Phase transition

A phase transition is the alteration in state of matter among the four basic recognized aggregative states: solid, liquid, gaseous and plasma. In some cases two or more states of matter can co-exist in equilibrium under a given set of temperature and pressure conditions, as well as external force fields (electromagnetic, gravitational, acoustic).

Introduction

Matter is known four aggregative states: solid, liquid, and gaseous and plasma, which are sharply different in their properties and characteristics. Physicists have agreed to refer to a both physically and chemically homogeneous finite body as a phase. Or, using Gybbs's definition, one can call a homogeneous part of heterogeneous system: a phase. The reason behind the existence of different phases lies in the balance between the kinetic (heat) energy of the molecules and their energy of interaction. Simplified, the mechanism of phase transitions can be described as follows. When heating a solid body, the kinetic energy of the molecules grows, distance between them increases, and in accordance with the Coulomb law the interaction between them weakens. When the temperature reaches a certain point for the given substance (mineral, mixture, or system) critical value, melting takes place. A new phase, liquid, is formed, and a phase transition takes place. When further heating the liquid thus formed to the next critical temperature the liquid (melt) changes to gas; and so on. All said phase transitions are reversible; that is, with the temperature being lowered, the system would repeat the complete transition from one state to another in reverse order. The important thing is the possibility of co-existence of phases and their reciprocal transition at any temperature.

Transition types

Four aggregative states of matter are distinguished, but phase transitions can be of n-order (kind). The classification was introduced by P. Erenfest in 1933. His idea about the transition order is based on expanding the function of chemical potential \( m(\Delta T, \Delta P) \) in a Taylor series in terms of the \( dT \) and \( dP \) powers. The chemical potential of a single-component system is the Gibbs's energy, referring to one particle of this component:

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\mu = G/N.
\]

If the first order terms are other than zero, then the first-order transition takes place. If the first order terms go to zero and the second order terms are other than zero, the second-order transition takes place, and so on.
First-order phase transitions
In the course of first-order transitions (PhT1) a change of the aggregative state of a substance takes place: melting/solidification (crystallization), vaporization/condensation, [[dissolution]/]crystallization, and sublimation/crystallization. At its transition point PhT1 is characterized by:

- abrupt change in the values of characteristic functions, and in the physical properties of the system;
- presence of discontinuity in the first-order derivatives of the characteristic functions and properties of the system (heat capacity, vaporization heat, viscosity, density, entropy, enthalpy, isobaric-isothermic potential, etc.), and in their physical parameters (temperature, pressure, intensity of an electrical, magnetic or gravitational field, etc.); and
- presence of a region of metastable state.

Second-order phase transitions
Second-order phase transitions (PhT2) take place without changes of the aggregative state of the substance and are in fact structural rearrangements. Examples of PhT2 are the change of crystallographic modification of a solid body, transition of a diamagnetic to paramagnetic, superfluidity and superconductivity. In the case of PhT2 the structural rearrangement occurs at exactly one point (Curie point, lambda-point, critical point) and is characterized by:

- abrupt change in the values of characteristic functions and in the physical properties of the system under continuous and smooth variation of the system-affecting factors;
- vanishing values of the first-order derivatives of the characteristic functions and properties of the system (heat capacity, vaporization heat, viscosity, density, entropy, enthalpy, isobaric-isothermic potential, etc), and in their physical parameters (temperature, pressure, chemical potential, magnetic field induction, electric field intensity, acoustic field frequency, size of heterogeneous surface, etc.), but with the presence of discontinuity of the functions of the second-order derivatives;
- absence of heat absorption or release by the system at the critical point; that is, by exchangeability of the general number of bonds, for instance hydrogen bonds, that provide interaction between the elements of system (as many bonds get destroyed in the course of structural rearrangements, so many new ones are formed);
- absence of a metastable state region, and abrupt structure change at the transition point; and
The classic theory of PhT2 was elaborated by L. Landau in 1937. He interpreted PhT2 as a structural rearrangement (change symmetry) in a system, likely to take place in the presence of at least two phases. Since intensity and character of interaction of the particles comprising the system depend not only on their nature and composition but also on the values of the factors affecting the system, the structure reflects the thermodynamic state of the system in its equilibrium. Interacting, the molecules form a cluster (the cluster theory) of random shape, structure and size. Changes in the system’s external parameters, such as temperature, pressure, intensity of the electric, magnetic, acoustic and gravitational fields, mass transfer energy, and introduction of solids (surface energy) or soluble impurities into the system, all result in changes in the system’s thermodynamic state. When the external influence to which the system is exposed changes smoothly, a gradual "quantitative" pile-up takes place, which then abruptly changes to a new "quality", that is a new relative positioning of particles, or the size or composition of clusters, in other words, of everything that manifests itself as a new property of the system. Since, basically, PT2 is brought about by changing the value of any external influence, the factor space is scattered with local extremums, which can be positioned at most different distances in relation to one another.

References


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