

diffraction patterns until a process is developed for the preparation of individual crystals of the various types for examination. This problem is complicated by the fact that the lower hydrates cannot be prepared in aqueous solution by ordinary processes because of the high temperature required. The x-ray powder patterns indicate the existence of the various forms associated with marked distinctions in structural relationships.

Assistance on the part of Professor G. L. Clark in the x-ray studies is gratefully acknowledged.

Summary

1. The structural relationships existing between the numerous forms of the hydrated perchloric acids have been discussed and the experimental justification for the conclusions drawn has been indicated.

2. Two new forms of hydrated magnesium perchlorates, diaquo- and tetraquo-magnesium perchlorate, were predicted from a study of the various hydrates of perchloric acid and the conditions for their preparation described.

3. Vapor pressure studies involving the use of the various forms of hydrated magnesium perchlorates have been made and the dehydrating efficiency of the anhydrous form compared to that of other highly intensive desiccants.

4. x-Ray powder diffraction patterns of the various hydrates of magnesium perchlorate have been prepared.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 316]

THE ENTROPIES OF SOME SIMPLE POLYATOMIC GASES CALCULATED FROM SPECTRAL DATA

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Introduction

Knowledge of the nature of the energy levels of diatomic molecules has now advanced to such a state that when appropriate data are available it is possible to calculate specific heats and entropies with great accuracy and with results in which we may be entirely confident, as has been shown by comparisons between calculated values and those obtained from specific heat data.

The polyatomic molecule in most cases offers considerably greater difficulties, and for those of the most general type there is as yet probably no case in which data are available for making any exact calculation. However, in two special cases the computation becomes very much sim-

plified, namely, the symmetrical rotator type of molecule, and the molecule having a linear configuration in the normal state; for several, examples of these data are available. Two of the symmetrical rotator molecules, ammonia and methane, have been treated by Villars,¹ but unfortunately the spectra of these gases have not been fully interpreted as yet, and one of the moments of inertia of ammonia may be in some doubt.

It is the purpose of this paper to treat four of the linear polyatomic molecules for which accurate spectroscopic data have recently been published, and which appear to be understood in sufficient detail so that we may be quite confident in the results of our calculations. After our calculations were completed our attention was called to a letter from W. H. Rodebush in the *Physical Review*² in which calculated values for the entropies of carbon dioxide and nitrous oxide were given. The former agrees approximately with our results but the value for nitrous oxide seems to be too low by about 0.2 entropy unit, apparently due to the use of the incorrect moment of inertia for this gas which is given in the paper of Plyler and Barker.³ In view of this fact, and since none of the details of the calculations were given in the letter of Rhodebush, we believe it may be of value to give our results as originally planned.

The methods of calculating entropies from spectral data have been the subject of so many papers⁴ that it seems unnecessary to discuss our computations in any detail, except in regard to some points which are more or less special for the particular molecules involved.

The Linear Triatomic Molecules Carbon Dioxide, Nitric Oxide and Hydrogen Cyanide

Vibrational Energy Levels.—The infra-red and Raman spectra of gaseous carbon dioxide,⁵ nitrous oxide^{3,5c} and hydrogen cyanide^{5a,6} have been investigated and we have conclusive evidence that the molecules are linear in the normal state, that carbon dioxide is symmetrical and that nitrous oxide is unsymmetrical. Molecules of the general type of which these are examples have three normal modes of vibration which we shall designate by the symbols ν_1^5 , ν_2 and ν_3 .⁷ The second and third are

¹ Villars, *Phys. Rev.*, **38**, 1552 (1931).

² Rodebush, *ibid.*, **40**, 113 (1932).

³ Plyler and Barker, *ibid.*, **38**, 1828 (1931), and see below.

⁴ For example: Giauque, *THIS JOURNAL*, **52**, 4808 (1930); Rodebush, *Chem. Rev.*, **9**, 319 (1931).

⁵ (a) See Schaefer and Matossi, "Das Ultrarote Spektrum," Julius Springer, Berlin, 1930, for references; (b) Sleator, *Phys. Rev.*, **38**, 147 (1931); (c) Dickinson, Dillon and Rasetti, *ibid.*, **34**, 582 (1929); (d) Houston and Lewis, *Proc. Natl. Acad. Sci.*, **17**, 229 (1931).

⁶ Badger and Binder, *Phys. Rev.*, **37**, 800 (1931).

⁷ We shall use the convention that the fundamental modes of oscillation are designated by subscripts in order of increasing frequency. The type of motion is designated

longitudinal or "valence" vibrations of relatively high frequency. In carbon dioxide ν_2 is "inactive" since it produces no changes in electric moment in the symmetrical molecule, but in the other two molecules it is weakly active. The other type of oscillation ν_1^δ is the one with which we shall be chiefly concerned since it is of relatively low frequency. It is a motion in which the two molecular bonds are bent with respect to each other, and the molecule is periodically deformed from its linear condition. In the case of a strictly harmonic oscillator the excited levels of the ν_1^δ vibration are degenerate with a weight of $v_1^\delta + 1$, where v_1^δ is the vibrational quantum number of the state.⁸ In the actual molecules the degeneracy is partly removed by the non-harmonic nature of the oscillation, and is probably completely removed when the molecule is rotating.

Unfortunately some of the $v_1^\delta + 1$ levels do not combine with the ground level in absorption, but their energy may be determined indirectly if absorptions from a known excited level to these states are observed. One simply adds the energy of the observed transition to the energy of the initial level.

In the case of carbon dioxide the situation is further complicated by the fact that the energy of the states $v_1^\delta = 2$, $v_2 = 0$, and of the state $v_1^\delta = 0$, $v_2 = 1$ are very nearly equal. This case has been discussed by Fermi⁹ on the assumption that in the unperturbed case these energies would be exactly equal, so that there would be a single degenerate state of weight 4. He shows that in the case of coupling between the two types of oscillation concerned, a resonance effect causes the degenerate state to split into three, one of which is still degenerate with a weight of 2, and he calculates the separation of the new levels with the aid of an estimated coupling energy. His discussion is obviously too simplified to take account of the situation in carbon dioxide in an exact way, and the agreement between calculation and the Raman spectrum must to some extent be fortuitous, but it is very important in calling attention to an effect which may be rather common in polyatomic molecules where the chance is great that vibrational levels of different types of oscillation may nearly coincide.

Fortunately, with the assistance of the infra-red and Raman spectra together we are able to find the energies of most of the states which are important for our purposes, and for a few others we may make a sufficiently accurate estimate. At this point we should like to correct an impression which seems to be fairly general to the effect that the Raman spectrum alone yields sufficient information for making the type of calculations by the superscript; δ indicates a deformation oscillation, that is, one in which the motion is principally a bending of a molecular bond, and its absence a longitudinal or valence oscillation. An inactive vibration is indicated by i in the superscript.

⁸ The problems with which we are here concerned are discussed by Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).

⁹ Fermi, *Z. Physik*, **71**, 250 (1931).

with which we are here concerned. Usually about two-thirds of the necessary data has to be obtained from infra-red investigations.

Rotational Energy.—It is found that for the linear polyatomic molecules the energies in the lower oscillational states are quite accurately given by a formula of the same type as that applicable to the diatomic molecules.

$$E = E_{\text{vib.}} + j(j+1) \frac{\hbar^2}{8\pi^2 I}$$

The stretching of the molecule due to rotation seems to be negligible, that is, I may be taken constant for a given vibrational state. But for nitrous oxide and hydrogen cyanide the data are sufficiently accurate to show that it is different for different oscillational levels. The difference is so small, however, and the higher levels contribute so little to the entropy at ordinary temperature, that we are perfectly justified in taking I constant and in calculating the rotational and vibrational entropies separately, just as is frequently done for diatomic molecules.

The moment of inertia of nitrous oxide given in the paper of Plyler and Barker³ is a misprint, and we have calculated our value from the constants given for the bands at 17μ and 8μ . For the moment of inertia of carbon dioxide we have taken the mean of the value given by Houston^{5d} and one given in a private communication to one of us by E. F. Barker (70.6×10^{-40} from infra-red data).

Due to the large moment of inertia the partition function sum may be very accurately replaced by the integral and we obtain, in the case of nitrous oxide or hydrogen cyanide

$$Q_{\text{rot.}} = \sum_0^{\infty} (2j+1) e^{-j(j+1)\sigma} = \int_0^{\infty} (2j+1) e^{-j(j+1)\sigma} dj = \frac{1}{\sigma} = \frac{8\pi^2 I k T}{h^2}$$

Since carbon dioxide is symmetrical and the oxygen nuclei have no spin, only half the rotational levels are permitted in any given oscillational state. Due to the symmetry properties of the oscillations, in some cases the even levels will be permitted and others the odd ones. We must consequently write for the total partition function

$$Q = \sum_0^{\infty} (4j+1) e^{-2j(2j+1)\sigma} \sum_{\text{ev.}} p e^{-E_{\text{vib.}}/kT} + \sum_0^{\infty} (4j+3) e^{-(2j+1)(2j+2)\sigma} \sum_{\text{odd}} p e^{-E_{\text{vib.}}/kT}$$

The first part of the expression takes care of the vibrational states in which the even rotational levels are permitted, and the second part of the remainder. But as σ becomes small, the sums taken over the rotational levels will approach the same value whether the even or the odd levels are summed. Consequently we may, to a very good degree of approximation, write

$$Q \approx \frac{1}{2} \sum_0^{\infty} (2j+1) e^{-j(j+1)\sigma} \sum e^{-E_{\text{vib.}}/kT}$$

and

$$Q_{\text{rot.}} \approx \frac{1}{2} \int_0^{\infty} (2j+1) e^{-j(j+1)\sigma} dj = \frac{1}{2\sigma} = \frac{4\pi^2 I k T}{h^2}$$

The data employed in our calculations and some of the steps are given in Table I. It should be noted that the entropies calculated as above described do not contain the part due to spin and are the values which may be compared with the results of specific heat measurements. We may call them the "virtual" entropies and shall designate them by the symbol S^* . To obtain the absolute entropies we should presumably add, in the case of nitrous oxide, $R \ln 9$, and in the case of hydrogen cyanide $R \ln 6$.

TABLE I

CALCULATION OF THE ENTROPIES OF CARBON DIOXIDE, NITROUS OXIDE AND HYDROGEN CYANIDE AT 298.2°A.

The symbol p indicates the weight of a degenerate state or the number of states having the same or nearly the same energy.

	State			CO ₂		N ₂ O		HCN		
	v_1^{δ}	v_2	v_3	$E_{\text{vib.}} (\text{cm.}^{-1})$	p	$E_{\text{vib.}} (\text{cm.}^{-1})$	p	$E_{\text{vib.}} (\text{cm.}^{-1})$	p	
Vibrational States	0	0	0	0	1	0	1	0	1	
	1	0	0	669	2	589.0	2	710	2	
	2	0	0	$\left. \begin{array}{l} 1285 \\ 1316^a \\ \sim 1340^b \\ 1388 \end{array} \right\}$	1	$\left\{ \begin{array}{l} 1167.3 \\ 1179.6^c \end{array} \right.$	1	~1411	3	
			1		2					
	0	1	0		1388	1	1285.4	1	~2090	1
	3	0	0		~2000	6	~1750	4	~2112	4
	1	1	0	~1868			2			
$Q_{\text{vib.}}$				1.088		1.133		1.068		
$T(d \ln Q_{\text{vib.}}/dT)$				0.281		0.372		0.232		
$I \times 10^{40}$				70.4		65.95		18.79		
$Q_{\text{rot.}}$				265.1		496.6		141.5		
$S_{\text{vib.}}$				0.726		0.987		0.592		
$S_{\text{rot.}}$				13.071		14.318		11.823		
$\frac{3}{2} R \ln M$				11.275		11.276		9.818		
$\frac{5}{2} R \ln 298.2 + S_0$				25.996		25.996		25.996		
$S_{298.2}^*$				51.07		52.58		48.23		
					$R \ln 9 =$	4.365	$R \ln 6 =$	3.559		
$S_{298.2}$ (absolute)				51.07		56.94		51.79		

^a 1316 = 669 + 647. ^b 1340 \approx 2 \times 669. ^c 1179.6 = 589.0 + 590.6

The only gas of the above three for which accurate data are available for comparison seems to be carbon dioxide. Using the calorimetrically determined entropy of carbon, the entropy of oxygen calculated by Giauque and Johnston¹⁰ and the free energy and heat of formation of carbon dioxide as given in the "International Critical Tables," we find for the entropy of

¹⁰ Giauque and Johnston, THIS JOURNAL, 51, 2300 (1929).

this gas 50.0 entropy units at 298.2°A. The heat of formation may be a little uncertain, and if we use the value accepted by Lewis and Randall we obtain 50.5, a somewhat better check.

There are some data on hydrogen cyanide but when they are considered together with the calculated entropies they are found to be inconsistent. We shall reserve a discussion of the situation until somewhat later as we expect to redetermine the heat of combustion of hydrogen cyanide, in this Laboratory.

Acetylene.—Acetylene has been the subject of careful spectroscopic investigations¹¹ which show it to be a linear molecule. Unfortunately there is a slight uncertainty in regard to some of the vibrational states. An interpretation of the spectrum given by Mecke¹² seems to be not quite correct in some details since his designation of several bands is not in agreement with transition rules which seem to be on a good theoretical basis. Acetylene has in all five normal modes of oscillation, but only three of these and some of their combinations are of sufficiently low frequency to contribute appreciably to the entropy at ordinary temperatures. The lowest frequency $\nu^{\delta i}$ is not known directly but may be estimated from some combination bands to be about 620 ± 20 cm.⁻¹. This uncertainty introduces a possible error of about 0.04 entropy units in the calculation, and consequently is not serious.

The moment of inertia has been determined for several vibrational states but may be considered constant for the levels with which we are concerned. Due to the spins of the hydrogen nuclei and the absence of any in the carbon nuclei we have a situation similar to that found in the hydrogen

TABLE II
THE ENTROPY OF ACETYLENE AT 298.2°A.

$\nu^{\delta i}$	Vibrational states			p	
	State	ν_2^{δ}	ν_3^{δ}		
0	0	0	0	1	$I = 23.509 \times 10^{-40}$ $Q_{\text{rot.}} = \frac{1}{2\sigma} = 88.51$ $Q_{\text{vib.}} = 1.181$ $T (d \ln Q_{\text{vib.}}/dT) = 0.5390$ $S_{\text{rot.}} = 10.892$ $S_{\text{vib.}} = 1.401$ $^{3/2} R \ln M = 9.710$ $^{5/2} R \ln 298.2 + S_0 = 25.996$ $S_{298.2}^* = 48.00$ $R \ln 4 = 2.754$ $S_{298.2}(\text{abs.}) = 50.75$
1	0	0	~ 620	2	
0	1	0	729.3	2	
2	0	0	~1240	3	
1	1	0	1328.5	4	
0	2	0	~1460	3	
3	0	0	~1860	4	
2	1	0	~1970	6	
0	0	1	1975	1	
1	2	0	~2070	6	
0	3	0	~2190	4	

¹¹ Levin and Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928); Hedfield and Mecke, *Z. Physik*, **64**, 151 (1930).

¹² Mecke, *ibid.*, **64**, 173 (1930).

molecule. Alternate rotational levels have a weight of one, and the remainder a weight of three, but whether it is the odd or even levels which have the greater weight depends on the symmetry of the oscillational state. It is easily shown, however, that at temperatures high enough so that the rotational sum may be replaced by integrals the expression for Q reduces to the following

$$Q = Q_{\text{rot.}} \cdot Q_{\text{vib.}} \approx \frac{1}{2} \int_0^{\infty} (2j + 1) e^{-j(j+1)\sigma} dj \times Q_{\text{vib.}}$$

$$= \frac{4}{2\sigma} Q_{\text{vib.}}$$

The use of this expression gives us the absolute entropy, including the part due to spin. If the factor 4 is omitted we obtain the "virtual" entropy.

Summary

1. The calculation of the entropies of linear polyatomic molecules from spectroscopic data is shown to be similar to and only slightly more complicated than similar calculations for diatomic molecules.

2. The entropies of carbon dioxide, nitrous oxide, hydrogen cyanide and acetylene at 298.2°A. have been calculated from spectral data. The "virtual" entropies (those to be compared with calorimetric data) are found to be 51.07, 52.58, 48.23 and 48.00 entropy units, respectively. The absolute entropies are 51.07, 56.94, 51.79 and 50.75, respectively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE THERMAL DECOMPOSITION OF ORGANIC COMPOUNDS FROM THE STANDPOINT OF FREE RADICALS. II. EXPERIMENTAL EVIDENCE OF THE DECOMPOSITION OF ORGANIC COMPOUNDS INTO FREE RADICALS

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In a recent paper² there was proposed an explanation for the decomposition of paraffin hydrocarbons based on the assumption that the unimolecular decomposition consists of the primary rupture of a C-C bond, with the formation of free radicals,³ followed by the decomposition of those

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² Rice, *THIS JOURNAL*, **53**, 1959 (1931).

³ The following is a bibliography of some of the more recent work in which the thermal production and reactions of free radicals are studied: (a) Taylor, *Am. Phil. Soc.*, **65**, 90 (1926); (b) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (c) Schultze and Müller, *Z. physik. Chem.*, [B] **6**, 267 (1929); (d) Paneth, *ibid.*, [B] **7**, 155 (1930); (e) Paneth and Lautsch, *Nature*, **125**, 564 (1930); (f) Taylor and Jones, *THIS JOURNAL*, **52**, 1111 (1930); (g) Paneth and Herzfeld, *Z. Elektrochem.*, **8**, 9 (1931); (h) Paneth and Lautsch, *Ber.*, **64**, 2702 (1931); (i) Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932).