

The Superficial Density of the Energy of Natural Vibrations

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combination corresponding to the dissociation of the molecular state, whereas the thermochemical dissociation energies are the lower values counted from the lowest atomic term combination. In thermochemical calculations concerning organic compounds generally energy values corresponding to the tetravalent 5S state of carbon are to be taken into account, the energy values given for CO, CN having to be modified according to $C(^5S) = C(^3P) + 33800 \text{ cm}^{-1}$.⁴ The heat of sublimation of carbon into 5S carbon atoms calculated from these results is 170 kcal.

¹ A. G. Gaydon and W. G. Penney, *Proc. Roy. Soc. A* **183**, 374 (1945).

² L. Gerö and R. Schmid, *Zeits. f. Physik* **111**, 588 (1939), **115**, 47 (1940).

³ J. G. Valatin, in the course of publication.

⁴ R. Schmid and L. Gerö, *Zeits. f. Physik* **105**, 36 (1937).

The Crystal Structure of Polonium

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Santa Fe, New Mexico
September 12, 1946

PRELIMINARY results of the investigations of various physical properties of polonium in this laboratory indicate that polonium undergoes a phase transformation at about 75°C . This was first discovered in experiments by one of the writers (C.R.M.) in measuring the thermal coefficient of electrical conductivity of thin polonium films. A plot of these data exhibits an abrupt decrease of electrical conductivity which is attributed to a phase change. This transformation has been further identified by x-ray diffraction powder photographs. For this work about 100 micrograms (0.5 curie) of pure polonium were vacuum distilled into a capillary about 0.3-mm diameter and 0.01-mm wall thickness at residual gas pressure below 10^{-6} mm of mercury. The metal was concentrated in a short length of the capillary by two successive vacuum distillations in a closed system under a thermal gradient. The capillary was outgassed before use for about 20 hours at 425°C at 10^{-6} mm of mercury pressure. Diffraction patterns have been obtained of three samples using copper and iron radiation. Because of the load formed by the radioactive disintegration of the polonium, the patterns change with time. This change is being followed in an effort to obtain knowledge of the Po-Pb system. The rate of formation of lead is approximately 0.5 percent per day. The photographs used for structure determination were taken from freshly prepared samples so that the lead content was less than 2 percent.

The crystal structure of polonium was studied by electron diffraction by Rollier, Hendricks, and L. R. Maxwell.¹ These workers interpreted the pattern obtained by transmission of thin films of polonium about 100Å thick as that of a monoclinic structure. Table I shows a comparison of their data with those of this investigation. Column 1 gives the ring number, columns 2 and 3 give $1/d^2$ and the intensity estimate for the ring as reported by Rollier, Hendricks, and Maxwell, columns 4 and 5, 6 and 7 give $1/d^2$ and intensity of the low temperature and high temperature forms of polonium, respectively. It appears that the earlier investigation was carried out on a mixture of the two phases.

TABLE I.

Ring No.	Reported in reference (1)	Intensity	$1/d^2$	Low temperature form		High temperature form	
				Intensity	$1/d^2$	Intensity	$1/d^2$
1	VS	0.0890	to 0.0940	VS	0.0897	VS	0.0932
2	M	.1580				S	.1550
3	MS	.1804		S	.1791		
4	W	.2175				MS	.2169
5	MW	.2481				MS	.2489
6	W	.2642		MW	.2692		
7	W	.3634		W	.3560		
8	VW	.370				M	.3735
9	M	.4068				MS	.4047
10	M	.4480		M	.4486		
11	VW	.46				W	.4669
12	S	.5310		MW	.5364	MS	.5279
13	W	.7170		VW	.7177	W	.7155
14	VW	.8000		W	.8062		
15	W	.8465				MW	.8396
16	W	.8953		W	.8978	VW	.8714
17	MW	.9920		VW	.9860	VW	.9947
18	VW	1.149		F	1.164	VW	1.151
19	VW	1.248		VW	1.253		
20	W	1.473		VW	1.519	VW	1.458
						F	1.489
21	VW	1.627		F	1.607	F	1.613
						F	1.638

The high temperature form is present in the capillary when the surroundings are at room temperature. The polonium is maintained above the transition temperature by the heat evolved in stopping its alphas (theoretically 27.42 calories/curie/hour). The low temperature form was found after the capillary had been cooled for several hours in an air stream at about -10°C .

Complete structures have not yet been worked out for the two forms of polonium. Preliminary calculations show that the low temperature form fits a simple cubic lattice with $a = 3.34\text{Å}$. It has been pointed out to us by Dr. W. H. Zachariasen that the high temperature form can be indexed as a simple rhombohedron with $a = 3.36\text{Å}$ and $\alpha = 98^\circ 13'$. A rough density determination is being made.

This work is being carried out under contract between the University of California and the Manhattan District, Corps of Engineers, War Department.

¹ Rollier, Hendricks, and Maxwell, *J. Chem. Phys.* **4**, 648 (1936).

The Superficial Density of the Energy of Natural Vibrations

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July 26, 1946

WHEN solving different physical problems one is often confronted with the necessity of summing up the energy of natural vibrations of a restricted body.

The solution of this problem for the case of the electron gas is known to correspond to Sommerfeld's theory of metals. A calculation of the energy of acoustic vibrations gives according to Debye the thermal energy of a solid body. Finally, Planck's law of the blackbody radiation corresponds to a summation of the energy of electromagnetic vibrations. In all the above-mentioned cases, however, this summation has always been carried out without taking into account the boundary conditions,

i.e., neglecting the effect due to the superficies of the vibrating body.

Our having taken into account this effect^{1,2} leads to a calculation of the superficial density (in Gibbs's sense of the term) of the energy of natural vibrations. For the first of the above problems this superficial density gives a correct idea of the main features of the surface tension of metals. For the second problem a calculation of this kind results in establishing the dependence of the specific heat of dispersed bodies and the surface tension of solid bodies on the temperature. By considering the third problem along the same lines the surface tension of the radiation has been calculated.

While solving the first problem¹ it was essential to bear in mind that the electrons when fixed on the boundaries of the body cannot occupy energy levels with quantum numbers equaling zero. It was also important to estimate the error due to the substitution of the integration for a summation of the energy of natural vibrations. The latter process requires a determination of the number of whole points in the sphere. By effecting these calculations on the basis of Vinogradoff's paper³ we derived the following equation for the calculation of the surface tension of metals

$$\sigma = 56,400(\gamma/A)^{1/3} \text{ dyne} \cdot \text{cm}^{-1}, \quad (1)$$

where A is atomic weight and γ is density of the metal, $\text{g} \cdot \text{cm}^{-3}$.

A comparison with experimental data has shown that Eq. (1) expresses the order of magnitude and the dependence of the surface tension on the density of the electron gas.

An important factor in the solution of the second problem² is the fact that for an entirely free surface, account should be taken of the presence of the Rayleigh and transitional (from ordinary to Rayleigh) waves. This could be only done by considering a vector problem.

By making use of Lamb's⁴ solution of the problem of the vibrations of the infinite thin plate, we derived the following equation for the specific heat of a non-compressible solid body:

$$c_v = 9Nk \left[\frac{4}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{x}{e^x - 1} \right] + \frac{4.26 N^{2/3} k F^{2/3} l^{2/3}}{V^{2/3}} \left[\frac{6}{x^2} \int_0^x \frac{\xi^2 d\xi}{e^\xi - 1} - \frac{2x(e^x - 1) + x^2 e^x}{(e^x - 1)^2} \right] \quad (2)$$

which at low temperature passes into:

$$c_v = \frac{467.56}{V_m \cdot x^3} + \frac{61.3F}{V_m^{2/3} x^2 \cdot N_A^{1/3}} \quad (3)$$

In these equations N is the number of atoms contained in the body in question, with volume V , surface F , and length of edge of base l ; x and ξ have the same meaning as in the Debye theory: $x = h\nu_{mx}/kT$; $\xi = h\nu/kT$; V_m is molecular volume; N_A is Avogadro's number.

The first terms in Eqs. (2) and (3) are the usual expressions for the specific heat of a solid body according to the Debye theory. An estimation of the second term in Eq. (3) shows that a measurement of the specific heat of

dispersed bodies (catalysts and activated charcoal, for example) at low temperature may serve as a method for determining their specific surface. The difference in the specific heat of activated charcoal and graphite, for example, as established by Simon and Swain,⁵ corresponds to the specific surface of charcoal in its order of magnitude.

The authors wish to express their gratitude to Professor I. E. Tamm and Professor M. A. Leontovitch for a number of valuable suggestions made by them while discussing the results of the present investigation at the different stages of its progress.

¹ A. Brager and A. Schuchowitzky, *Acta Physicochimica U.S.S.R.* **21**, 13 (1946).

² A. Brager and A. Schuchowitzky, *Acta Physicochimica U.S.S.R.* (in press).

³ I. Vinogradoff, *Trans. (Trudy) Stekloff Math. Inst. Acad. Sci. U.S.S.R.* **9**, 17 (1935).

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⁵ F. Simon and R. Swain, *Zeits. f. physik. Chemie* **B28**, 189 (1935).

Upper and Lower Bounds to Rayleigh's Frequency for a Vibrating System

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April 18, 1946

THE variation method of quantum mechanics has been extended by D. H. Weinstein² to yield upper and lower bounds for the eigenvalues of the wave equation. The method of Weinstein may be extended to the frequencies of a system of coupled harmonic oscillators. The characteristic equation of the system may be written as

$$V k_i = \lambda_i T k_i,$$

where V and T are the real symmetric potential and kinetic energy matrices, respectively, k_i is a real eigenvector (normal mode), and λ_i is the corresponding real positive eigenvalue ($\lambda_i = 4\pi^2 \nu_i^2$, where ν_i is the frequency). The secular equation for vibrations thus contains two non-commutable symmetric (real Hermitian) matrices, and in this respect differs from the wave equation of quantum mechanics, which contains a single Hermitian operator (the Hamiltonian). However the secular equation may be made isomorphic with the wave equation by transforming to a representation in which T is reduced to the unit matrix and V remains symmetric. The method of Weinstein may then be applied. Alternatively, the method with modifications may be applied directly to the secular equation in its original form. In either case the following result is obtained.

At least one eigenvalue, λ_i , lies within the range

$$\mu_1 \pm (\mu_2 - \mu_1)^{1/2},$$

where

$$\mu_1 = (k' V k) / (k' T k),$$

$$\mu_2 = ((V k)' T^{-1} (V k)) / (k' T k).$$

k is an arbitrary (variation) vector. Primed and unprimed vectors are row and column vectors, respectively. $\mu_1 = 4\pi^2 \nu^2$, where ν is the frequency of the system when it is forced by means of constraints to vibrate in a non-normal mode k .³ μ_1 and μ_2 are positive or zero. If k is an eigenvector, k_i , $\mu_1 = \lambda_i$, and $(\mu_2 - \mu_1)^{1/2} = 0$. If k is not an eigenvector,