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results indicated in Table IV. It is interesting to note that the constant G , usually assumed equal to H in the treatment of pyramidal type molecules, is nearly equal to H for heavy halogen atoms, but is considerably greater than H for light halogen atoms bound to the central boron.

Using these force constants we have calculated the frequencies ν_3 and ν_4 to be expected for the compounds containing the B^{10} isotope. The results agree well with the observed values as indicated in the table. The fact that the frequency ν_4 has little isotopic shift indicates that

the symmetry modes are very nearly the normal modes in these cases.

Finally in Table IV, columns 10 and 11 are presented values of the internuclear distances calculated directly from the values of K by Badger's rule.¹³ The agreement with the internuclear distances determined by electron diffraction experiments⁴ is much better than would have been expected, judging from the experience of previous investigators.

¹³ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934); **3**, 710 (1935).

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The Entropy of Carbon Tetrachloride

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A new calculation of the entropy of carbon tetrachloride has been made from Raman spectra and electron diffraction data. The effect of the isotopes of chlorine has been investigated. A new value of the calorimetric entropy has been computed from recent (and in part unpublished) thermal data. The agreement of the entropies is sufficiently good as to leave little reason to doubt the validity of the spectroscopic calculations

SOME time ago Yost and Blair¹ noted a difference of about three entropy units between the entropy of carbon tetrachloride calculated from the existing thermal data² and a value of the entropy which they calculated from spectroscopic data by statistical methods. Assuming that the thermal data were substantially correct, they suggested that the discrepancy arose in the statistical calculation from uncertainty about the vibrational states of the molecule. The purpose of their note was to point out the dubious value, in their opinion, of spectroscopic entropy calculations made on the basis of the customary assumption that molecular vibrations are quasi-harmonic. In view of the good spectroscopic data available and the straightforward interpretation of the vibrational structure of carbon tetrachloride, it seemed to us unlikely that uncertainties of the sort suggested by Yost and Blair could account for the discrepancy between the thermal and spectroscopic

entropies. Rather it appeared that the difficulty probably lay in the experimental thermal data. We have had put at our disposal some new unpublished heat capacity data for carbon tetrachloride. Furthermore we have made a new calculation of the statistical entropy, thoroughly investigating several possible sources of the disagreement. The theoretical and calorimetric data have been found to agree well within the limits of the probable experimental error in the latter.

STATISTICAL ENTROPY

It appeared worth while to refine the statistical computations by taking into account the isotopes Cl^{35} and Cl^{37} . The presence of these isotopes creates five different isotopic configurations for carbon tetrachloride, and the final value of the entropy has been obtained from the entropies of the configurations. It is to be remarked that the symmetry numbers of the various configurations are not uniformly twelve. At first sight, this variance in symmetry number might be thought

¹ Yost and Blair, *J. Am. Chem. Soc.* **55**, 2610 (1933).

² Latimer, *J. Am. Chem. Soc.* **44**, 90 (1922).

to affect the entropy considerably. However, because the isotopic ratio ordinarily remains fixed (i.e., no separation of isotopes occurs), the effect of isotopes on symmetry number may be disregarded. This neglect may be briefly justified as follows:

The only term in the entropy expression containing the symmetry number is of the form³

$$\frac{X!Y!Z!}{N_1!N_2!\cdots\sigma_1^{N_1}\sigma_2^{N_2}\cdots}, \quad (1)$$

which occurs in the expression for the γ -weight of the gas whose entropy is being calculated. In (1) the symbols X , Y and Z denote the actual numbers of the various atoms which have combined chemically to form the different kinds of molecules which make up the gaseous system. These molecules, the actual numbers of which are denoted by N_1 , N_2 , \cdots , possess, respectively, the symmetry numbers σ_1 , σ_2 , etc. In a mole of gaseous carbon tetrachloride, for example, there will be N carbon tetrachloride molecules ($N=6\times 10^{23}$) which are made up of X carbon atoms ($X=6\times 10^{23}$) and Y chlorine atoms ($Y=24\times 10^{23}$). Eq. (1) may be written for this system:

$$\frac{X!Y!}{N!\sigma^N}. \quad (2)$$

When the Y chlorine atoms are sorted into Y_1 Cl^{35} atoms and Y_2 Cl^{37} atoms, (2) becomes

$$\frac{X!Y_1!Y_2!}{N_1!N_2!\cdots N_5!\sigma_1^{N_1}\sigma_2^{N_2}\cdots\sigma_5^{N_5}}, \quad (3)$$

in which the subscripts of the N 's denote the various isotopic configurations of carbon tetrachloride.

Taking the mole fractions of the several configurations to be those corresponding to purely fortuitous molecular formation from chlorine isotopes whose abundance ratio is Y_1/Y_2 , we find

³ See Ehrenfest and Trkal, Proc. Sect. Sci. Amstr. 23, 162 (1921), Eq. (20), p. 170. Similar expressions are reproduced in Tolman, *Statistical Mechanics* (Chemical Catalog Company, New York, 1927), Eq. (246), p. 127; and in Fowler, *Statistical Mechanics* (Cambridge, 1929), Eq. (292), p. 102. A quantum mechanical justification of the use of symmetry number at high temperatures (above 100°K) will be found in the discussion given by Mayer, Brunauer and Mayer, J. Am. Chem. Soc. 55, 27 (1933).

that expressions (2) and (3) are numerically identical. That is to say, the presence of the isotopes may be neglected insofar as its effect on tetrahedral symmetry is concerned. Giauque and Overstreet⁴ have proved this for diatomic molecules in a different but fundamentally equivalent way. Incidentally they have shown (reference 4, p. 1735) that at high temperatures (specifically, at 298°K), the formation of the isotopic configurations of Cl_2 is strictly according to chance.

Langseth⁵ has obtained the Raman spectrum of carbon tetrachloride under high dispersion, and has observed vibrational frequencies for the three most prominent isotopic configurations. By utilizing these observed values in conjunction with the formulas of Rosenthal⁶ for isotopic frequency shifts, a complete set of frequencies has been worked out. These frequencies, in reciprocal centimeters, are listed in Table I.

Isotopic type I is CCl_4^{35} , type II $\text{CCl}_3^{35}\text{Cl}^{37}$, etc. For certain of the configurations, the degenerate vibrations split into groups of frequencies. The frequency values listed for these vibrations are weighted means of the individual frequencies. In addition, the triply degenerate ν_3 happens to be split into a doublet because of accidental resonance with the sum of ν_1 and ν_4 . The extent of the splitting is small enough, however, that no appreciable error is introduced into the entropy by using an average of the two doublet components. This average frequency is listed for ν_3 in Table I.

For the calculation of rotational entropy, the moments of inertia were obtained from the accurate electron diffraction data of Pauling and Brockway.⁷ The value of the carbon-chlorine

TABLE I. Frequencies and degeneracies.

Isotopic Type	$\nu_1(1)$	$\nu_2(2)$	$\nu_3(3)$	$\nu_4(3)$
I	461.5	219.0	777	315.5
II	458.3	216.6	775	314.6
III	455.2	215.8	772	312.8
IV	452.1	215.0	769	311.4
V	448.9	212.8	767	310.2

⁴ Giauque and Overstreet, J. Am. Chem. Soc. 54, 1731 (1932).

⁵ Langseth, Zeits. f. Physik 72, 350 (1931).

⁶ Rosenthal, Phys. Rev. 46, 760 (1934).

⁷ Pauling and Brockway, J. Chem. Phys. 2, 867 (1934); J. Am. Chem. Soc. 57, 2684 (1935).

TABLE II.

Isotopic Type	Mole Fraction	Entropy at 298°K					Entropy at 348.5°K				
		Trans.	Rot.	Vib.	Total	Fraction	Trans.	Rot.	Vib.	Total	Fraction
I	0.3319	40.97	28.51	9.36	78.84	26.17	41.76	28.97	11.39	82.12	27.26
II	0.4215	41.01	28.55	9.43	78.99	33.30	41.80	29.02	11.46	82.28	34.68
III	0.2008	41.05	28.59	9.51	79.15	15.89	41.84	29.05	11.53	82.42	16.55
IV	0.0425	41.08	28.63	9.58	79.29	3.37	41.87	29.10	11.59	82.56	3.51
V	0.0033	41.12	28.67	9.67	79.46	0.26	41.91	29.14	11.67	82.72	0.27
Sum of Fractional Entropies						78.99					
$-R \ln \sigma (\sigma=12)$						<u>-4.94</u>					
Net Entropy of CarbonTetrachloride:						74.05					

TABLE III. Heat capacity of carbon tetrachloride.
Calories per mole $0^\circ\text{C} = 273.10^\circ\text{K}$.

$T^\circ\text{K}$	C_p	$T^\circ\text{K}$	C_p
<i>Solid 1</i>		<i>Solid 2</i>	
18	3.81	230	29.65
20	4.98	240	29.82
25	6.78	<i>Liquid</i>	
30	8.09	260	31.68
40	10.07	270	31.31
50	11.32	280	31.00
60	12.45	290	30.60
70	13.70	300	31.04
80	14.80	310	31.63
* * *	* * *	320	32.19
100	16.68	330	32.78
120	18.50		
140	20.14		
160	21.74		
180	23.51		
200	25.70		
220	28.12		

CONCLUSION

At low temperatures the heat capacity of carbon tetrachloride is considerably larger than the earlier measurements indicated. The discrepancy between the value of the thermal entropy cited by Yost and Blair and the spectroscopic entropy is thus to be ascribed to erroneous heat capacity data, chiefly below 70°K . It is difficult to estimate closely the accuracy of the value of the thermal entropy given here. The entropy below 20°K may be in error by as much as 0.15 E.U. In the region between 80° and 140° there remain uncertainties in the heat capacity data which could conceivably affect the entropy to the extent of 0.5 E.U. We believe, however, that the value of the thermal entropy may be safely considered to be within 0.7–0.8 E.U. of the true value.

To bring the spectroscopic entropy into exact agreement with the present value of the thermal entropy requires a symmetry number in the neighborhood of 10. This number is uncertain by two or three units because of the doubt about the

TABLE IV. Calculation of the entropy of carbon tetrachloride.

	298°K	348.5°K
0° – 10°K , T^3 -extrapolation ^a	0.25	0.25
10° – 85°K , graphical (B & B)	16.21	36.29
85° – 225.4°K , graphical (Stull)	20.08	
Transition, $1080.8/225.4$ (J & L)	4.79	4.79
225.4° – 250.2°K , graphical (Stull)	3.08	3.08
Fusion, $577.2/250.2$ (J & L)	2.31	2.31
250.2° – 298°K , graphical (Stull)	5.45	5.45
298° – 348.5°K , graphical	—	5.05 ^b
Vaporization	25.94 ^c	20.55 ^d
Compression: $R \ln 114.5/760$	–3.76	—
$R \ln 730/760$	—	–0.08
Calorimetric entropy, cal./deg./mole	74.35	77.69
Spectroscopic entropy, this research	74.05	77.33
“ “ Yost & Blair	74.3	—

^a $C_p = aT^3$, where $a = 0.75 \times 10^{-3}$ cal/deg⁴/mole.

^b Heat capacity data extrapolated graphically from 334°K .

^c Int. Crit. Tab., Vol. III, p. 215.

^d J. H. Mathews, J. Am. Chem. Soc. 48, 562 (1926).

heat capacity data. It is therefore seen that accurate thermal data are a prime necessity for a valid determination of σ . A trustworthy evaluation of σ is also dependent upon a satisfactory analysis of vibrational frequencies and upon freedom of the thermal entropy of the crystalline state from such effects as have been studied by Giauque and his associates.¹⁰ For carbon tetrachloride, however, the vibrational analysis is assuredly correct, and it appears likely that the entropy of the crystal is free from orientation effects of the sort found in N_2O , CO and H_2O . We believe therefore that the agreement which we have obtained between thermal and statistical entropies indicates the reliability of calculations based on the sort of spectroscopic data we have utilized.

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¹⁰ Giauque and Johnston, J. Am. Chem. Soc. 50, 3221 (1928). Clayton and Giauque, *ibid.* 54, 2610 (1932). Blue and Giauque, *ibid.* 57, 991 (1935).