

## An Experimental Contribution to the Problem of Diamond Synthesis

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## An Experimental Contribution to the Problem of Diamond Synthesis

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Pressure up to 30,000 kg/cm<sup>2</sup>, and in one case 45,000 kg/cm<sup>2</sup>, has been applied to graphite alone, or to graphite seeded with diamonds, at temperatures above 2000°C. In order to maintain temperatures for times of the order of seconds it is necessary to make the apparatus large, a commercial 1000-ton press being used to generate the pressure. Two methods were used, external heating with rapid transfer of the heated specimen to the pressure vessel and application of pressure, and internal heating by a modified thermite reaction set off by the pressure itself. No detectable transformation of graphite to diamond was found in any of the experiments. In the experiments with internal heating it was established that the rate of inversion of diamond into graphite at a temperature above the melting point of molybdenum is a function of the pressure. The individual points are considerably scattered, but the

mean points lie roughly on a straight line running from 100 percent graphitization at 15,000 kg/cm<sup>2</sup> to 0 percent at 30,000 kg/cm<sup>2</sup>. Linear extrapolation would, therefore, indicate reversible transition from graphite to diamond at higher pressures. It has not been possible to check this by direct experiment. The graphite formed from diamond under these conditions has the same x-ray structure as ordinary graphite, indicating that there are no previously unknown modifications of graphite in the present range to complicate the problem. In an appendix the theoretical evidence is considered and the conclusion drawn that linear extrapolation of the equilibrium curve between graphite and diamond from data up to 1000°C gives too high values of pressure in a range above 2000° where the velocities become appreciable, and that the equilibrium curve more probably curves upward.

### INTRODUCTION

IN order to achieve the transition from graphite to diamond, it is necessary not only to produce conditions such that the stability of diamond is higher than that of graphite as indicated by the thermodynamic potentials, but it is also necessary to reach temperatures so high that the transition will run with appreciable velocity. Within the last twenty-five years improved values of the thermodynamic parameters, in particular the heats of combustion, have revised previous estimates of the relative stability of diamond and graphite. At 0° absolute the discussion of Rossini and Jessup<sup>1</sup> indicates that the most probable pressure of reversible transition from graphite to diamond is 13,000 kg/cm<sup>2</sup>. This pressure increases with increasing temperature at a rate depending on the thermodynamic parameters, in particular on specific heat and thermal expansion. I had found how to handle pressures of the order of magnitude of tens of thousands of kg/cm<sup>2</sup> as a matter of routine in the laboratory at room temperature, and had proved such pressures impotent to produce the transition,<sup>2</sup> which will not run at pressures as high even as 400,000 kg/cm<sup>2</sup>. The controlling

factor under ordinary conditions is, therefore, the velocity of transition. Judging by the known velocity of inversion of diamond into graphite at atmospheric pressure, temperatures of the general order of 2000°C or more would seem to be necessary if the transition is to run appreciably in the times available in the laboratory.

The natural method of attaining temperatures of this magnitude would be by internal electrical heating, and I did make various experiments with fine wires electrically heated within the pressure medium. The technical difficulties of any such method were evidently great, however, both because of the greatly enhanced thermal conductivity of ordinary substances under high pressure and because of increased chemical reactivity at high temperatures. Although methods of electrically heating the specimen *in situ* in the pressure vessel doubtless are not ruled out, it seemed to me that other methods, such as external heating, rapid transfer to the pressure vessel and rapid application of pressure, would be instrumentally more feasible. It was also obvious that any such method as this would have to be carried out on a fairly large scale if temperatures were to be maintained for times sufficient to allow the transition to run appreciably. My previous experiments up to pressures of 50,000 kg/cm<sup>2</sup> had been carried out in vessels

<sup>1</sup> F. D. Rossini and R. S. Jessup, *J. Research Nat. Bur. Stand.* **21**, 491-513 (1938).

<sup>2</sup> P. W. Bridgman, *J. App. Phys.* **12**, 461-469 (1941).

of only 0.25-inch internal diameter. Rough calculations indicated that in order to maintain temperatures in the reactive region for times of the order of several seconds, which was long enough to seem worth while, an increase would be necessary in the linear dimensions of eight-fold, or a 500-fold increase in mass. Apparatus of this magnitude was beyond my own unaided resources, and I was fortunate to obtain the sponsorship and financial support of three commercial companies, which considered the extension of range of conditions beyond those previously utilized in attacking this problem to be sufficient to justify their support. Dr. Zay Jeffries was primarily responsible for making the contacts; the companies were: General Electric, Carborundum, and Norton. Work began under an agreement with these companies in January, 1941. The goal set for the apparatus was 30,000 kg/cm<sup>2</sup> in a region 2 inches in diameter and several inches long at a temperature above 2000°C, 2500° if possible.

The apparatus was set up and the experiments made in the Dunbar Laboratory of Harvard University. The actual experimental manipulations were conducted by various members of the Norton Company, who were responsible for many of the details of the construction. Especially to be mentioned are: Dr. R. R. Ridgway, Associate Director of Research, Mr. E. J. van der Pyl, during the stages of construction and the early experiments, and in the later stages Dr. S. S. Kistler and Mr. W. M. Wheildon. Mr. L. P. Jensen skillfully performed much of the difficult machine work.

#### THE APPARATUS AND METHOD

Pressure was produced by a 1000-ton press, of a regular commercial model manufactured by the Watson Stillman Company, with a few minor changes to adapt it to the particular requirements. The ram of the press was 20 inches in diameter, and was actuated by oil, the pressure in which could be raised to 6400 p.s.i. to develop the maximum thrust. The oil pressure was developed by a commercial hydraulic intensifier with 30 to 1 ratio of areas. The large piston of the intensifier was driven by air pressure, stored in a large tank capable of supporting 250 p.s.i. The air pressure was generated by a

3-hp compressor. In operation, pressure in the intensifier was brought to the predetermined maximum by establishing connection with the air reservoir, and then by suddenly opening a valve to the 20-inch ram, pressure was rapidly generated by the action of the ram on the piston, 2 or 1.5 inches in diameter, of the high pressure chamber. The major part of the stroke, before contact was made with the contents of the high pressure vessel, was produced by an auxiliary piston, mounted within and concentrically with the 20-inch ram, so that a stroke of only a few inches was necessary with the 20-inch ram, thus speeding up the action.

The high pressure container was made conical in shape, and the general method of construction was similar to that used in my first experiments to 50,000 kg/cm<sup>2</sup>. In this apparatus external support is given automatically as pressure increases by the thrust on the piston, which drives the whole vessel into external conical supporting rings. The internal diameter of the pressure vessel was 2 inches and the mean external diameter 8 inches. The external supporting block was 10 inches thick and 36 inches external diameter; this was made compound of five disks each 2 inches thick, instead of a single piece, for facility in heat treatment. In the first experiments the whole two inches internal diameter was used, the high pressure piston being 2 inches in diameter; in the later experiments this was reduced to 1.5 inches, combined with various tapered removable liners, to facilitate disassembly and to minimize effects of fracture. In the course of the work several of the containing vessels fractured and several of the supporting disks. The fractures are to be ascribed in part to the fact that it was not possible under wartime conditions to get the desired grades of steel, but there is doubtless in addition a scale effect, making it more difficult with the larger apparatus to reach the 50,000 that had been attained with the original smaller apparatus. The pistons were a source of major difficulty. At first these were of Carboloy; only once was the full 30,000 attained with a Carboloy piston and this fractured after a brief interval. Small test pistons cut from the material of the larger pistons supported more than 50,000, thus indicating a true scale effect. The problem was finally solved by the use of

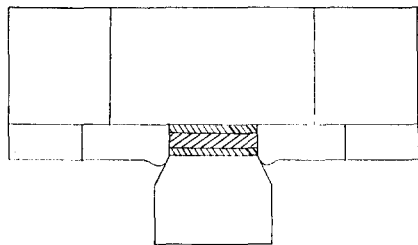


FIG. 1. Method of applying 45,000 atmospheres to hot graphite disk between refractory disks.

steel pistons, which Mr. Whieldon found how to make of the Ajax steel of the Cyclops Steel Company, giving them the special heat treatment, including low temperature soaking, recommended by the manufacturers.

Two types of experiment were performed. In the first a block of graphite was heated to the desired temperature, transferred as rapidly as possible to the pressure chamber and pressure applied. The heating was electrical, by the resistance of the specimen itself. Two graphite electrodes were pressed against the specimen, and current from a transformer capable of delivering 75 kw at 7.5 v stepped down from 2300 v was passed through the specimen until the desired temperature, as indicated on an optical pyrometer, was reached. The graphite block was 1.5 inches in diameter and 2 inches long. When the desired temperature was reached, which might take something of the order of 1 minute, the heating current was broken, the electrodes swung away from the specimen, the specimen pushed home in the pressure chamber by the auxiliary piston, and pressure applied. This sequence of operations was all automatically controlled and consumed altogether about 7 seconds, which was considerably longer than was called for in the original specifications. This time could have been shortened but did not seem worth while in view of the present substitution of the second type of experiment. At first, during the first type of experiment, the 1.5-inch graphite block was pushed by a 2-inch piston into a refractory liner with 0.25-inch thick walls. The expectation was that the refractory, which under normal conditions had little mechanical strength, would crush under the piston, allowing the transfer of full load to the graphite. It developed, however, that under pressures of these magnitudes the refrac-

tory assumes so much compressive strength that pressure on the graphite by no means reached the desired value. For this reason the design was later modified, using a 1.5-inch piston, acting directly on the graphite, the refractory liner now being appropriately mounted inside the removable tapered steel liner already mentioned.

In the second type of experiment external electrical heating was replaced by internal heating, produced by a reaction of the thermite type. At first the thermite reaction was used merely to supplement the external heating, in order to compensate for loss of temperature during the unexpectedly long time of transfer to the pressure vessel. This was done by pushing the heated graphite into contact with a thermite charge previously placed inside the pressure vessel. Under these conditions the thermite nearly always failed to ignite, indicating that the surface temperature of the graphite had fallen to less than 1300°C at the moment of contact. In the modified arrangement, the major part of the pressure vessel, inside a refractory liner of graphite, was filled with a modified thermite mixture, capable of giving a higher temperature than the conventional thermite. Embedded in the center was a piece of graphite containing in the later experiments seeds of diamond. Pressure was applied to the cold set-up by suddenly opening the valve to the ram. The mixture contained an igniting arrangement such that when pressure reached a predetermined value, usually between 10,000 and 15,000 kg/cm<sup>2</sup>, the mixture was ignited. The balance of the stroke necessary to bring pressure up to maximum was short, and since the piston was already in motion, required only a small fraction of a second. The reaction was non-explosive in character. One could thus be sure that maximum pressure and temperature were present in the apparatus simultaneously. Pressure was maintained at its maximum while the contents cooled by conduction.

#### THE EXPERIMENTS AND RESULTS

The experiments with external heating encountered many instrumental difficulties. The preliminary heating of the graphite was usually to 2800°C. Finally a run was made in which it seemed reasonably certain that 30,000 kg/cm<sup>2</sup> had been applied to graphite at temperatures

well above 2000°C and probably nearer 2500°C. Analysis by the Chemical Laboratory of the Norton Company showed no evidence of any transformation to diamond. The initial material of these experiments was highly purified graphite made in the electric furnace by the Norton Company and had an initial density around 1.9. After exposure to these high temperatures and pressures the theoretical density of 2.25 was permanently acquired. At lower temperatures, however, it proved surprisingly difficult to permanently increase the density by pressure alone, and at room temperature the volume elasticity of commercial graphite of 1.9 density is almost perfect. This may result in very large piston displacements on applying pressure, which on more than one occasion led to the erroneous anticipation that the transition had been effected.

One modified experiment with external heating was made. In this, pressure was pushed to the neighborhood of 45,000 kg/cm<sup>2</sup>, but at the expense of an unknown decrease in the effective temperature. In order to attain this high pressure, advantage was taken of a phenomenon which I had previously utilized<sup>3</sup> in my experiments combining high pressure with shearing stress. It is possible, in small localized regions, to reach much higher stresses than can be attained in homogeneously stressed regions because of the support afforded by the surrounding unstressed parts. The experimental arrangements are indicated in Fig. 1. The plane face, 1.5 inches in diameter, of a truncated Carboloy cone, compresses a disk of graphite 0.25 inch thick against the plane face of a massive steel block hardened to maximum hardness. In order to minimize lateral escape of the graphite, the disk is surrounded by a retaining ring of alloy steel in which the Carboloy cone embeds itself. The retaining ring was heat treated to hardness about 40 on the Rockwell *C* scale. The graphite disk was heated to a preliminary 2800°C electrically as in the other method, and then swept by the onrushing piston into forcible contact with the massive block. Direct contact between metal parts and the hot graphite was prevented by refractory disks. Because of the small travel distances, the time interval between cessation of

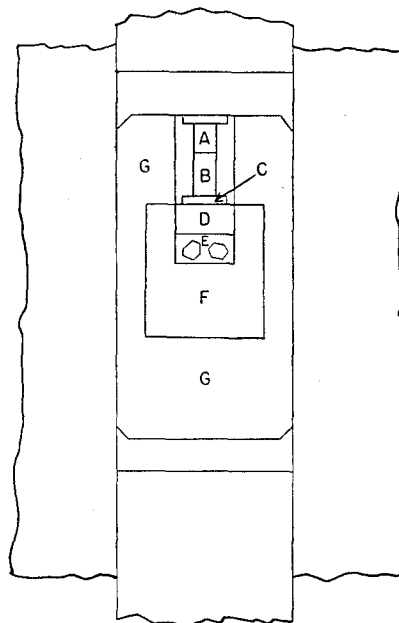


FIG. 2. Apparatus for combining internal heating with pressure. A, tetracene; B, empty space; C, shear plate of hardened steel; D, "igniter" charge; E, diamond seed crystals embedded in powdered graphite; F, main charge for exothermic reaction; G, massive graphite. The other parts are of steel.

heating and the maximum pressure was notably less than in the previous method, but on the other hand, because of the smaller mass of graphite, cooling was more rapid. The result of the experiment was negative. There was copious and dramatic evidence of the magnitude of the stress in the manner in which the graphite was extruded laterally into the retaining steel ring, and there was also evidence of the high temperatures on the surfaces surrounding the graphite in the way in which cracks in the hardened steel had been melted together again. It would be hazardous to estimate the maximum temperature in the interior of the graphite, and the times, and I shall not attempt it. One of the factors to be considered in any calculation is that the mechanical energy of the lateral extrusion was sufficient to raise the temperature 500°C.

The second type of experiment, with internal heating, involved much preliminary work, both to get the proper geometrical arrangements so that ignition of the charge would reliably occur, and also to find the proper chemical compositions for the charge to develop the required amount of

<sup>3</sup> P. W. Bridgman, *Phys. Rev.* **48**, 825-847 (1935).

heat. The conventional thermite mixture was entirely unsuitable, being difficult to ignite, and not developing enough heat. The general arrangement finally adopted is shown in Fig. 2. The reaction is initiated by impact of a fractured shear plate against a pellet of "tetracene." This sets off the "igniter" charge, which in a typical case consisted of 0.080 g sugar and  $\text{KClO}_3$  mixture plus 0.360 g Mg and  $\text{Na}_2\text{O}_2$  mixture. The igniter charge in turn sets off the main charge. The composition of the main charge, which in the final experiments weighed 25 g, varied according to the temperature to be reached. The mixture giving the highest temperature was compounded out of 25 percent of a mixture of Mg and  $\text{Na}_2\text{O}_2$  and 75 percent of a mixture of Mg and  $\text{KClO}_3$ , the latter containing 30 percent excess Mg. For the lowest temperature 13 grams of the mixture just specified was mixed with 12 grams MgO. The temperatures to be expected were calculated by W. F. Moy of the Research Staff of Norton Company and varied from  $6350^\circ\text{K}$  for the first to  $3000^\circ\text{K}$ . The calculation was on the basis of 100 percent efficiency, all the heat being assumed retained in the reacting mass. It would have been difficult to apply all the corrections involved in making a satisfactory calculation of the difference between the theoretical maximum temperature and that actually reached. The time of the reaction is an element of uncertainty; it was not explosive and there was no external indication when the piston was pushed home as to whether the reaction had run or not. The actual temperature was, therefore, roughly obtained by using a small disk of molybdenum embedded in the mixture. This was always found to have been fused with mixtures giving a theoretical maximum temperature of  $3660^\circ\text{K}$  or higher. Allowing an increase of the melting point of molybdenum of  $100^\circ$  above normal for the effect of pressure, this would indicate a loss from the theoretically calculated maximum temperature of not more than  $700^\circ$ .

The experiments with internal heating differed from those with external heating in that diamond seed crystals were used. Three of these were usually used in each experiment, weighing approximately 0.1 g apiece. They were embedded in a graphite capsule weighing about 0.6 g. The degree of graphitization produced was de-

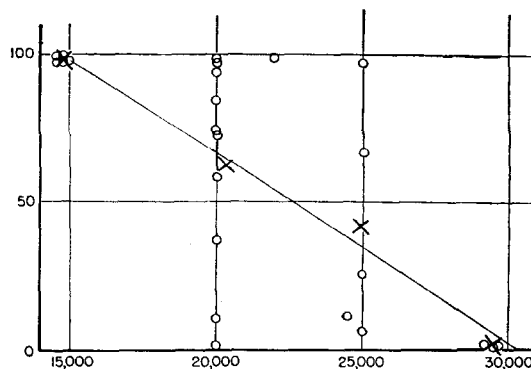


FIG. 3. Percentage of graphitization plotted as ordinate against pressure in  $\text{kg}/\text{cm}^2$  as abscissa. The crosses show the group averages and the circles the individual readings.

termined by the Chemistry Section of the Norton Company under the direction of Dr. N. W. Thibault, by treatment with perchloric acid and weighing the unaltered residue.

The first experiments were made at a constant pressure of  $20,000 \text{ kg}/\text{cm}^2$  with a variety of temperatures. In these experiments total graphitization was found at the higher temperatures and none at all at the lower temperatures. X-ray analysis showed that the graphitized diamond had the same crystal structure as normal graphite. This establishes the fact that the problem is not complicated by the existence of previously unknown intermediate modifications between diamond and graphite. An experiment at  $30,000 \text{ kg}/\text{cm}^2$  at a temperature where there was no graphitization also established the absence of any transition in the reverse direction from graphite to diamond.

In spite of this negative result, indicating that the transition would not run under the conditions attainable with the apparatus, it appeared that positive indications might possibly be attained as to the location of the transition pressure in this temperature range. If this could be done, the whole diamond problem would obviously be much nearer solution. After some trial, for the experimental conditions were somewhat sensitive, a proper mixture, that is, a temperature, was found such that at this temperature graphitization was only partial. Now keeping the mixture and, therefore, presumably the temperature constant the percentage of graphitization was determined as a function of pressure in the range from  $15,000$  to  $30,000 \text{ kg}/\text{cm}^2$ . The results

are shown in Fig. 3. The five runs at 15,000 all gave practically 100 (99.9) percent graphitization, and the three at 30,000 all practically 0 percent (0.2, 1.0, and 0.3 percent). The intermediate runs at 20,000 (11 points), and 25,000 (5 points) show a wide degree of scattering, but the trend is unmistakable, and, as a matter of fact, the averages at 20,000 and 25,000 lie not far out of line with the points at 15,000 and 30,000.

A literal interpretation of these results would, therefore, indicate by extrapolation that above 30,000 kg/cm<sup>2</sup> at this temperature, that is, slightly above the melting point of molybdenum, the percentage of graphitization will be negative, or in other words that the transition from graphite to diamond will actually go under these conditions. The true significance of these results is obscured by the scattering of the points, the complexity of the experimental conditions, and the possibility of a region of indifference between graphite and diamond. It would seem that these experiments have at least established an effect of pressure on the transition, of which there was no previous direct evidence. Further experiments are obviously called for, but at this stage of the investigation the time limit on the contractual relations with the three companies expired, and there is no present prospect that I will be able to continue the investigation.

#### APPENDIX

Two points require comment in this appendix.

In the first place there is considerable superficial resemblance between the first experiments with external heating and experiments, also negative, by Günther, Geselle, and Rebentisch,<sup>4</sup> published in 1943. These experimenters also heated graphite externally, which was then swept by a rapidly moving piston into the pressure vessel. The initial temperature was between 3000 and 3200°C. The graphite specimen was small, being in the form of a thin disk of unspecified thickness and 8 mm in diameter. All parts of the apparatus were of steel. No method of automatic external support of the steel was employed, but merely conventional methods of shrunk on members. Momentary pressures as high as 120,000 kg/cm<sup>2</sup> and static pressures of 100,000 kg/cm<sup>2</sup> were claimed. Stresses of these magnitudes in steel under these conditions may, I believe, be absolutely ruled out, so that it is probable that the pressures and temperatures actually reached were materially less than those claimed. Friction and binding of

the steel pistons (not corrected for) would account for too high stresses, and the small size of the specimen for too high temperatures.

The second point concerns the calculation from thermodynamic data of the relation between pressure and temperature for the reversible transition. The fundamental data, which by universal consent seem to have been accepted as best, are summarized in a paper by Rossini and Jessup in 1938,<sup>1</sup> supplemented by slightly improved data in the paper by Prosen, Jessup, and Rossini<sup>5</sup> of 1944. In the 1938 paper Rossini and Jessup also discussed the most probable relation between pressure and temperature for the reversible transition, and this discussion has been accepted by other authors as the basis for various estimates as to the transition parameters. All these estimates agree in predicting, for temperatures of 2000° or more, pressures considerably higher than 30,000. For example, Leipunskii<sup>6</sup> estimates 60,000 kg/cm<sup>2</sup> at 2000°C and Goranson<sup>7</sup> 50,000 kg/cm<sup>2</sup> at 1000°C. Some comment seems, therefore, called for on the degree of probability that can be attached to an extrapolation of Rossini and Jessup's equation.

The great improvement effected by Rossini and Jessup over previous work was in a better value for the heat of combustion. Recent methods of manufacture have produced a graphite pure enough to give reproducible and reliable values for the heat of combustion, so that in determining the energy content of carbon compounds it is now possible to dispense with the expensive procedure of burning diamonds, which had previously been necessary because of the inferior quality of the available graphite. The difference of the heats of combustion between diamond and graphite enters into the free energy of transition from diamond to graphite, so that a much improved value for this was possible, which was calculated by Rossini and Jessup. But it is important to notice that the improvement affects only the constant term in the free energy. The terms involving the variation of free energy with pressure and temperature are in no wise affected by the work of Rossini and Jessup and continue to rest on the old measurements with unsatisfactory grades of graphite.

The relations of the various factors may be exhibited by writing the equation for the difference of free energy in the form:

$$\Delta F(p, \tau) = \Delta H_0 - \tau \Delta S_0 + \left\{ \int_{\tau_0}^{\tau} \Delta C_p d\tau - \tau \int_{\tau_0}^{\tau} \frac{\Delta C_p}{\tau} d\tau \right\} + \int_{p_0}^p \Delta v dp.$$

Here  $F$  is the Gibbs thermodynamic potential, defined as  $F = E - \tau S + pv$ , where the letters have their customary significance.  $\Delta F$  is defined as  $\Delta F \equiv F(\text{diamond}) - F(\text{graphite})$ .  $\Delta H_0$  is by definition the difference of total heats at an arbitrary temperature  $\tau_0$  at atmospheric pressure  $\{ \Delta H_0 = H_{\tau_0}(\text{diamond}) - H_{\tau_0}(\text{graphite}) \}$  and may be obtained experimentally from the difference of heats of combustion.  $\Delta S_0$  is by definition the difference of entropies at  $\tau_0$  and atmospheric pressure.  $\{ \Delta S_0 = S_{\tau_0}(\text{diamond})$

<sup>5</sup> E. J. Prosen, R. S. Jessup, and F. D. Rossini, *J. Research Nat. Bur. Stand.* **33**, 447-449 (1944).

<sup>6</sup> O. I. Leipunskii, *Uspekhi Khimii* **8**, 1519-1538 (1939).

<sup>7</sup> R. W. Goranson, *Sci. Mon.* **51**, 528 (1940).

<sup>4</sup> P. L. Günther, P. Geselle, and W. Rebentisch, *Zeits. f. anorg. allgen. Chem.* **250**, 357 (1943).

$-S_{\tau_0}(\text{graphite})\}$ .  $\Delta C_p$  is the difference of  $C_p$  at atmospheric pressure and is a function of temperature.  $\{\Delta C_p = C_p(\text{diamond}) - C_p(\text{graphite})\}$ .  $\Delta v$  is the difference of volume  $\{\Delta v = v(\text{diamond}) - v(\text{graphite})\}$  and is intrinsically negative. The integration with respect to pressure is performed at temperature  $\tau$  from atmospheric pressure to  $p$ . The transition always runs either with decreasing  $F$  or, in the limit at equilibrium, with no change in  $F$ . Under ordinary conditions the phase which has the larger  $F$  is the unstable phase.

If it can be assumed that at atmospheric pressure  $\Delta C_p$  becomes and remains zero above a certain temperature, then above this temperature  $\Delta F$  is approximately linear in pressure and temperature. This is the assumption that has been made by various authors in extrapolating to higher temperatures. The data have been directly determined only to 1100°C and Rossini and Jessup have been careful in their paper to state that this is the range of applicability of their formulas. What now is the probability of a vanishing of  $\Delta C_p$  above a certain temperature and an eventual linear course of the curve? From the theoretical point of view, as suggested by Dulong and Petit's law, and neglecting electronic contributions, it would be expected that eventually  $C_v$  rather than  $C_p$  would become equal at high temperatures. But now  $C_p$  and  $C_v$  for diamond and graphite differ by an abnormally large amount. The relation is given by the formula

$$C_p = C_v - \tau \left( \frac{\partial v}{\partial \tau} \right)_p^2 / \left( \frac{\partial v}{\partial p} \right)_\tau.$$

The difference between  $C_p$  and  $C_v$ , particularly at the higher temperatures, is abnormally large for diamond both because its compressibility is abnormally small, being 30 times less than that of graphite, and because its thermal expansion appears to rise abnormally rapidly. The formulas for best volumes quoted by Rossini and Jessup indicate that at 1000°K the thermal expansion of diamond is 36 percent greater than that of graphite. Altogether, the excess of  $C_p$  over  $C_v$  is 60 times greater for diamond than graphite at 1000°K and increases further with rise of

temperature. At this temperature  $C_p$  for diamond is 15 percent greater than  $C_v$ . Furthermore, the best formula quoted by Rossini and Jessup for specific heats gives a reversal of sign for the difference of  $C_p$  at 1100°C.

Altogether it is, therefore, probable that above 1000°K the contribution of the terms  $\int_{\tau_0}^{\tau} \Delta C_p d\tau - \tau \int_{\tau_0}^{\tau} \frac{\Delta C_p}{\tau} d\tau$  to the thermodynamic potential tends to become increasingly negative. This means that the transition curve is not linear, but the slope,  $d\tau/dp$ , rises increasingly, and the pressure obtained by linear extrapolation becomes increasingly too high.

Another much rougher and more elementary argument indicates the plausibility of an upward curvature of the equilibrium line. The slope of the transition line is, according to Clapeyron's equation:

$$d\tau/dp = \tau \Delta v / L.$$

Any variations in  $\Delta v$  may be expected to be of relatively minor importance because of the abnormally large absolute value of  $\Delta v$  for this transition, with the result that any effects of pressure and temperature on  $\Delta v$  would be expected to be of less importance than for more normal substances. Also the variation in latent heat may be expected to be relatively small in view of the direct experimental results which I have found for a large number of polymorphic transitions measured under pressure. This leaves outstanding, therefore, that  $d\tau/dp$  is approximately proportional to the absolute temperature, and therefore the equilibrium line curves upward.

All things considered, it would seem to me that there are possibilities of such large uncertainties in the calculation of the thermodynamic parameters of the transition line in the extrapolated temperature region, between 2000° and 3000°C, that little more than an indication as to orders of magnitude can be expected. Greater weight should, I believe, be attached to the location of the curve suggested by the experimental determination of the change with pressure of the inversion velocity as described in this paper.