Liquid Critical Properties of Elements and Compounds. 8. Organic Sulfur, Silicon, and Tin Compounds (C + H + S, Si, and Sn)

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This is part 8 of a series of contributions by the critical properties group of the IUPAC Commission I.2 on Thermodynamics, Subcommittee on Thermodynamic Data. It presents all known experimental data for the critical constants of organic sulfur compounds (6 sulfides, 2 disulfides, 7 thiols, and 4 thiophenes), four organic silicon compounds, and one organic tin compound. Recommendations are given together with uncertainties. Critical temperatures have been converted, where warranted, to the ITS-90 scale.

Part 8 presents experimental data for 24 compounds. For 15 of them, there is only a single investigation. Very limited experimental information is available for organic sulfur compounds, even less is available for organic silicon compounds, and only a single organic tin compound (tetramethylstannane) has been investigated.

The presentation and evaluation of the experimental data follow the guidelines of Ambrose *et al.* in parts 1 and 2 of this series [95-amb/you, 95-amb/tso]. Succeeding parts have been by Tsonopoulos and Ambrose [95-tso/amb], Gude and Teja [95-gud/tej], Daubert [96-dau], Tsonopoulos and Ambrose [96-tso/amb], and Kudchadker *et al.* [2001-kud/amb]. The recommended values are given in Table 1, while all known data have been collected in Table 2. Where appropriate, the data on which the recommended values are based are indicated by an asterisk. Critical temperatures enclosed in parentheses are not new measurements; they are the values at which investigators determined the critical pressure or critical density. The references follow the format [year-first three letters of first author/first three letters of second author and, where required, a sequence number].

Organic Sulfur Compounds (C + H + S)

Sulfides. Most of what is known about the critical properties of sulfides is based on measurements made in 1924 or earlier. The only recent measurements have been made by Wilson's group at Wiltec Research [94-wil; 2000-von/wil], using a flow method. Wilson typically uses a cell (which is connected to inlet and outlet pumps) with a capacity of 0.1 L, stirs the sample during the experiment by rocking the cell, but disconnects the rocking mechanism when observations are made.

These recent measurements on diethyl sulfide have confirmed the much earlier T_c values of Ferretto [00-fer] and Vespignani [03-ves], as well as the T_c and p_c results of Berthoud and Brum [24-ber/bru]. They have also confirmed that Vespignani's p_c value is much too high (while his value

for ethyl methyl sulfide is shown in a later section to be, most likely, too low).

Ferretto's direct determination of T_c for the first three sulfides is supported by later work. However, for the two unstable sulfides, di(3-methylbutyl) sulfide and di(3-propenyl) sulfide, which were investigated only by him, T_c was determined by back-calculating from measurements on mixtures of the sulfide with diethyl ether. As shown in Table 2, these indirectly determined T_c's have considerable uncertainties. (This is also true of Ferretto's results for diethyl disulfide and 3-methyl-1-butanethiol.)

Disulfides. In addition to the indirect determination of the T_c of diethyl disulfide by Ferretto (see previous paragraph), we only have the recent investigation of dimethyl disulfide by Teja's group [90-ans/tej], which also resulted in an approximate T_c value, because an explosion occurred at approximately 615 K. Considering the high heating rate used and the thermocouple lag, the actual T_c would be expected to be above 615 K, and thus this figure should be considered as very approximate.

Thiols. Although we have Teja's results for four thiols [90-tej/ans; 90-ans/tej], there are no recent data to check the 1900−1924 values. The only exception is the critical density of methanethiol by Janik and Janik [61-jan/jan], which was based on liquid and vapor densities at (20−80) °C determined by neutron scattering. Even Teja's measurements raise questions about the carbon number dependence of the critical density of alkanethiols (minimum at CN = 3?). However, Teja [2000-tej] more recently noted that his result for the critical density of 1-propanethiol is very approximate, as it was based on an extrapolation of two meniscus disappearance measurements. Accordingly, a large uncertainty is recommended for the critical density of 1-propanethiol.

Thiophenes. Only thiophene has been studied by more than one investigator, starting in 1885. (It is not clear how Schiff [1885-sch] determined T_c and p_c; he apparently calculated the critical constants with the van der Waals equation of state, but his paper also makes reference to capillary measurements in the range 17.6 to 84.0 °C.) Benzo[*b*]thiophene and dibenzothiophene have been inves-

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Table 1. Recommended Values of Critical Properties of Organic Sulfur (C + H + S), Silicon (C + H + Si), and Tin (C + H + Sn) Compounds

	molar mass, M/g·mol^{-1} [a]	T_c/K[b]	(±)	p_c/MPa	(±)	ρ_c/g·cm^{-3}	(±)	V_c/cm^3·mol^{-1}	Z_c[c]
				Sulfides					
dimethyl sulfide	62.135 64	503	(1)	5.53	(0.10)	0.305	(0.005)	203.7	0.269
ethyl methyl sulfide	76.162 52	533	(1)	4.25	(0.4)				
diethyl sulfide	90.189 4	557.8	(0.2)	3.90	(0.02)	0.284	(0.005)	317.6	0.267
di-*n*-butyl sulfide	146.296 92	650	(2)	2.48	(0.10)				
di(3-methylbutyl) sulfide	174.350 68	664	(15)						
di(3-propenyl) sulfide	114.211 4	653	(10)						
				Disulfides					
dimethyl disulfide	94.201 64	615	(10)						
diethyl disulfide	122.255 4	642	(10)						
				Thiols					
methanethiol	48.108 76	470	(2)	7.23	(0.20)	0.327	(0.010)	147	0.272
ethanethiol	62.135 64	499	(2)	5.49	(0.20)	0.300	(0.010)	207	0.274
1-propanethiol	76.162 52	537	(1)	4.6[d]	(0.2)	0.266	(0.020)	286	0.295
1-butanethiol	90.189 4	570	(1)	4.0[d]	(0.2)	0.278	(0.010)	324	0.273
3-methyl-1-butanethiol	104.216 28	594	(10)						
1-octanethiol	146.296 92	667	(7)			0.29	(0.02)	504	
cyclohexanethiol	116.227 28	684	(25)			0.29	(0.02)	401	
				Thiophenes					
thiophene	84.141 76	580	(1)	5.70	(0.10)	0.385	(0.015)	219	0.259
tetrahydrothiophene	88.173 52	632	(1)	5.4[d]	(0.2)				
benzo[*b*]thiophene	134.201 64	764	(2)	4.76	(0.20)	0.354	(0.007)	379	0.284
dibenzothiophene	184.261 52	897	(2)	3.86	(0.20)	0.360	(0.007)	512	0.265
				Organic Silicon Compounds					
methylsilane	46.144 14	352.4	(?)						
tetramethylsilane	88.224 78	448.6	(0.05)	2.821	(0.005)	0.244	(0.001)	361.6	0.2735
tetraethylsilane	144.332 3	605	(2)	2.50	(0.20)	0.246	(0.005)	587	0.292
methylenebis(trimethyl)silane	160.406 8	573.9	(0.6)	1.99	(0.04)				
				Organic Tin Compound					
tetramethylstannane	178.849 28	521.8	(0.05)	2.981	(0.005)				

[a] Molar masses based on carbon = 12.011, hydrogen = 1.007 94, sulfur = 32.066, silicon = 28.0855, tin = 118.710. [b] Temperatures are expressed on the ITS-90 scale. [c] $Z_c = p_c V_c/RT_c$, where R = 8.314 472 J·mol^{-1}·K^{-1}. [d] Calculated with method 6; see text and Table 3.

tigated by Steele's group [91-chi/kni; 91-chi/kni-1] with a method that is based on DSC and density measurements in the critical region; see part 7 of this series [2001-kud/amb] for a description of this method.

Steele's T_c and ρ_c values are obtained by fitting the DSC and density data, but p_c requires extrapolation of their carefully measured vapor pressures (up to 0.27 MPa) to T_c. This is method 6 (see Table 3), which is conditionally acceptable as a source of "experimental-quality" critical pressures. Because of the limited p_c data for organic sulfur compounds, we examine below the estimation of p_c's with method 6.

Calculation of Critical Pressure with Method 6. Table 3 states for method 6: "critical pressure by extrapolation of vapor pressure curve". This method has become more important than had originally been anticipated (as noted above, it is the method used in the recent work of Steele to estimate the critical pressure), and thus it is timely to expand the discussion given in part 1 [95-amb/you] of the difference between methods 5 and 6.

Method 5 generally refers to critical pressures obtained by fitting an equation to the results of high-quality experimental measurements of vapor pressure made up to and normally including the critical temperature. Therefore, "method 5" p_c's can be accepted as experimental values, even in those cases where the vapor pressure measurements may stop short, by a few kelvins, of the critical temperature. Furthermore, "method 5" p_c's have the advantage that they are internally consistent with the vapor pressure of the compound—the same way that "method 7 (orthobaric density measurements)" ρ_c's are internally consistent with the orthobaric (saturated) vapor and liquid densities of the compound.

Method 6, on the other hand, involves *extrapolation* by an amount undefined of vapor pressure measurements made at temperatures up to an unstated temperature below the critical. The question, then, is under what conditions "method 6" p_c's can be included in Table 2 (and, therefore, also in Table 1).

The first and absolute condition is that the critical temperature must have been determined experimentally. The other conditions involve some judgment, but it is important that the measurements be made on very pure samples (at least 99% purity), with equipment and techniques that have been used extensively and successfully (such as those by Rossini, by the Bureau of Mines at Bartlesville, OK (a tradition continued by Steele), by Ambrose, and by a few others). Steele and Ambrose now use the Wagner equation to extrapolate their vapor pressure data, but reliable extrapolations can also be made with the Antoine equation.

The use of the Antoine equation to estimate the critical pressure is mentioned (and was used) by Dreisbach [55-dre], who refers to a private communication from Thomson; see also [46-tho]. If the critical pressure calculated at T_c with the Antoine equation (with Antoine coefficients fit to lower-pressure data) is multiplied by the factor 1.07, it will agree with known p_c data to within ±3%. (It is also noted by Dreisbach that, since the ratio T_b/T_c increases with increasing carbon number in a given family (for example, normal alkanes), it follows that the factor should gradually decrease.)

Ambrose in his early work also used this approach but multiplied the "Antoine" p_c by 1.08. (For example, see his estimates for ketones [75-amb/ell] in part 7 [2001-kud/amb].) Here we tested this approach for those organic

Table 2. Critical Properties from the Literature

ref	values reported in nonstandard units	T_{90}/K	p/MPa	ρ/g·cm^{-3}	method[a]	authors
	DIMETHYL SULFIDE (2-Thiapropane): Molar Mass = 62.135 64 g; CASRN = 75-18-3					
00-fer	231.2 °C	504.4*			1	Ferretto
03-ves[b]	231.29 °C, 56.14 atm	504.4*	5.688		1	Vespignani
23-her/neu	(229.0 ± 0.2) °C	502.2*		0.301*	1, 7	Herz and Neukirch
24-ber/bru[c]	229.9 °C, 54.6 atm	503.0*	5.53*	0.3089*	1, 7	Berthoud and Brum
	recommended values	503 ± 1	5.53 ± 0.10	0.305 ± 0.005		
	ETHYL METHYL SULFIDE (2-Thiabutane): Molar Mass = 76.162 52 g; CASRN = 624-89-5					
00-fer	259.66 °C	532.8*			1	Ferretto
03-ves	259.66 °C, 41.9 atm	532.8*	4.25		1	Vespignani
	recommended values	533 ± 1	4.25 ± 0.4			
	DIETHYL SULFIDE (3-Thiapentane): Molar Mass = 90.1894 g; CASRN = 352-93-2					
00-fer	284.67 °C	557.8*			1	Ferretto
03-ves	284.60 °C, 47.1 atm	557.8*	4.77		1	Vespignani
24-ber/bru[d]	283.8 °C, 39.1 atm	557.0	3.96	0.2842	1, 7	Berthoud and Brum
2000-von/wil		557.8* ± 0.1	3.897* ± 0.001		2a, c	VonNiederhausern et al.
	recommended values	557.8 ± 0.2	3.90 ± 0.02	0.284 ± 0.005		
	DI-n-BUTYL SULFIDE (5-Thianonane): Molar Mass = 146.296 92 g; CASRN = 544-40-1					
94-wil[e]	(360 ± 2) psi	650 ± 2	2.48		2a, c	Wilson
	recommended values	650 ± 2	2.48 ± 0.10			
	DI(3-METHYLBUTYL) SULFIDE (2,8-Dimethyl-5-thianonane): Molar Mass = 174.350 68 g; CASRN = 544-02-5					
00-fer[f]	(391 ± 13) °C	664			1	Ferretto
	recommended value	664 ± 15				
	DI(3-PROPENYL) SULFIDE (4-Thia-1,5-heptadiene):[g] Molar Mass = 114.2114 g; CASRN = 592-88-1					
00-fer[h]	(380 ± 8) °C	653			1	Ferretto
	recommended value	653 ± 10				
	DIMETHYL DISULFIDE (2,3-Dithiabutane): Molar Mass = 94.201 64 g; CASRN = 624-92-0					
90-ans/tej[i]		>615			1c	Anselme and Teja
	recommended value	615 ± 10				
	DIETHYL DISULFIDE (3,4-Dithiahexane): Molar Mass = 122.2554 g; CASRN = 110-81-6					
00-fer[j]	(369 ± 4) °C	642			1	Ferretto
	recommended value	642 ± 10				
	METHANETHIOL (Methyl Mercaptan): Molar Mass = 48.108 76 g; CASRN = 74-93-1					
24-ber/bru	196.8 °C, 71.4 atm	470	7.23	0.3315*	1, 7	Berthoud and Brum
61-jan/jan		(470)		0.3225*	7	Janik and Janik
	recommended values	470 ± 2	7.23 ± 0.20	0.327 ± 0.010		
	ETHANETHIOL (Ethyl Mercaptan): Molar Mass = 62.135 64 g; CASRN = 75-08-1					
00-fer	228 °C	501			1	Ferretto
03-ves	228.3 °C, 63.5 atm	501.4	6.43		1	Vespignani
24-ber/bru	225.5 °C, 54.2 atm	498.6*	5.49*	0.2996	1, 7	Berthoud and Brum
	recommended values	499 ± 2	5.49 ± 0.20	0.300 ± 0.010		
	1-PROPANETHIOL (N-Propyl Mercaptan): Molar Mass = 76.162 22 g; CASRN = 107-03-9					
90-tej/ans		536.6 ± 0.3		0.266	1c	Teja and Anselme
		(537)	4.6 ± 0.2		6	this work
	recommended values	537 ± 1	4.6 ± 0.2	0.266 ± 0.020		
	1-BUTANETHIOL (N-Butyl Mercaptan): Molar Mass = 90.1894 g; CASRN = 109-79-5					
90-tej/ans[k]		570.1 ± 0.3		0.278 ± 0.005	1c	Teja and Anselme
		(570)	4.0 ± 0.2		6	this work
	recommended values	570 ± 1	4.0 ± 0.2	0.278 ± 0.010		
	3-METHYL-1-BUTANETHIOL (Isopentyl Mercaptan): Molar Mass = 104.216 28 g; CASRN = 541-31-1					
00-fer[l]	(321 ± 3) °C	594			1	Ferretto
	recommended value	594 ± 10				
	1-OCTANETHIOL (N-Octyl Mercaptan): Molar Mass = 146.296 92 g; CASRN = 111-88-6					
90-ans/tej[m]		667.3 ± 6.3		c. 0.29	1c	Anselme and Teja
	recommended values	667 ± 7		0.29 ± 0.02		
	CYCLOHEXANETHIOL (Cyclohexyl Mercaptan): Molar Mass = 116.227 28 g; CASRN = 1569-69-3					
90-ans/tej[n]		684 ± 22		c. 0.29	1c	Anselme and Teja
	recommended values	684 ± 25		0.29 ± 0.02		
	THIOPHENE: Molar Mass = 84.141 76 g; CASRN = 110-02-1					
1885-sch	(302.7 ± 0.1) °C, (55.0 ± 0.4) atm	576	5.57		8	Schiff
1888-paw	317.3 °C, 47.7 atm	590.4	4.83		1	Pawlewski
56-kob/rav[o]	(585 ± 2) °F, (826 ± 10) psi, (2.6 ± 0.1) cm^3·g^{-1}	580*	5.695*	0.385	3, 5	Kobe et al.
62-che/mcc[o]		579.4* ± 0.1			1	Cheng et al.
	recommended values	580 ± 1	5.70 ± 0.10	0.385 ± 0.015		
	TETRAHYDROTHIOPHENE: Molar Mass = 88.173 52 g; CASRN = 110-01-0					
62-che/mcc[p]		632.0 ± 1			1	Cheng et al.
		(632)	5.4 ± 0.2		6	this work
	recommended value	632 ± 1	5.4 ± 0.2			

Table 2. (Continued)

ref	values reported in nonstandard units	T_{90}/K	p/MPa	ρ/g·cm^{-3}	method[a]	authors
	BENZO[*b*]THIOPHENE (Thianaphthene): Molar Mass = 134.201 64 g; CASRN = 95-15-8					
91-chi/kni-1		764 ± 2	4.76 ± 0.10	0.354 ± 0.007	4, 6, 7	Chirico *et al.*
	recommended values	764 ± 2	4.76 ± 0.20	0.354 ± 0.007		
	DIBENZOTHIOPHENE: Molar Mass = 184.261 52 g; CASRN = 132-65-0					
91-chi/kni		897 ± 2	3.86 ± 0.08	0.360 ± 0.007	4, 6, 7	Chirico *et al.*
	recommended values	897 ± 2	3.86 ± 0.20	0.360 ± 0.007		
	METHYLSILANE: Molar Mass = 46.144 14 g; CASRN = 992-94-9					
67-ott/tho	79.3 °C	352.4			?	Otto and Thomas
	recommended value	352.4 ± ?				
	TETRAMETHYLSILANE: Molar Mass = 88.224 78 g; CASRN = 75-76-3					
	$T_{90} - T_{68} = -0.039$ K at 449 K					
76-hic/you		450.4	2.814		1	Hicks and Young
77-cip/all		451 ± 1		0.197	1	Cipollini and Allen
77-mcg/mck	(361 ± 8) cm^3·mol^{-1}	448.60* ± 0.01	2.821* ± 0.001	0.244* ± 0.005	1, 5, 7	McGlashan and McKinnon
78-van[q]				0.25 ± 0.01	9	Van Loef
93-mcl/bar		(448.6)		0.2436* ± 0.0001	7	McLure and Barbarin-Castillo
	recommended values	448.6 ± 0.05	2.821 ± 0.005	0.244 ± 0.001		
	TETRAETHYLSILANE: Molar Mass = 144.3323 g; CASRN = 631-36-7					
71-hic/you	25.68 atm	603.7*	2.602*		1	Hicks and Young
91-ste/chi		606* ± 1	2.400* ± 0.024	0.246 ± 0.005	4, 6, 7	Steele *et al.*
	recommended values	605 ± 2	2.50 ± 0.20	0.246 ± 0.005		
	METHYLENEBIS(TRIMETHYL)SILANE (Hexamethyldisilmethylene): Molar Mass = 160.4068 g; CASRN = 2117-28-4					
82-mcl/nev		573.9 ± 0.3	1.99 ± 0.02		1	McLure and Neville
	recommended values	573.9 ± 0.6	1.99 ± 0.04			
	TETRAMETHYLSTANNANE: Molar Mass = 178.849 28 g; CASRN = 594-27-4					
	$T_{90} - T_{68} = -0.040$ K at 522 K					
78-hug/mcg		521.77* ± 0.02	2.9813 ± 0.0005		1, 5	Hugill and McGlashan
91-chr/tra		521.8* ± 0.5			1	Christou *et al.*
	recommended values	521.8 ± 0.05	2.981 ± 0.005			

[a] For methods see Table 3. [b] Kobe and Lynn [53-kob/lyn] report the p_c value of [03-ves] incorrectly as 54.16 atm. [c] Berthoud and Brum [24-ber/bru] report 229.9 °C on pages 146, 154, and 159; 227.9 °C and 54.6 atm on page 150; and 54.5 atm on page 159. [d] Kobe and Lynn [53-kob/lyn] report the ρ_c value of [24-ber/bru] incorrectly as 0.279 g·cm^{-3}. [e] Measured in a flow cell at four flow rates and extrapolated to zero residence time. [f] t_c was back-calculated from two measurements on mixtures with diethyl ether: 404.34 and 378.16 °C; average = 391.25 °C. [g] Kudchadker *et al.* [68-kud/ala] name this compound, incorrectly, 4-thiaheptane (di-*n*-propyl sulfide). [h] t_c was back-calculated from two measurements with diethyl ether: 388.33 and 372.47 °C; average = 380.38 °C. [i] Only one observation of the critical point could be made; dimethyl disulfide decomposed explosively as T_c was approached. [j] t_c was back-calculated from two measurements on mixtures with diethyl ether: 365.10 and 372.76 °C; average = 368.93 °C. [k] Teja and Anselme [90-tej/ans] observed a slow decrease of T_c with time. [l] t_c was back-calculated from two measurements on mixtures with diethyl ether: 323.82 and 318.02 °C; average = 320.92 °C. [m] They observed that T_c decreased with time. Pennwalt, the supplier of this compound, called it thiooctane. [n] They observed that T_c decreased with time. The extrapolation was based on the first two measurements. Pennwalt, the supplier of this compound, called it thiocyclohexane. [o] Cheng *et al.* [62-che/mcc] observed no decomposition, whereas Kobe *et al.* [56-kob/rav] noted "appreciable" decomposition, though that did not prevent determination of the critical point. [p] Due to sample decomposition, measurements were extrapolated to zero time to give the "true critical temperature". [q] Van Loef [78-van] estimated the critical density by comparing log D (selfdiffusion coefficient) versus T_c/T plots of tetramethylsilane at various densities with those of carbon tetrachloride at different isochores expressed in terms of reduced densities.

Table 3. Key to Methods of Critical Point Determination (Reprinted with permission from 95-amb/you. Copyright 1995 American Chemical Society)

1.	visual—in glass tube
2.	visual—in cell with windows
3.	nonvisual—pVT measurements
4.	other nonvisual methods
5.	critical pressure measurements combined with vapor pressure measurements up to the critical point
6.	critical pressure by extrapolation of vapor pressure curve
7.	orthobaric density measurements
8.	equation of state, thermodynamic study
9.	calculation from another physical property
10.	literature survey
(a)	with stirring
(b)	instrumental detection of critical point
(c)	special feature of apparatus

Table 4. Comparison of Critical Pressures with Values Calculated with the Antoine Equation

compound	T_c/K	p_c/MPa		ratio
		exp	Antoine	
dimethyl sulfide	503	5.53	5.080	1.089
ethyl methyl sulfide	533	4.25	4.200	1.012
diethyl sulfide	557.8	3.90	3.582	1.089
di-*n*-butyl sulfide	650	2.48	2.274	1.091
methanethiol	470	7.23	6.749	1.071
ethanethiol	499	5.49	5.070	1.083
thiophene	580	5.70	5.311	1.073

sulfur compounds with known p_c's, using vapor pressure data from the Bureau of Mines [49-wad/kno, 66-osb/dou, 80-osb/sco]. Generally, the vapor pressure data go up to 0.27 MPa, the same upper limit in Steele's measurements

on benzo[*b*]thiophene [91-chi/kni-1] and dibenzothiophene [91-chi/kni]. The comparisons given in Table 4 support a ratio of 1.08 ± 0.01; they also suggest that the reported value for the p_c of ethyl methyl sulfide [03-ves] is most likely too low.

Taking into account the uncertainty in T_c (1 K uncertainty leads to about 1% uncertainty in p_c), we make the following recommendations for the critical pressures of three compounds for which we have assessed the uncer-

tainty in their critical temperature as ±1 K (see Tables 1 and 2).

1-propanethiol	(4.6 ± 0.2) MPa	method 6
1-butanethiol	(4.0 ± 0.2) MPa	method 6
tetrahydrothiophene	(5.4 ± 0.2) MPa	method 6

These values have been included in Tables 1 and 2. The justification for doing so is the high quality of the underlying vapor pressure data [66-osb/dou]. Most of the vapor pressure data in the literature are not of sufficiently high quality, nor do they cover a sufficiently wide temperature range, to justify their use in the estimation of critical pressures. Furthermore, this approach is unreliable for associating compounds, such as alcohols and carboxylic acids.

Organic Silicon Compounds (C + H + Si)

Of the four organic silicon compounds investigated, only tetramethylsilane has been studied extensively, by a variety of methods. Tetramethylsilane and, to a lesser extent, tetraethylsilane and tetramethylstannane (next section) have attracted interest because of their spherical symmetry.

Tetramethylsilane was investigated by five groups, more than any other compound in part 8. Hicks and Young [76-hic/you] used the sealed tube method to determine T_c and p_c; they also measured the vapor pressure up to the critical region but made no claim that those measurements supported their p_c value. Cipollini and Allen [77-cip/all] also used the sealed tube method, to determine T_c and ρ_c. Perhaps the most precise investigation was carried out by McGlashan and McKinnon [77-mcg/mck], who determined T_c and then measured the vapor pressure and orthobaric volumes from 373 K to T_c. Our recommendations are based on the results of McGlashan and McKinnon, with somewhat larger uncertainties than they reported. Their T_c and p_c values are close to those of Hicks and Young, while their ρ_c is close to the indirect determination by Van Loef [78-van] and, especially, the orthobaric measurements of McLure and Barbarin-Castillo [93-mcl/bar].

Organic Tin Compound (C + H + Sn)

Hugill and McGlashan [78-hug/mcg] investigated tetramethylstannane with an apparatus similar to that of Ambrose [67-amb/bro], but modified to enable measurements on mixtures, as by Young [72-you]. They observed that both T_c and p_c increased with time (at rates, respectively, of 0.025 K·h⁻¹ and 1 kPa·h⁻¹), apparently due to thermal decomposition. They made four measurements within 10 h and determined the values in Table 2 by making a linear extrapolation to time zero. Christou *et al.* [91-chr/tra] confirmed the T_c result of Hugill and McGlashan.

Overview of Recommendations (Table 1)

Table 1 summarizes the recommended critical values given in Table 2. It also includes, where appropriate, the critical volume, V_c, and the critical compressibility factor, $Z_c = p_c V_c / R T_c$ ($R = 8.314\ 472$ J·mol⁻¹·K⁻¹ [99-moh/tay]). A comparison of the recommendations for the Z_c's of alkanethiols raises questions about the high value for 1-propanethiol, 0.295. This may suggest that the "method 6" p_c value calculated here, 4.6 MPa, is too high. However, it is more likely, as noted earlier, that the value for ρ_c, 0.269 g·cm⁻³, is too low. It is unlikely that the critical density of alkanethiols should have a minimum at CN = 3.

Registry Numbers Supplied by the Authors: Dimethyl sulfide, 75-18-3; ethyl methyl sulfide, 624-89-5; diethyl sulfide, 352-93-2; di-*n*-butyl sulfide, 544-40-1; di-(3-methylbutyl) sulfide, 544-02-5; di(3-propenyl) sulfide, 592-88-1; dimethyl disulfide, 624-92-0; diethyl disulfide, 110-81-6; methanethiol, 74-93-1; ethanethiol, 75-08-1; 1-propanethiol, 107-03-9; 1-butanethiol, 109-79-5; 3-methyl-1-butanethiol, 541-31-1; 1-octanethiol, 111-88-6; cyclohexanethiol, 1569-69-3; thiophene, 110-02-1; tetrahydrothiophene, 110-01-0; benzo[*b*]thiophene, 95-15-8; dibenzothiophene, 132-65-0; methylsilane, 992-94-9; tetramethylsilane, 75-76-3; tetraethylsilane, 631-36-7; methylenebis(trimethyl)silane, 2117-28-4; tetramethylstannane, 594-27-4.

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