

Metastable phases, phase transformations, and phase diagrams in physics and chemistry

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Abstract. Concepts of a ‘phase’ and a ‘phase transition’ are discussed for stable and metastable states of matter. While condensed matter physics primarily considers equilibrium states and treats metastable phases as exceptions, organic chemistry overwhelmingly deals with metastable states. It is emphasized that many simple light-element compounds — including most hydrocarbons; nitrogen oxides, hydrides, and carbides; carbon monoxide CO; alcohols and glycerin — are also metastable at normal pressure in the sense that they do not correspond to a minimum Gibbs free energy for a given chemical composition. At moderate temperatures and pressures, the phase transformations for these metastable phases are reversible with the fulfilment of all laws of equilibrium thermodynamics over the entire range of experimentally accessible times. At sufficiently high pressures ($> 1–10$ GPa), most of the metastable molecular phases irreversibly transform to lower-energy polymer phases, stable or metastable. These transitions do not correspond to the equality of the Gibbs free energy for the involved phases before and after the transition and so they are not first-order in the ‘classical’ sense. At normal pressure, the resulting polymer phases can exist at temperatures above the melting point of the original metastable molecular phase, as the examples of polyethylene and polymerized CO dramatically illustrate. As pressure is increased further to 20–50 GPa, the PV contribution to Gibbs free energy gives rise to stable high-density atomic phases. Many of the intermediate-energy polymer phases can likely be synthesized by methods of ‘classical’ chemistry at normal pressure.

1. Concept of a phase of a substance in physics and chemistry

The phenomenon of phase transitions belongs, to an equal extent, to the field of investigation of both physicists and chemists. The idea of a ‘phase’ of matter was introduced by J W Gibbs [1] to designate the state of bodies with a definite ‘phase’, i.e., with a certain set of momenta and coordinates of particles (atoms or molecules) composing the matter. For equilibrium states with a minimum thermodynamic potential, Gibbs suggested the term ‘phase of dissipated energy’.

Later, the meaning of the term ‘phase’ underwent a certain evolution; at present, the definitions of the ‘phase of matter’ differ slightly in the physical and chemical literature. Thus, according to [2, 3], the ‘phase’ is a thermodynamically equilibrium state of a substance differing in physical properties from other possible states (phases) of the same substance. The terms ‘equilibrium state’, ‘stable phase’ mean that this is a state with a minimum value of thermodynamic potential (Gibbs potential in the case of variable temperature and pressure) among all possible states.

At the same time, according to [4–6], the ‘phase’ is a part of a system that is homogeneous in chemical composition and thermodynamic properties and separated from other parts (phases) by interfaces. The difference between these definitions is that in chemistry the condition of thermodynamic equilibrium is, as a rule, not applied to the ‘phase’. In physics, the thermodynamic nonequilibrium is assumed to exist, in principle, but is subject to a proviso: “... Sometimes a nonequilibrium metastable state of a material is also called ‘phase’ (metastable phase)” [2]. Gibbs used the term ‘passive resistance forces’ instead of the concept of ‘metastability’, by analogy with ‘dry’ friction [1].

This seemingly insignificant difference in the definitions adopted in physics and chemistry may lead to dramatic consequences. An incomplete understanding of the specificity of metastable molecular organic and inorganic compounds frequently leads to quite erroneous treatment of experimental data concerning phase transitions in these systems. This paper is devoted to an analysis of quasi-

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equilibrium and nonequilibrium phase transformations in metastable phases.

2. Metastable phases are ‘pariahs’ in classical thermodynamics

A metastable state is any state that corresponds to a local minimum in configurational space separated by a barrier from the state corresponding to the deepest minimum (stable state). A ‘metastable phase’ is a nonequilibrium state of a substance whose properties change reversibly at the time of experiment or observation. The metastability is ensured by the existence of an energy barrier in the path of transformation of the system into low-lying energy states (Fig. 1). Since the barrier separating metastable from stable states is never infinite in reality, at finite temperatures (and, with allowance for quantum fluctuations, even at a zero temperature), there is always a probability of passing into a stable state in a certain time; i.e., there is always a characteristic ‘lifetime’ of a metastable phase. Thus, the existence of a ‘metastable phase’ unavoidably introduces the factor of time (kinetics), which is absent in thermodynamics. Therefore, strictly speaking, in classical thermodynamics no metastable phases can exist, since in infinite times the system should relax irreversibly into an equilibrium state. However, this rigorous approach is by no means constructive, since it excludes the possibility of analyzing the thermodynamic properties of numerous existing metastable phases of substance for many of which the ‘lifetime’ formally can exceed the age of the universe. The duration of the investigations of phases in a metastable state can vary in a wide range from 10^{-12} to 10^8 s. Apart from short-lived metastable phases of matter, such as overheated and undercooled liquids and undercooled vapor, there also exist long-lived solid metastable phases. A number of metastable crystalline modifications, e.g., diamond and stishovite (a dense modification of silica), have a field of thermodynamic stability at high pressures. Some metastable phases, such as white phosphorus and silicon clathrates, have no stability fields at positive pressures, although they are possibly conditionally stable with respect to other condensed phases at negative pressures (although not to the gaseous phase, which at negative pressures has an infinitely large value of the Gibbs free energy). Some metastable

modifications, e.g., fullerite C_{60} , have no stability region at any pressures and temperatures. The metastable phases that have no P – T stability fields include all glasses and amorphous solids. In a certain range of values of the P and T parameters, the solid metastable phases can exist infinitely long as compared to any reasonable experimental times. Moreover, with changing pressure and temperature, the metastable phases can undergo reversible phase transformations in which all laws of equilibrium thermodynamics are fulfilled (these transformations correspond to the equality of the Gibbs free energy for the phases involved). Such phase transitions can be accompanied by both a reversible change in the structure of the substance (e.g., one- and two-dimensional polymerization of fullerite C_{60} upon heating under pressure; changes in the short-range order upon compression in glassy SiO_2 or in amorphous ice H_2O) and in their aggregate state (e.g., upon melting and crystallization of white phosphorus). A mixture of phases can also be metastable. Thus, Gibbs considered, as an example, a mixture of hydrogen and oxygen, which at moderate temperatures does not transform into the H_2O equilibrium phase for infinitely long times (from the viewpoint of experimental times) [1].

Interestingly, in statistical physics to date constructive methods for testing a system for metastability have been absent. In other words, one can determine whether the system is in a local or in a ground (deepest) minimum only by enumerating all the minima and by comparing their depths. With changing P – T parameters, the ‘lifetime’ of a metastable phase can substantially change and, after reaching certain pressures and temperatures, there arises a probability (substantially differing from zero) of overcoming barriers in experimentally reasonable times (see Fig. 1). Diamond at room temperature can ‘live’ virtually infinitely; at 1400 K, it transforms into graphite in a few months; at 1700 K, in a few hours. White phosphorus under normal conditions (room temperature and normal pressure) exists virtually eternally, while at 700 K it crystallizes into stable red phosphorus in several days. Therefore, diamond or white phosphorus can be considered as long-lived (virtually everlasting) metastable phases under normal conditions and as short-lived metastable phases at high temperatures. Thus, with changing P – T parameters, the metastable phases leave the quasi-equilibrium zone of reversibility (Fig. 2) and relax to thermodynamically equilibrium phases, frequently through intermediate (in energy) states (see Fig. 2). Thus, amorphous and glassy modifications of substances crystallize upon heating; stishovite transforms upon heating to 850 K into glassy silica (as an intermediate state in the course of transformation into equilibrium cristobalite); diamond upon heating under normal pressure in an inert medium transforms into graphite (as was already mentioned above); fullerite C_{60} upon heating under pressure transforms into graphite or diamond through intermediate polymerized and amorphous carbon states; hydrogen–oxygen mixtures begin to react and form H_2O upon heating to above 700 K.

All these transitions to more equilibrium states represent fundamentally irreversible, kinetic processes, which are accompanied by a decrease in the Gibbs free energy and by a corresponding release of heat and are not phase transformations in the strict sense. As a result, for metastable phases we can consider, instead of equilibrium phase diagrams, a nonequilibrium kinetic diagram of transformations (see Fig. 2), part of which (a P – T zone of reversibility) is

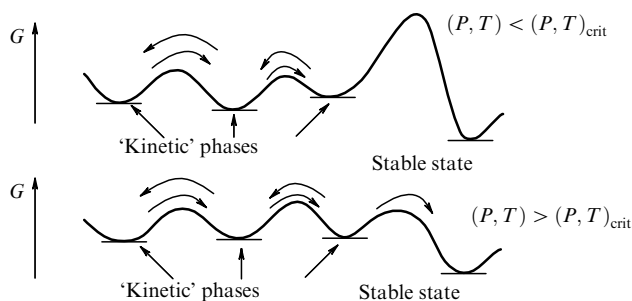


Figure 1. Minima in configurational space corresponding to metastable (kinetic) and stable states of phases. As the temperature and pressure change, reversible transformations between various metastable phases are possible. At pressures and temperatures below critical, no transition to a stable state with a minimum value of the Gibbs free energy occurs in experimentally accessible times. After some critical temperatures and pressures are reached, the energy barrier separating the metastable phases from the stable state decreases and an irreversible transformation into a stable phase can occur in the experimental times.

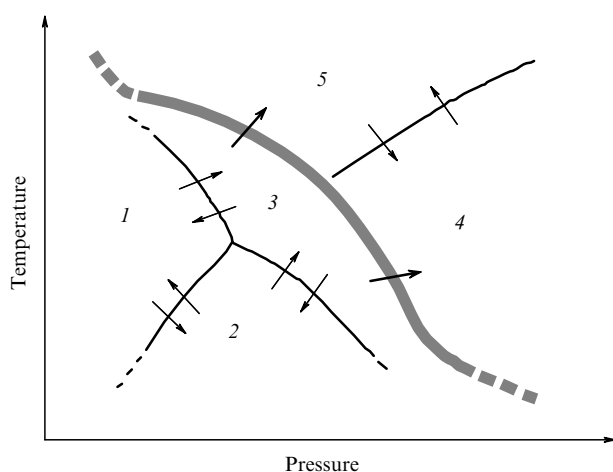


Figure 2. A generalized diagram of transformations of metastable phases. The shaded band corresponds to a zone of irreversible relaxation of metastable phases into equilibrium states; it separates the quasi-equilibrium and equilibrium P - T fields. Inside each field, the transitions between metastable phases (1-2, 2-3, 1-3) and stable phases (4-5) are reversible. The transformations 3-4 and 3-5 from metastable phases into stable states are irreversible.

quasi-equilibrium. We emphasize that the dimensions of the quasi-equilibrium part of the phase diagram depends (logarithmically weakly) on the time of observation or experiment. All these considerations are well known, generally speaking, but in physics the concept of metastable phases is usually considered as marginally exotic. Most of the simple substances that are studied by physicists are stable phases. When analyzing properties of metastable phases, the rigor of thermodynamics is sacrificed to the convenience of description, since in a certain P - T range we can 'forget' the metastable character of phases. Problems appear when we approach the boundaries of the quasi-equilibrium part of the transformation diagram (see Fig. 2), where we should 'recollect' the metastable state of the phases and where the laws of equilibrium thermodynamics stop being fulfilled.

3. Chemistry is the realm of metastable phases

When moving from elemental substances and simple compounds to more complex compounds, especially to organic ones, the proportion between stable and metastable phases changes dramatically. The overwhelming majority of condensed phases of organic compounds are metastable; i.e., they do not correspond to a minimum of the Gibbs free energy for a given elemental composition [7]. For even more complex systems of biological nature, 100% phases are metastable. This means that as the compounds become more complex, the proportion of thermodynamically equilibrium phases becomes progressively smaller and in reality we live in a world of predominantly metastable phases. As a result, the property of equilibrium disappears from the definition of a 'phase' in chemistry and frequently the phase diagrams in chemistry are in fact transformation diagrams (see Fig. 2) with corresponding zones of quasi-equilibrium and irreversible relaxation. Thus, the 'divide' between condensed-matter physics and chemistry in a certain sense is determined by the degree of prevalence of metastable phases among the objects being investigated.

4. At the junction between physics and chemistry: Simple molecular compounds of light elements

Thus, the main objects investigated in physics are stable phases of elemental substances and simple compounds, whereas chemistry mainly studies metastable phases of complex compounds. Problems and misunderstandings usually arise in the frontier field when studying phase transitions in molecular substances based on light element compounds, including simple compounds in the C-O-N-H system. In view of the relative simplicity of these compounds, the physicists usually consider them as 'their' objects, frequently even being ignorant of the fact that the overwhelming majority of condensed phases of these compounds are not thermodynamically equilibrium states. Thus, for example, such a simple compound as molecular ethylene C_2H_4 does not represent the ground state of the system and polyethylene $C_{2n}H_{4n}$ represents a lower-lying energy modification [8]. And what phase of the CH_2 composition is equilibrium at normal pressure? The answer is sufficiently unexpected: the equilibrium state for this composition is a mixture of phases of solid carbon (graphite) and methane (CH_4) in the proportion 1 : 1. Moreover, in the equilibrium concentration diagram for C-H at normal pressure in a wide temperature range there exist only pure hydrogen, graphite, and a single compound, namely, methane, whereas numerous other molecular phases such as ethylene, acetylene, benzene, etc. are metastable with respect to the transition to a mixture of methane and graphite in a corresponding proportion. That this is the case can easily be seen from data on the binding energies for the related molecules [9, 10]: 430 kJ mol⁻¹ for H_2 , 1642 kJ mol⁻¹ for CH_4 , 2225 kJ mol⁻¹ for C_2H_4 , 753 kJ mol⁻¹ for CH_2 , and 1626 kJ mol⁻¹ for C_2H_2 ; the cohesion energy for graphite is 712 kJ mol⁻¹; and the energies of formation of the condensed phases from the molecules CH_2 , C_2H_4 , C_2H_2 , C_6H_6 , CH_4 , etc. do not exceed a few tens of kJ mol⁻¹. At very high temperatures at normal pressure, the molecular states of intermediate compositions in the gaseous phase correspond to the minimum Gibbs free energy (Fig. 3). As temperature decreases and attendant condensation of carbon occurs, the situation changes; most of the molecular phases are only in local minima and are separated by a high energy barrier from the equilibrium state — a mixture of graphite and methane (see Fig. 3). In a similar way, in the equilibrium phase diagram of the C-O-H system, only compounds such as H_2O , CH_4 , and CO_2 are present apart from pure components, whereas other compounds, e.g., all alcohols, are metastable phases (although they melt and boil reversibly, similar to white phosphorus). The fact that many hydrocarbons at normal pressure are not in an equilibrium state has long been known to chemists (see, e.g., [11] and references therein). At the same time, the 'working' range of pressures and temperatures usually employed in chemistry ($T < 500$ K, $P < 1$ GPa) corresponds, as a rule, to the quasi-equilibrium field in the P - T transformation diagram (see Fig. 2), where the metastable states of the phases studied can be 'forgotten'.

In recent years, however, the above substances have been studied in a wider P - T range ($P > 10$ GPa), outside the quasi-equilibrium zone, but their metastability is frequently ignored [12-18]. Sometimes experimentalists study P - T phase diagrams of different molecular compounds of the same composition, e.g., acetylene C_2H_2 and benzene C_6H_6

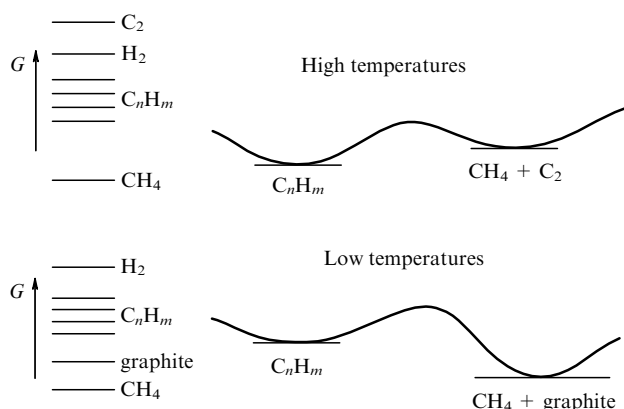


Figure 3. Gibbs free energies for carbon, hydrogen, and hydrocarbons at high temperatures (gaseous phases) and low temperatures (condensed phases). At high temperatures, most gaseous phases based on various hydrocarbon molecules are equilibrium. At low temperatures, the only equilibrium phase is a mixture of methane CH_4 and graphite in appropriate proportion, whereas the hydrocarbons of intermediate compositions exist in a metastable state owing to the existence of an energy barrier for the transition to a mixture of methane and graphite.

[12, 13], without even asking themselves the question of which of the substances is a stable phase. The correct answer is none; both substances are metastable phases. In the quasi-equilibrium field of pressures and temperatures (see Fig. 2), the properties, structure, and aggregate state of such substances change reversibly; however, at sufficiently high pressures, there begin irreversible transformations into lower-lying energy states, e.g., into polymerized phases. In particular, acetylene C_2H_2 and benzene C_6H_6 transform irreversibly into polymer phases and then into amorphous diamond-like carbon saturated with hydrogen (a-C:H) [13, 14, 16, 17]. In this case, the nonequilibrium part of the kinetic diagram of transformations is realized (see Fig. 2).

Apart from hydrocarbons and alcohols, which are all organic substances, there exist, of course, numerous other examples of metastable ‘kinetic’ phases of simple molecular substances. Thus, in the N–H system at normal pressure there is only one equilibrium phase, namely, ammonia NH_3 , whereas molecular phases such as NH_2 , N_2H_2 , N_2H_4 , HN_3 , etc. are metastable with respect to the decomposition into ammonia and molecular nitrogen N_2 (the corresponding binding energies are as follows: N_2 , 942 kJ mol⁻¹; NH_2 , 710 kJ mol⁻¹; NH_3 , 1158 kJ mol⁻¹; N_2H_2 , 1154 kJ mol⁻¹; N_2H_4 , 1696 kJ mol⁻¹; and HN_3 , 1328 kJ mol⁻¹ [9]). In the N–O system, the molecular phases N_2O , NO_2 , N_2O_3 , N_2O_4 , and N_2O_5 are metastable as well (the corresponding binding energies for these molecules are 1103 kJ mol⁻¹ for N_2O ; 927 kJ mol⁻¹ for NO_2 ; 1590 kJ mol⁻¹ for N_2O_3 ; 1908 kJ mol⁻¹ for N_2O_4 ; and 2153 kJ mol⁻¹ for N_2O_5 [9]). In the C–N system, the molecular phases CN, NCN, CNC, CCN, and C_2N_2 also are metastable with respect to the decomposition into solid carbon and molecular nitrogen [10]. Many molecular compounds including phosphorus and sulfur are also metastable phases.

The reason why so many long-lived metastable ‘kinetic’ phases are encountered among the compounds of light elements and only few are found among the compounds of heavy elements lies in the small size of molecules consisting of atoms of light elements. In this case, the distance between the atoms of light elements inside the molecule is noticeably

smaller than that between atoms from different molecules. The molecules are bound by van der Waals forces, which are two orders of magnitude smaller than the interactions inside the molecules. At distances corresponding to a minimum of the potential of intermolecular interaction, the small molecules look almost spherical and the separation of the substance into molecules is well defined. For large molecules such as MgO, SiO₂, etc., the dimensions of the molecules are comparable to their spacing, and the weak intermolecular interactions are replaced by stronger ionic or covalent interactions; in this case, the treatment of molecules as isolated structural units in a condensed medium becomes incorrect. It can easily be understood that the molecular substances ‘go away’ from the quasi-equilibrium P – T field upon compression just in that range of pressures in which the distance between the molecules becomes comparable to the distance between atoms inside the molecules, which corresponds to a severalfold decrease in the specific volume of the substance. The characteristic values of the bulk moduli of substances with a molecular interaction reach several GPa; consequently, the characteristic pressures of ‘irreversibility’ are on the order of 10 GPa.

It is well known that metastable substances cannot exist for a long time at temperatures exceeding the melting temperature of the stable phase [8]. In particular, the metallic high-pressure modifications of hydrogen and oxygen and the polymer modification of nitrogen can potentially exist in a metastable state at normal pressure only at ultralow temperatures, below the melting temperatures of stable molecular phases. However, if the initial molecular phase is itself metastable, then the lower-lying (in energy) modifications obtained from the molecular phase can, certainly, exist in a metastable state at temperatures above the melting point of the molecular phase [8]. As a characteristic example of such a metastable phase, we considered [8] polyethylene, whose temperature stability significantly exceeds that of the condensed phases of molecular ethylene and is fundamentally restricted by the methane–graphite liquidus line. We emphasize once again the irreversibility of transformations of metastable molecular phases into polymer modifications: upon annealing such polymer phases, they certainly do not go back into molecular states.

5. Metastable molecular carbon monoxide CO

In view of the active investigation in recent years of phase transformations under pressure in molecular carbon monoxide (see [18–20] and references therein) and the erroneous treatment of the experimental data obtained, we consider this system separately. At normal pressure, only one compound, CO_2 , is present in the equilibrium concentration phase diagram of the carbon–oxygen system. (The energy of formation of CO_2 is 1598 kJ mol⁻¹; that of CO, 1071 kJ mol⁻¹ [10].) The molecular condensed phases of CO are metastable with respect to decomposition into a mixture of solid carbon (graphite) and CO_2 , which distinguishes the CO compound from its isoelectronic analog N_2 , for which the molecular phases at normal pressure are equilibrium. When studying the phase diagram of CO at high pressures, a transformation into a polymerized modification of CO, which is considered erroneously as a high-pressure phase of the molecular phase, was revealed [18, 19].

In fact, the polymerization of the metastable molecular phase CO at $P \sim 4$ – 5 GPa is a nonequilibrium kinetic

transformation into a lower-lying energy state. According to the results of a computer simulation, the polymerization of CO is accompanied by significant heat release [20]. The polymerized CO phase is metastable at normal pressure up to high temperatures (400–700 K) [19], which is much higher than the melting temperature of the molecular crystal of CO. As in the case of polyethylene, there is nothing surprising in the high thermal stability of the polymerized CO, since the polymerized phase represents a more equilibrium state rather than a high-pressure phase of the molecular modification. Upon heating the polymerized CO phase at normal pressure, a significant amount of heat is released, which also has been erroneously ascribed by Lipp et al. [19] to the existence of energy stored in the polymerized phase (excessive as compared to the molecular phase), which enters into the Gibbs free energy in the form of PV terms. Meanwhile, the simple estimate of the difference between the PV terms for the polymerized phase and the molecular modification at $P \sim 4$ GPa yields a value of ~ 0.5 – 1 kJ mol⁻¹, which is smaller by an order of magnitude than the observed values. In reality, the observed energy release appears to be related to the transition of the polymerized CO phase to an equilibrium state in the form of a mixture of CO₂ and solid carbon (it is these products that are observed after annealing the CO polymer). Note that the picture of nonequilibrium transformations of the molecular CO phase under pressure can be even more complicated; in particular, a disproportionation of the CO compound into C₂O₃ and C₃O₂ modifications can occur, which, in turn, can polymerize [19–21]. In any case, the polymerization of CO under pressure is a nonequilibrium transformation into a lower-lying energy state, similar to the polymerization of ethylene C₂H₄, acetylene C₂H₂, and benzene C₆H₆ under pressure.

6. Stable and metastable phases under strong compression

Thus, the majority of molecular phases of light-element compounds are by no means stable at a given chemical composition and in their equilibrium low-pressure concentration phase diagrams there are only a few phases, such as C, O₂, H₂, N₂, H₂O, CO₂, CH₄, NH₃. We mentioned above that high pressures can serve as a factor in reducing the energy barrier for the transformation of metastable molecular phases into more equilibrium states. At the same time, at sufficiently high pressures the equilibrium concentration phase diagrams themselves can change because of the different PV contributions from the phases of different densities; in particular, a series of unsaturated hydrocarbons can become more energetically advantageous than a mixture of condensed phases of methane and carbon. As a result, sufficiently complex polymerized phases can arise in light-element systems upon compression, not only as energetically intermediate states upon the transformation of nonequilibrium molecular phases, but also as ground-state modifications that are most stable under high pressure. In particular, under certain pressures, the formation of higher hydrocarbons becomes favorable, which is quite important for the abiogenic synthesis of oils (at normal pressure, all oils naturally consist of metastable hydrocarbon phases) [11, 22].

In the case of compounds, a situation can also arise where the molecular phase, stable at low pressures and temperatures, upon compression becomes metastable with respect to a mixture of phases of other compositions; i.e., in

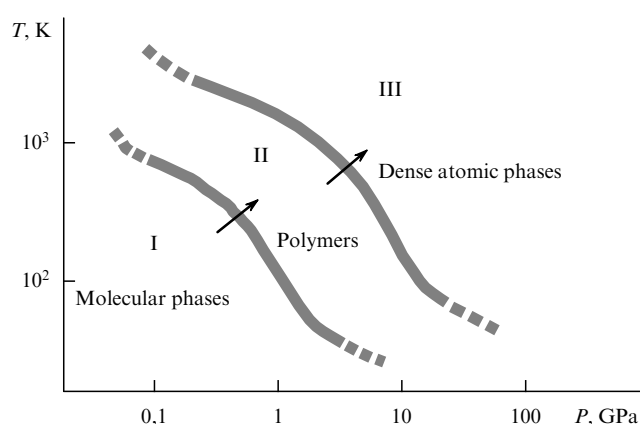


Figure 4. Generalized P – T diagram of transformations for molecular phases. For most of the molecular compounds of light elements, the transitions from zone I to zone II and from zone II to zone III are irreversible kinetic transformations.

Fig. 2 the zone lying at low P – T parameters is really equilibrium and the transition to the zone of nonequilibrium is related to the change in the type of stable phase rather than to a decrease in the barrier for the transition. In addition, if at high pressures the system is to some extent ‘open’ to volatile components, then the phase equilibria in it can change substantially [23].

Thus, all P – T diagrams of molecular compounds of light elements can arbitrarily be divided into three zones (Fig. 4). Zone I corresponds to moderate temperatures and pressures (10–1000 K, < 1 – 10 GPa), at which the Gibbs free energy is almost completely determined by the binding energy of atoms in molecules. Most molecular substances in this zone are in a metastable state.

Zone III is located in the field of ultrahigh pressures (> 20 – 50 GPa), where the Gibbs free energy of most phases is substantially determined by the PV term. The substances in this zone are, as a rule, in a stable state and represent a mixture of simple dense equilibrium modifications (diamond, CO₂, H₂O, etc.). In particular, at pressures in the megabar range ($P > 20$ – 50 GPa) at moderate temperatures the PV contribution to the Gibbs free energy favors the transition of all unsaturated hydrocarbons into a solid solution of hydrogen in diamond; and at high temperatures, it favors the formation of a mixture of diamond and hydrogen. As was noted above, for many hydrocarbons at ultrahigh pressures, indeed the formation of amorphous diamond-like carbon saturated with hydrogen (a-C:H) was observed [13, 14, 16, 17].

Zone II corresponds to intermediate pressures ($P \sim 1$ – 20 GPa) and temperatures (200–1500 K). In this zone, the formation of a large number of both ‘kinetic’ and equilibrium (at a given pressure) polymerized phases is possible. The contributions to the Gibbs free energy from intramolecular and intermolecular interaction and from the PV term for these phases are comparable in magnitude. It should only be remembered that these modifications, as a rule, are not high-pressure phases of the molecular substances, since most molecular substances at normal pressure are themselves metastable. The experiments at ultrahigh pressures in this case indicate which energetically intermediate polymer phases can exist. It is obvious that many of these unusual polymer phases can be synthesized by ‘chemical’ methods at normal pressure.

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