Zero-Point Energy of Molecular Crystals

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Additional information on J. Chem. Phys.

LETTERS TO THE EDITOR

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Zero-Point Energy of Molecular Crystals

Sufficient data are available to calculate the zero-point energy of some simple molecular crystals. These values may be compared with the corresponding heats of sublimetion calculated to 0°K. The zero-point energy may be calculated from the relation:

$$E(0°K) = \int_0^{\nu \, (max)} F\nu^2(h\nu/2)d\nu = 2.25\theta_{(max)} \text{ calories.}$$

The heats of sublimation were calculated to 0°K from the best recent available data. The results are given in Table I.

In order for the crystal state to exist the sum of the zero-point energy, the attraction potential and the repulsion potential must be negative. From the table it is seen that the ratio of the zero-point energy to the heat of sublimation is greater for the crystal of lighter mass particles. Hence a crystal of the lighter mass particles is the less stable one, in virtue of its high zero-point energy. Further it is reasonable to say that the more negative the above-mentioned sum, the more stable is the lattice to a change of state. As evidence for this the melting points of the monatomic solids in the table increase with the heat of sublimation. Likewise do the melting points of the diatomic solids. Of the latter the value for nitric oxide suggests the existence of (N_2O_4) units. The hydrogen halide crystals have an additional factor entering into the attraction potential, namely the electrostatic potential between the permanent dipoles.

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TABLE I.

	M.W.	$\theta_{(max)}$	$E(0°K)$	$\Delta H(0°K)$	M.P.	$E(0°K)/\Delta H(0°K)$
He [2]	4.	9	20	24(4°K)	0.9	84%
Ne [1]	20.2	63	142	425	24.4	33.
A [1]	39.9	85	191	1830	83.9	10.
H₂ [3]	2.	91	205	216(20°K)	14.	95.
N₂ [4]	28.	68	153	1636	63.3	9.
CO [5]	28.	80	179	1845	68.1	10.
NO [6]	30.	119	268	3680	109.5	7.
O₂ [7]	32.	91	204	2083	54.7	10.
HCl [8]	36.46	128	290	4845	161.	6.
HBr [9]	80.92	92	207	5428	184.6	4.
HI [10]	127.9	73	164	6250	.222.3	3.

[1] *Landolt-Bornstein Physical Tables.*
[2] Keesom and Keesom, Proc. Acad. Sci. Amst. **35**, 736 (1932).
[3] Fowler and Stern, Rev. Mod. Phys. **4**, 697 (1932).
[4] Giauque and Clayton, J.A.C.S. **55**, 4882 (1933).
[5] Giauque and Clayton, J.A.C.S. **54**, 2619 (1932).
[6] Giauque and Johnston, J.A.C.S. **51**, 3208 (1929).
[7] Giauque and Johnston, J.A.C.S. **51**, 2300 (1929).
[8] Giauque and Wiebe, J.A.C.S. **50**, 116 (1928).
[9] Giauque and Wiebe, J.A.C.S. **50**, 2200 (1928).
[10] Giauque and Wiebe, J.A.C.S. **51**, 1447 (1929).

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A Reaction Produced by Light of Very Short Wave-Length

When light from a capillary discharge tube filled with hydrogen at a pressure of 1–2 mm of Hg passes for some time through a fluorite window into air at atmospheric pressure there is formed on the *outside* of the window a light film showing metallic luster. The film can be removed by swabbing the window with absorbent cotton moistened with alcohol.

A more prolonged use of the tube gives rise to a deposit of white powder on top of the film which can easily be brushed off with dry cotton. Both deposits tend to prevent the passage of wave-lengths 1250–1500 Angstroms through the window. An imperfection in the fluorite casts a shadow in such a manner that no deposit is formed at a point where a straight line from the end of the capillary through

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the imperfection cuts the surface of the fluorite.

The powder has been found to be insoluble in distilled water but soluble in dilute hydrochloric acid. It forms after a shorter period of time if the air is moist than if it has been carefully dried. It is possible that light of extremely short wave-length activates the oxygen of the air so that either (1) calcium oxy-fluoride (perhaps) is formed directly, or (2) hydrogen peroxide is produced first and then reacts with CaF_2 to form the deposit. In the latter case it might be expected that a very strong solution of H_2O_2 applied to the window would produce some effect upon it, but upon making this test not the slightest effect could be detected. As yet nothing further is known about the nature of the deposit or of the reaction which causes it.

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Note on the sp^3 Configuration of Carbon, and Correction to Part III on CH₄

In part III[1, 2] of my recent series on CH₄, I overlooked Edlén's[3] new measurements and classifications for the spectra of C I, N II and O III, which appeared just as my article was being completed. The previously unknown sp^3 ^5S state has been found by Edlén in N II and O III, and may now be located in carbon I at approximately 4.1 volts above the ground state s^2p^2 ^3P by extrapolation from N II and O III with the aid of the irregular doublet law. A more accurate, in fact quite remarkable, method of extrapolation based on theoretical considerations has subsequently been developed by Bacher and Goudsmit.[4] It places ^5S at 4.3 volts in carbon. Thus ^5S is not quite as high above the ground state as my previous estimate 5–8 volts based on the Slater-Condon-Johnson F-G relations, but is much closer to this estimate than to the value 1.6 volts so often quoted in the literature. It is somewhat accidental that my estimate was as close as it is, for in applying these relations, I used the experimental values of the sp^3 ^1D and sp^3 ^1P terms, viz., 9.65 and 9.66 volts, usually listed in spectroscopic tables, such as for example Bacher and Goudsmit's book.

Edlén finds that the terms at these positions are certainly due to some other configuration, probably s^2pd. The true sp^3 ^1D and sp^3 ^1P levels have not yet been detected spectroscopically, but may be located by Bacher and Goudsmit's new method at 12.9 and 14 volts, respectively. (Because ^3S of N II was obviously out of line with ^1P and ^1D of C I in the old classification, I suggested in part III that ^3S was due to some other configuration than sp^3; it is now evident that the old ^1D, ^1P were the real culprits.) With the new classification and for more extensive data, the Johnson formulas fit experiment very much better than previously, in fact unusually well for F-G relations. The revised and extended version of Table I of part III is given in Table I.

TABLE I. *Energies, in volts, relative to the ground state s^2p^2 ^3P.*

	Observed			Calculated		
	C I	N II	O III	C I	N II	O III
sp^3 ^5S	[4.3]	5.8	7.4	(4.3	5.8	7.4)
sp^3 ^3S	13.0	19.2	24.4	(13.3	19.2	24.4)
sp^3 ^3D	7.9	11.4	14.8	8.2	11.8	15.2
sp^3 ^1D	[12.9]	17.8	23.1	12.6	18.5	23.7
sp^3 ^3P	9.3	13.5	17.6	(9.3	13.5	17.6)
sp^3 ^1P	[14.0]	20.6	26.0	13.7	20.2	26.1

The "observed" values in square brackets, unlike the others, are not really spectroscopic, but have been computed by Bacher and Goudsmit with their new extrapolation method. Their results are reliable to a few tenths of a volt, and better than the estimates 12.1 and 14.8 for ^1D, ^1P which Edlén obtained with the irregular doublet law. The calculated values have been obtained by the Johnson formulas given in part III, with the parameters chosen so as to yield the proper positions for ^5S, ^3S, ^3P. The corresponding magnitudes of the parameters are those labelled "empirical" in Table II; they would not be much altered if three other states were fitted instead of ^5S, ^3S, ^3P. We make this selection for the three because it makes the maximum deviation between the calculated and observed values in Table I less than with most other choices and so represents a closer approximation to the method of least squares. The Bacher-Goudsmit procedure is sufficiently accurate that it is not important that one of the three states fitted has been located in C I by this procedure rather than spectroscopically.

The values in parentheses are those obtained in part III for carbon by fitting ^1P, ^3D, ^3P with the old classification. We have also listed for comparison the results of Beardsley's theoretical calculations by means of approximate wave functions obtained by a variational method. It is seen that the new classification largely removes the previous qualitative disagreement between the empirical values of the Johnson parameters and those computed by Beardsley.

With the empirical values of the parameters listed in Table II, one calculates from Eqs. (7) and (8) of part III

[1] J. H. Van Vleck, J. Chem. Phys. **2**, 20 (1934).

[2] The following minor errata may be noted in part II (ibid. **1**, 219, 1933): add $\frac{3}{2}(1-\cot^2 \theta) \sin^2 \theta N_{\pi\pi}+\cot^2 \theta N_{ss}$ to the expression (41); in the line before (41) read $\mathfrak{R}=0$ for $N=0$.

[3] B. Edlén, Zeits. f. Physik **84**, 746 (1933); I am indebted to Professor Bowen for calling my attention to this reference and to the use of the irregular doublet law in connection with it.

[4] Bacher and Goudsmit have as yet published only a preliminary abstract on their method; Phys. Rev. **45**, 559 (1934). They have, however, very kindly informed me of the results of the application to carbon in advance of their detailed paper.