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ON THE QUESTION OF THE RELATION BETWEEN THE SHAPE OF CRYSTALS AND THE THERMODYNAMIC CONDITIONS OF THEIR GROWTH

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Works of recent years on the synthesis of diamonds ([1–6]) have shown that there is a close connection between the shape of diamond crystals and the thermodynamic parameters of synthesis (P and T). In this connection it is of interest to find an analytical dependence between the equilibrium shape of crystals and the thermodynamic parameters under which they are formed. In doing so we take into account that the shapes assumed by diamond crystals under synthesis conditions are not, in particular because of the extremely rapid nature of this process, final equilibrium shapes, but evidently reflect a tendency toward acquiring an equilibrium shape. This follows already from the fact that most artificial diamonds are characterized by combinations of two or more simple forms, one of which predominates. At the same time it is assumed that the predominant form is the equilibrium form toward which the crystal tended under the given synthesis conditions.

Several methods are known for determining the equilibrium shapes of a crystal as a function of the thermodynamic conditions of their growth. Thus, the rule for determining G-faces, which is applicable to certain types of lattices, is derived from the regularity of crystal growth and the formation of two-dimensional nuclei under conditions of thermodynamic equilibrium. In the Gibbs–Wulff method ([7,8]) it is assumed that the shape of a crystal is equilibrium if the free energy of the crystal is minimal; here the free energy is represented as the sum of the volume E_V and E_S–the surface free energy. In this case, for equal volumes the crystal assumes the shape that corresponds to the minimum of E_S. In the method of Stranski and Kaischew ([9]) it is assumed, as applied to all surface plane nets, that to detach one particle it is necessary to expend a certain average work of detachment, and on this basis the equilibrium shapes are calculated.

Figure 1. Dependence of the quantities α_{ok} (a), α_{od} (b), and α_{dk} (c) on temperature and pressure.

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Both these methods, as well as the rule for determining G-faces, use the Thomson–Gibbs equation ([10]), which relates the ratio of the vapor pressure of a crystal of finite size to an infinite one with the temperature and the size of the crystal. However, these methods do not establish a direct connection between the equilibrium shape of the crystal and the corresponding thermodynamic parameters (P and T).

We have attempted to outline such a connection by considering not the process of crystal growth itself, the course of which is usually determined by the simultaneous action of several factors (temperature, pressure, concentration, impurities, etc.), but only the final crystal shapes to which this process leads. Such an approach makes it possible to take into account only those factors that play the dominant role in the occurrence of one or another form of crystalline polyhedra, namely pressure and temperature.

For thermodynamic systems in which P and T exert a dominant influence on the shape of crystals, there should, in our opinion, exist a relatively simple relation between the indicated parameters and the equilibrium shape of the crystalline polyhedron that is part of the given system.

Let us assume that the number of faces (Γ), vertices (B), and edges (P) of a convex crystal-

the crystalline polyhedron are variable quantities that we can specify. In view of the existence of a functional relation between G, B, and P, found by Euler ($G = P - B + 2$), one of these variables (P) may be omitted, since it is a function of the other two. We introduced the quantities G and B as additional parameters of the thermodynamic system; since the normals to the faces represent the direction of possible crystal growth, and the number of vertices is the number of different combinations of these faces. Then the ratio $G/B = \theta$ is the average number of faces incident on one vertex or, evidently, the mean degree of freedom of the growth of faces from one vertex. Drawing an analogy with a homogeneous system, one may represent the quantity θ as the number of faces per phase, where by a phase one may regard a vertex linking a definite combination of faces.

Fig. 1. Dependence of the quantities α_{ok} (a), α_{od} (b), and α_{dk} (c) on temperature and pressure.
1—at 1900°K; 2—1700°K; 3—1500°K; 4—at 10^5 atm.; 5—$5 \cdot 10^4$ atm.; 6—$3 \cdot 10^4$ atm.

Proceeding from the fact that the shape of a crystal is the result of definite reactions, we attempted, on the basis of the law of mass action ([11]), to find

a dependence between the thermodynamic parameters and the crystal shape, assuming that the ratio G/B is proportional to the total number of molecules of all components of one phase of a homogeneous system. In this case the expression of the law of mass action for different values of θ takes the form

$$K(P,T) \sim aP^{-\theta}T^{\theta(\frac{C}{R}+1)} \exp\left(-\frac{\theta q}{RT}\right), \tag{1}$$

where a is a constant independent of the crystal shape, C is the specific heat, and q is the chemical heat of reaction, which are close for different forms.

In connection with the adopted assumptions, we cannot directly determine the quantity $K(P,T)_i$ for different (i) crystal forms. However, one may say that the ratio of the quantities $K(P,T)_i$ for different forms

$$\alpha_{ij} = K(P,T)_i / K(P,T)_j, \tag{2}$$

where i and j are definite crystallographic forms, reflects the preferential formation of one of them under particular thermodynamic parameters. In this sense we considered the possibility of the formation of different forms of diamond crystals under various thermodynamic conditions (for diamond $q = 1897$ J/mole, $C = 6.8$; 7.6; 8.4 cal/deg $\cdot$ mole at 1500, 1700, 1900°K, respectively ([12,13]).

The results of these calculations according to the formulas

$$\alpha_{\text{ok}} = \frac{K(P,T)_{\text{okt}}}{K(P,T)_{\text{kub}}} \approx P^{-0.58}T^{0.58(\frac{C}{P}+1)} \exp\left(-0.58\frac{q}{RT}\right), \tag{3}$$

$$\alpha_{\text{od}} = \frac{K(P,T)_{\text{oct}}}{K(P,T)_{\text{dodec}}} \simeq P^{-0.48}T^{0.48(\frac{C}{P}+1)} \exp\left(-0.48\frac{q}{RT}\right), \tag{4}$$

$$\alpha_{\text{dk}} = \frac{K(P,T)_{\text{dodec}}}{K(P,T)_{\text{cub}}} \simeq P^{-0.1}T^{0.1(\frac{C}{R}+1)} \exp\left(-0.1\frac{q}{RT}\right) \tag{5}$$

are presented in Fig. 1.

From Fig. 1 (curves **4, 5, 6**) it follows that, as the temperature increases at constant pressure, crystals of dodecahedral habit may be encountered more often than those of cubic habit, and at the same time the relative number of crystals of octahedral habit increases with increasing temperature in comparison with the number of crystals of dodecahedral and cubic habits.

As the pressure increases at constant temperature, the calculations give the opposite picture (Fig. 1, curves **1, 2, 3**).

The calculated data obtained agree qualitatively well with the experimental results ([1]-[6]). Unfortunately, we do not know of statistical data on the quantitative distribution of diamonds of different habit as a function of temperature or pressure during synthesis that would make it possible to perform a quantitative assessment of the agreement between the experimental data and the calculations.

It is not difficult to note (Fig. 1) that the dependence of crystal shape on temperature is more sharply expressed than on pressure and, consequently, maintaining it is more important in the process of diamond synthesis. Obviously, the considerable scatter of crystal shape from experiment to experiment under identical synthesis conditions is due mainly to deviations of the temperature from the specified value and, possibly, to considerable temperature fluctuations in the cell.

Table 1

Estimate of the thermodynamic parameters of growth of crystals from the "Mir" tube

Quantity	Value
Ratio of the numbers of crystals of octahedral and dodecahedral habit ([14], [15])	~ 10
Ratio of the total areas of octahedral and dodecahedral surfaces	$\sim (1 \div 2) \cdot 10^2$
Estimate of changes in crystal shape introduced in the subsequent time periods after formation of the tube (dissolution, abrasion, breakage of crystals, etc.), as well as those associated with the distribution of diamonds of different habit over horizons	~ 2
Approximate value of the ratio of the total areas of octahedral and dodecahedral surfaces immediately after formation of the diamonds	$\sim (2 \div 4) \cdot 10^2$
Estimated value of the thermodynamic parameters at which the diamonds in the "Mir" tube grew (assuming $\gamma_0 = \alpha_{\text{od}}$ (Fig. 1b))	$P = (4 \div 6) \cdot 10^4$ atm.$T = 1700 \div 1750$°K

On the basis of the calculations carried out using statistical data on the habit of natural diamonds ([13], [14]), one may say that, on average, they grew at high temperatures of the order of $1700 \div 2000$°K and at not very high pressures of the order of $3 \cdot 10^4 \div 6 \cdot 10^4$ atm. The results of an analogous estimate of these parameters for the "Mir" tube are summarized in Table 1.

Obviously, the estimates we have obtained are approximate in character, which is connected with the assumptions made regarding the constancy of the quantities a, C, and q for all crystal forms, the independence of the quantities a and q from temperature and pressure, and a number of other unaccounted factors that could substantially affect the shape of the crystals (impurities, concentration fluctuations, etc.). At the same time, the qualitative agreement of the calculated data obtained with the experimental data makes it possible to regard the proposed approach as expedient.

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Note: Figure translations are in progress. See original paper for figures.