THE DYNAMICAL THEORY OF THE DIAMOND LATTICE.

Part III. The Diamond-Graphite Transformation.

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1. Introduction.

IT is common knowledge that diamond is spontaneously transformed to graphite or black carbon at high temperatures. There have been many investigations to find out whether the transformed substance is really graphite or contains any other modification of carbon and to determine the exact temperature of transformation of diamond. That the transformed substance consists of minute crystals of graphite has been established by two Hungarian investigators Emerich Szarvasy and Béla Lányi.[1] They found that the transformation was rapid at 1760° C. but unchanged diamond was still present. On Röntgen examination, they found that the relative intensities of the stronger graphite lines are the same in natural or artificial Acheson graphite and in graphite formed from diamond by graphitization. The size of the sub-microscopic crystals of graphite formed from diamond at 2000° C. was about the same as those of graphite produced from methane. G. Friedel and G. Ribaud[2] who have studied the weak birefringence in diamond have also studied the transformation of diamond to graphite and they find the temperature of transformation to be 1885° C. P. Libeau and M. Picon[3] have also studied the transformation with their technique of high temperature heating and they place the temperature of the rapid transformation at about 2000° C. At lower temperatures they find that the transformed substance consists not only of graphite but also of black diamond which gives the same X-ray pattern[4] as diamond itself. M. de Kay Thompson and P. K. Frölich[5] have also studied the conversion of diamond to graphite

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[1] Emerich Szarvasy and Béla Lányi, *Math. Naturw. Anz. Ungar. Akad. Wiss.*, 1931, **48**, 137.

[2] G. Friedel and G. Ribaud, *Comptes Rendus*, 1924, **178**, 1126.

[3] P. Libeau and M. Picon, *Comptes Rendus*, 1924, **179**, 1059.

[4] W. Gerlach, *Zeit. f. Anorg. und Alg. Chemie*, 1924, **137**, 331.

[5] M. de Kay Thompson and Per K. Frölich, *Trans. Amer. Electro-chem. Soc.*, 1923, **43**, 161.

at various temperatures for various times of heating confirming that the transformed substance is graphite by Brodie's Test. They place the temperature of slow transformation at 1650° C. and rapid transformation at 1750° C. and remark that diamonds turn black at 1200° C. due to the numerous cracks causing the absorption of light by total reflection. If this explanation is genuine, it seems to offer also an explanation for the blackening noticed by P. Libeau and M. Picon at such temperatures. The conclusion of Vogel and Tamman[6] who have studied the conversion of diamond, that diamond starts converting to graphite at 1000° C. appears to require modification in the light of the remark of M. de Kay Thompson and P. K. Frölich. There are many others who have studied the transformation from the time of Francis I who burnt a portion of diamond at the focus of a large concave mirror. Among them are Jacquelain,[7] v. Schrötter,[8] Moisson,[9] Rose[10] and Hon. C. A. Parsons and A. A. C. Swinton.[11]

The purpose of this paper is to explain as to how the graphite structure can be derived from that of diamond by a simple transformation and also to calculate the temperature at which diamond transforms to graphite. The calculated temperature is in satisfactory agreement with the experimental determinations. The ideas followed up here seem to be not very special to the diamond-graphite transformation itself but can have extensions for similar types of transformation of other substances.

2. The Diamond-Graphite Transformation.

It has been shown by X-ray analysis that the diamond structure[12, 13] is made up of two cubic face-centred lattices interpenetrating one another in a manner such that an atom of one lattice is equally nearest to four atoms of the other lattice, the C-C distance being 1·54 Å and the edge of the unit cubic cell being 3·56 Å. Bernal,[14] Hassel and Mark[15] and others have shown that the graphite structure is made up of series of parallel plane equidistant layers of carbon atoms and that each layer is a hexagonal net of atoms such that half the atoms in a layer lie directly along the lines parallel to the c-axis through half the atoms of *both* the adjacent layers and the other half lie along

6 R. Vogel and G. Tamman, *Zeit. f. Phy. Chemie*, 1910, 69, 598.

7 Jacquelain, *Ann. d. Chim. et Phy.*, 1847, 20, 468.

8 A. R. v. Schrötter, *Sitzungsber. Akad. Wiss.* (*Wien*), 1871, 63, 465.

9 H. Moisson, *The Electric Furnace*; *Comptes Rendus*, 1893, 117, 423.

10 G. Rose, *Monatsber. Berliner Akad.*, 1872, p. 685.

11 Hon. C. A. Parsons and A. A. C. Swinton, *Proc. Roy. Soc.* (*A*), 1907, 80, 184.

12 W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.* (*A*), 1913, 89, 27.

13 W. Ehrenberg, *Zeit. f. Kristall.*, 1926, 63, 320.

14 J. D. Bernal, *Proc. Roy. Soc.* (*A*), 1924, 106, 749.

15 O. Hassel and H. Mark, *Zeit. f. Phy.*, 1924, 25, 317.

the lines parallel to the c-axis through the centres of the hexagons of the adjacent layers, the C-C distance being 1·42 Å and the distance between the layers being 3·41 Å. Knowing the above structures of diamond and graphite, one can now raise a very natural and important question as to how we can derive the graphite structure from the diamond structure. In the following we have proposed a solution for the above question and have calculated the temperature at which diamond converts to graphite, which agrees well with the experimental determinations of the said temperature.

In Part I,[16] it has been pointed out by the author that the vibration of the two cubic face-centred lattices of diamond is Raman-active but infra-red inactive and that it has the frequency 1332 cm.$^{-1}$ We now seek the origin for the conversion of diamond to graphite in the above vibration which is triply degenerate. When the temperature of the crystal is raised or when its internal energy is increased, the amplitude of the vibration increases. At a definite increase of the amplitude, we will show in the following that the instability of diamond sets in. We will first give the purely geometrical aspect of the problem and then present its physical aspect in which we have followed a method for calculating the temperature at which the lattice vibration is of sufficient amplitude to favour the diamond-graphite transformation.

3. The Geometrical Aspect of the Transformation.

In the following we will show that the diamond structure can be transformed to a graphite-like structure by the following elementary operations:—

(a) A definite displacement of the two cubic face-centred lattices of diamond relative to one another along a particular direction (Figs. 1 and 2).

(b) A definite homogeneous dilatation of the whole crystal along the same direction (Fig. 3).

(c) A definite homogeneous gliding of the planes obtained by the above two transformations perpendicular to the same direction (Fig. 4.)

(a) If we displace the two cubic face-centred lattices of diamond relative to one another along a diagonal of the unit cubic cell by 1/12 the length of the diagonal or increase the length of the C-C bonds parallel to the diagonal by a third of it, we get a structure which resembles apparently the graphite structure and which we call it as the a-pseudo-graphite structure. The following are its properties:—

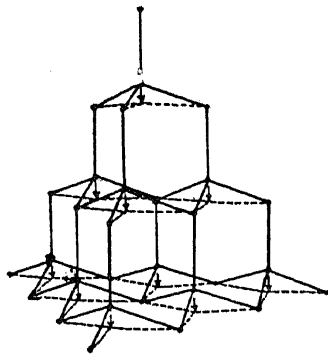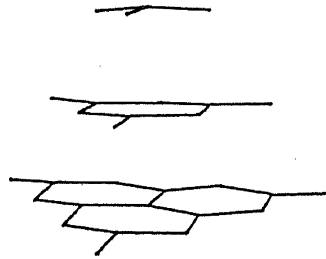[16] N. S. Nagendra Nath, *Proc. Ind. Akad. Sci.* (*A*), 1934, 1, 333.
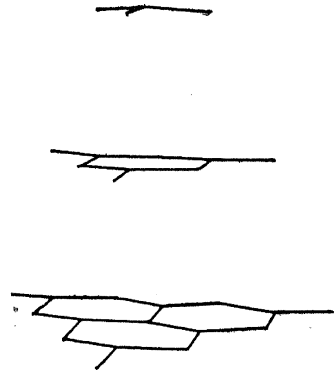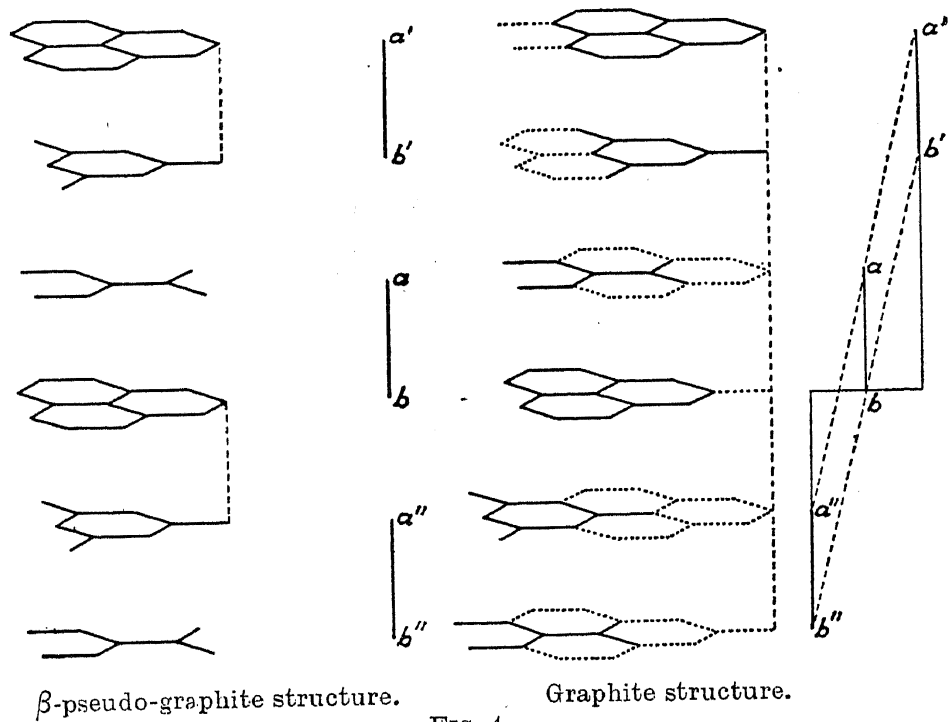
FIG. 1.   FIG. 2.   FIG. 3.

FIG. 1—Diamond structure→ α-pseudo-graphite structure.
FIG. 2—α-pseudo-graphite structure.
FIG. 3—β-pseudo-graphite structure.

β-pseudo-graphite structure.   Graphite structure.

FIG. 4.

(1) The α-pseudo-graphite structure is similar to the graphite structure in that it is made up of equidistant parallel plane layers of carbon atoms, each layer being a hexagonal net. But half the atoms in a layer A are directly along the normals to the planes through half the atoms of only one

of the adjacent layers B and the same set of half the atoms in A are directly along the normals to the planes through the centres of the hexagons of the remaining adjacent layer C ; the remaining set of half the atoms in the layer A will be directly along the normals to the planes through half the atoms in the layer C and the same atoms in A will be directly along the normals through the centres of the hexagons in B.

(2) Assuming the C-C distance in diamond to be $1 \cdot 54$ Å, we can easily calculate the C–C distance in a plane of the α-pseudo-graphite structure. It is $1 \cdot 54$ sin $[\cos^{-1} (-\frac{1}{3})]$ Å $= 1 \cdot 54 \times 2 \sqrt{\frac{2}{3}}$ Å $= 1 \cdot 45$ Å. This agrees pretty closely with $1 \cdot 42$ Å in graphite determined by X-ray analysis.

(3) The distance between the plane layers in the α-pseudo-graphite structure is $(1 \cdot 54 + 1 \cdot 54/3)$ Å or $2 \cdot 05$ Å while it is $3 \cdot 41$ Å in graphite.

(b) This transformation is only a simple homogeneous dilatation of the α-pseudo-graphite structure along a normal to its planes by the ratio $3 \cdot 41/2 \cdot 05$ or $1 \cdot 66$. We will call the transformed structure after the above operation as the β-pseudo-graphite structure which is practically identical with the graphite structure in the C–C distance, the distance between the layers and the structure of atoms in each layer except the symmetry of the planes taken as a whole. For example, every plane is a plane of reflection in the case of the graphite structure while it is not so in the case of the α- or β-pseudo-graphite structures. The next process to be described consists in transforming the β-pseudo-graphite structure into the graphite structure.

(c) The successive plane layers in the β-graphite structure may be symbolically represented by

$$. \quad . \quad . \quad A \quad B \quad C \quad A \quad B \quad C \quad . \quad . \quad .$$

and those in graphite may be represented by

$$. \quad . \quad . \quad A \quad B \quad A \quad B \quad A \quad B \quad . \quad . \quad .$$

where all the atoms in any of the planes A, B, C cannot be superposed on the atoms of any one of the remaining by the motion of the plane along a normal to the parallel planes. This is obvious in virtue of the property (1) in (a).

The required transformation of the β-graphite structure to the graphite structure is accomplished by considering a particular kind of gliding motion of the planes of the β-graphite structure. It consists in moving all the planes along a C-C direction lying in the planes with two adjacent planes as a rigid unit such that an unit suffers relative displacements with its adjacent units, which are equal in magnitude to the C-C distance but are opposite in sign. A clear pictorial representation of the transformation is given in the preceding figures.

4. The Physical Aspect of the Transformation.

It is clear from the above that there exists a simple continuous process by which we can derive the graphite structure from that of diamond. We shall now discuss its bearing on the physical aspect of the transformation.

We know that both diamond and graphite are normally stable substances. The stability of a crystal implies that the energy of the normal configuration is a minimum for all infinitesimal displacements of the lattice. With this idea in view, let us now discuss the course of the energy curve during the diamond-graphite transformation. While discussing it, *we ignore the forces between the layers in graphite as they are, we hope, exceedingly feeble compared to the valence forces in the planes.* As the process starts from diamond, the energy of the lattice increases in accordance with the fact that the energy of normal diamond is minimum for all infinitesimal displacements of the lattice. Similarly, starting from graphite to diamond the energy of the lattice also increases. As the process under consideration is a continuous one, the above means the existence of at least one stage at which the energy of the lattice is maximum, *i.e.*, a stage at which the energy of the lattice no longer increases either from the diamond side or the graphite side. But there cannot be more than one such stage or else it would imply the existence of minima of energy or of stable configurations in between the maxima distinct from those of diamond or graphite which seems to be highly physically improbable. In other words, the above considerations mean that there exists a single finite potential barrier between the diamond and the graphite states. We will call the stage of the lattice having the energy of the peak of the barrier as the α-stage.

If we now increase the thermal energy of diamond which is exhibited as the vibrational energy of its atoms, to such an extent that it will have the energy of the α-stage, the immediate instability of diamond will set in. Since diamond requires a definite temperature to possess a definite heat content from the thermal point of view, we can calculate the temperature at which diamond becomes unstable if we know the energy of the lattice at the α-stage.

The next question will be as to how to plot the energy curve during the process of transformation quantitatively. It appears to be exceedingly difficult to give even a fairly reasonable answer to this question. But we make here an approximation which will not be perhaps far from the truth. We know from molecular spectra that the course of the potential energy curve of a diatomic molecule is given for a fair approximation by a Morse function. In the case of diamond, we will assume a Morse function characterised by the constants D and *a* for all the chemical bonds in it. As the

Morse function is generally valid for fairly large variations of the internuclear distance of a diatomic molecule, we can assume the Morse function of the C–C bonds in diamond to be valid so long as diamond is stable. That is, the Morse function of the C–C bonds in diamond may be regarded as valid till the α-stage. To get an approximate function for the energy curve between the α-stage and the graphite state, we think of the transformation of the graphite structure to that of diamond. Regarding the C–C bonds in the layers of graphite to be all identical in character so far as our calculations are concerned here, we assume a Morse function characterised by the constants D′ and a′ for all the C–C bonds in graphite and also assume that it is valid between the graphite state and the α-stage. One may say that our approximation is weak in this case for we have ignored the forces between the layers. It is no doubt a defect, but it is one which cannot be remedied immediately and justifiably. However, we believe a part of the defect is compensated for in our assumption that the C–C bonds in the planes of the graphite structure will have the same character till the α-stage instead of the fact that there is a gradual weakening of the C–C bonds in the planes and the gradual appearance of the C–C bonds perpendicular to the planes.

The dissociation energy D of a normal C–C bond[17] is $72 \cdot 6$ K. cal./gm. mol. We know from the data on the Raman spectra of organic compounds that the force constant of the C–C bond is in the neighbourhood of about 4×10^5 dyn./cm., the expression for the force constant from the Morse formula being $2D a^2/N$. From this, it follows that a is $\approx 2 \times 10^8$. Now we can regard the dissociation energy of a C–C bond in graphite to be $1\frac{1}{3}$ times that in diamond for it is observed by Roth[18] and his collaborators that the heats of combustion of diamond and graphite are practically identical. So D′ is $96 \cdot 8$ K. cal./gm. mol. We now assume that the force constant of a C–C bond in graphite is about $1\frac{1}{3}$ times that in diamond. To this assumption, we attach no physical significance whatsoever ; we are only aiming at an approximate value of the force constant of a C–C bond in graphite. With this assumption $a′ \approx 2 \times 10^8$.

Let $r′$ be the internuclear distance of the C–C bonds parallel to the line of displacement and r be the internuclear distance of the other C–C bonds

[17] K. Fajans, *Ber. der Deut. Chem. Ges.*, 1920, 53, 643; 1922, 55, 2826.

Prof. K. Fajans gives the values 75 K.cal./gm. mol. and 100 K. cal./gm. mol. for D and D′ respectively. The value $72 \cdot 6$ K. cal./gm. mol. for D has been taken from the work of Prof. E. Hückel. This difference does not affect our calculations in this paper to any appreciable extent.

[18] W. A. Roth and H. Wallasch, *Ber. der Deut. Chem. Ges.*, 1913, 46 (1), 896.

W. A. Roth, *Zeit. f. Electrochem.*, 1915, 21, 3.

W. A. Roth and G. Naeser, *Zeit. f. Electrochem.*, 1925, 31, 461.

equally inclined to the line of displacement. As we proceed from the diamond state to the α-stage r' is a definite function of r as there is only one co-ordinate during that interval.

If E_α corresponds to the energy gained by a gram-atom of the diamond lattice when it comes to the α-stage,

$$E_\alpha = \frac{D}{2}\left[\left\{1-e^{-2(r'_\alpha - 1\cdot54)}\right\}^2 + 3\left\{1-e^{-2(r_\alpha - 1\cdot54)}\right\}^2\right]$$

$$= \frac{3D'}{2}\left\{1-e^{-2(r_\alpha - 1\cdot42)}\right\}^2 \tag{1}$$

where $2D$ and $3D'/2$ are the dissociation energies of gram-atoms of diamond and graphite respectively and r's are given in Ångstrom units and their values at the α-stage are denoted by the subscript α. Solving the equation (1), we find

$$r'_\alpha = 1\cdot68\text{ Å} \quad \text{and} \quad r_\alpha = 1\cdot50\text{ Å}.$$

Hence the α-stage in the process of the transformation occurs when the two cubic face-centred lattices are displaced apart along a diagonal of the unit cell by $(1\cdot68-1\cdot54)$ Å or $0\cdot14$ Å. We also find

$$E_\alpha = 2920\text{ cals./gm. atom.}$$

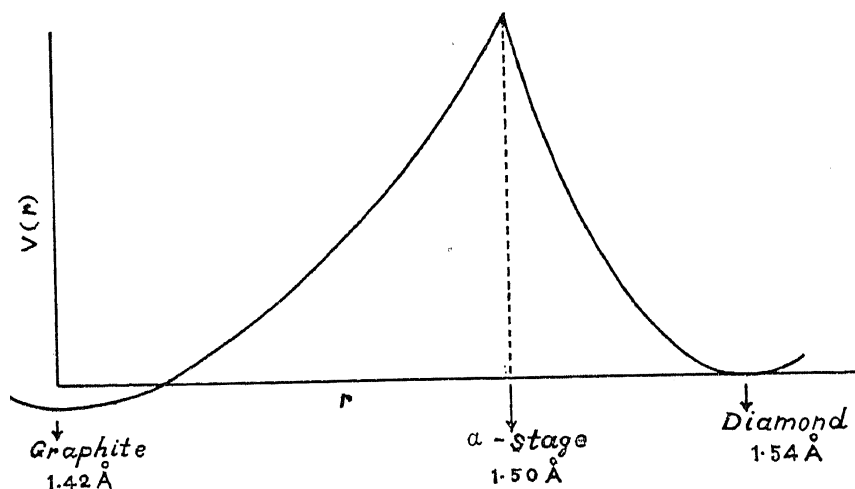The potential energy curve of the transformation is drawn in Fig. 5.

FIG. 5—The potential energy curve between the diamond and the graphite states as a function of r. The initial energy of the diamond lattice is taken as zero.

The above calculations mean that the diamond lattice will only be stable if the change in the C–C distance parallel to the line of displacement does not exceed $0\cdot14$ Å. So, if we increase the thermal energy of diamond which is exhibited as the vibrational energy of its atoms to such an extent that the lattice vibration will have an amplitude of $0\cdot14$ Å, the instability

of diamond will set in. Since the lattice vibration is triply degenerate, the maximum heat content of diamond without its being unstable is 2920×3 $=8760$ calories/gm. atom. We make now a calculation of the temperature at which the instability of diamond will set in and at which diamond will have the maximum heat content.

Using the Einstein formula for the heat content, we get

$$\frac{3 \, R \, \Theta}{\exp (\Theta/T) - 1} = 8760 \tag{2}$$

where $\Theta = h\nu/k$, where the frequency ν corresponds to the characteristic frequency expressed in absolute units. If we assume that the characteristic Einstein frequency of diamond has a magnitude equal to the Raman frequency 1332 cm.$^{-1}$ (in wave numbers), we get $\Theta = 1907$. Solving (2), we get

$$T \approx 2290 \text{ A.}$$

$$\approx 2000° \text{ C.}$$

The temperature T may also be calculated by the use of the Nernst-Lindemann formula for the heat content of a crystal, which gives satisfactory results for the specific heat of diamond at higher temperatures. According to it

$$\frac{3}{2} R \left[\frac{\Theta}{\exp (\Theta/T) - 1} + \frac{\Theta/2}{\exp (\Theta/2T) - 1} \right] = 8760 \tag{3}$$

where the value for Θ is 1940 as given by Nernst and Lindemann[19] themselves. Solving the equation (3), we get

$$T \approx 2110 \text{ A.}$$

$$\approx 1850° \text{ C.}$$

These calculations of the temperature at which diamond converts to graphite stand in good agreement with the experimental determinations which lie between 1650° C. and 1885° C., the temperature of rapid transformation being about 1750° C. according to M. de Kay Thompson and P. K. Frölich and Emerich Szarvasy and Béla Lányi.

The author is highly thankful to his professor Sir C. V. Raman for his great and helpful interest in this work.

5. Summary.

The transformation of the diamond structure to the graphite structure is explained in terms of three elementary operations, one of which is a definite displacement of the two cubic face-centred lattices of diamond relative to one another. It is shown here that for a certain displacement of the

[19] W. Nernst and F. A. Lindemann, *Ber. Berliner Akad.,* 1911, 1, 494; *Zeit. f. Electrochem.,* 1911, 17, 817.

component lattices, diamond attains maximum energy of its configuration and becomes unstable. The temperature at which diamond becomes unstable and transforms to graphite is calculated and is shown to be in good agreement with the experimental determinations.

The ideas followed up here seem to be not very special to the diamond-graphite transformation itself but can have extensions for similar types of transformation of other substances.

Note added in proof.—While this paper was in the Press, two papers by W. Lasareff have appeared (*Jour. Phys. Chem.*, 1935, **39**, 913; *Physica*, 1935, **2**, 737) in which he has calculated the dissociation energy of a C–C bond in diamond. The value given in *Physica* is 132 ± 3·5 K. cals./mol. for D, departing greatly from the values known till now which range between 70—80 K. cals. Lasareff has argued that a carbon atom in diamond is in the (^{5}S) state while a carbon atom in the gaseous state is in the (^{3}P) state and that the difference between the energies of these two states has to be considered when calculating the dissociation energy of a C–C bond in diamond by the help of the data regarding the sublimation heat. However, it should be noted that this great change in the dissociation energy of a C–C bond does not affect our calculations of E_a, as Da^2 the coefficient of the quadratic term r^2 does not vary for it is equal to NK/2 where N is the Avogadro number and K is the force constant of the C–C bond whose value has been assumed to be $\approx 4 \times 10^5$ dyn./cm. Thus a change in D with the corresponding change in a affects only higher order terms. Thus our results should not be affected to a great extent by a change in D. We have made calculations of a, a', r_a, r_a' and E_a assuming Lasareff's value for D (D' = 4D/3 = 176 K. cal./mol.). The value of a is $1·48 \times 10^8$ cm.$^{-1}$ and the values of r_a and r_a' are the same old values 1·50Å and 1·68Å respectively. E_a would be 3040 cals./gm. atom. It follows from the above that T is $\approx 2080°$C. according to the Einstein formula and that it is $\approx 1900°$C. according to the Nernst-Lindemann formula. These values are again in agreement with the experimental determinations.