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Metastable phases and ‘metastable’ phase diagrams

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Abstract

The work discusses the qualitative nature of phase transitions for metastable states of substances. The objects of the physics of condensed media are primarily the equilibrium states of substances with metastable phases viewed as an exception, while in chemistry the overwhelming majority of organic substances under investigation are metastable. It turns out that at normal pressure many simple molecular compounds based on light elements (these include: most hydrocarbons; nitrogen oxides, hydrates, and carbides; carbon oxide (CO); alcohols, glycerin) are metastable substances too, i.e. they do not match the Gibbs free energy minimum for a given atomic chemical composition. At moderate temperatures and pressures, the phase transitions for particular metastable phases are reversible throughout the entire experimentally accessible time period with the equilibrium thermodynamics laws obeyed. At sufficiently high pressures (1–10 GPa), most molecular phases irreversibly transform to more energy efficient polymerized phases. These transformations are not consistent with the equality of the Gibbs free energies between the phases before and after transition, i.e. they are not phase transitions in the ‘classical’ meaning. The resulting polymeric phases at normal pressure can exist at temperatures above the melting one for an initial metastable molecular phase. Striking examples of such polymers are polyethylene and a polymerized modification of CO. Many energy-intermediate polymeric phases can apparently be synthesized by the ‘classical’ chemistry techniques at normal pressure. At higher pressures (10–100 GPa) polymerized modifications transform to a mixture of simple stable phases.

The phase transition effect falls equally within the areas of physical and chemical research. The notion of the ‘phase’ was introduced by Gibbs [1] as a condition of a substance with a certain ‘phase’, meaning a set of pulses and coordinates of the particles (atoms or molecules) that make up a substance. At a later time, the meanings of the term ‘phase’ have evolved so that currently the definitions of a phase of a substance used in the literature in physics and chemistry are somewhat different [1–6]. In chemistry, a thermodynamic equilibrium condition is not mandatory for a phase. In physics, a thermodynamic non-equilibrium is allowed in principle but with reservations of the kind in [2]; sometimes the non-equilibrium metastable state of a

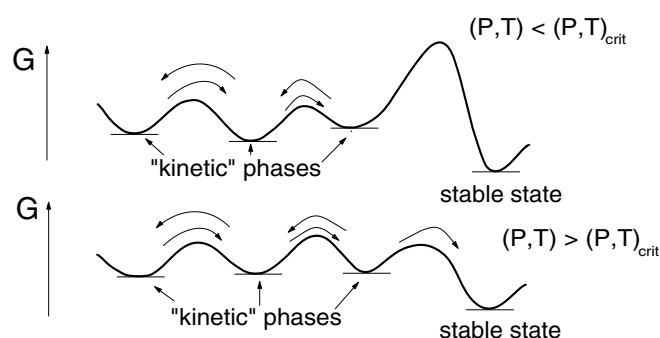


Figure 1. Energy minima in the configuration space. At pressures and temperatures below threshold values metastable 'kinetic' phases can transform into one another but cannot transit to the ground stable state with the minimal Gibbs free energy. At threshold P, T -parameters $(P, T)_{\text{crit}}$ the irreversible transitions from the 'kinetic' phases to the stable modification occur for the experimental times.

substance is also called the 'phase (metastable phase)'. This seemingly minor distinction in the definitions accepted in physics and chemistry has a profound meaning. An incomplete understanding of the peculiarities of metastable molecular organic and inorganic compounds often gives rise to an erroneous interpretation of the experimental data on phase transitions in these systems. In the present paper, we focus on the analysis of quasi-equilibrium and non-equilibrium phase transformations in metastable phases.

The name 'metastable phase' is given to a non-equilibrium state of a substance whose properties change reversibly over the period of experiment or observation. Strictly speaking, there are no metastable phases in classical thermodynamics, as the system, through the infinity of time, should irreversibly relax to the equilibrium state. However, there are some long-lived metastable solid phases whose lifetime at normal conditions exceeds the timescale of the Universe, and their existence cannot be neglected. Time periods of the investigation of phases in their metastable state may vary over a wide range from 10^{-12} to 10^9 s. A number of metastable crystalline modifications, such as diamond, have a high-pressure region of thermodynamic stability. Other metastable modifications, for instance, fullerite C_{60} and amorphous solids, have no stability region at any pressure and temperature at all. In a certain range of the P, T -parameters, metastable phases can undergo reversible phase transformations with all the equilibrium thermodynamics laws obeyed (the transformations match the Gibbs free energy equality for the corresponding phases), and with a reversible change of the structure of substances or even of their aggregate state (for example, during the melting and crystallization of white phosphorus). A phase mixture can be metastable too. Thus, Gibbs considered, by way of example, a mixture of hydrogen and oxygen; at moderate temperatures the mixture does not transform to the equilibrium phase H_2O in an indefinitely long time [1].

A metastable condition of the phases is provided for by the existence of the energy barrier on the way of the transformation of the system into low-lying energy states in configuration space (see figure 1). It is interesting to note that the statistical physics still lacks effective ways of checking the system for metastability. In other words, there is no possibility of determining whether the system is in the local minimum or in the deepest one than through the enumeration of all the minima and through the comparison of their depths. On reaching certain pressures and temperatures, a high probability of overcoming the corresponding energy barriers within the time of the experiment (figure 1) arises; in this case, the metastable phases go beyond the quasi-equilibrium area of reversibility (figure 2) and relax, often through energy-

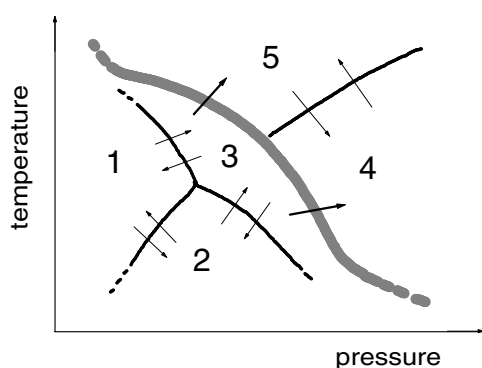


Figure 2. Transitional phase diagram of initially metastable phases. The grey band corresponds to the irreversible non-equilibrium relaxation of metastable phases to the stable modifications and separates the quasi-equilibrium and equilibrium P, T -regions. Inside these regions the transformations (1–2, 2–3, 1–3 and 4–5) are reversible. The transitions 3–4 and 3–5 are irreversible.

intermediate states, to thermodynamically equilibrium phases (figure 2). Thus, on heating, the amorphous modifications of substances crystallize; diamond, if heated at normal pressure in an oxygen-free atmosphere at 1400–1700 K, transforms to graphite; the white phosphorus melt at temperatures ~ 700 K crystallizes into violet–red phosphorus. Fullerite C_{60} on heating under pressure transforms to graphite or diamond through the intermediate polymerized and amorphous carbon states. A hydrogen–oxygen mixture on heating above 700 K begins reacting to form H_2O .

All these transitions to more equilibrium states are fundamentally irreversible kinetic processes, accompanied by the decrease in the Gibbs free energy and the corresponding release of heat; they are not phase transformations in the strict sense of the word. Accordingly, for the metastable phases one should examine a non-equilibrium diagram of kinetic transformations (a transitional diagram; figure 2), which is partially (the P, T -reversibility region) in quasi-equilibrium, rather than an equilibrium phase diagram. We emphasize here that the sizes of the quasi-equilibrium area of the phase diagram depend on the period of observation or experiment. These are commonly known considerations, but in physics the notion of the 'metastable phases' is of somewhat exotic character since most simple substances studied by physicists qualify as stable phases.

When passing from elemental substances and simple compounds to more complex compounds, especially to those of organic nature, the ratio between stable and metastable phases radically changes. The overwhelming majority of condensed phases of organic compounds are metastable, i.e. they do not match the Gibbs free energy minimum for a given composition of elements [7]. For yet more complex systems of biological nature, metastable are 100% of the phases. In other words, as compounds become more complex, the proportion of thermodynamically equilibrium phases goes down, so we materially live in the world of predominantly metastable phases. As we see, in chemistry the property of equilibrium falls outside the concept of the 'phase', and the phase diagrams in fact are often transitional diagrams (figure 2) with their respective quasi-equilibrium and irreversible relaxation regions. Thus, the demarcation line between physics and chemistry of condensed media in a certain sense lies in the degree of occurrence of the metastable phases among the objects of research.

So, the objects of research in physics are primarily the stable phases of elemental substances and simple compounds, while chemistry is basically preoccupied with the metastable phases of complex compounds. The difficulties and ambiguities usually arise in the border region when investigating the phase transitions in molecular substances based on light element compounds, including simple compounds in the system C–O–N–H. Because of a relative simplicity of these compounds, physicists look upon them as 'their' objects; in so doing they are often unsuspecting of the fact that the vast majority of the condensed phases of

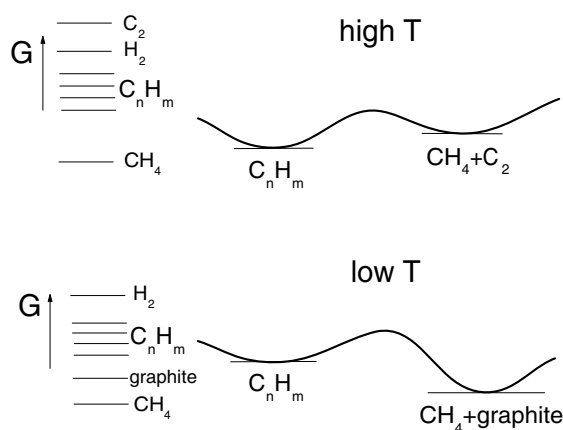


Figure 3. The Gibbs free energy for carbon, hydrogen and hydrocarbons at high temperatures (gas phases) and low temperatures (condensed phases). At low temperatures the equilibrium state is the methane–graphite mixture, and all other hydrocarbons are in metastable state.

the compounds in question are not thermodynamically equilibrium states. For example, as we mentioned in [8] molecular ethylene C_2H_4 is not the ground state of the system; in particular, polyethylene $C_{2n}H_{4n}$ is a more low-lying energy modification [8]. Here we underline that, as regards the given composition, it is the mixture of solid carbon (graphite) and methane (CH_4) in the ratio of 1:1 that will constitute an equilibrium state. Thus, the only substances present in the equilibrium concentration diagram C–H at ambient pressure over a wide temperature range are pure hydrogen, graphite, and a single compound, methane, while other numerous molecular phases like ethylene, acetylene, benzene are metastable with respect to the transition to the methane–graphite mixture in the proper ratio. That this assertion is true can be clearly seen from the data on the bonding energies of molecules [9, 10]: for H_2 —430 kJ mol⁻¹, CH_4 —1642 kJ mol⁻¹, C_2H_4 —2225 kJ mol⁻¹, CH_2 —753 kJ mol⁻¹, C_2H_2 —1626 kJ mol⁻¹, the cohesive energy for graphite—712 kJ mol⁻¹; the energies of the formation of condensed phases from the molecules CH_2 , C_2H_4 , C_2H_2 , C_6H_6 , CH_4 , etc do not exceed tens of kJ mol⁻¹.

For example, reaction of the decomposition of C_2H_4 in a gas state into the mixture of CH_4 plus solid carbon mixture is accompanied by the heat release and energy lowering $1642 \text{ kJ mol}^{-1} + 712 \text{ kJ mol}^{-1} - 2225 \text{ kJ mol}^{-1} = 129 \text{ kJ mol}^{-1}$. For the condensed phases of CH_4 and C_2H_4 this principal result does not change since the values of enthalpy of evaporation (8.3 kJ mol⁻¹ for CH_4 ; 13.5 kJ mol⁻¹ for C_2H_4) and enthalpy of melting (0.94 kJ mol⁻¹ for CH_4 ; 3.3 kJ mol⁻¹ for C_2H_4) are much lesser values in comparison with enthalpy of decomposition. The same is true for the polyethylene. So, both molecular ethylene and its low-lying polymeric phase—polyethylene—are metastable phases in comparison with methane–graphite mixture.

At extremely high temperatures and low pressure in a gas medium the molecular states at the intermediate compositions match the Gibbs free energy minimum (figure 3). The situation changes with the decrease in temperature and carbon condensation: most hydrocarbon molecular phases are to be found only within the local minima and are separated from the equilibrium state, the graphite–methane mixture, by a high energy barrier (figure 3). In a similar way, the only compounds present in the equilibrium concentration diagram in the system C–O–H, besides pure components, are H_2O , CH_4 and CO_2 , while other compounds, including, for example, CO, alcohols or glycerin, are metastable phases (although they melt and boil

reversibly). The fact that most hydrocarbons at ambient pressure are not in the equilibrium state has been known to chemists for quite a time (see, for example, [11] and references therein). On the other hand, the effective range of pressures $P \sim 1$ GPa and temperatures $T \sim 500$ K, employed in chemistry, corresponds to the quasi-equilibrium region in the P, T transitional diagram (see figure 2), where a researcher can 'forget' about the metastable state of the phases under investigation. In recent years, however, the substances in question have been studied over a wider P, T range ($P > 10$ GPa) beyond the threshold values of P, T [12–18]. In the process, the studies have often involved the P, T phase diagrams of different molecular compounds of the same composition, for example, acetylene C_2H_2 and benzene C_6H_6 [12, 13] (the phases of both substances are metastable). In the quasi-equilibrium region of pressures and temperatures (figure 2) the properties, structure, and aggregate state of such substances change reversibly; however at sufficiently high pressure, the irreversible transformations to more low-lying energy states, including polymerization, begin. In particular, acetylene and benzene irreversibly transform to the polymeric phases, and then to amorphous diamond-like carbon saturated by hydrogen a-C:H [13, 14, 16, 17]. In so doing, the non-equilibrium part of the transitional diagram is realized (figure 2).

Metastable substances cannot exist for any significant time at temperatures above the melting temperature of a stable phase [8]. In particular, high-pressure metallic modifications of hydrogen and oxygen, and a polymeric modification of nitrogen at ambient pressure can potentially exist in the metastable state only at ultralow temperatures below the melting temperatures of stable molecular phases. However, as was noted in [8], if the initial molecular phase is metastable by itself, then more low-lying energy modifications obtained from it can undoubtedly exist in the metastable state at temperatures above the melting temperature of the molecular phase in question. The work [8] has offered a good example of such metastable state, namely, polyethylene, whose temperature stability is far in excess of the one for the condensed phases of molecular ethylene, being fundamentally limited by the methane–graphite liquidus line. We again point out the irreversibility of the transformation under pressure of metastable molecular phases to polymeric modifications: on annealing, such molecular phases never transform back to the molecular states.

In addition to hydrocarbons and alcohols, which are nevertheless organic substances, there are, of course, other numerous examples of metastable 'kinetic' phases of simple inorganic substances. Thus, in the system N–H at normal pressure there is only one equilibrium phase, ammonia NH_3 , while NH_2 , N_2H_2 , N_2H_4 , HN_3 and other molecular phases are metastable in relation to the decomposition to ammonia and molecular nitrogen (the respective molecule bonding energies are: 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, HN_3 —1328 kJ mol⁻¹ [9]). In the system N–O, the metastable molecular phases are N_2O , NO_2 , N_2O_3 , N_2O_4 , N_2O_5 (the respective molecule bonding energies are: N_2O —1103 kJ mol⁻¹, NO_2 —927 kJ mol⁻¹, N_2O_3 —1590 kJ mol⁻¹, N_2O_4 —1908 kJ mol⁻¹, N_2O_5 —2153 kJ mol⁻¹ [9]). There is also the system C–N where the molecular phases CN, NCN, CNC, CCN, C_2N_2 , C_3N_4 [10] are metastable with relation to the decomposition to solid carbon and molecular nitrogen. Metastable phases are some alkalis, acids and many other molecular compounds with the participation of the phosphorous and sulfur atoms.

Let us discuss separately such a system as molecular carbon oxide. In recent years, the phase transformations under pressure in this system have been intensively studied ([18–20] and references therein), but the experimental data obtained have often been interpreted erroneously. In the equilibrium concentration diagram in the carbon–oxygen system at normal pressure there is only one compound present, CO_2 (its formation energy is 1598 kJ mol⁻¹, CO —071 kJ mol⁻¹ [10]). The CO molecular condensed phases are metastable with regard to the

decay into the mixture of solid carbon (graphite) and CO_2 ; this distinguishes the CO compound from its isoelectronic analogue, N_2 , for which the molecular phases at ambient pressure are equilibrium. The examination of the CO phase diagram at high pressures has revealed the transformation to a CO polymerized modification, erroneously taken to be a high-pressure phase of the molecular phase [18, 19]. In actuality the polymerization of the CO metastable molecular phase at $P \sim 4\text{--}5$ GPa constitutes a non-equilibrium kinetic transformation to a more low-lying energy state. According to computer simulation data, the CO polymerization is followed by a considerable emission of heat [20]. The CO polymerized phase is metastable at normal pressure up to high temperatures (400–700 K) [19], which is much higher than the melting temperature of the CO molecular crystal. As with polyethylene, it is hardly surprising that polymerized CO demonstrates a high thermal stability, since a polymerized phase is not a high-pressure phase of a molecular modification but is a lower-lying energy state. On heating the CO polymerized phase at normal pressure, a significant amount of heat is released, which was mistakenly ascribed by the authors of [19] to the energy stored up in a polymerized phase (and being in excess of that of a molecular phase) at the expense of the PV -terms in the Gibbs free energy. At the same time, a simple calculation of the difference of the PV -terms for the polymerized phase as against the molecular modification for the transition pressure of $P \sim 4$ GPa gives the value of $\sim 0.5\text{--}1$ kJ g⁻¹, which is an order less than the observed values. In reality, the observed release of energy is apparently associated with the transition of the CO polymerized phase to an equilibrium state of the mixture of CO_2 and solid carbon (these are precisely the products found after the annealing of polymer CO) [22]. Note that the pattern of non-equilibrium transformations under pressure of the CO molecular phase can be more complicated; in particular, under pressure a disproportionation of the CO compound into C_2O_3 and C_3O_2 modifications which, in turn, are polymerized is possible [19–22]. In any event the polymerization of CO under pressure is a non-equilibrium transformation to a more low-lying energy state similar to the polymerization of acetylene C_2H_2 and benzene C_6H_6 under pressure.

The reason that there are so many long-lived metastable ‘kinetic’ phases among the light element compounds is the small size of the corresponding molecules and strong covalent interatomic bonding in these molecules. The distance between the atoms of light elements inside a molecule is noticeably less than the distance between the atoms of different molecules. The molecules are bonded by the van der Waals forces which are two orders weaker than the interaction inside the molecules. At the distances that correspond to the minimum of an intermolecular interaction potential, the molecules appear quite small, and the separation of the substances into molecules is determined quite well. It is easy to understand that molecular substances subjected to pressure within a particular range reach the boundaries of the quasi-equilibrium P, T region, provided the distance between molecules becomes comparable to the distances between the atoms inside a molecule, which involves a several times decrease in the volume of substances. Characteristic values of the bulk modulus of substances with molecular interaction amount to units of GPa; hence, characteristic pressures of ‘irreversibility’ are of the order of 10 GPa.

Thus, the majority of molecular phases of the light element compounds are not stable for a given chemical composition, while in the equilibrium concentration diagrams at low pressures and temperatures there are only several phases, such as C, O_2 , H_2 , N_2 , H_2O , CO_2 , CH_4 , NH_3 . As we noted above, high pressures can be a contributory factor for lowering the energy barrier for the transformation of the metastable molecular phases to more equilibrium states. At the same time, at sufficiently high pressures the equilibrium concentration diagrams themselves can undergo changes because of the different contributions of the PV -terms for the phases of a variable density; in particular, a number of unsaturated hydrocarbons can become more advantageous in terms of energy than the mixture of condensed phases of methane and

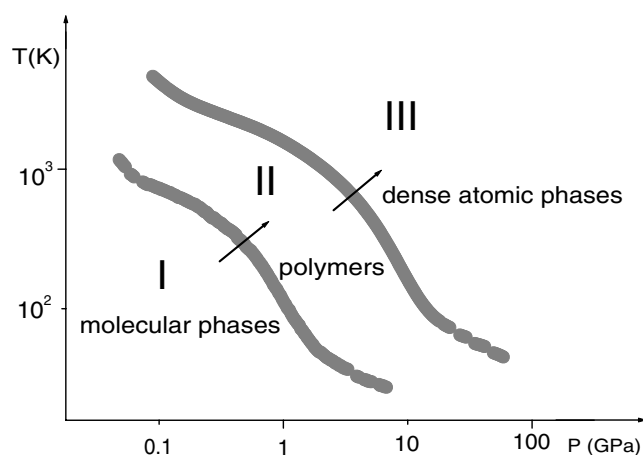


Figure 4. General kind of transitional P, T -phase diagram of molecular low- Z -element compounds. In most cases the transitions between the phases from zone I to zone II and from zone II to zone III are non-equilibrium 'kinetic' transformations.

carbon. As a result, sufficiently complex polymerized phases in the light element systems may emerge at compression not only as intermediate-energy states during the transformation of the non-equilibrium molecular phases, but also as the most stable at high-pressure ground modifications. For example, at certain pressures the formation of higher hydrocarbons becomes beneficial, which is of great importance for abiogenous petroleum synthesis (petroleum at normal pressure is, of course, composed of the metastable phases of hydrocarbons) [11, 23].

To sum up, all P, T -diagrams of the light element molecular compounds can be arbitrarily divided into three zones (figure 4). Zone I includes moderate pressures and temperatures (1–10 GPa, 10–1000 K), at which the Gibbs free energy of the phases is almost completely determined by the bonding energy of atoms in molecules. Most molecular substances in this zone are in the metastable state. Zone III involves ultrahigh pressures (20–50 GPa), at which the Gibbs free energy of the majority of the phases is largely determined by a PV -term. The substances in this zone are in the stable state, as a rule, and represent the mixture of simple solid equilibrium modifications (diamond, CO_2 , H_2O , etc). Specifically, at megabar pressures $P \sim 20\text{--}50$ GPa and moderate temperatures the PV -contribution to the Gibbs free energy facilitates the transition of all unsaturated hydrocarbons to a solid hydrogen solution in diamond; at higher temperatures it brings about the formation of a diamond–hydrogen mixture [24]. As was pointed out above, the formation of amorphous diamond-like carbon saturated with hydrogen $\alpha\text{-C:H}$ was, indeed, observed for many hydrocarbons at ultrahigh pressures [13, 14, 16, 17]. Zone II corresponds to intermediate pressures $P \sim 1\text{--}20$ GPa and temperatures 200–1500 K, at which 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, intermolecular interaction and the PV -contributions for these phases are comparable in magnitude. One should however remember that the modifications in question are not, as a rule, the high-pressure phases of molecular substances, since the majority of molecular substances at ambient pressure are metastable themselves. The high-pressure experiments in this case suggest what intermediate-energy polymeric phases of a substance can exist. Evidently, many of these uncommon polymeric phases, e.g. polymeric benzene and polymeric CO, can be synthesized through 'chemical' techniques at normal pressure, much like well-known polyethylene and polyacetylene.

The grey zones in the transitional diagrams on figures 2 and 4 can be exemplified by the actual phase diagrams, e.g. the transitional diagram of C₆₀ [25] and of benzene [12]. Phase boundaries between molecular phases of benzene and polymer modification and (or) a-C:H phase in figure 8 in [12] correspond to the grey zones of irreversible transitions. There are three areas in the *P, T*-transitional phase diagram of C₆₀, figure 2 in [25]: the region of molecular phases, the region of polymeric and amorphous carbon modifications and the ‘stable’ region of graphite and diamond. The boundaries between these regions precisely correspond to the grey zones in figures 2 and 4 of the present paper. Actually almost all so-called ‘phase diagrams’ of molecular substances in the reference books are in fact transitional diagrams with the corresponding ‘grey zones’ of irreversibility.

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