

Thermochemical Investigations on Organic Sulfur Compounds

IV. On Thermochemical Sulfur Bond Energy Terms

STIG SUNNER

Department of Organic Chemistry, University of Lund, Lund, Sweden

From modern values of heats of combustion of sulfur compounds the different sulfur bond energies have been computed. Assuming the heat of sublimation of graphite and sulfur to be 138 and 66.3 kcal.gatom⁻¹, respectively, the following values have been obtained: $E_{C-S} = 61.5$ kcal., $E_{C=S} = 115$ kcal., $E_{S-H} = 87.5$ kcal. and $E_{S-S} = 67$ kcal.

The following heats of formation at 20° C have been computed from combustion experiments: 5-Thianonane ΔH_f° (liq) = -52.7 ± 0.45 kcal. mole⁻¹; Methyl isothiocyanate ΔH_f° (s) = 18.7 ± 0.30 kcal. mole⁻¹ and 1-Pentanethiol ΔH_f° (liq) = -36.2 ± 0.20 kcal.mole⁻¹.

For many problems in organic thermochemistry it is very useful — and some times necessary — to have reliable bond energy data available. Recently, Cottrell made a careful compilation of bond dissociation as well as thermochemical bond energy data¹. The given values for sulfur bond energies originate partly from old determinations of heats of combustion. It therefore seemed desirable to check these values. Besides, it was judged possible to increase the constancy of obtained data for the same bond by comparing pairs of compounds with almost the same intramolecular environment and then relate the energy of the differing bonds to each other*. The application of this method is often successful — the calculation of the S—S bond energy may illustrate this approach.

THE C—S BOND ENERGY

Reliable values for heats of formation of dialkylsulfides are available for 3-thiapentane² and 5-thianonane. A comparison between the thiaalkane and the corresponding normal alkane gives the heat of substitution of a CH₂-group for a sulfur atom (Table 1).

* Cf. the group equivalent method, see Refs.^{4,5}.

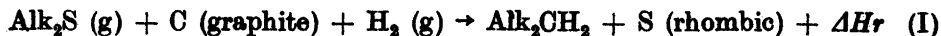


Table 1. Comparison between heats of formation of thiaalkanes and alkanes.

Alk.	ΔH_f kcal.mole ⁻¹		ΔH_r kcal.
	Alk ₂ S	Alk ₂ CH ₂	
Et	-19.9	-35.00 ^a	-15.1
Bu	-40.3	-54.75 ^a	-14.4
Alk ₂ = (CH ₂) ₂	-15.14 ^a	-29.43 ^a	-14.3

^a The average between the value -14.96 ± 0.25 kcal. obtained at the US Bur. Mines, Bartlesville⁶ and our value -15.32 ± 0.20 kcal.⁷

From ΔH_r , the C—S thermochemical bond energy, E_{CS} , is calculated in terms of E_{CC} , the heat of atomization of sulfur, $\Delta H_a(\text{S})$, and the well known increment in the heat of formation per CH₂-group (4.926 kcal.)⁸.

$$E_{\text{CS}} = \frac{1}{2} (E_{\text{CC}} + \Delta H_a(\text{S}) + \Delta H_r + 4.926) \quad (1)$$

Using the values $E_{\text{CC}} = 66.2$ kcal.¹ and $\Delta H_a(\text{S}) = 66.3$ kcal.¹ we get $E_{\text{CS}} = 61.2$ and 61.5 kcal. for Et₂S and Bu₂S, respectively.

An estimate of E_{CS} may also be obtained in the same way from the known heat of formation of thiacyclohexane, assuming the ring to be strainless. The calculation leads to $E_{\text{CS}} = 61.6$ kcal. Within the expected errors the three values are identical. We therefore use the average and put

$$E_{\text{CS}} = 61.5 \text{ kcal.}$$

This value is primarily valid for straight chain dialkyl and unstrained ring sulfides but will also be used for the calculation of the thermochemical sulfur-hydrogen and sulfur-sulfur bond energies.

THE C=S BOND ENERGY

A direct determination of the C=S bond energy is at present not possible due to the fact that thiones without electron-interfering neighbors are not stable as monomers. The few exceptions known have no unambiguous structure; cyclohexanthione exists in two protomeric forms, *viz.* cyclohexanthione and 1-mercapto-cyclohexen⁹. In compounds available for an experimental investigation the heat of formation of a C=S bond is made up of two quantities, the (by definition) invariable C=S bond energy and the energy supplied by interaction between the C=S group and its environment **. However, it is

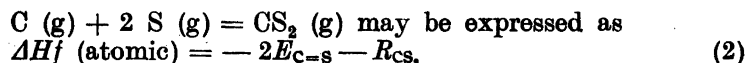
** As in the case of the C=O bond, the C=S bond energy implicitly includes the stabilizing energy from the interaction between the C=S and $\overset{+}{\text{C}}-\overset{-}{\text{S}}$ structures.

possible to give a relation between the bond energy and the interaction energy (resonance energy) for resonating molecules containing a C=S bond.

Pauling estimated the C=S bond energy to be 103 kcal. and the resonance energy for CS₂ to be 11 kcal., for COS 20 kcal.; for CO₂ the resonance energy is 33 kcal.¹⁰ Using data for CS₂ and COS from *Selected Values*¹¹, the heats of formation of monoatomic gaseous carbon¹⁰ and sulfur¹⁰ and the estimated C=S bond energy 103 kcal., the resonance energy for CS₂ becomes 23 kcal. per mole, and for COS 28 kcal. per mole. Either the C=S bond energy or the resonance energies for COS and CS₂ must be in error. If the resonance energies given by Pauling are correct, a C=S bond energy of about 112 kcal. should be expected.

From bond distances (see Pauling) and from infrared measurements¹² it is implied that the character of the resonance in CO₂, COS and CS₂ is the same, the three structures X=C=Y, $\bar{X}-C\equiv\bar{Y}$, $\bar{X}\equiv C-\bar{Y}$ contributing equally (X, Y = O, S). Under these circumstances the decrease in interaction energy from CO₂ over COS to CS₂ is in accordance with the weaker C—S bonds compared with the C—O bonds. It thus seems justified to use the values of the resonance energies given by Pauling as fairly good approximations.

The endothermicity of the reaction



where $E_{\text{C-S}}$ is the energy of the C=S bond and R_{CS_2} the resonance energy of CS₂.

From the heat of formation of gaseous CS₂¹¹ and gaseous monoatomic carbon¹ and sulfur¹:

$$E_{\text{C-S}} = 121 - 0.5 R_{\text{CS}_2} \text{ kcal.} \quad (3)$$

Using $R_{\text{CS}_2} = 11$ kcal., $E_{\text{C-S}} = 116$ kcal.

Analogously, for COS (using $E_{\text{C-O}} = 162$ kcal.¹):

$$E_{\text{C-S}} = 134 - R_{\text{COS}} \quad (4)$$

$R_{\text{COS}} = 20$ kcal. gives $E_{\text{C-S}} = 114$ kcal.

It should be possible to determine the C=S bond energy more precisely from the heat of combustion of a compound with a small resonance energy. The resonance energy of the alkyl isocyanates, according to Pauling, is 7 kcal. and for the thiocyanates it should be less than that. We therefore redetermined the heat of combustion of methylisothiocyanate and found

$$\Delta H_f = 27.1 \text{ kcal. per mole}$$

in good agreement with Thomsen's value of 28 kcal. Using Cottrell's bond energy values, we found

$$E_{\text{C-S}} + R_{\text{MeNCS}} = 118 \text{ kcal.} \quad (5)$$

If we put $R_{\text{MeNCS}} = 3$ kcal., we get $E_{\text{C-S}} = 115$ kcal.

The somewhat arbitrary choice of resonance energy values gets support from equations (3) to (5). These equations combine to give:

$$R_{\text{COS}} = 0.5 R_{\text{CS}_2} + 13 \quad (6)$$

$$R_{\text{COS}} = R_{\text{MeNCS}} + 16 \quad (7)$$

R_{MeNCS} is of course positive but should be less than 7 kcal., a probable value is 3—5 kcal. Thus, $23 > R_{\text{COS}} > 16$, it is believed that 19—21 kcal. should be a fair estimate. The limits for the R_{CS_2} value will then be $20 > R_{\text{CS}_2} > 6$, and probably $16 > R_{\text{CS}_2} > 12$. The apparently proportional decrease in interaction energy in the series, CO_2 , COS and CS_2 favors the low limit value of $R_{\text{COS}} = 19$, which gives $R_{\text{CS}_2} = 12$, $R_{\text{MeNCS}} = 3$ and $E_{\text{C=S}} = 115$ kcal. We will therefore use this value as a fairly good estimation of the C=S bond energy.

$$E_{\text{C=S}} = 115 \text{ kcal.}$$

Pauling and Sherman deduced the resonance energy of MeNCS to be 10 kcal. From this value, according to equation (3)—(5), $R_{\text{COS}} = 26$ kcal. and thus $R_{\text{CS}_2} = 26$ kcal. which is not very probable. It is worth noticing that equations (3) to (5) are based only on

1) the assumption that it is possible to express the energy of a resonating molecule as a sum of constant bond energies plus a resonance energy term (which in fact only indicates the deviation from the constancy of the bond energies);

2) experimental data of heats of combustion;

3) the values of bond energies given by Cottrell; concerning the $E_{\text{C=N}}$ -term value, which differs appreciably from previous values in the literature, reference is made to the further discussion.

These assumptions being essentially correct, the equations (3) to (5) relate the resonance energy terms for different compounds to each other. The conclusion as to the probable value of the thermochemical C=S bond energy is drawn from the fair assumption that the interaction energy changes in a regular manner in the series CO_2 , COS and CS_2 .

Cottrell prefers to incorporate the resonance energy term into the value of the thermochemical bond energy and gets $E_{\text{C=S}} = 121$ kcal. both for COS and CS_2 . This agreement is reached by using the value $E_{\text{C=O}} = 175$ kcal. which is calculated for CO_2 and which also includes the resonance energy term. However, from Cottrell's data, the calculated atomic heat of formation of MeNCS exceeds the experimentally determined value by 3 kcal.; for MeNCO the calculated value exceeds the experimental by as much as 22 kcal. if $E_{\text{C=O}} = 175$ kcal. is used. Excluding the resonance energy from the bond energy term and using $E_{\text{C=O}} = 162$ kcal. (Ketones; Cottrell) and $E_{\text{C=S}} = 115$ kcal. (this paper) the resonance energy of MeNCS becomes 3 kcal. (assumed value) and the calculated atomic heat of formation of MeNCO still exceeds the experimental value by 9 kcal. The heat of combustion of methyl isocyanate was determined by Lemoult in 1898¹³ and might be seriously in error. This suspicion is strengthened by the fact that Pauling¹⁰, Glockler¹⁴, Syrkin and Dyatkina¹⁵ and others have used the heat of formation of MeNCO to calculate the C=N bond energy and give values between 90 and 94 kcal. while Cottrell, who has used a deter-

mination of the heat of formation of *n*-butyl isobutylidene amine from Coates and Sutton¹⁶ obtains the much higher value of 112 kcal. (Recalculated from Pauling's values for heats of atomization of carbon and nitrogen it becomes 105 kcal.).

A comparison between the heats of formation of the following pairs of compounds also indicates an abnormal situation for the pair methyl isothiocyanate and methyl isocyanate (Table 2).

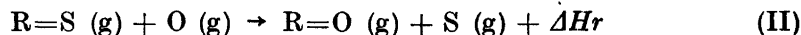


Table 2.

R =	ΔH_r kcal.
OC =	-54.1
SC =	-53.3
MeNC =	-34.7
(NH ₂) ₂ C =	-50.5

THE S-H BOND ENERGY

The S-H bond energy was calculated from the known heats of formation of 1-pentanethiol, 2-propanethiol and hydrogen sulfide. From the heat of formation of H₂S Cottrell calculates $E_{SH} = 87.7$ kcal.¹ In order to obtain an E_{SH} value for a normal mercaptane we determined the heat of combustion of 1-pentanethiol and found the heat of formation of the gaseous substance to be $\Delta H_f = -26.7$ kcal.*. A comparison between 1-pentanethiol and *n*-pentane gives the desired value of E_{S-H}



$$E_{CH} - E_{CS} - E_{SH} = -58.0 \quad (7)$$

$E_{CH} = 90.5$ kcal.¹ and $E_{CS} = 61.5$ gives $E_{SH} = 87.0$ kcal. Recently, the Bartlesville group has determined the heat of formation of 2-propanethiol¹⁸. From their result one gets $E_{SH} = 87.5$ kcal. Thus a value of 87.5 kcal. for E_{S-H} can be adopted with fair confidence.

$$E_{S-H} = 87.5 \text{ kcal.}$$

THE S-S BOND ENERGY

High precision determinations of heats of combustion of disulfides are lacking in the literature. However, Franklin and Lumpkin¹⁹ burned the dimethyl- and diethyl disulfides in a static bomb system. Their result for 2-methyl-2-propanethiol shows a fairly good agreement with the value from the US Bureau of Mines group¹⁷ and the results obtained seem to be accurate within ± 1 kcal.

* The average has been used between the values obtained at the US Bureau of Mines, Bartlesville, ΔH_f° (liq) = -36.12 kcal.¹⁷ and in this laboratory, ΔH_f° (liq) = -36.23 kcal.

The S—S bond energy may be obtained from a comparison between the heats of formation of 3-thiapentane and diethyldisulfide, $\Delta H_f(g) = -21.4$ kcal.*.

$\text{Et} - \text{S} - \text{Et}(g) + \text{S}(g) \rightarrow \text{Et} - \text{S} - \text{S} - \text{Et}(g); \Delta H = -67.8$ kcal. (IV) which gives $E_{\text{SS}} = 67.8$ kcal.

In the same manner one gets from dimethyldisulfide, $\Delta H_f = -7.2$ kcal., and dimethylsulfide, $\Delta H_f = -6.9$ kcal.¹¹, $E_{\text{SS}} = 66.6$ kcal. **.

From the heats of formation of liquid H_2S_2 ¹¹ and H_2S ¹¹ and an estimation of the heat of vaporization of H_2S_2 using Klages equation⁴ ($\Delta H_{\text{vap}} = 8.0$ kcal.), $E_{\text{SS}} = 59$ kcal.. However, the calculated value of the heat of formation of H_2S_2 can be appreciably in error and therefore no particular emphasis can be put on this E_{SS} -value.

Pauling has used the heat of atomization of rhombic sulfur to calculate E_{SS} ¹⁰. $\Delta H_a(\text{S}) = 66.3$ kcal. is combined with the heat of vaporization for $\text{S}(\text{rh}) \rightarrow \text{S}_8(g)$, 24.35 kcal.²¹, which gives $E_{\text{SS}} = 63.3$ kcal. However, this result is believed to be only of limited value for disulfides, considering the increased opportunity for intramolecular interaction in the S_8 -ring as compared with that in a normal disulfide. Therefore, for organic disulfides the value

$$E_{\text{SS}} = 67 \text{ kcal.}$$

will be adopted.

HEATS OF COMBUSTION ***

Materials. The samples of 5-thianonane and methyl isothiocyanate were prepared and purified at this laboratory. The thianonane was repeatedly distilled at different pressures, all fractions during the last distillation boiled at the same constant temperature, b.p.₃₅ $95.10 \pm 0.05^\circ$, b.p.₇₁ $112.20 \pm 0.05^\circ$, n_D 1.4572. The methyl isothiocyanate was purified after distillation by repeated sublimations to constant m. p.

The pentanethiol was obtained from the U.S. Bureau of Mines, Thermodynamics Laboratory, Bartlesville, U.S.A., as "Samples of API—BM certified sulfur compounds purified at the Laramie Station of the Bureau of Mines and made available by American Petroleum Institute Research Project 48 A on the Production, Isolation and Purification of Sulfur Compounds and the Measurement of their Properties"****.

Apparatus and method. The calorimeter and accessory apparatus, experimental procedure and method of calculation have been described in detail previously^{7,22}.

Units of measurement and auxiliary quantities. The results of the combustion experiments are expressed in terms of the defined calorie equal to 4.1840 abs. joules and refer to the isothermal process at 20° and to the true mass. The molecular weights were computed from the 1951 table of international atomic weights. The observed values for the heat of the bomb process were corrected to obtain values for the energy of the idealized combustion reaction in which all the reactants and products are in their standard states at 20° and no external work is performed. The corrections, which include those from the formation of nitric and nitrous acids and for the dilution of sulfuric acid were made as described by Sunner^{7,22}. The heats of formation of water and carbon dioxide at 20° were taken to be 68.355 and 94.050 cal.g⁻¹, respectively.

* Franklin and Lumpkin give the value -20.0 . From Scott *et al.*²⁰ the heat of vaporization is deduced to be 11.1 kcal. which gives $\Delta H_f(g) = -21.4$ kcal.

** Cottrell deduces $E_{\text{SS}} = 70$ and 67 kcal. for diethyl- and dimethyldisulfide, respectively.

*** Together with B. Lundin.

**** We are indebted to Dr. Guy Waddington and Mr. Ward Hubbard of the Thermodynamics Laboratory, U. S. Bureau of Mines, Bartlesville, for furnishing this sample.

Energy equivalent of the calorimeter. The energy equivalent of the calorimeter has been given elsewhere²² as $S_B = 5251.3 \pm 0.4$ cal. per I.U. (= interval unit, equals 1.35° C). A minor change in the system gave $S_B = 5255.1$ cal. per I.U.

Heat of combustion of paraffin oil. Paraffin oil has been used as an auxiliary substance. Table 3 gives the results of two series of determinations of the heat of combustion of the oil.

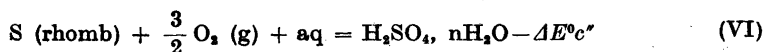
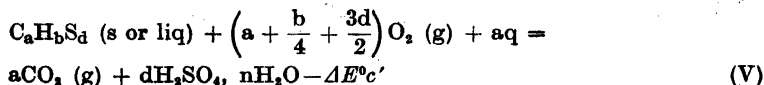
Table 3. Heat of combustion of paraffin oil. The head lists S_B the energy equivalent of the calorimeter excluding the charge of substance (s), which is included in S_F ; q_{CO_2} , the heat of solution of carbon dioxide and q_{wc} the Washburn corrections. The columns list the amount of oil burned, the corrected increase in temperature in interval units, the heat of combustion of the fuse, the correction for the formation of nitrogen acids and the heat of combustion of the paraffin oil under standard conditions.

Oil mg mass	ΔT_{corr} I.U.	q_{fuse} cal.	q_N cal.	$-\Delta E^{\circ}c/M$ cal. per g mass.
$S_B = 5251.3$ cal. per I.U., $S_F = 0.8$ cal. per I.U., $q_{CO_2} = 5.1$ cal., $q_{wc} = 0.8$ cal.				
474.52	1.00216	14.7	9.4	11027.1
471.55	0.99616	17.3	9.6	11025.5
471.61	0.99600	15.2	9.6	11026.9
471.05	0.99450	14.0	9.6	11025.8
470.98	0.99483	15.8	9.4	11025.9
			Average	11026.2
$S_B = 5255.1$ cal. per I.U.				
471.08	0.99441	15.3	9.4	11027.8
469.27	0.99010	14.2	9.7	11025.6
472.70	0.99754	14.9	9.5	11027.1
471.75	0.99507	14.3	9.6	11024.3
473.03	1.01869	12.6	9.7	11025.8
473.22	0.99847	13.7	9.4	11026.5
			Average	11026.2

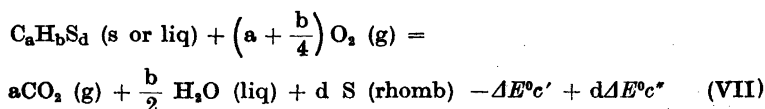
Average for both series $-\Delta E^{\circ}c/M = 11026.2$ cal. per g mass.

Correction for the heat of formation of sulfuric acid. The application of the Washburn corrections to the combustion of a compound containing sulfur means that the heat of combustion has been calculated for an idealized process, the final state of which is made up of CO_2 (g, 1 atm) and a diluted sulfuric acid, H_2SO_4 , nH_2O ; n usually being about 115.

In order to minimize the influence from possible systematic errors due to the presence of sulfur, the heat of combustion of rhombic sulfur has been determined under strictly comparable conditions and the final reaction has been calculated for the formation of rhombic sulfur:



Subtracting d times VI from V gives:



The value of $\Delta E^{\circ}c''$ for $n = 115$ is given in Table 4 for four different series of experiments.

Table 4.

Sample	Investigator	Amount of sulfur milliatoms	$-\Delta E_c^*$ (115) cal. per milliatom of sulfur
1	A	5	143.05 \pm 0.05
1	B	5	143.05 \pm 0.05
1	B	8	143.10 \pm 0.10
2	B	5	143.20 \pm 0.10

Average for all determinations 143.10 \pm 0.05 cal. per millimole of H_2SO_4 , 115 H_2O *.
Deviations from a final dilution of H_2SO_4 , 115 H_2O are accounted for by using SVCTP values of heats of formation of sulfuric acid at different dilutions ¹¹.

RESULTS

The results of the individual combustion experiments are presented in Table 5.]

Table 5. Results of combustion experiments. $S_B = 5251.3$ cal. per I.U., 5255.1 cal. (x)

Sample mg mass	Oil mg mass	ΔT_{corr} I.U.	q_{fuse} cal.	q_N cal.	$-\Delta E_c^*/M$ cal. per g mass.
-------------------	----------------	---------------------------	--------------------	---------------	---------------------------------------

5-Thianonane.

$M = 146.290$, $D_4^{20} = 0.840$, $S_F = 0.6$ cal., $q_{CO_2} = 4.7$ cal. $q_{wc} = -0.4$ cal.

354.17	151.81	0.99528	15.4	10.2	8967.4
334.24	171.60	0.99947	16.1	10.7	8969.9
343.71	161.02	0.99498	15.4	10.7	8968.9
350.36	157.44	1.00053	16.2	10.8	8973.8
371.50 x	137.21	0.99722	15.6	10.7	8972.8
Average					8970.6

Methyl isothiocyanate.

$M = 73.118$, $D_4^{20} = (1.1)$, $S_F = 0.5$ cal., $q_{CO_2} = 4.9, 5.0, 4.6$ cal., $q_{wc} = 0.0$ cal.

188.36	355.52	0.974528	14.9	12.5	4223.2
341.23	247.71	0.985021	14.0	13.6	4229.8
237.57	315.75	0.949528	16.7	14.0	4227.6
Average					4227

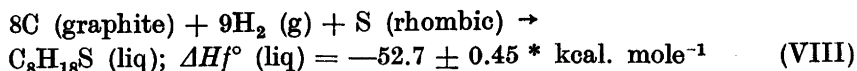
1-Pentanethiol.

$M = 104.212$, $D_4^{20} = 0.85$, $S_F = 0.6$ cal., $q_{CO_2} = 4.7$ cal., $q_{wc} = -0.4$ cal.

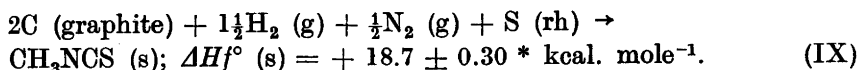
388.86	138.53	0.99671	13.8	10.9	8084.8
403.96	129.46	1.00509	15.1	11.0	8084.3
413.60 x	120.61	1.00282	15.0	10.0	8082.8
364.54	157.83	0.99365	15.5	10.4	8084.6
Average					8084.1

* This value is 0.3 kcal. higher than that obtained at the US Bureau of Mines, Bartlesville.

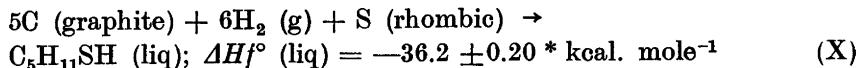
From the results the following values of ΔH_f (liq) and ΔH_f (g) have been computed at 20° C.:



The heat of vaporization was estimated from boiling point *versus* pressure data. Stull's compilation²³ of vapor pressures gives 12.8 kcal. mole⁻¹; our own data 12.0 kcal. mole⁻¹. The average value, 12.4 kcal. mole⁻¹, has been used. For



The heat of vaporization was calculated from vapor pressure data²⁴ to + 8.4 kcal. mole⁻¹. Thus, ΔH_f (g) = + 27.1 kcal. For



ΔH_{vap} was estimated from vapor pressure data to 9.5 kcal. mole⁻¹. Thus ΔH_f (g) = -26.7 kcal. mole⁻¹.

Acknowledgement. This work has been supported by a grant from the *Swedish Natural Science Research Council*.

REFERENCES

1. Cottrell, T. L. *The Strengths of Chemical Bonds*, Butterworths Sci. Publ., London 1954.
2. Scott, D. W., Finke, H. L., Hubbard, W. N., McCullough, J. P., Oliver, G. D., Gross, M. E., Katz, C., Williamson, K. D., Waddington, G. and Huffman, H. M. *J. Am. Chem. Soc.* **74** (1952) 4656.
3. *Selected Values of Properties of Hydrocarbons*, Natl. Bur. Standards Circ. 461, Washington 1947.
4. Klages, F. *Chem. Ber.* **82** (1949) 358.
5. Franklin, J. L. *Ind. Eng. Chem.* **41** (1949) 1070.
6. McCullough, J. P., Finke, H. L., Hubbard, W. N., Good, W. D., Pennington, R. E., Messerly, J. F. and Waddington, G. *J. Am. Chem. Soc.* **76** (1954) 2661.
7. Sunner, S. *Studies in Combustion Calorimetry Applied to Organo-sulfur Compounds* (Diss.) University, Lund 1949.
8. Prosen, E. J. and Rossini, F. D. *J. Research Natl. Bur. Standards* **34** (1945) 263.
9. Dines Shandra Sen *J. Indian Chem. Soc.* **13** (1936) 268.
10. Pauling, L. *Nature of the Chemical Bond*, Cornell University Press, Ithaca N. Y. 1945.
11. *Selected Values of Chemical Thermodynamic Properties*, Natl. Bur. Standards Circ. 500, Washington 1950.
12. Robinson, D. Z. *J. Chem. Phys.* **19** (1951) 881.
13. Lemoult, M. *Compt. rend.* **126** (1898) 43.
14. Glockler, G. *J. Chem. Phys.* **19** (1951) 124.
15. Syrkin, Y. K. and Dyatkina, M. E. *Structure of Molecules and the Chemical Bond*, Translated Ed., Interscience Publishers Inc., New York 1950.

* Twice the "overall" standard deviation.

16. Coates, G. E. and Sutton, L. E. *J. Chem. Soc.* 1948 1187.
17. Hubbard, W. N., Katz, C. and Waddington, G. *J. Phys. Chem.* 58 (1954) 142.
18. McCullough, J. P., Finke, H. L., Scott, D. W., Gross, M. E., Messerly, J. F., Pennington, R. E. and Waddington, G. *J. Am. Chem. Soc.* 76 (1954) 4796.
19. Franklin, J. C. and Lumpkin, H. E. *J. Am. Chem. Soc.* 74 (1952) 1023.
20. Scott, D. W., Finke, H. L., McCullough, J. P., Gross, M. E., Pennington, R. E. and Waddington, G. *J. Am. Chem. Soc.* 74 (1952) 2478.
21. Guthrie, G. B. Jr., Scott, D. W. and Waddington, G. *J. Am. Chem. Soc.* 74 (1954) 1488.
22. Sunner, S. and Lundin, B. *Acta Chem. Scand.* 7 (1953) 1112.
23. Stull, D. R. *Ind. Eng. Chem.* 39 (1947) 517.
24. Bauer, H. and Burschkies, K. *Chem. Ber.* 68 (1935) 1238.

Received March 16, 1955.