THE ENTROPIES OF POLYATOMIC MOLECULES

Sir:

Very recently spectroscopic and specific heat data have been employed in the estimation of the entropies and symmetry numbers of polyatomic molecules in the vapor state.[1] We wish to point out that such calculations may be of uncertain value for molecules containing many atoms. To illustrate this for an apparently favorable case we have made entropy calculations for the tetrachlorides of carbon, silicon, titanium and tin. The Raman spectra of these substances[2] have been studied theoretically by a number of investigators and they are in substantial agreement regarding the interpretation of the experimental results. The molecular dimensions[3] have been determined by the electron diffraction method. Latimer,[4] by specific heat measurements from low temperatures (39°K. with CCl_4), determined the entropies of the liquids at 25° and good vapor pressure data[5] are available for completing the calculation of the entropies of the gases at the customary standard state of one atmosphere and 25°. The results of the calculations together with the data used are presented in the table. The numbers in parentheses adjoining the symbol ω are the multiplicities of the vibrational levels. To calculate "S°_{298} spectroscopic" it was assumed, in accordance with the results of electron diffraction experiments, that the symmetry number is 12, *i. e.*, that the chlorine atoms are at the corners of a regular tetrahedron.

Substance	$\omega_1(1)$ cm.$^{-1}$	$\omega_2(2)$ cm.$^{-1}$	$\omega_3(3)$ cm.$^{-1}$	$\omega_4(3)$ cm.$^{-1}$	ΔH Vap. at 25°, cal.	V. p. at 25°, mm.	Cl–Cl distance, Å.
CCl_4	459	217	775	313	7730	114.5	2.98
$SiCl_4$	422	148	608	220	7184	235	3.29
$TiCl_4$	386	119	491	139	8960	13.38	3.61
$SnCl_4$	367	104	401	136	9472	24.0	3.81

Substance	S° Trans. cal./deg.	S° Rot. cal./deg.	S° Vib. cal./deg.	S°_{298} Spec. cal./deg.	S°_{298} Third law cal./deg.	Difference cal./deg.
CCl_4	40.99	28.78	9.51	74.3	71.2	3.1
$SiCl_4$	41.29	29.35	13.53	79.2	78.3	0.9
$TiCl_4$	41.62	29.90	17.81	84.4	81.5	2.9
$SnCl_4$	42.56	30.22	19.37	87.2	86.8	0.4

The differences between the calculated entropies and those obtained from thermal measurements are, in at least two cases, larger than corresponds to the experimental error usually allowed to the measured quantities involved. The data for carbon tetrachloride are probably better than

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(1) Dietz and Andrews, *J. Chem. Phys.*, **1**, 62 (1933); Mayer, Brunauer and Mayer, THIS JOURNAL, **55**, 27 (1933).

(2) Kohlrausch, "Der Smekal-Raman Effekt," J. Springer, Berlin, 1930, pp. 49, 215.

(3) Wierl, *Ann. Physik*, **8**, 521 (1931).

(4) Latimer, THIS JOURNAL, **44**, 90 (1922).

(5) "International Critical Tables," Vol. III, pp. 213, 214 (for CCl_4 and $SnCl_4$); Wintgen, *Ber.*, **52**, 724 (1919) (for $SiCl_4$); Arii, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **8**, 714 (1929); *cf. Chem. Abs.*, **24**, 277 (1930) (for $TiCl_4$).

those for the other three tetrachlorides, yet the difference is greatest for that substance. In all cases the symmetry number would turn out greater than 12 (59 for CCl_4) if the results were used to calculate that quantity.

On the assumption that some more fundamental difficulty is not involved, it is possible that the differences found are to be ascribed to incomplete knowledge of the vibrational states of non-linear polyatomic molecules. Accordingly, great accuracy cannot, at present, be ascribed to the results of spectroscopic entropy calculations for polyatomic molecules in those cases where all of the necessary energy levels are not accurately known and correctly interpreted. For the approximate estimation of free energies[6] such entropies are, however, often of considerable value.

[6] Kassel, THIS JOURNAL, **55**, 1351 (1933).

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RECEIVED MAY 1, 1933 PUBLISHED JUNE 6, 1933

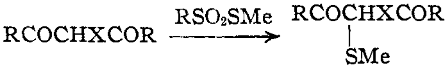
THE METHYLENE DISULFONES[1]

Sir:

These substances are of considerable interest as cogeners of Sulphonal. The general methods of preparation, outlined as early as 1877,[2] are expressed

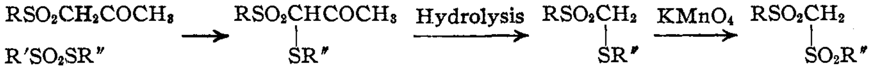
$$\left.\begin{array}{l} CH_2I_2 + 2HSR \xrightarrow{-2HI} \\ CH_2O + 2HSR \xrightarrow{-H_2O} \end{array}\right] \longrightarrow CH_2(SR)_2 \longrightarrow CH_2(SO_2R)_2$$

In the past month a simple modification of the former scheme was described by Stutz and Shriner which, by obviating the isolation of mercaptan, greatly reduces the offensive odor of the process. Unfortunately, the yields were not very good, and the methylene disulfides, though less volatile, have persistent and unpleasant odors. These drawbacks can be avoided completely by an extension of the work of Brooker and Smiles.[3] They showed



$$RCOCHXCOR \xrightarrow{RSO_2SMe} \begin{array}{l} RCOCHXCOR \\ \quad\;\; | \\ \quad\; SMe \end{array}$$

By applying this to sulfonyl ketones I developed a process (1931)[4] whereby disulfones were obtained with no obnoxious intermediate at all.



$$\begin{array}{l} RSO_2CH_2COCH_3 \\ R'SO_2SR'' \end{array} \longrightarrow \begin{array}{l} RSO_2CHCOCH_3 \\ \quad\;\; | \\ \quad\; SR'' \end{array} \xrightarrow{Hydrolysis} \begin{array}{l} RSO_2CH_2 \\ \quad\;\; | \\ \quad\; SR'' \end{array} \xrightarrow{KMnO_4} \begin{array}{l} RSO_2CH_2 \\ \quad\;\; | \\ \quad\; SO_2R'' \end{array}$$

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[1] Stutz and Shriner, THIS JOURNAL, **55**, 1242 (1933).

[2] Claesson, *J. prakt. Chem.*, **15**, 176 (1877).

[3] Brooker and Smiles, *J. Chem. Soc.*, 1723 (1926).

[4] D. T. Gibson, *ibid.*, 2637 (1931).