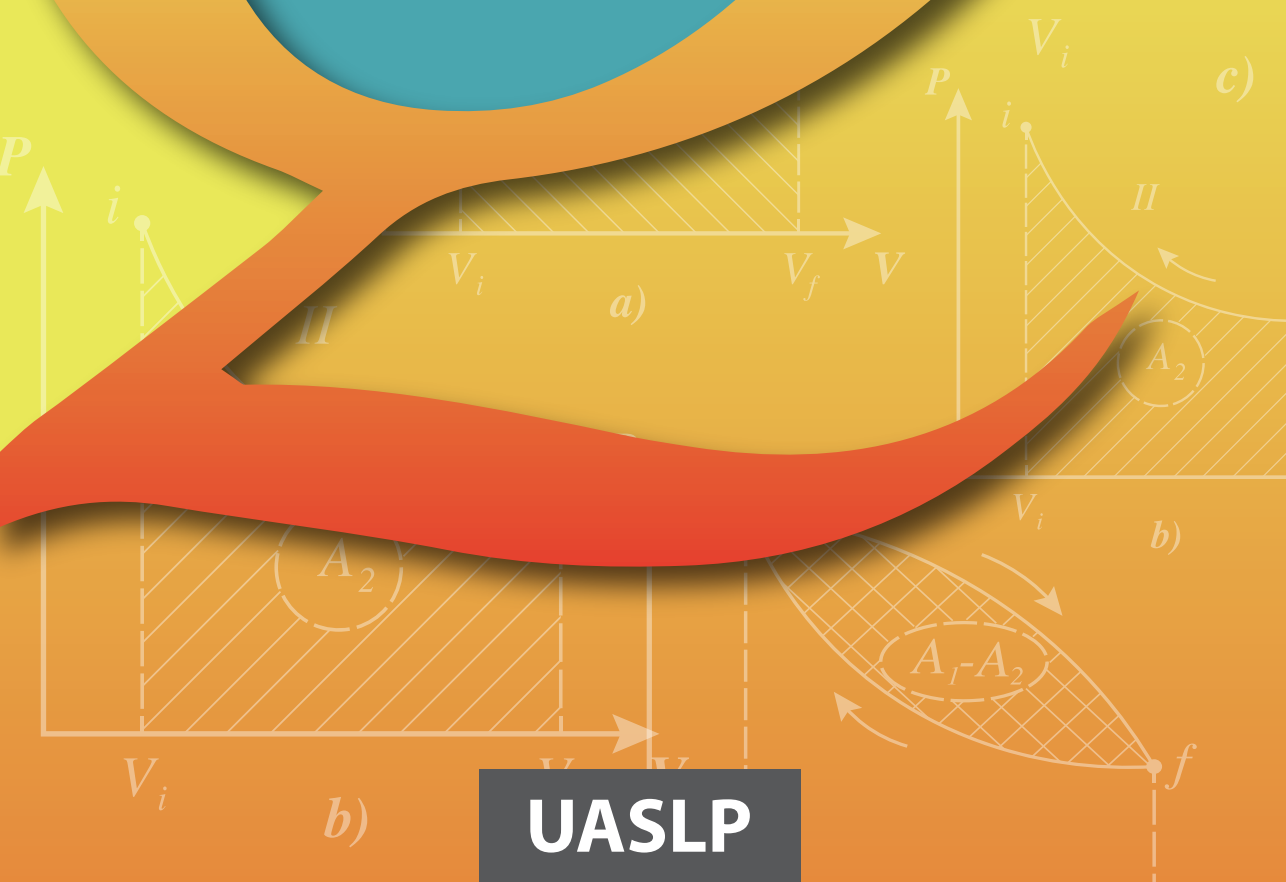# Lectures on Termodynamics and Phase Diagrams

Viatcheslav Andreevich Mishurnyi

UASLP

Lectures on Termodynamics
and Phase Diagrams

Lectures on Termodynamics and Phase Diagrams

Viatcheslav Andreevich Mishurnyi

UASLP
Universidad Autónoma
de San Luis Potosí

INSTITUTO DE
INVESTIGACIÓN EN
COMUNICACIÓN ÓPTICA

Viatcheslav Andreevich Mishurnyi
Instituto de Investigación en Comunicación Óptica

CONTENT

INTRODUCTION

This book is the result of several years of teaching of the Faculty of Science in physical engineering and optoelectronics at the Autonomous University of San Luis Potosi (UASLP). It is devoted to the essential, in my opinion, area of material science and technology: thermodynamics related to various phase diagrams. I realized that there was a lack of appropriate literature that would clearly and thoroughly explain the necessary topics for students. I have tried to present the material simple, and accessible to students of different levels of education. Thus, to understand it, you only need to be familiar with the concepts of differential and integral calculus.

The book consists of six chapters. The first and second chapters are concerned with the basic concepts of thermodynamics, that are used in the construction and analysis of various phase diagrams: the first law of thermodynamics, the equation and function of state, thermodynamic work, properties of the ideal gas and the Carnot cycle. The second law of thermodynamics is outlined on the basis of these essentials and the concept of entropy is introduced. These two chapters, although they review basic concepts in classical thermodynamics, have been included in the text after some hesitation to make the subsequent sections of the book clearer and to produce a more complete and self-contained work. An attentive reader familiar with the basic concepts of thermodynamics will be able to skip this part, aimed especially for beginning students, without compromising their understanding.

In the third chapter, thermodynamic functions such as internal energy, enthalpy or heat, Gibbs and Helmholtz energies are studied. The fundamental Gibbs equation and the general conditions for thermodynamic equilibrium in any complex system are also discussed here. On the basis of these conditions, in chapters four, five, and six the phase diagrams of various systems are discussed, starting with the one-component system and continuing with the two-component, three-component, and multicomponent systems. Here I discuss in detail the state diagram for A^3B^5 systems and solid solutions on their basis. These materials are used widely today to fabricate various optoelectronic devices such as laser diodes, LEDs, detectors, and photovoltaic converters. I analyze in detail the conditions of the solution decomposition in the regular model,

as well as the state diagram of multicomponent systems and methods of experimental and theoretical study of these diagrams.

Of course, a text like this could be continued and expanded. Subsequent editions may be supplemented by a presentation of nucleation theories and models, and details of crystal growth theory (Czochralski, Bridgman, fusion zone), as well as descriptions of such technologies as liquid, gas, and molecular epitaxy.

CHAPTER 1

FUNDAMENTAL PRINCIPLES OF THERMODYNAMICS

1.1 General Concepts

Generally speaking, the bulk of problems in mechanics are solved by using the idealization that any system composed of several bodies is considered as a set of material dots located in their own center of gravity. In the frame of this idealization, the state of the mechanical system can be determined at any moment, if the coordinates of speed, and acceleration in terms of time are known. The coordinates, the speed and the acceleration of the material dots are determined from the time radio-vector $r(t)$ function, which fixes the position of each one of dots and its first and second derivatives, respectively. When, in addition to all this, the forces acting upon the system are also determined, Newton's second law applies, and a system of differential equations can be written relating these forces with the acceleration of the bodies of the system. In order to solve the system of equations, it is necessary to know the initial conditions, that is, the position and speed of all the system's dots at a given point in time. The solution of this problem, allows the calculation of the trajectory of the movement of the bodies, which completely describes the dynamic behavior of the mechanical system under consideration.

In contrast to mechanics, thermodynamics studies the physical processes that occurr in macroscopic bodies or systems, which contain an enormous amount of particles (atoms, molecules, electrons, etc.). It is impossible to determine the values of each of the variables needed to describe the system of the macroscopic bodies. However, for many technical and scientific purposes this is not necessary, because many phenomena in thermodynamic systems can be described using generalized properties of the system. This means that there is no need to determine the coordinates, velocity, or acceleration of each particle. In other words, many of the properties observed in macroscopic bodies are investigated through a set of average parameters that describe the behavior of the system as a whole. It is not necessary to consider the intricacies of their atomic

or molecular structure or the precise values of the position and velocity of each individual particle.

The objectives of thermodynamic studies are to understand the behavior of different thermodynamic or physical-chemical systems, which involve a specific region of space containing the substances under investigation in given quantities. The space outside the system's location is referred to as external environment. Examples of simple thermodynamic systems unclude a crystal, an alloy, gas within a container, a salt solution, and so on.

Likewise, thermodynamics also studies more complex systems composed of single substance in different physical states. These systems are referred to heterogeneous systems. An example of one heterogeneous system is one composed of ice, water, and vapor contained in a closed container.

A system is considered open if it allows for an exchange or transfer of substance with the environment. On the other hand, a closed system does not permit any exchange of substances with the environment. An isolated system is characterized by the absence of both energy and material interchange with the environment.

The principles of thermodynamics were established in the 19th century through the analysis of thermal energy efficiency indicators and its conversion into work by the first steam machines. A common example of a thermodynamic system is a cylinder in which vapor is compressed and expands in another phase of thermodynamics. In the system, the pressure (P) and temperature (T) of the vapor in the cylinder are essential parameters to describe the processes that occur. Let us call these physical magnitudes parameters or thermodynamic variables. Another important parameter is the volume, that is determined by the position of the piston inside the cylinder. In analyzing the work produced by the cylinder in an internal combustion machine, additional parameters such as the chemical composition of the fuel and the mixture of air and gasoline vapor at the moment of entry into the cylinder should be considered. For a complete description of a thermodynamic system, a number of microscopic parameters must be taken into account. These parameters can include the chemical composition, the pressure, temperature, volume, and the concentration of a substance dissolved in another substance.

A wide variety of physical and chemical phenomena can occur in any given thermodynamic system. These include different chemical reactions and substance transformations from one physical state to another, such as the melting of a metal or evaporation of water. If different temperatures exist in different parts of the system, heat conduction will occur between the parts, leading to an exchange of heat. Similarly, if the pressure is not equal at different regions of the system, there will be currents or microscopic flows of the substance in liquids and gases within the system. Concentration gradients can also lead to the dissemination of substances from regions of high concentration to regions of low concentration within the system. As a result of the above-mentioned processes, the system can become unstable, causing the thermodynamic parameters of the system to change over time.

Nevertheless, numerous experiments show that if external conditions remain constant, the system eventually reaches an equilibrium state if sufficient time is allowed. In such state phase transitions, chemical reactions, the substance concentration redistribution in solutions and other processes have already occured. The temperature throughout the system is uniform, the concentrations in different regions of the system becomes equal, i.e. all parts of the system are uniformly mixed, and therefore the pressure in the system are equal. Consequently, if the external conditions do not change over a given period of time, then the thermodynamic parameters characterizing the system over the same time do not change either. Thus, the concept of thermodynamic equilibrium is conceived as the state of a system in "thermodynamic idleness", which is maintained by the absence of external influences on the system.

A homogeneous system, i.e. a system in which the macroscopic properties of any of its parts are equal in any portion of it, is in a thermodynamic state of equilibrium called a phase. Thermodynamic systems can be composed of one or more phases. For instance, a quartz crystal is a one phase system; a salt crystal in contact with a saturated aqueous salt solution forms a two-phase system; water, ice and vapor that are in equilibrium inside a closed container represent a three coexisting phase system.

Any thermodynamic system can be found in different states of equilibrium. Let us consider, for example, a hermetic container with water as a thermodynamic system, which is heated to 90°C. Let us suppose that the container initially has room temperature and is not insulated, allowing heat exchange

with the environment. In this situation, the system is not in equilibrium since the room temperature is around 20°C and the system is subjected to progressively higher temperatures for the container and, simultaneously, lower for the water. As a consequence, heat conduction and convection processes occur. By approaching the container with a hand, heat can be perceived (radiation in the infra-red region of the spectrum). However, as the water continues to cool down, there will be a moment where the temperature becomes the same at all points within the system, reaching room temperature, and so, the processes of heat conduction, convection and net heat radiation emission come to an end. If, on the other hand, the container is placed in a refrigerator at a temperature of 2°C, then the heat conduction, convection, and radiation processes will continue until the system reaches a new state of equilibrium, adopting the new room temperature of 2°C. The key difference between the two experiments lies in the difference between the thermodynamic parameters of temperature, volume, and final resulting density acquired by the water.

The parameters of a thermodynamic state are macroscopic characteristics that describe the state of one system as a whole. They can be measured relatively easily, but their ability to fully describe the system is limited. For a thermodynamic system with multiple components and phases, the number of parameters needed for a complete characterization will be discussed in detail later. For simple homogeneous systems, however, it is sufficient to know three parameters of the state: volume (V), pressure (P), and temperature (T). In this case, the equilibrium of the state of a system can be characterized by a point in a three-dimensional diagram known as the T–P–V diagram. In practice, this three-dimensional diagram can be simplified by representing the state of the system through plane cuts of two parameters, such as P and V, with the third parameter (in this case, the temperature T) indicated alongside.

Let us suppose that some changes occur in the system that affect the magnitudes of the thermodynamic parameter. In this case, let us assume that the system responds rapidly to these changes, such that within any given time interval, the values of the thermodynamic parameters reach equilibrium, i.e., the rate at which the internal processes responsible for the "homogenization" of the system occur is considerably lower than the rate of relaxation. Using a sufficiently slow process, we can transfer the system from an initial state i to a final

state *f*. In the *PV* diagram, the process of the system from *i* to *f* can be represented by means of a curve that connects these points. Obviously, all points of the curve represent a set of equilibrium states infinitely close to each other, and this process is called equilibrium. Processes in equilibrium are also known as reversible processes, because when external conditions change backwards, the system can be reversed back from the final state to the initial one by passing through all the states originally reached, although this time in the opposite direction. It is clear that equilibrium states are an idealization of actual states.

Now assume that the system is not subject to the action of any internal or external forces. Under such conditions, the system is said to be in a state of mechanical equilibrium. If in a system in a mechanical state no spontaneous changes occur in its internal structure, i.e., no chemical reaction or phase change occurs, the system is in chemical equilibrium. Finally, thermal equilibrium is reached in a system in mechanical and chemical equilibrium when the temperature is equal at any point and there is no heat interchange with the environment. When conditions of all three forms of equilibrium are satisfied, the state of the system is defined as a thermodynamic system in equilibrium in which no changes occur. For this reason, the thermodynamic state in equilibrium can be described using thermodynamic parameters that are independent of time. If one of the above equilibrium variables, mechanical, chemical or thermal, is not satisfied, the system will be in an unstable thermodynamic state.

Imagine now that, for example, destabilizing internal and external forces are applied. As a result of such impact on the system, macroscopic flows, turbulence, wave effects, acceleration of some parts in relation to others, etc. may occur. As these processes proceed, the thermodynamic system will pass through a series of unstable states.

If the pressure varies in different parts of the system, it cannot be used to characterize or describe the whole system. If there are chemical reactions or phase transformations in the system, it becomes clear that the concentration of components involved in these processes depends on the time and position in space of these components. Lastly, if there is temperature difference between the system and the environment, there will be temperature gradients within the system. In view of the above, temperature in this case will not be considered as a thermodynamic parameter.

Thus, if the conditions of mechanical, chemical and thermal equilibrium are not met, the system cannot be described in the language of thermodynamic coordinate, which describes the system as a whole.

Any thermodynamic system is made of components. The name "component" is given to individual substances that, in their smallest ammount, are sufficient to construct the whole system. Likewise, the system is assumed to be in a state of equilibrium. In other words, components can be defined as the independent parts forming the system. To illustrate this, consider the following examples:

1.- The system water–ice–vapor. In this system there is but one component and that is water, which is a chemical homogeneous substance. It would be incorrect to consider Hydrogen as a component of the system, since its quantity in water is conditioned by the Oxygen content, and therefore they are not independent. Similarly, the same can be said with regards to Oxygen. Based on the above, in this example we have three phases and one single system.

2.- The mixture of Nitrogen, Oxygen, Argon, Carbon Dioxide, and Water Vapor gases that compose the air at ambient temperature. The system has five components, since the amount of each gas in the mixture is independent of the amounts of the other gases. This is an example of a system with five multiple components and one single phase.

3.- The aqueous solution of sodium chloride. This is a system of two components, $NaCl$ and H_2O. Although the molecules of $NaCl$ dissociate in the water into Na^+ and Cl^- ions, their amounts are interrelated, which by definition, $NaCl$ is represented in the system as one component, while the system is treated as two components with one phase.

4.- A system composed of chemical substances for instance: $CaCO_3 \leftrightarrow CaO + CO_2$.

The arrows show that a disassociation occurs in the system, as well as the formation of Calcium Carbonate. In this case, there are three fundamental parts: Calcium Oxide CaO, Carbon Dioxide CO_2 and Calcium Carbonate $CaCO_3$. However, only two components, such as CaO and CO_2, are really needed to form the whole system, as in this case, and so only two of the three parts that compose this system will be considered as components. Which two should we choose in this case? – It really does not matter. For instance, if we build the system of CaO and CO_2, a chemical reaction will produce $CaCO_3$. On the other hand, we can consider $CaCO_3$ and CaO as components of the same system, and the dissociation of $CaCO_3$ will result in formation of CO_2.

From the previous examples, it is clear that the number of components in a system may be equal or less than the number of its parts or elements.

1.2 The Equation and Function of State

Let us imagine a closed system containing a given amount of gas. Assume that volume (V), temperature (T) and pressure (P) of the gas can be measured. It is established experimentally that if the temperature and volume of gas are constant, the pressure of the gas also remains constant. Hence, the system is in a state of equilibrium. If V and P are the magnitudes that remain constant, then the temperature of the gas will correspond to a unique value of T. Similarly, when P and T have certain fixed values, the volume of the gas cannot change. Thus, the system under consideration will be described by three thermodynamic parameters T, P and V, and, characteristically, only two of these parameters can be independent. Consequently, for a gas in a state of equilibrium, there is a certain dependence between these three parameters, which analytically relates their magnitudes. Such dependence is called the equation of state of the system in equilibrium or simply the equation of state.

For any thermodynamic system there exists its own equation of state, but this equation cannot always be written by simple mathematical functions. In the case of a gas with a relatively low pressure, the equation of state can be described in a simple manner $PV = RT$, where R is known as "the constant of gases (8.314 $J{\cdot}K^{-1}mol^{-1}$)". This equation is already known from the general physics course and is called the ideal gas equation of state. The properties of this equation will be analyzed next. Let us suppose that the equation of state of the ideal gas is solved with respect to V, i.e., the volume is represented as a function of T and P.

$$V=V(T,P) \tag{1.1}$$

If infinitesimal changes occur in the system during the transition of the equilibrium state from one point to another, then, logically, these changes are accompanied by infinitesimal changes in temperature, volume and pressure which are described by dT, dP and dB. In this case, from (1.1) we deduce that

$$dV = \left.\frac{\partial V}{\partial T}\right|_{P} dT + \left.\frac{\partial V}{\partial P}\right|_{T} dP \tag{1.2}$$

where the partial derivative $\left.\frac{\partial V}{\partial T}\right|_{P}$ means an infinitesimal change in volume due to an infinitesimal change in temperature at a constant pressure. Analogically, the partial derivative $\left.\frac{\partial V}{\partial T}\right|_{T}$ shows how the volume changes due to a change in pressure, while maintaining a constant temperature. It can be observed that each partial derivative in the equation (1.2) can be a function of T and P.

If the equation is solved with regards to P, then $P=P(T,V)$, and correspondingly

$$dP=\left.\frac{\partial P}{\partial T}\right|_{V}dT+\left.\frac{\partial P}{\partial V}\right|_{T}dV. \qquad (1.3)$$

The temperature can also be expressed as a function of P and V

$$dT=\left.\frac{\partial T}{\partial P}\right|_{V}dP+\left.\frac{\partial T}{\partial V}\right|_{P}dV. \qquad (1.4)$$

Let us now suppose a general case in which the function F depends on the thermodynamic state parameters, which we shall call x, y, z. By definition, this function will be called a state function if its value depends only on the state parameters and not on the processes that precede the establishment of such a state. Consequently, the difference between the value of F_1 of this function for state 1 and F_2 for state 2, is due only to the values of $x1$, $y1$, $z1$ and $x2$, $y2$, $z2$, and is independent on the process or trajectory of transition from state 1 to state 2. As an example, we consider potential energy. For a body with a mass (m), located at height h_1, the potential energy is $E_1=mgh_1$ and for height h_2 respectively $E_2=mgh_2$. Since the difference $E_2 - E_1=mg(h_2 - h_1)$ between the first and second state does not depend on which trajectory the body traveled, then according to the definition, given above, the potential energy is a function of state.

One more example of a state function is the product PV. Suppose that a gas in the state of initial equilibrium is characterized by the values of P_1 and V_1 which are the state parameters of P and V. Let us assume that after a series of transformations, this gas reaches its final state of equilibrium, in which the values of the pressure and volume are equal to P_2 and V_2. Thus, the function PV

acquires values of P_1V_1 until P_2V_2, which depends only on the values of the state parameters P and V in states 1 and 2, which are completely independent of the transition trajectory from 1 to 2.

Suppose there is a functional dependence between the three parameters x, y, z, that is, there is a relation $f(x, y, z)=0$.

In principle, this relation can be rewritten for z as a function of x and y

$$z=F(x, y). \tag{1.5}$$

Let $F(x, y)$ be a state function. If infinitesimal transformations occur in the system, the change of $F(x, y)$ com be written as

$$dF = \left.\frac{\partial F(x, y)}{\partial x}\right|_y dx + \left.\frac{\partial F(x, y)}{\partial y}\right|_x dy. \tag{1.6}$$

The differential is called the total or exact differential, where

$$\int_1^2 dF(x, y) = F_2(x_2, y_2) - F_1(x_1, y_1). \tag{1.7}$$

$F1(x1, y1)$ and $F2(x2, y2)$ are, respectively, values of the function F in the initial state 1 and in the final state 2. It is clear that one of the mathematical properties of the state function is that its closed contour integral is zero. Such integral represents the evolution of the system, that starts in some initial state 1, transforms, but returns to the same state from which it departed, i.e., 1.

$$dF(x,y)=0$$

Once this condition is met, the opposite is also valid, i.e. if the closed contour integral of the function $F(x, y)$ is equal to 0, then it is a function that, if we refer it to the properties of matter, can be considered as a state function. Let us suppose that

$$dF(x,y)=M(x,y)dx + N(x,y)dy, \tag{1.8}$$

where $M(x, y)$ y $N(x, y)$ are functions with independent variables x and y. It is easy to show that, if the condition known as the Euler relation

$$\frac{\partial M(x, y)}{\partial y} = \frac{\partial N(x, y)}{\partial x} \tag{1.9}$$

there exists a function $F(x, y)$ whose total differential is expressed by reference (1.8). To understand this, let us assume that function $F(x,y)$ exists, then, by definition, its total differential can be written as

$$dF(x, y) = \frac{\partial F(x, y)}{\partial x}\bigg|_{y} dx + \frac{\partial F(x, y)}{\partial y}\bigg|_{x} dy. \tag{1.10}$$

If (1.8) y (1.10) are compared, it can be seen that

$$M(x, y) = \frac{\partial F(x, y)}{\partial x} \qquad N(x, y) = \frac{\partial F(x, y)}{\partial y}. \tag{1.11}$$

If in the expression (1.11) we differentiate $M(x, y)$ in relation to y, and $N(x, y)$ in relation to x, then we obtain

$$\frac{\partial M(x, y)}{\partial y} = \frac{\partial^2 F(x, y)}{\partial x \partial y} \qquad \frac{\partial N(x, y)}{\partial x} = \frac{\partial^2 F(x, y)}{\partial x \partial y}. \tag{1.12}$$

Since in (1.12) the part on the right-hand sides of both equations are the same, the left-hand sides are exactly the same, that corresponds to the Euler relation (1.9). If the Euler relation is not met, that is, if

$$\frac{\partial M(x, y)}{\partial y} \neq \frac{\partial N(x, y)}{\partial x}. \tag{1.13}$$

Then, in this case there is no function for which the expression (1.10) would be a total differential. This statement is simple to demonstrate. Suppose that function $F(x,y)$ exists. If we repeat the previous reasoning, we obtain the condition (1.9), which contradicts inequality (1.13). This means that if the Euler relation is not satisfied, then the state function $F(x,y)$ does not exist, and $dF(x,y)$ cannot be a total differential, but simply represents an infinitesimal change in some variable F.

1.3 Work

Suppose a force field is applied to a given thermodynamic system. Under the influence of such field, work can be performed. In this situation, the system is able to perform external work, for example, the work to replace a load due to the expansion of the piston inside the cylinder. Likewise, work can be done by compression of the gas inside the cylinder. In the first case, we will conventionally say that the work done by the system over external bodies is positive work, and in the second case, it is negative work. In the general case, the amount of work is determined by the force under the action of which it is performed, and the total displacement that the force produces. In principle, one part of a system can produce work on another part of it. This kind of work is called internal work and can be produced, for example, by the interaction of molecules, atoms, or electrons within the system. In thermodynamics, only the external work done by the interaction of the system with surrounding bodies is analyzed, received or produced, and the internal work is disregarded.

As discussed earlier, the system in thermodynamic equilibrium must satisfy the following conditions:
1.- Mechanical equilibrium. For this, it is necessary that external and internal forces compensate each other within the system.
2.- Chemical equilibrium. The structure and chemical properties do not change in time.
3.- Thermal equilibrium. The temperature of the system is constant and coincides with the surrounding temperature.

Let us consider that the thermodynamic system is in equilibrium and the environment remains unchanged. In such circumstances, no displacement occurs, neither inside nor outside the system, therefore no work is performed. Nevertheless, if unbalanced forces interact with the system, the state of mechanical equilibrium is lost and, as a consequence of this:
– Effects such as the acceleration of some particles in relation to others, macroscopic currents, turbulences, etc. may occur in the system.
– As a result of the above-mentioned phenomena, temperature differences between the system and the environment may surge; likewise, inside the system temperature gradients may appear.
– The chemical equilibrium condition is lost and chemical reactions with a finite speed will begin to occur, as well as concentration of constituent elements of the system and phase transformations.

Thus, the interaction of external forces causes a transition of the thermodynamic system, that is in equilibrium, into a series of nonequilibrium states. If the forces applied to the system are sufficiently dynamic, the thermodynamic parameters characterizing the whole system (pressure, temperature, concentration, volume and others), can no longer be used to analyze its behavior. That is why equilibrium thermodynamics uses a certain idealization, in which the forces acting on the system are considered infinitesimal and change very slowly. In the frame of this idealization, the processes occuring in the system can be characterized as quasi-static or quasi-equilibrium. In a quasi-static process, the system is always infinitely close to thermodynamic equilibrium, and therefore, all the states through which the system passes can be described by their thermodynamic parameters. For this reason, the equation (if known) can also be used to analyze the behavior of the system.

As a result, the quasi-static processes are idealizations used in the study of various thermodynamic systems, and the conditions for the realization of these processes can never be fully satisfied experimentally.
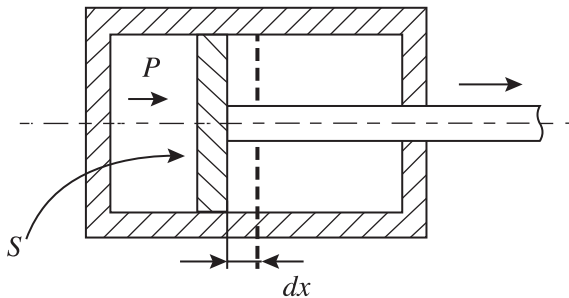
Fig. 1.1. To a definition of work in thermodynamic.

Let us imagine a cylinder with a piston (Fig. 1.1). Where we denote the pressure of the gas inside the cylinder as P and the area of the cylinder is S. As a result, the force applied to the cylinder is equal to PS. If under the action of this force the piston travels a distance dx, then the system performs an infinitesimal work on the environment, and the magnitude of this work is $đW = PSdx$. But $Sdx = dV$, dV represents an infinitesimal change of volume. Finally,

$$đW = PdV. \qquad (1.14)$$

The reason why a horizontal line is used on the symbol $đW$ to illustrate work performed by the system will be explained at the end of this section.

Now suppose that under the action of force PS the piston travels a certain distance, and the volume inside the cylinder changes from V_i to V_f. Thus, the amount of work performed by the system is equal to

$$W = \int_{V_i}^{V_f} PdV. \tag{1.15}$$

If the pressure inside the cylinder is constant, this integral can be easily calculated. In the case when the piston moves with acceleration, P and V become functions of time and the analytical integration of equation (1.15) gets complicated, although we must remember that all integrals of a continuous function that does not diverge can always be calculated numerically. Suppose that the gas expansion process inside the cylinder is quasi-static. In that case, the pressure inside the system can be considered as a thermodynamic parameter, and therefore, utilizing the equation of state of the system, the pressure can be described as a function of T and V. If the laws of temperature change are already known (for example, in the case of an isothermal process the temperature is constant), the pressure can be expressed as function of the volume. This way, the integral in (1.15) would be determined.

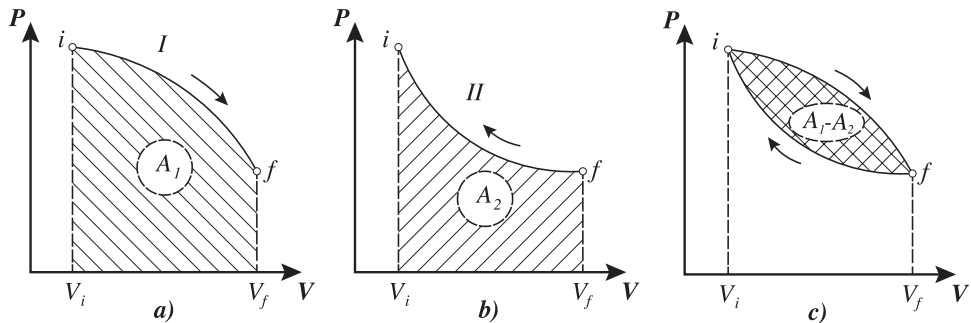**Fig. 1.2. a) Work W₁ done by the gas during expansion from volume Vᵢ to volume Vf (positive); b) Work W₂ done by the gas during compression from volume Vf to volume Vᵢ (negative); c) The looped cycle W₁-W₂ when the gas returns ti the original state.**

The system performs work by moving the piston due to expansion of gas inside the cylinder. This process is schematically shown in Fig. 1.2.*a*, the change in pressure and gas volume is characterized by curve *I*, with intial and final points *i* and *f*, respectively. The amount of work W_1 produced by the system can be determined by integrating (1.15), corresponding to the shaded area under curve *I*. Fig. 1.2.*b* shows the process of gas compression in a cylinder under the action of external forces. The work W_2 expended during this process corresponds to the shaded area under curve *II*, along which the compression process occurs. In Fig. 1.2.*a*, the work is positive, and in Fig. 1.2.*b*, it is negative. Curves *I* and *II* drawn together in Fig. 1.2.*c* illustrate the situation when the gas in the cylinder returns to the initial state, and the initial and final positions in the system in the first and second processes are equal. The closed process represented in Fig. 1.2.*c* is called a cycle, and the shaded area between curves *I* and *II* corresponds to the difference between W_1 and W_2, i.e., the work produced by the system in this cycle. The direction of the processes is marked by arrows in Fig. 1.2.*c* indicating that the work is positive. If the processes were realized in the opposite direction, the sum of the works would be negative.

The *P-V* diagram in Fig. 1.3 shows initial and final positions of the stationary states relative to a certain thermodynamic system characterized by the parameters P_i, V_i, T_i and P_f, V_f, T_f. There are many different trajectories along which a system can move from one state *i* to another state *f*. For instance, first the system at constant pressure can be delivered from one point *i* to another (this is the isobaric process), then at constant volume it moves from point *a* to point *f* (isochoric process). In this case, the work performed is equal to the area limited at the top by the horizontal line *i–a*. Another variable may be the trajectory *i–b–f*, to which corresponds the work under the area below the line *b–f*. The series of isobaric and isochoric short lines connecting points *i* and *f*, as well as the continuous curve between these two points, illustrate two more possible trajectories of system transition from the initial state to the final state. It is clear that the work produced by a thermodynamic system depends not only on the initial and final states of the system, determined by the positions of points *i* and *f*, but also on the intermediate states taken by the system before reaching the final state *f*. In other words, the trajectory along which the system moves affects the amount of work, and so the work cannot be a function of the thermodynamic system, since a given state determines a fixed value for the physical or thermodynamic variables that define it. As a consequence, the infinitesimal value *đW* in expression (1.9) is not a total

differential. In order to underline this situation, the horizontal line in the symbol $đ$ denotes an infinitesimal work produced by the thermodynamic system and exerted on it.
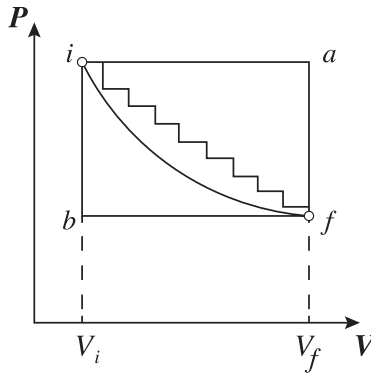

Fig. 1.3. Variable ways of transition of the thermodynamic system from state *i* to state *f*.

1.4 The First Principle of Thermodynamics and the Simplest Thermodynamic Processes

One of the main concepts of thermodynamics is the internal energy U of the system, that represents all forms of motion of the particles that compose the system, energy storage at the electronic level, as well as interactive energy between them. Internal energy consists of rotational energy, motion energy, undulatory motion of particles, internal energy of molecules, as well as interactions between them, intra- and interatomic, nuclear etc. The reserve of internal energy depends only on the state of the system and, therefore, can be considered as one of the characteristics of the state. In other words, the internal energy is a function of the state of the thermodynamic system.

There are different methods to modify the internal energy of the system. As an example, let us analyze a thermodynamic system such as a container with a certain amount of water. If the container is heated, after a period of time, the water will increase its initial temperature T_1 to a final T_2. Let us assume that inside the container we place a cylinder with blades (paddle wheel). The cylinder is then coiled with a cable electrically charged on one end. As the charge goes down, the paddle wheel starts to rotate. Consequently, the water temperature raises from an initial T_1 to a final temperature which can reach T_2. So, this

temperature increase is only due to the work being produced on the system. Thus, the internal energy of the system increases due to the heat interchange with the environment, and in the second case, mechanical energy is trasmitted to the system, which the system absorbs. Since the initial and final states of the system and the increase of its internal energy coincide in both cases. We can conclud that heat and mechanical work are equivalent. Heat is measured in the same units as energy, viz: Joules, ergs, etc. The mechanical equivalent of heat, or energy is called Calorie, that is equal to 4.180 Joules. Historically, the Calorie has been defined as the amount of heat energy needed to be applied to one gram of water to increase its temperature by one degree, and by international convention, an interval between 14.5 and 15.5 °C is chosen to standardize this unit of calorie. It should be clarified that neither heat nor work is a form of energy, rather they are forms of energy transmission.

We point that thermodynamic quantities whose values are proportional to the number of particles in the mass of a body are called extensive quantities, in contrast to intensive quantities, that in general case do not depend on the mass. Therefore, the internal energy of a body is an extensive quantity, since it proportional to the number of particles (mass). Examples of intensive quantities are temperature of a body, pressure of a gas inside a balloon, various types of fields (gravitational, electric, magnetic, etc.).

Suppose that as a result of some process a thermodynamic system receives a certain amount of heat ΔQ from the environment. This heat can be consumed by possible phase transitions, such as fusion, sublimation, or evaporation, and partially or completely by heating the system. In this case, the energy state of the system changes regardless of how the heat transmitted to the system was expanded: phase transitions change the interaction or bonding energy of atoms or molecules, while heating increases the kinetic energy of the system. Therefore, part of the heat received by the system is spent on changing its internal energy.

Likewise, some of the absorbed heat can be used to perform external work. Let us heat the gas contained in a cylinder with a piston, and assume that there is a load on the external surface of this piston. Since the volume of gas increases with the temperature, useful work is produced, because as the piston is displaced upward, it lifts the load.

So, the heat absorbed by a thermodynamic system can be expended either by changing the internal energy of the system or by the external work produced. When this happens, the law of conservation of energy is always met and the equation of the balance of energy can be written in the following form

$$\varDelta Q = \varDelta U + \varDelta W \qquad\qquad (1.16)$$

This expression is known as the first law or the first principle of thermodynamics, $\varDelta Q$ is the heat received by the system, $\varDelta U$ is the sum of all internal energy, and $\varDelta W$ is the total amount of external work performed. Since the internal energy U of the system is a function of state, then, its infinitesimal change $\varDelta U = dU$ is the total differential. As shown in section 1.3, the work depends on the trajectory along which the system moves from the initial state to the final state, and consequently, W is not a function of state and dW cannot be a total differential. Likewise, the infinitesimal change of temperature is also not a total differential of the function, which can be shown mathematically in general terms. This leads to the demonstration that the infinitesimal change in $\varDelta Q$, which is Euler condition (1.9), is not met. Similarly, one can show that $\varDelta Q$ is not a function of state by simple reasoning. Equation (1.16) represents $\varDelta Q$ as the sum of infinitesimal quantities. As pointed out earlier, one of these quantities, namely U is a function of state and consequently dU is a total differential, at the same time, since W is not a function of state and hence $\varDelta W = dW$ is simply an arbitrary infinitesimal quantity that does not correspond to a state differential. In view of this, the sum of these two quantities, that is, their linear combination, also cannot be a total differential either and consequently, Q is not a function of state. In other words, the sum of the total differential (dU) and the infinitesimal magnitude dW cannot be a total differential according to Euler linear condition. On the other hand, the algebraic difference of the two infinitesimal quantities ($\varDelta Q = d\,Q$ and $\varDelta W = dW$) can be the total differential, as is inferred from the first principle, when purifying and expressing the internal energy of the system in the form $dU = dQ - dW$. Therefore, the first law of thermodynamics can be written in its differential form as

$$dQ = dU + dW \qquad\qquad (1.17)$$

In this expression, the sign d represents infinitesimal changes of heat and work, according to the adopted terminology, reflecting the fact that neither Q, nor W is the

functions of state. Properly speaking, $đQ$ and $đW$ cannot be total differentials for the simple reason that they characterize two different processes by which the thermodynamic system can interchange energy with the environment. Therefore, the quantities $đQ$ and $đW$ do not reflect the behavior of the system in any way, but simply characterize its energy interaction with the environment. That means that the internal energy of the system can be changed by heat introduced or extracted from the system, or by external work received or produced. At the same time, dU is a total differential of the internal energy of the system, which is a function of state and describes the properties of the system as a whole. Let us analyze with the help of the first law of thermodynamics the simplest case where a system interchanges, in various ways, heat and work with the environment. Let us assume that the work produced on the system or system is due only to the change in volume, then $đW=PdV$ and therefore the first law of thermodynamic can be

$$đQ = dU + PdV \qquad (1.18)$$

Let us now consider the following processes:

1. Isochoric process.
These describe the processes in which the volume V is maintained constant, and the system can interchange heat with the environment. Since in the isochoric $dV=0$, the expression of the first law of thermodynamics takes the form

$$đQ = dU \qquad (1.19)$$

this means that all heat is used to change the internal energy. If, as a result of the absorption Q of heat units, the temperature of the system changes from T_i to T_f, then the calorific capacity for $V = const$ is determined by

$$c_V = \frac{Q}{T_f - T_i} \qquad (1.20)$$

2. Isobaric process.
In this process the pressure remains constant and the system can exchange heat with the environment. When a certain amount of heat is absorbed, the internal energy of the system will increase and the system will now be able to perform

an external work. Suppose that in an isobaric process, when heat is absorbed Q, the internal energy increases from U_1 to U_2, and the volume from V_1 a V_2. Then, based on the first law of thermodynamics, we can write

$$Q = U2 - U1 + P \int dV = U2 - U1 + P(V2 - V1) \qquad (1.21)$$

For these isobaric processes it is relevant to introduce a new variable or thermodynamic parameter which is very useful to analyze them, combining the following energies

$$H = U + PV \qquad (1.22)$$

The new function is called enthalpy or heat function. It is also a function of state, since it is represented as a linear combination of two functions of state U and PV. In this specific case of isobaric processes, in which $P=const$, the magnitude dQ turns out to be a total differential

$$đQ_p = dH \qquad (1.23)$$

The heating capacity at a constant pressure can be now expressed in terms of the enthalpy H

$$c_P = \left.\frac{\partial Q}{\partial T}\right|_P = \left.\frac{\partial H}{\partial T}\right|_P \qquad (1.24)$$

This way, in the processes that occur at a constant pressure the enthalpy H has analogous properties to those of the internal U in processes with constant volume.

3. Isothermal process.
To maintain a constant temperature during this process, the system is placed in a thermostat. Let us see the dependence of the internal energy on temperature and volume (since only two of the three parameters P, T y V are independent, then, for example, pressure can be represented in relation to T and V). So, let us express the new state function U in terms of these two variables that completely define the system, T and V, to show $U=U(T,V)$. In this case, we get

$$dU = \left.\frac{\partial U}{\partial T}\right|_V dT + \left.\frac{\partial U}{\partial V}\right|_T dV \qquad (1.25)$$

In the isothermal process $dT=0$

$$dU = \frac{\partial U}{\partial V}\bigg|_T dV \qquad\qquad (1.26)$$

Let us substitute (1.26) in (1.18)

$$Q = \frac{\partial U}{\partial V}\bigg|_T dV + PdV = \left[\frac{\partial U}{\partial V}\bigg|_T + P\right]dV \qquad\qquad (1.27)$$

Therefore, from (1.27) in an isothermal process, heat partly contributes to an increase of the internal energy of the system, and partly to the performance of external work.

4. Adiabatic process.

In this process, the system is necessarily wrapped with a membrane that blocksor prevents the passage of heat from or into it, and is called an insulating or adiabatic wall, which completely excludes the heat exchange with the environment. Since $dQ=0$, we can conclude from the first thermodynamic principle that $dU=-dW$. Consequently in an adiabatic process, if the system performs useful work on the external environment, it is only due to a decrease of internal energy. If work is realized on the system, then the internal energy of the system will increase. Work is thus now equal to the change in internal energy, which is a function of state. Work is consequently independent now from the trajectory along which the system moves from the initial to the final state.

1.5 The Ideal Gas

The ideal gas is a gas whose state is determined by the well-known equation $PV=nRT$. Here n is the number of moles in the constituting substance of the gas, and R is the gas constant, that represents the amount of work performed by one mol of gas ($n=1$) in an isobaric process when its temperature is raised by one degree.

Let us examine a process in order to determine the internal energy of an ideal gas. For this purpose, let us consider the experiment carried out by Joule, which demonstrates that a gas temperature does not increase when it is expanded in the vacuum. Joule's experiment is schematically presented in Fig. 1.4.
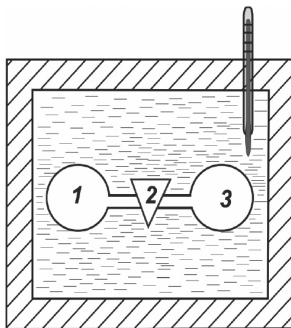
Fig. 1.4. Diagram of the Joule experiment.

This drawing shows two containers *1* and *3* connected by a tube and a valve *2* located inside a calorimeter. Container *1* is filled with gas at a given pressure (P) and temperature (T), while in the container *3* there is vacuum. After thermal equilibrium is established, according to the readings of the thermometer, valve *2* is opened and the gas flows from container *1* to container *3* until the pressured equalizes. As a result of this experiment, Joule observed that when the volume occupied by the gas is doubled, the temperature variations recorded by the thermometer were negligible, meaning no heat was transferred between the containers, and the calorimeter lecture was zero for all practical purposes. Small changes in temperature observed in the thermometer, were associated with the use of a real gas in the experiment. If an ideal gas were used, the temperature variations would be zero. For this reason, $\Delta Q = 0$ for an ideal gas. In addition, since the system did not perform external work during the experiment, then ΔW is also zero. Thus, from the first law of thermodynamics we conclude that $\Delta U = 0$, which means that the internal energy of a gas does not change during free expansion. If T and V are chosen as independent variables, then in the experiment shown in Fig. 1.4 we have

$$dU = \frac{\partial U}{\partial T}\bigg|_V dT + \frac{\partial U}{\partial V}\bigg|_V dV = 0. \tag{1.28}$$

Since during the experiment $\Delta T = dT = 0$, then, since dU turned out to be zero

$$\frac{\partial U}{\partial V}\bigg|_T = 0. \tag{1.29}$$

To satisfy the condition that dU is zero. This indicates that the internal energy of an ideal gas is independent with regards to the volume. If we consider U as a function of T and P, we get that

$$dU = \frac{\partial U}{\partial T}\bigg|_P dT + \frac{\partial U}{\partial P}\bigg|_T dP = 0. \tag{1.30}$$

For $dT = 0$ and $dU = 0$, as in the previous case, it is inferred from this equation that

$$\frac{\partial U}{\partial P} = 0. \tag{1.31}$$

Thus, if in a process of free expansion of a real gas its temperature barely changes, this indicates that internal energy U does not depend on either V or P, but is only a function of T. Consequently, we postulate that for a real gas, this applies rigorously:

$$PV = RT, \quad \frac{\partial U}{\partial V} = 0, \quad \frac{\partial U}{\partial P} = 0 \quad U = U(T). \tag{1.32}$$

Since $dW = PdV$, then

$$dQ = dU + dW \tag{1.33}$$

In this case $dQ = dU$. Thus, the calorific capacity at constant volume can be written as

$$c_V = \frac{\partial U}{\partial T}\bigg|_V = \frac{\partial U}{\partial T} \quad \text{y} \quad dU = c_V dT. \tag{1.34}$$

Since the internal energy of an ideal gas depends only on temperature, the partial derivative $\frac{\partial U}{\partial T}\bigg|_V$ coincides with the total derivative.

$$c_V = \frac{\partial Q}{\partial T}\bigg|_V = \frac{\partial U}{\partial T}\bigg|_V = \frac{\partial U}{\partial T}, \text{y} \quad dU = c_V dT. \tag{1.35}$$

Now the first law of thermodynamics can be written as

$$đQ = c_V dT + PdV \qquad (1.36)$$

Let us review the simplest processes that occur in an ideal gas.

1. Isochoric process.
Since in an isochoric process $V = const$, then the gas does not perform any external work. Correspondingly, all heat transmitted to the gas is consumed by the increase of its internal energy and of (1.36)

$$đQ = dU = c_V dT \qquad (1.37)$$

If the temperature increased from T_1 to T_2, then (1.37) is integrated within these limits and we find the heat received by the ga

$$\Delta Q = \Delta U = c_V(T_2 - T_1) \qquad (1.38)$$

2. Isobaric process.
In this process $P = const.$

$$đQ = dU + PdV = c_V dT + PdV \qquad (1.39)$$

$$c_V = \frac{\partial Q}{\partial T}\bigg|_V = \frac{\partial U}{\partial T}\bigg|_V \qquad (1.40)$$

From the equation of state $PV = RT$ for one mole of gas we have

$$PdV + VdP = RdT \qquad (1.41)$$

For constant pressure,

$$đQ = c_V dT + PdV = c_V dT + RdT = (c_V + R)dT = c_P dT \qquad (1.42)$$

After that, the so-called Mayer formula can be obtained

$$c_P = c_V + R \qquad (1.43)$$

From this we can observe that

$$Q = c_P(T_2 - T_1) = H_2 - H_1 \quad \text{and} \quad W = P(V_2 - V_1) \tag{1.44}$$

3. Isothermal process.
At $T = const$ and $đQ = C_V dT + PdV$, we fin

$$đQ = PdV = đW \tag{1.45}$$

Therefore, in this case, all the heat received is converted into work and $\Delta Q = \Delta W$. From the ideal gas equation, we have

$$P = \frac{RT}{V} \tag{1.46}$$

$$đQ = đW = RT\frac{dV}{V} \tag{1.47}$$

$$Q = W = RT\int_{V_1}^{V_2} \frac{dV}{V} = RT\ln\frac{V_2}{V_1} \tag{1.48}$$

4. Adiabatic process.
In this case $đQ=0$, and hence the equation of the first principle has the form

$$c_V dT + PdV = 0 \tag{1.49}$$

From the equation (1.41) we get

$$dT = \frac{PdV}{R} + \frac{VdP}{R} \tag{1.50}$$

Considering Mayer's formula $c_p = c_v + R$, from (1.49) we have

$$c_V\frac{PdV}{R} + c_V\frac{VdP}{R} + PdV = 0 \tag{1.51}$$

$$c_P PdV - RPdV + c_V dP + RPdV = 0 \tag{1.52}$$

or

$$-c_P PdV = c_V VdP \tag{1.53}$$

Designating

$$\frac{c_P}{c_V} = \chi .$$

(1.54)

Then

$$-\chi \frac{dV}{V} = \frac{dP}{P}$$

(1.55)

Integrating within the limits of V_1 to V_2 and P_1 to P_2, we have

$$\ln\left(\frac{V_1}{V_2}\right)^{\chi} = \ln\frac{P_2}{P_1},$$

(1.56)

or

$$P_1 V_1^{x} = P_2 V_2^{x}$$

(1.57)

and, in a general form

$$PV^x = Const$$

(1.58)

This is the Poisson's equation, which is graphically represented by a scalene hyperbola, called in this case adiabatic. The mathematical ratio of χ (Poisson's ratio) is always greater than one, and therefore the adiabatic curve is more pronounced than the isothermal curve. Since

$$P_1 V_1^{x} = P_2 V_2^{x}$$

(1.59)

and

$$P = \frac{RT}{V}$$

(1.60)

then

$$RT_1 V_1^{x-1} = RT_2 V_2^{x-1}$$

(1.61)

or

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\chi-1}$$

(1.62)

Since the exponent $(\chi - 1)$ in (1.62) is a positive one, it is obvious that thetemperature of the gas decreases in an adiabatic expansion, and increases during compression. The adiabatic curve is more pronounced than the isothermal one, therefore, in the adiabatic process, the pressure of the expanding gas decreases due to an increase in its volume and it is associated cooling. From the equation $dV = c_V \, dT$, we can conclude that the positive external work in the process is equal to $c_V \, (T_1 - T_2)$ and is performed by reducing the internal energy of the gas.

Fig. 1.5 shows all possible idea gas functions such as isochoric, isobaric, isothermal and adiabatic in various coordinates: *P-V*, *P-T* and *T-V*.
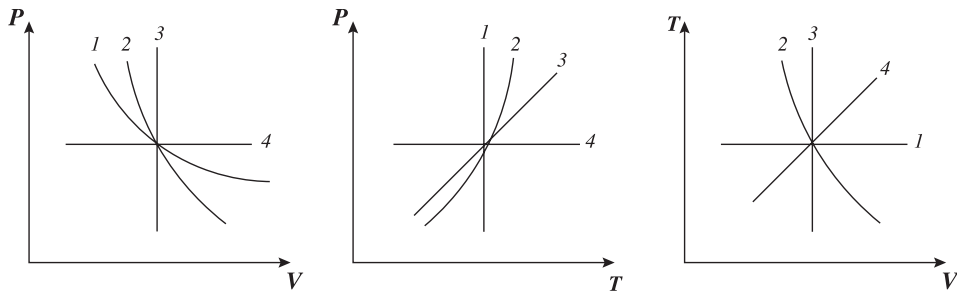

Fig. 1.5. Isothermal (1), adiabatic (2), isochoric (3) and isobaric (4) functions of an ideal gas are shown in the planes of different coordinates: P-V, P-T and T-V.

CHAPTER 2.

SECOND LAW OF THERMODYNAMICS

2.1 Reversible and Irreversible Processes and the Carnot Cycle

Imagine a thermodynamic system tied to some balance with blocks and ropes in such way that the system itself can exercise external work on its environment. Suppose the system is in contact with some thermal reservoirs with which it can interchange heat. We shall call masses and heat reservoirs "the system's immediate surroundings" since between them and the system there exists a direct relationship. As a result of a certain process due to interaction with its immediate surroundings, the system goes from the initial thermodynamic state i to the final state f. At the same time, due to the work performed therein, some of the weights that are hanging increase their potential energy (they are raised), and some other part diminishes their potential energy (they are lowered). Furthermore, some heat reservoirs transferred a certain amount of heat to the system, while others received heat from it. If, at the end of the process, this thermodynamic system, as well as the weights and heat reservoirs return to the initial state without any changes in their immediate surroundings, then the process will be called reversible. If, on the other hand, these conditions cannot be achieved, then the process is called irreversible.

In real processes, dissipative phenomena always occur, leading to energy dispersion. The effects of this type include thermal conductivity, viscosity, electric resistance, magnetic hysteresis, friction, etc. By definition, for a process in a thermodynamic system to be reversible, it is necessary that the work done by the system is given back to it when the process is performed in the reverse order. Theoretically, this is possible only if in the process under consideration there is no dissipative phenomena. Since such a condition cannot be satisfied: reversible processes in thermodynamics are an abstract idealization. It is worth noting that classical mechanics also uses similar idealizations, for instance: material points (particles), bodies moving without friction, weightless ropes, etc.

Suppose, that it is necessary to carry out a process that involves the transformation of heat into work. Let us analyze one of these processes consisting of isothermal

expansion of a gas. In such case, the gas temperature remains constant and the internal energy does not change. Nevertheless, as the gas expands, the pressure in the system decreases, and as soon as it becomes equivalent to the atmospheric pressure, the process ends. Therefore, in order to continue with the production of work using the same gas, it is necessary to return the system back to the starting point, that is, to run what is called a cycle, using some additional complementary processes. When we reviewed the properties of an ideal gas, it was shown that the isothermal curve and the adiabatic curve are different. As shown in Fig. 2.1.*a*, the isothermal curve *1* is called equilateral hyperbola, and the adiabatic curve *2* is called scalene hyperbola. From this it can be concluded that a combination of two isothermal and two adiabatic curves can be used to form a cycle as seen in Fig. 2.1.*b*, which is called the Carnot cycle. Analyzing this cycle in detail, we assume that the isothermal and adiabatic processes that correspond to it are reversible. As this is done, we realize that these processes are most convenient to perform work, because in the first case all transferred heat is converted into work, and in the second case all work is done due to the internal reduction of the heat of the gas.

The Carnot Cycle is represented by 2 adiabatic and two isothermal curves in Fig. 2.1.*b* in the coordinate plane *P–V*. These four curves intersect at points *1, 2, 3*, and *4*. Curves *1–2* and *3–4* are isothermal with their corresponding temperatures T_1 and T_2, where $T_1 > T_2$. Curves *2–3* and *4–1* are adiabatic curves.
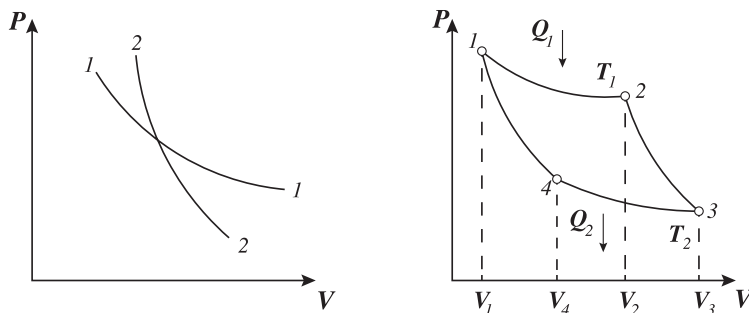
Fig. 2.1. a) Isothermal (1) and adiabatic (2) curves in the coordinate plane P-V; b) The Carnot cycle.

During the cycle, the following four processes occur:
  1.- The reversible isothermal expansion of a gas along the isothermal curve *1–2*, showing the corresponding changes in pressure and volume. During this

process, the heat Q_1 that is transmitted to the heater gas at temperature T_1, is totally transformed into work W_1

$$Q_1 = W_1 = RT_1 \ln \frac{V_2}{V_1}$$

Its magnitude is equal to the area under the curve which goes from point *1* to *2* (*1*, V_1, V_2, *2*).

2.- The reversible adiabatic expansion of a gas from point *2* to *3*. When this happens, the gas temperature decreases from T_1 to T_2, and the positive work generated by it is equal to

$$W_2 = c_V(T_1 - T_2)$$

This is represented in the diagram by the area (*2*, V_2, V_3, *3*).

3.- The reversible isothermal compression of the gas from *3* to *4*. This process takes place while performing external work on the gas, and it is equals to the amount of heat transferred from the gas to the refrigerant, which has a temperature T_2. In the isothermal process, the internal energy of an ideal gas does not change. The work performed on the gas in this process is negative and equal to
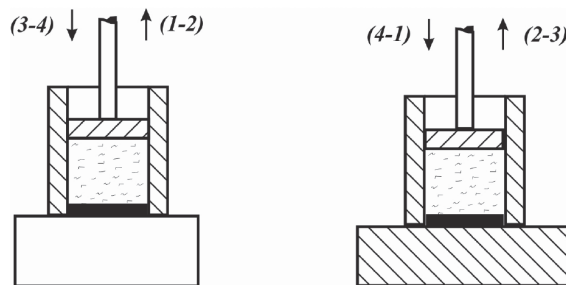
$$Q_2 = W_3 = -RT_2 \ln \frac{V_3}{V_4}$$

Fig. 2.2. a) The heater and the refrigerator (1-2), (3-4): isothermal processes; b) An ideal thermo-insulator (2-3), (4-1): adiabatic processes.

4.- The reversible adiabatic compression of the gas from point *4* to *1*, produced by the external work. The work performed by the gas in this process is

$$W_4 = c_V(T_1 - T_2)$$

The idealized Carnot cycle we have just analyzed can be represented with the diagram in Fig. 2.2. This figure shows a cylinder filled with an ideal gas. The piston slides on the walls of the cylinder without friction, and both components are made of thermally insulating material, while the bottom of the cylinder is made of a material ideal for thermal conductivity. Let us assume that at the beginning the gas has temperature T_1, volume V_1, and pressure P_1. We place the cylinder on a huge grate having a temperature T_1, which we shall call "heater" or "heat source", now we gradually remove the load from the piston, allowing the gas to reversibly expand to volume *2* at temperature T_1, carrying out the isothermal process *1*, *2* (Figs. 2.1 and 2.2).

Having reached state *2*, we pull the heat source, place the cylinder on the heat insulating template, and further reduce the load on the piston, causing an adiabatic expansion of the gas (process *2–3*). When the volume V_3 is reached, the gas temperature will decrease due to its expansion to T_2 (Fig. 2.2.*b*). After that,the heat insulating template is removed from the base of the cylinder and placed on the surface having a temperature T_2 equal the gas temperature at that moment. This cooler body we shall call "refrigerator". Now, let us now reversibly and isothermally compress the gas to T_2, reducing the volume from V_3 to V_4, the value of which we shall determine later. Having reached volume V_4, we take out the refrigerator and place the base of the cylinder back on the insulating template. We continue to compress the gas, now performing an reverse adiabatic compression. In this case, the temperature will rise as the gas is compressed by the external work done on it to achieve compression, a process that yields energy as a result of work performed. The compression stops when the temperature reaches T_1 again.

The algebraic sum of all performed work in a cycle is equal to

$$W = R(T_1 \ln \frac{V_2}{V_1} - T_2 \ln \frac{V_3}{V_4}). \tag{2.1}$$

In the *P–V* diagram (Fig. 6b), this work is represented by the area of a curvilinear figure (*1, 2, 3, 4*). In this sketch, the volumes V_1, V_2, y V_3 can be arbitrary, while V_4 must have a determined and unique value as a condition for the system to return to the initial state.

Let us determine volume V_4. For the adiabatic curve (*2–3*)

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\chi - 1}$$

For the adiabatic curve (*4–1*)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\chi - 1},$$

where

$$\frac{V_2}{V_3} = \frac{V_1}{V_4}, \quad \text{or} \quad \frac{V_3}{V_4} = \frac{V_2}{V_1}. \tag{2.2}$$

If the volumes V_1, V_2 y V_3, which, as we mentioned earlier, can be determined arbitrarily, then the value of V_4, can be found and cannot be arbitrary, but is given by the equation (2.2), which allows the gas to return to the initial state, thus closing the cycle. Using (2.2), the total work of the gas (2.1) produced by the reversible Carnot machine can be written as

$$W = R(T_1 - T_2) \ln \frac{V_2}{V_1}. \tag{2.3}$$

At this moment, we define that the work relationship with regards to the heat absorbed from the heat source we named "heater" in this process, Fig. 2.1.*b*, the isothermal at T_1 in this cycle, determines the efficiency of the machine to execute the Carnot cycle we are examining

$$\eta = \frac{W}{Q_1}. \tag{2.4}$$

The total amount of heat Q_1 received from the heater is

$$Q_1 = RT_1 \ln \frac{V_2}{V_1}.$$

Therefore,

$$\eta = \frac{R(T_1 - T_2) \ln \dfrac{V_2}{V_1}}{RT_1 \ln \dfrac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1}. \tag{2.5}$$

From the equation (2.5), it can be seen that the efficiency of a reversible and ideal Carnot machine can never be equal to 100% when operating between two thermal reservoirs having the temperatures T_1 and T_2, at which the colder (isothermal T_2) is a real temperature, which is always higher than the temperature absolute zero. Also in this machine, both isothermal and adiabatic processes are used, which are the most convenient for obtaining high efficiency. For this reason, in any real machine operating between the same temperatures T_1 and T_2, that is, between the reservoir or heat source from which heat is taken to perform work at temperature T_1, and the one to which it gives heat T_2, the efficiency will always be lower than in (2.5), mainly because any cycle other than the Carnot cycle will, by definition, involve processes other than isothermal and adiabatic. In addition, due to the always present dissipative effects, all real processes are irreversible and always require the loss of useful work, and, consequently, a decrease in efficiency. Thus, the efficiency of a reversible Carnot machine is a limit or a maximum superior value that can never actually reached for any real thermal machine operating between the temperature of the heater T_1 and the temperatures of the cooler T_2, respectively.

Obviously, the efficiency of a Carnot machine can be determined in a different way using the following reasoning: in a heater's cycle a certain amount of heat is removed or absorbed Q_1. In the same cycle a certain amount of heat is transmitted to the refrigerator Q_2, being $Q_2 < Q_1$. It is clear that the difference $Q_1 - Q_2$ becomes useful work, so the efficiency of the Carnot machine is expressed by the relation

$$\eta' = \frac{Q_1 - Q_2}{Q_1}. \tag{2.6}$$

The expression (2.6) is more general than (2.5), which is valid only for reversible Carnot machines, that means only for the following $\dot{\eta} = \eta$. From which we obtain

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}. \quad \text{or} \quad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \tag{2.7}$$

Let us analyze the results of the processes occuring in the Carnot machine in one cycle:

  1.- The source of high temperature called "heater" loses an amount of heat Q_1.

2.- Q_2 is the amount of heat transmitted to the cold source we have called "refrigerator".

3.- The difference $Q_1 - Q_2$ is the net heat transformed into useful work W.

After the cycle is finished, the gas returns to its original state at the beginning and, therefore, its internal energy does not change.
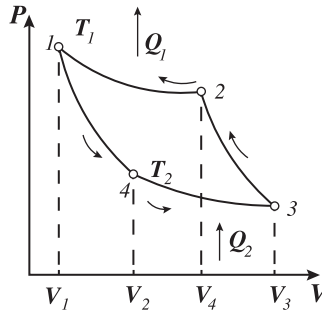

Fig. 2.3. The inverse Carnot cycle.

The machine under consideration, that performs mechanical work in a given cycle, is called the direct Carnot machine. If the direction of the cycle is reversed, as shown in Fig. 2.3, then this will be the inverse Carnot machine. In this machine, the cycle consists of the following reversible processes:

1.- The expansion of the gas from volume V_1 to volume V_2 occurs simultaneously with the cooling from T_1 to T_2 along adiabatic *1–4*. In this process, the system performs an external work and its quantity is proportional to the area *1, 4, V_2, V_1*, and the work is positive.

2.- The gas expansion from volume V_2 to volume V_3 maintaining T_2 constant along isothermal *4 – 3*. In this process, the system also performs an external work which is proportional to the area *4, 3, V_3, V_2*.

3.- The gas compression from volume V_3 to volume V_4 as it is heated from temperature T_1 to temperature T_2 along adiabatic *3–2*. This work is performed when consuming an external work (this is negative) determined by the area *3, 2, V_4, V_3*.

4.- The gas compression of volume V_4 up to the initial volume V_1 at a constant temperature T_1 and along isothermal *2–1* which is also due to an external work, which is proportional to the area *1, 2, V_4, V_1*.

It follows that the amount of mechanical work performed by the machine during the cycle is negative. In other words, for the inverse Carnot machine to work, it is

necessary to consume external work proportional to the area *1*, *2*, *3*, *4* and equal to $Q_1 - Q_2$. During the cycle of the inverse Carnot machine, the following changes take place:

1.- A compression work is performed on the gas that equals to $Q_1 - Q_2$.
2.- Q_2 is the amount of heat removed from the refrigerator.
3.- Q_1 is the amount of heat transferred to the heater.

Thus, the inverse Carnot machine allows heat to be removed from the cold body and transferred to a hotter one, that is, it operates as a refrigerator or refrigeration machine. The efficiency of the inverse Carnot machine can be found the same way as the direct one, using the formula (2.5). That is why, if the direct Carnot machine is converted into a inverse one or into a refrigerating machine, then its efficiency will not change.

The Carnot machine is an idealization, useful in other physics disciplines as well, such as material points or particles, frictionless pulleys, electric circuits, resistanceless cables, and many more.

2.2 Clausius Postulate and the Second Principle of Thermodynamics

Clausius postulate, also known as one of the variants of the second principle of thermodynamics, was formulated on the basis of a generalization of a large number of experimental observations. According to this postulate, heat cannot itself transfer from a cold body to a hot one. The expression "itself" implies that the processes of heat transfer from a cold body to a hot one cannot occure spontaneously, since they require the participation of some other agent or physical process. In other words, the transfer of heat from a cold body to a hot body requires an additional process that makes the first possible, that is, taking heat from the cold body and transferring it to one that has a higher temperature or is "hotter". This situation, in which an auxiliary process is required to take heat away from a cold body and deliver it to a hot one, we describe as a process that requires "compensation". Clausius defines these processes requiring compensation as negative processes. On the contrary, processes that occur by themselves in an isolated system and, by definition, do not require additional processes, are considered as positive processes. An example is the transfer of heat from a cold body to a hot one and the conversation of heat into work.

Using the above definitions, one can elaborate a way to formulate the second principle of thermodynamics:

> *"In an isolated system, positive processes are unique and occur by themselves, that means they do not need compensation, while negative processes can only take place with compensation processes which must occur simultaneously to make it possible".*

Let us illustrate this formulation of the second principle of thermodynamics with the examples analyzed in Section 2.1, that take place in the direct and reverse Carnot machines.

1.- Let us suppose that the reversible direct Carnot machine works in an isolated system. Therefore, in a Carnot machine cycle, a negative process of transformation of heat into mechanical work takes place, compensated by a positive process of heat transmission from the heater to the refrigerator. See Figs. 2.1.*b* and 2.2.*a*.

2.- Now, let us consider the work utilized by the Carnot inverse reversible machine in an isolated system. In this case, during the cycle two processes also occur. During the first one, heat is removed from the refrigerator (which is the source of heat that corresponds to the isothermal with the lower temperature) and it is transmitted to the heater (the source corresponding to the isothermal with the highest temperature in the cycle), during the second, work is transformed into heat. The first process (negative), is completely compensated by the second positive process.

2.3 The Carnot Theorem for Reversible and Irreversible Cycles and the Absolute Temperature

The efficiency of any reversible Carnot machine operating between the same heat source "hot" and another source "cold" (with a lower temperature of former) are the same and do not depend on the type or phase state of the substances used to produce a thermodynamic cycle between these heat sources in these machines.

This principle is called Carnot's theorem. To demonstrate this theorem, suppose that the system is connected to a hot heat source and another, which we have called "cold", the two machines having in common the fact of being connected to those same sources. Also, suppose they function as two inversible Carnot machines. Assume, that the first machine uses an ideal gas, while in the second, any real

substance is used. Let us consider that the temperatures of the hot heat source and the cold heat source are T_1 y T_2, respectively, and let us make the arrangements so that work W that these machines produce are equal.

   1.- The hot source yields a heat amount Q_1.

   2.- Work is produced W.

   3.- The cold source receives a heat amount $Q_2=Q_1-W$ which is "surplus" heat.

   4.- The cycle's efficiency is therefore: $\eta_1 = \dfrac{W}{Q_1}$

Considering now a cycle of work W by the second machine, that operates between the same heat sources, but this time working with a substance, we have accordingly:

   1.- The hot source yields a heat amount Q_1.

   2.- Work is produced W.

   3.- The cold source receives a heat amount Q_1-W.

Now assume for a moment that the efficiency of the second machine η_2 is higher than the first. If

$$\eta_2 > \eta_1 \ \text{ or } \ \frac{W}{Q_2} > \frac{W}{Q_1},$$

then it must be that Q_1-Q_2 in order to satisfy this inequality.

Now let us start machine I in the opposite direction, maintaining its efficiency unchanged. The gas is compressed at the expense of the useful work produced by the second machine. In such case, both machines together form a device that works by itself and independently, as all work produced by machine II is spent for compression of gas in machine I. In this machine, the heat balance of the refrigerator is determined by the ratio

$$(Q_1 - W) - (Q_2 - W) = Q_1 - Q_2 \tag{2.8}$$

Since the difference between Q_1 and Q_2 is positive, the expression (2.8) determines the heat amount lost by the heat source, called refrigerator, during the working cycle of such device. During this cycle, the "hot" heat source or heater receives the amount of heat, also defined by the difference Q_1-Q_2. Consequantly, during the operation of an insulated device, Q_1-Q_2 is the amount of heat transferred from the cold body to the hot one. Incidentally, it is important to mention here that this transition

(negative process) is not accompanied by any compensation by a positive process, which contradicts the Clausius postulate. This contradiction arises as a consequence of the initial assumption that $\eta_2 > \eta_1$. As a result, this assumption is not true and

$$\eta_2 \leq \eta_1$$

If we convert the machine *II* backwards and convert the machine *I* to a direct one, then, by analogy with the previous reasoning we have the following

$$\eta_1 \leq \eta_2$$

from this, we conclude that these expressions can only be simultaneously true if the equality $\eta_1 = \eta_2$, is assumed.

Fundamental independence of efficiency of a reversible Carnot machine on the type and phase state of the substance is a consequence of expression (2.5), in which the factors haracterizing the properties of the ideal gas are simply not demanded, but are expressed only in terms of temperature of the substances "hot" or "cold". For this reason, the Carnot cycle is valid not only for a gas, but also for any liquid or solid substance.

We are now going to demonstrate that between two heat reservoirs, the heater and the refrigerator, no machine can be more than efficient than the Carnot machine.

First, we shall demonstrate that the efficiency of any reversible cycle at temperatures T_1 and T_2 ($T_1 > T_2$) is always lower then the efficiency of a Carnot machine operating in the same range of temperatures of the heater and the refrigerator, T_1 y T_2, respectively.
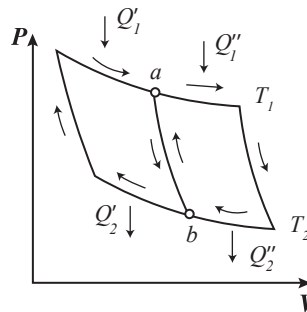

Fig. 2.4. Division of the Carnot cycle into two.

Let us divide Carnot cycle into two cycles, as shown in Fig. 2.4, using the adiabatic *ab*. Thus, both adiabatic processes occurring along *ab* in the two new cycles are mutually compensated, since they are directed in opposite directions. That is why the initial cycle is equivalent to the two new cycles. It becomes clear that it cannot only be divided, but also arranged with adiabats from different Carnot cycles. In this case, if in these cycles use heaters and refrigerators with different temperatures, the resulting cycle will be, for example, as shown in Fig. 2.5.
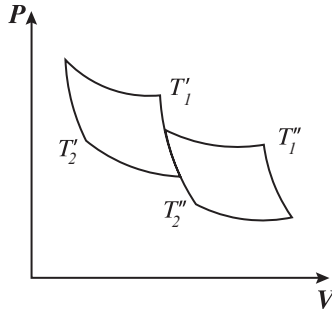
Fig. 2.5. 2 different Carnot cycles with different refrigerators and heaters.

Let us analyze the arbitrary reversible cycle represented in Fig. 2.6. In this cycle, the temperature changes continuously from T_1 to T_2. Regarding this arbitrary cycle, let us describe the Carnot cycle that operates between the same temperatures, in which we draw a series of adiabatic cycles spaced at infinitesimal intervals.

Fig. 2.6. Presentation of the Carnot cycles as a sum of elementary cycles.

After this operation, the Carnot cycle ends up divided into a series of elementary cycles. From the points of intersection of the adiabatics with the arbitrary inversible

cycle, we will draw segments of the isotherm as indicated in Fig. 2.6. Now, we can see that this reversible arbitrary cycle can be presented as a series of elementary Carnot cycles with different temperatures within the interval between T_1 and T_2. The efficiency of the elementary cycles is equal to:
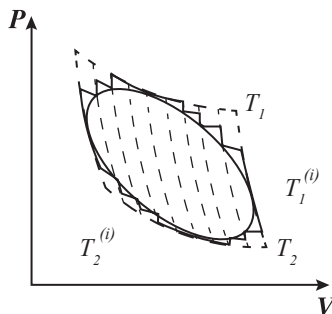
$$\eta^{(i)} = \frac{T_1^{(i)} - T_2^{(i)}}{T^{(i)}} = 1 - \frac{T_2^{(i)}}{T_1^{(i)}}. \tag{2.10}$$

The efficiency of the elementary cycles into which the Carnot cycle, described around an arbitrary inversible cycle, is equal to:

$$\eta = 1 - \frac{T_2}{T_1} \tag{2.11}$$

From Fig. 2.6 it can be seen that $T_1 > T_1^{(i)} > T_2^{(i)} > T_2$ and, therefore,

$$\frac{T_2^{(i)}}{T_1^{(i)}} > \frac{T_2}{T_1} \tag{2.12}$$

where

$$\eta^{(i)} < \eta \tag{2.13}$$

which means that of all reversible cycles we can conceive of that operate between T_1 and T_2, the most convenient one for obtaining useful work from, that is to say the most efficient one, is the Carnot cycle.

Now analyze any irreversible machine. In such a machine certain irreversible processes occur, which reduce the useful work produced by the cycle. In other words, the efficiency is reduced. For example, the processes in irreversible machine are always accompanied by some friction. This means that part of the heat induced to the system will be spent in work to overcome the force of friction. It is also clear that if heat conduction occurs in certain parts of the machine, some of the heat that comes from the heater will be consumed in warming up those parts and it will dissipate uselessly. In this fashion, when irreversible processes exist, a part of the work produced will be lost to friction so that it will not be taken advantage of by turning it into useful work. In view of this,

the efficiency of the irreversible machine (*I*) will always be lower than that of the reversible Carnot machine (*II*), and the inequality (2.11) will always be true:

- Due to the losses associated with the irreversible processes in machine (*I*);
- Due to the difference between the processes occurring in machine (*I*) vs. the isothermal and adiabatic processes taking place in machine (*II*).

For the reversible Carnot machine $\dfrac{Q_1 - Q_2}{Q_1} = \dfrac{T_1 - T_2}{T_1}$ where:

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} \qquad \text{or} \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{2.14}$$

From a vast number of experiments, we know that when measuring the temperature of one given body, different types of thermometers may show different readings. In other words, the value of experimental measurements of temperature depend on the type of thermometer being used or the material of given body. One definition of the Kelvin scale can be formulated like this: "The reason of two temperatures in the Kelvin scale is equal to the reason of the heat shed by the heat source or heater and the heat transferred to the cold source or refrigerator, in a cycle in which the reversible Carnot machine operates between two heat sources at these temperatures".

2.4 Entropy

Like in the previous paragraph, we are going to divide the Carnot cycle into two cycles with the help of an intermediate adiabatic *ab* (Fig. 9), which, as mentioned before, are equivalent to the initial cycle. Heats Q_1 and Q_2 can be represented as the sum

$$Q_1 = Q_1' - Q_1'' \qquad \text{and} \qquad Q_2 = Q_2' - Q_2''$$

For each of the two new cycles (Fig. 2.4) it can be annotated

$$\frac{Q_1'}{T_1} = \frac{Q_2'}{T_2} \tag{2.15}$$

$$\frac{Q_1''}{T_1} = \frac{Q_2''}{T_2}. \tag{2.16}$$

Adding (2.15) and (2.16), we obtain

$$\frac{Q_1^{'}}{T_1} + \frac{Q_1^{''}}{T_1} = \frac{Q_2^{'}}{T_2} + \frac{Q_2^{''}}{T_2}.$$

(2.17)

It is obvious that if the initial cycle is divided in several segments with the help of several intermediate adiabats, then (2.17) can now be written in a generalized form as follows:

$$\sum \frac{Q_1^{(i)}}{T_1} = \sum \frac{Q_2^{(i)}}{T_2}.$$

(2.18)

In such case, if a given quantity of Carnot cycles in which heaters and refrigerators are used at different temperatures composed of adiabats, as shown in fig. 2.6, then the expression (2.17) for n number of cycles in annotated in the form

$$\sum_{i=1}^{n} \frac{Q_1^{(i)}}{T_1^{(i)}} = \sum_{i=1}^{n} \frac{Q_2^{(i)}}{T_2^{(i)}},$$

(2.19)

where i is the number of cycles in an interval from 1 to n

If we now consider the elementary cycles, in which infinitesimal quantities of heat $đQ_1$ and $đQ_2$ are transferred, then for each one of these cycles

$$\frac{đQ_1}{T_1} = \frac{đQ_2}{T_2}.$$

(2.20)

Let us assume that we have a reversible cycle that is not a Carnot cycle. We shall divide this cycle into a large number of elementary Carnot cycles, as shown in Fig. 2.7. It follows that any reversible cycle can be represented by a set of such elementary cycles which are adiabatic, and that the error arising from replacing a continuous curve by a series of linear steps can be reduced to an infinitesimal value by tending to an eigenlimit. Then the operation (2.19) is transformed into the expression

$$\int \frac{đQ_1}{T_1} = \int \frac{đQ_2}{T_2}$$

(2.21)

or

$$\int \frac{dQ_1}{T_1} - \int \frac{dQ_2}{T_2} = 0$$

(2.22)
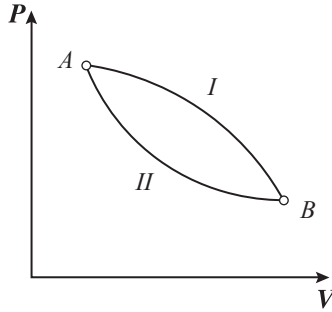
Fig. 2.7. To the definition of entropy.

Since Q_1 is transmitted from the heater to the object, and Q_2 in turn from the object to the refrigerator, the heat has different signs: dQ_1 can be considered as positive and dQ_2 as negative. Therefore equation (2.22) represents an algebraic sum of the heat divided by the temperature $\dfrac{dQ}{T}$ along the contour, since the contour is closed, its closed curve integral is equal to zero

$$\oint \frac{dQ}{T} = 0$$

(2.23)

from (2.23) we see that the integrand is a function of state and therefore, if a reversible thermodynamic system moves from state A to state B, then the magnitude of the integral $\int_A^B \dfrac{dQ}{T}$ does not depend on the trajectory along which the transition takes place. In other words, the integral $\int_A^B \dfrac{dQ}{T}$ within the limits of A–B along an arbitrary trajectory I, is always equal to the integral of $\int_A^B \dfrac{dQ}{T}$ within the limits of A–B but calculated along another arbitrary trajectory II. See Fig. 2.7.

$$\int_A^B \frac{dQ}{T}\bigg|_I = \int_A^B \frac{dQ}{T}\bigg|_{II}$$

(2.24)

Let us demonstrate this expression. Assume that the system can be taken from state *A* to state *B*, as show in Fig. 2.7, using two reversible processes along trajectories *I* and *II*. Since each one of these processes is reversible, then the whole contour *A-I-B-II-A* is also reversible, for this contour, the Clausius integral is aplicable, i.e.

$$\oint \frac{đQ}{T}\bigg|_{AIBIIA} = 0$$

Dividing the contour of this integral in two, we have

$$\oint \frac{đQ}{T}\bigg|_{AIBIIA} = \int_A^B \frac{đQ}{T}\bigg|_I + \int_B^A \frac{đQ}{T}\bigg|_{II}$$

where the reversing the limits of the second integral, which changes sign from positive to negative, we obtain

$$\int_A^B \frac{đQ}{T}\bigg|_I = \int_A^B \frac{đQ}{T}\bigg|_{II}$$

which, in the end, needed to be demonstrated.

In view of the above, the infinitesimal magnitude $\frac{đQ}{T}$ is a total differential of the state function of the parameters. This function was first introduced by Clausius, who denoted it with the letter **S** and called it entropy, and the integral (2.23) was called the Clausius integral for any reversible cycle.

In this manner, the second law of thermodynamics can be written as

$$\frac{đQ}{T} = dS. \tag{2.25}$$

If the state parameters are known, entropy can always be calculated as a function of these parameters. Similarly, in solving a number of problems, it is often convenient to use entropy as a state-independent parameter with the same hierarchy in regards to temperature, pressure and volume, which

are state parameters of a thermodynamic system, but if necessary they can be considered as a function of state.

The entropy of a system can increase or decrease, depending on whether $đQ$ is positive or negative, since the absolute temperature T is always positive. Obviously, if the system receives heat, then the entropy increases, otherwise the entropy of the system decreases when the system yields heat. Since in adiabatic processes $đQ=0,$ in such cases the entropy of the system remains unchanged, and therefore the adiabat is called the curve of constant entropy or isentrope, and then process is called isentropic.

The entropy can be added. This means that the entropy of a system composed of several bodies is equal to the sum of the entropies of these bodies. For this reason, the entropy is an extensive magnitude. The physical units of entropy, as can be seen from (2.25) coincide with the units of specific heat capacity.

Most problems in thermodynamics are formulated by establishing relationships between different variable parameters of state that can be functionally related.

Next, we consider some of the mathematical properties that we need in thermodynamics, which follow from the methods and theory of the partial differential equations. The linear and quasi-linear differential equations, that have the following general form, are widely used in several disciplines of science and engineering:

$$dF = U_1 du_1 + U_2 du_2 + U_3 du_3 + ... + U_n du_n , \qquad (2.26)$$

where $u_1,$ $u_2,$ u_3 are independent variables, and $U_1,$ $U_2,$ $U_3,$ ... are functions of these variables.

In the theory of differential equations, it is shown that when the Euler condition (1.9) is satisfied, there is a so-called integration $\psi = \psi$ $(U_1, U_2, U_3,...)$, which, by multiplying the left part of equation (2.26), turns it into a total differential of the function. Note that if there are only two independent variables in (2.26), or, in other words, if the differential equation has the form

$$dF(x,y) = M(x,y)dx + N(x,y)dy . \qquad (2.27)$$

then, as the theory of differential equations prescribes, integration for it always exists.

As thoroughly discussed in previous sections, heat itself is not a function of state, since it only characterizes one of the possible ways in which a thermodynamic system can interchange energy with its environment, which means that $đQ$ is not a total differential, but only an infinitesimal amount. Multiplying $đQ$ by the reciprocal of the temperature allows us to convert this magnitude to the total differential of a function we have called the entropy S, so for $đQ$ the reciprocal of the temperature is the integration factor.

2.5. The General formulation of the Second Law of Thermodynamics.

By definition, the efficiency of any thermal machine is the ratio that exists between the difference in heat Q_1–Q_2, that is transformed into useful work, and the heat Q_1 transferred to the system. Therefore, for an irreversible thermal machine, the efficiency is given by the expression

$$\eta` = \frac{Q_1 - Q_2}{Q_1}$$

As shown earlier, for an irreversible Carnot machine, it also holds

$$\eta = \frac{T_1 - T_2}{T_1}$$

where $\eta`<\eta$. It means that

$$\frac{Q_1 - Q_2}{Q_1} < \frac{T_1 - T_2}{T_1} \quad \text{or} \quad 1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

so that

$$\frac{Q_2}{Q_1} > \frac{T_2}{T_1} \quad \text{and} \quad \frac{Q_2}{T_2} > \frac{Q_2}{T_1}$$

This way, if in an irreversible Carnot machine the ratio of heat to its temperature $\frac{Q_1}{T_1}$ is equal to the corresponding ratio of the heat extracted from

the refrigerator above its temperature $\dfrac{Q_2}{T_2}$, then, in an irreversible machine, $\dfrac{Q_1}{T_1}$ is less than $\dfrac{Q_2}{T_2}$ and therefore

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} < 0 \qquad (2.28)$$

In the following we shall adopt again the convention previously mentioned in section 2.4, where we eliminate the negative sign in Q_2 remembering that this is heat delivered to the refrigerator.

If we do again what we did before, sum up various Carnot cycles, then for the new Carnot composition we can rewrite the following

$$\sum \frac{Q_1^{(i)}}{T_1} + \sum \frac{Q_2^{(i)}}{T_2} < 0 \qquad (2.29)$$

Or, if we proceed with the integration, we obtain

$$\int \frac{đQ_1}{T_1} + \int \frac{đQ_2}{T_2} < 0 \qquad (2.30)$$

For the whole contour, if we take into account that Q_2 is negative
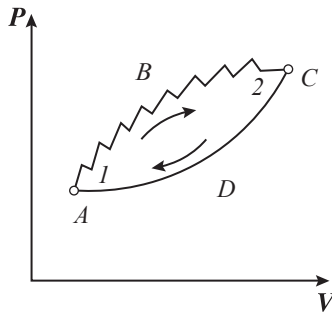
$$\oint \frac{đQ}{T} < 0 \qquad (2.31)$$

Fig. 2.8. To the definition of entropy.

Let us analyze the thermodynamic system for which, in two given states *1* and *2*, the entropy has values S_1 y S_2, respectively. With the help of an irreversible process, we will transfer the system from the initial state *1* to the final state *2,* along a jagged highly irreversible trajectory *ABC*, as shown in Fig. 2.8. After this, we return to the initial state of the system, but with the help of a reversible process along the *CDA* trajectory. Since the whole process in Fig. 2.8 is an irreversible process, then

$$\int_1^2 \frac{đQ}{T}\bigg|_{irrev} + \int_2^1 \frac{đQ}{T}\bigg|_{rev} < 0 \tag{2.32}$$

For the second process (reversible) transition from *2* to *1* we have

$$\int_2^1 \frac{đQ}{T}\bigg|_{rev} = S_1{-}S_2 \tag{2.33}$$

Substituting (2.33) in (2.32) we obtain

$$\int_1^2 \frac{đQ}{T}\bigg|_{irrev} < S_1{-}S_2 \tag{2.34}$$

It follows from formula (2.34) that if an infinitesimal change of state occurs in the thermodynamic system, then

$$\frac{đQ}{T} < dS \quad \text{o} \quad TdS < đS \tag{2.35}$$

Therefore, for the general form we have

$$TdS \geq đQ \tag{2.36}$$

As a result, any process in an isolated system always occurs in such a way and in such a direction that the net sum of the entropy in the system does not decrease. When the processes in the system are completed, the entropy reaches its maximum value. After that, the entropy can no longer increase, i.e., not a single process in the system will occur arbitrarily. At the same time, this means that the system has reached the point of thermodynamic equilibrium. For this reason, the second principle of thermodynamics, according to Clausius, can be formulated as follows: "The entropy of any isolated system always tends to its maximum".

In statistical mechanics, the second thermodynamic principle first received a clear interpretation in the classical works of Boltzmann. Without going into the detail of statistical mechanics, let us analyze its postulates, whichshow that the entropy of an isolated system does not decrease. To do this, we define the macro- and microstates of the system: a macroscopic state is understood as any state specified by the values of a limited set of thermodynamic parameters, such as energy, density, temperature, pressure, etc. On the contrary, a microscopic state is considered certain if the positions and velocities of all particles in a system are known. In view of this, the same values of the thermodynamic parameters of the system can be obtained from different positions and velocities of particles in the system. Therefore, any macroscopic state usually corresponds to a large number of microscopic state. Each of this microscopic states is depicted as a set of points - a six-dimensional space known as phase space and defined by three coordinate axes x, y, and z and by three axes for the velocity components V_x, V_y y V_z. If a number of mathematical operations are performed, then it is more convenient to use the motion or impulse components instead of velocity components

$$p_x = mV_x, \, p_y = mV_y, \, p_z = mV_z$$

Suppose that the phase space is divided into an infinite series of elementary six-dimensional cells with sides dx, dy, dz, dp_x, dp_y, and dp_z. Therefore, the volume dW of one of these elementary cells of the phase space is defined as

$$dW = dx \cdot dy \cdot dz \cdot dp_x \cdot dp_y \cdot dp_z$$

Obviously, some particle in the system can be localized in a cell if its coordinates lie within the limits from x to $x+dx$, from y to $y+dy$ and from z to $z+dz$, and for the velocity components V_x to V_x+dV_x, V_y to V_y+dV_y and V_z to V_z+dV_z. It is assumed that the movement of a particle inside a cell does not lead to any general or macroscopic change in the state of the system. Just as the macroscopic state of the system remains unchanged if certain particles inside the cell change their position. The position of the particles inside a cell in the phase space may change as a result of the interaction between them or when a force is applied due to fields interacting with the system.

That way, each macroscopic state can be formed by a series or set of microstates w, which is called thermodynamic probability for a given macrostate. The

probability of occurence of a macrostate in a system grows with the number of microstates that compose it. For instance, the probability of a state forming is smaller when all the particles are concentrated in an infinitesimal volume of the system and have velocities equal in magnitude and direction, since this state is formed by only one combination. In statistical physics it is shown that entropy increases with the number of microstates forming it. At the same time, this indicates a certain parallelism between the entropy S of the system and the thermodynamic probability w. In other words, there is a functional interdependence between them. Such dependence was first established by Boltzmann who showed it on the base of statistical considerations

$$S = k \ln(w) \qquad (2.39)$$

where k is Boltzman constant, equal to the gas constant rate R and *Avogadro number N*.

CHAPTER 3.

THERMODYNAMIC FUNCTIONS AND THE GENERAL CONDITION OF EQUILIBRIUM OF A THERMODYNAMIC SYSTEM

3.1 Thermodynamic Functions

Below is the combined expression of the first (1.18) and second (2.25) laws of thermodynamics for a system in equilibrium.

$$TdS = dU + PdV \text{ o } dU = TdS - PdV \tag{3.1}$$

In (3.1), we are going to analyze the internal energy U as a function of the parameters S and V. In this case, the partial derivatives of U for these parameters are respectively T and $-P$, respectively. In fact, if U is a function of S and V, then, by definition, its total differential is

$$dU = \left.\frac{\partial U}{\partial S}\right|_V dS + \left.\frac{\partial U}{\partial V}\right|_S dV \tag{3.2}$$

Equalizing (3.1) and (3.2) we obtain

$$\left.\frac{\partial U}{\partial S}\right|_V = T \qquad \left.\frac{\partial U}{\partial V}\right|_S = -P \tag{3.3}$$

Let us introduce the definition of the characteristic function. A characteristic function is a function whose partial derivatives for some of its state parameters are, in turn, equal to other state parameters. Therefore, by definition, U is a characteristic function, if it is considered as a characteristic function of the V and S parameters.Let us write (3.1) in general form

$$dU_1 = Xdx + Ydy \tag{3.4}$$

where

$$X = f_1(x,y) \text{ and } Y = f_2(x,y).$$

Let us solve the problem of changing variables in expression (3.4) so that the roles variables in one or both terms are reversed. In other words, we transform (3.4) into three total differentials of new functions

$$dU_2 = xdX + Ydy$$
$$dU_3 = Xdx + ydY$$
$$dU_4 = xdX + ydY$$

This transformation is known in mathematics as the Legendre transformation, it is performed by sequential subtraction from dU_1 of the differentials of the product of the corresponding conjugate variables $d(xX)$, $d(yY)$ and $d(xX+yY)$.

1.-We subtract from (3.1) the differential $d(TS)$. Then on the left part of the new expression we get

$$dU - d(TS) = d(U - TS)$$

On the right part we get

$$TdS - PdV - TdS - SdT = -Sdt - PdV$$

Finally

$$d(U - TS) = dF = -SdT - PdV, \tag{3.5}$$

where $(U - TS)=F$. The function F is called the Helmholtz function. If we consider F as a function of T and V then its complete differential is

$$dF = \frac{\partial F}{\partial T}\bigg|_V dT + \frac{\partial F}{\partial V}\bigg|_T dV \tag{3.6}$$

From (3.5) and (3.6) it is inferred that

$$\frac{\partial F}{\partial T}\bigg|_V = S, \quad \frac{\partial F}{\partial V}\bigg|_T = -P$$

Thus, the Helmholtz energy is a characteristic function for variables T and V, and their partial derivatives with respect to these variables are entropy and pressure.

2.- Considering that the second term in (3.1) is preceded by minus sign, we subtract the differential $-d(VP)$ from this equality. On the right side we get

$$dU + d(PV) = d(U + PV)$$

Correspondingly, on the left side of the new function we have:

$$TdS + PdV + VdP - PdV = TdS + VdP$$

We indicate that

$$H = U + PV \tag{3.7}$$

The function just obtained and introduced in paragraph 1.4 is called enthalpy and its total differential is equal to

$$dH = TdS + VdP \tag{3.8}$$

It is clear that

$$dH = \frac{\partial H}{\partial S}\bigg|_P dS + \frac{\partial H}{\partial S}\bigg|_S dP \quad \text{and} \quad \frac{\partial H}{\partial S}\bigg|_P = T, \; \frac{\partial H}{\partial S}\bigg|_S = V$$

It follows that the enthalpy is a function of the variables S and P.

3.- Subtracting differential $d(TS - PV)$ from (3.1), on the left side of the equation we have

$$dU - d(TS - PV) = d(U - TS + PV),$$

and correspondingly on the right side we have

$$TdS - PdV - TdS - SdT + PdV + VdP = -SdT + VdP$$

In other words

$$d(U - TS + PV) = -SdT + VdP$$

Denoting $U - TS + P$ as G. This function is called the Gibbs energy, so

$$dG = -SdT + VdP, \tag{3.9}$$

and

$$\frac{\partial G}{\partial T}\bigg|_{P} = -S, \; a \; \frac{\partial G}{\partial P}\bigg|_{T} = V$$

Therefore, the Gibbs energy is a characteristic function of the variables T and P. Expressions (3.1), (3.5), (3.8) and (3.9) for the differentials of thermodynamic functions are also called the fundamental thermodynamic identities. All four characteristic functions, often referred to as thermodynamic potentials, have been obtained. These functions are shown in the following table:

Characteristic Function	Parameters	Relationship in the Internal Energy	Partial Differential Equations
Internal Energy U (Isochoric-Isoentropic Potenetial)	V S	U	$\dfrac{\partial U}{dS}\bigg|_{V} = T$ $\dfrac{\partial U}{\partial V}\bigg|_{S} = -P$
Entalpy H (Isobaric-Isoentropic Potential)	P S	$U + PV$	$\dfrac{\partial H}{\partial S}\bigg|_{P} = T$ $\dfrac{\partial H}{\partial P}\bigg|_{S} = V$
Helmholtz Energy F (Isochoric-Isothermal Potential)	T V	$U - TS$	$\dfrac{\partial F}{\partial T}\bigg|_{V} = -S$ $\dfrac{\partial F}{\partial V}\bigg|_{T} = -P$
Gibbs Energy G (Isobaric-Isothermal Potential)	T P	$U-TS+PV=H-TS$	$\dfrac{\partial G}{\partial T}\bigg|_{P} = -S$ $\dfrac{\partial G}{\partial P}\bigg|_{T} = V$

Table 1. Thermodynamic potentials

3.2 Equilibrium in Thermodynamic Systems
with different External Conditions

Using the expression

$$TdS \geq dU + PdV \qquad (3.11)$$

obtained on the basis of the first and second thermodynamic principles, the thermodynamic equilibrium conditions can be formulated for a system under different external conditions. We mean that the equality in (3.11) corresponds to the state of equilibrium of the system, and the inequality corresponds to the state of non-equilibrium, when certain processes occur in the system.

Based on several external conditions, we shall analyze the five most important particular cases.

1.- Fully isolated constant volume system.
   The internal energy of an isolated system remains unchanged. That is why, when $U=const$ and $V=const$, then $dU=0$ and $dV=0$. From (3.11) it derives that

$$TdS \geq 0$$

Since $T>0$, then $dS>0$. This means that as certain processes occur under non-equilibrium conditions, the entropy of a system under extreme conditions increases ($dS>0$). Immediately after the completion of non-equilibrium process, the system comes to a state of equilibrium, and the entropy reaches its maximum value ($dS=0$). Thus, in the state of equilibrium $S=S_{max}$ and $d^2S< 0$.

2.- The system is located in a thermostat whose function is to maintain a constant temperature and, in addition, to maintain a constant volume.

   In the case of $T=const$ and $V=const$, from (3.11) it derives that

$$TdS \geq dU \quad \text{or} \quad dU - TdS = d(U - TS) \leq 0$$

Considering that $U–TS=F$, we have $dF\leq0$. Therefore, during the time needed for the system to approach equilibrium, the Helmholtz energy decreases ($dF<0$). In view of

this, under these external conditions, all irreversible processes in the system take place in such direction that the Helmholtz energy continuously diminishes until, finally, it reaches equilibrium at

$$dF = 0,\ F = F_{min}\quad \text{and}\quad d^2F > 0$$

3.- The system is again located in a thermostat, but this time under constant pressure. Under these conditions $T=const$ and $P=const$. Then, it follows from (3.11) that

$$dU - TdS + PdV \leq 0$$

or

$$dU - TdS + PdV = d(U - TS + PV) = dG \leq 0$$

If the system is in thermostat at constant pressure, then the Gibbs energy gradually decreases as the system approaches equilibrium. Just before the equilibrium $dG<0$, in the equilibrium $dG=0$. Thus, when $T=const$, the equilibrium condition is to reach the minimum of the Gibbs energy.

$$dG = 0,\ G = G_{min}\quad \text{and}\quad d^2G > 0$$

4.- The system occupies a constant volume and the entropy remains unchanged, i.e., $V=const$ and $S=const$.

From the inequality $dU–TdS+PdV\leq0$ we derive that $dU\leq0$. As a consequence, under such conditions, the internal energy of the system decreases and, when equilibrium is reached, has a minimum value ($dU=0$). This result is illustrative if we consider that in order to maintain the entropy unchanged, it is necessary to deprive the system of energy all the time and to deliver it to the environment or to external bodies. Otherwise, under irreversible processes, the entropy must increase.

5.- The system is under constant external pressure and the entropy remains unchanged. In this case $P=const,$ and $S=const$.

From $dU - TdS + PdV \leq 0$ we infer that

$$dU + PdV = d(U + PV) = dH \leq 0.$$

This means that the enthalpy and heat contained in the system continuously decrease in time ($dH<0$), and when equilibrium is reached, $dH=0$.

Table 2 summarizes the equilibrium conditions.

External constant parameters	Certain processes that occur in the system	Equilibrium conditions
U,V	$dS > 0,\ S$ - increases	$dS = 0,\ d^2S<0,\ S=S_{max}$
V,T	$dF < 0,\ F$ - decreases	$dF = 0,\ d^2F>0,\ F=F_{min}$
P,T	$dG < 0,\ G$ - decreases	$dG=0,\ d^2G>0,\ G=G_{min}$
V,S	$dU < 0,\ U$ - decreases	$dU=0,\ d^2U>0,\ U=U_{min}$
P,S	$dH < 0,\ H$ - decreases	$dH=0,\ d^2H>0,\ H=H_{min}$

Table 2. Equilibrium conditions.

3.3 Gibbs Fundamental Equation

In any heterogeneous system, along with the most simple thermodynamic processes like, for example, heat absorption or external work, phase transformations such as evaporation, fusion, crystallization can occur. In addition, chemical reactions may take place between the various components of the system. As a result of these processes, the number of particles in the composit states will change in time. These changes themselves imply changes in the thermodynamic functions or potentials we have just reviewed in sections 3.1 and 3.2. In other words, the thermodynamic functions in their general form must depend not only on the corresponding state parameters, such as, for example, P, T, or V, but also on the number of particles of the various components of the system $n_1, n_2, n_3,...n_k$, (or concentrations), which, as we have already mentioned, are also thermodynamic parameters. That is why, for the thermodynamic functions in their general form it is necessary to take into consideration their dependence on the number of particles of the components, i.e.,

$$U = U(S, V, n_1, n_2, n_3,...,n_k)$$
$$H = H(S, P, n_1, n_2, n_3,...,n_k)$$
$$F = F(T, V, n_1, n_2, n_3,...,n_k)$$
$$G = G(T, P, n_1, n_2, n_3,...,n_k)$$

Let us analyze the internal energy, for which it was previously shown that

$$dU = TdS - PdV \qquad (3.12)$$

On the right side (3.12), the first term is related to the influence of temperature and entropy on dU, and the second term describes the dependence of the internal energy differential on the work performed on the system or the system itself. It is natural to assume that, as before, the internal energy corresponding to the equal particles, but being in different phases, can be in general different. For this reason, the total sum of the internal energy of the system must also be associated with the energy consumption due to different chemical transformations or phase transitions from some part of the system to another. If, for example, we assume that the first component goes from one phase to another, than as a result of this transition the change in the number of particles of this component is equal to a negative value dn_1 (negative for one phase and positive for the other). Obviously, the change in internal energy ΔU_1 associated with this transition is proportional to the number of particles involved in the transition and can be written as $\mu_1 dn_1$

$$\Delta U_1 = \mu_1 dn_1$$

In this expression, μ_1 is a proportionality coefficient. Since dn_1 is dimensionless, μ_1 represents the value of the internal energy that corresponds to a particle in phase 1, component 1. In other words, for a multicomponent system, the proportionality coefficient μ_1 must be equal to the partial differential equation of the internal energy of the system with regards to n_1

$$\mu_1 = \frac{\partial U}{\partial n_1}\bigg|_{S,V}$$

Similarly, if chemical reactions or phase transformations result in changes in concentrations of other components, these changes will affect dU and can be annotated as:

$$\mu_2 dn_2, \ \mu_3 dn_3, \cdots, \ \mu_k dn_k$$

The total sum of the internal energy conditioned by the concentration changes of all system components is written as

$$\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots + \mu_k dn_k = \sum \mu_i dn_i$$

Let us show that in the presence of varibles S, V, n_1, n_2, n_3, ..., n_k in a multi-component system the corresponding expression has the form

$$dU = TdS - PdV + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{S,V,nj} dn_i \tag{3.13}$$

which is known as Gibbs Fundamental Equation. Therefore, if the internal energy of a thermodynamic system is a function of S, V, n_1, n_2, n_3, ..., n_k, then, by definition, the differential of this function is

$$dU = \left.\frac{\partial U}{\partial S}\right|_{V,n_i} dS + \left.\frac{\partial U}{\partial V}\right|_{S,n_i} dV + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{S,V,nj} dn_i \tag{3.14}$$

In (3.14), the derivatives of the internal energy in entropy and volume are evaluated with a constant n_i, i.e., for a system with a fixed composition. In this connection, the values of the derivatives must coincide with the corresponding known derivatives of the system in which there are no phase transitions, chemical reactions, or mass interchange, etc., i.e.,

$$\left.\frac{\partial U}{\partial S}\right|_{V,n_i} = \left.\frac{\partial U}{\partial S}\right|_{V} = T$$

$$\left.\frac{\partial U}{\partial V}\right|_{S,n_i} = \left.\frac{\partial U}{\partial V}\right|_{S} = -P$$

Thus, the relationship (3.13) is demonstrated. Analogously, considering the functions

$$H = H(S, P, n_1, n_2, n_3, \ldots, n_k)$$
$$F = F(T, V, n_1, n_2, n_3, \ldots, n_k)$$
$$G = G(T, P, n_1, n_2, n_3, \ldots, n_k)$$

The following variants can be obtained from the Gibbs Fundamental Equation

$$dH = TdS - VdP + \sum_{i=1}^{k} \left.\frac{\partial H}{\partial n_i}\right|_{S,P,nj} dn_i \tag{3.15}$$

$$dF = -SdT - PdV + \sum_i \left.\frac{\partial F}{\partial n_i}\right|_{T,V,\,n_j} dn_i$$

$$dG = -SdT + VdP + \sum_i \left.\frac{\partial G}{\partial n_i}\right|_{T,P,\,n_j} dn_i$$

(3.15)

The enthalpy has been previously defined as

$$H = U + PV.$$

Differentiating this equation, we obtain

$$dH = dU + PdV + VdP \tag{3.16}$$

Substituting (3.13) in (3.16), we have

$$dH = TdS - PdV + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{S,V,\,n_j}$$

$$dn_i + PdV + VdP = TdS + VdP + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{S,V,\,n_j} dn_i$$

(3.17)

Likewise, differentiating $F = U - TS$ and $G = U - TS + PV$ and substituting the expressions obtained from (3.13), we denote

$$dF = -SdT - PdV + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{T,V,\,n_j} dn_i \tag{3.18}$$

$$dG = -SdT + VdP + \sum_{i=1}^{k} \left.\frac{\partial U}{\partial n_i}\right|_{T,P,\,n_j} dn_i \tag{3.19}$$

Comparing of the Gibbs fundamental equations (3.13), (3.17), (3.18) and (3.19) it is seen that to the sum of the partial differential equations of U, H, F and G corresponds to the equal number of particles. In principle, it can be shown that the same partial differential equations of the thermodynamic (potential) functions have the same value with regard to the number of particles, i.e.,

$$\left.\frac{\partial U}{\partial n_i}\right|_{S,V,nj} = \left.\frac{\partial U}{\partial n_i}\right|_{S,P,nj} = \left.\frac{\partial F}{\partial n_i}\right|_{T,V,nj} = \left.\frac{\partial G}{\partial n_i}\right|_{T,P,nj} = \mu_1 \tag{3.20}$$

Nonetheless, we shall limit ourselves to the demonstration of this equality for the Gibbs energy, since for the other functions it can be demonstrated exactly the same way. This demonstration will be presented in the next section. For now, we note only that the equality (3.20) defines the chemical potential of the system that corresponds to one specific magnitude, i.e., equal to one particle of one of the characteristic functions. The Gibbs fundamental equations can be represented in the following forms

$$dU = TdS - PdV + \sum_i \mu_i \, dn_i$$

$$dH = TdS + VdP + \sum_i \mu_i \, dn_i$$

$$dF = -SdT - PdV + \sum_i \mu_i \, dn_i$$

$$dG = -SdT + VdP + \sum_i \mu_i \, dn_i$$

In all the formulas of this section (this and in the following ones) the number of particles $n_i,...,n_1,n_2,n_3,...,n_i,...,n_k$ can be replaced by their corresponding concentrations $x_1,x_2,x_3,...\ x_i,...,x_k$, when dealing with multiple component systems.

3.4 Thermodynamic Equilibrium Conditions in a Multi-Component System

The equilibrium conditions in various thermodynamic systems can be studied based on the analysis of any of the previously considered functions, *U, H, F,* or *G.* As it was shown earlier, the system is in equilibrium when each of these functions has a minimum value. For this reason, the study of the equilibrium states of a thermodynamic system is practically reduced to the determination of those conditions under which the differential of any these functions is zero. Thus, from the mathematical point of view, the functions *U, H, F,* or *G* turn out to be equivalent. Likewise, one of the thermodynamic parameters for the internal energy and enthalpy is the entropy *S*, that can be calculated but cannot be measured or changed. In this relation, from a practical and physical point of view, the most convenient are the Gibbs and Helmholtz energies, that depend on *T, P,* and *V,* i.e., depend on parameters that can be easily measured and changed. Therefore, in the

literature devoted to the study of equilibrium conditions of any thermodynamic system, it is these functions that are most often used. Later, when studying the construction of equilibrium phase diagrams, we will analyze in detail how the Gibbs energy behaves.

The general differential form of the Gibbs energy is written as

$$dG = -SdT + VdP + \sum_{i=1}^{k} \frac{\partial G}{\partial n_i}\bigg|_{T,P,\,n_j} dn_i$$

Assuming that we have an isolated system with k components and φ number of phases, the necessary condition for the equilibrium of the system is the invariance of temperature and pressure in all phases, so $T' = T'' = T''' =...= T^\varphi$ and $P' = P'' = P''' =...= P^\varphi$. In this case, dT and dP are zero. Thus,

$$dG_{T,P} = \sum \frac{\partial G}{\partial n_i}\bigg|_{T,P,\,n_j} dn_i$$

or

$$dG_{T,P} = \sum_{i=1}^{k} \frac{\partial G}{\partial n_i}\bigg|_{T,P,\,n_j} dn_i = \frac{\partial G}{\partial n_1}\bigg|_{T,P,\,n_2,n_3,n_4,...,n_k} dn_1 + \frac{\partial G}{\partial n_2}\bigg|_{T,P,\,n_1,n_3,n_4,...,n_k}$$

$$dn_2 + \frac{\partial G}{\partial n_3}\bigg|_{T,P,\,n_1,n_2,n_4,...,n_k} dn_3 +...+ \frac{\partial G}{\partial n_k}\bigg|_{T,P,\,n_1,n_2,n_3,...,n_{k-1}}$$

$$dn_k = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 +...+\mu_k dn_k$$

The general equilibrium condition is $dG|_{T,P} = 0$. If we substitute P and T into all phases, then possible changes in the system lead to a transition of components from one phase to another. Although such a transition is possible even for only some of these components, the system will not be in a state of equilibrium. As a result, one of the essential conditions of equilibrium is that such transitions are impossible because they have already been completed. If dG', dG'', dG'''... etc., are the Gibbs free energies of phase transitions, then

$$dG\big|_{T,P} = dG'\big|_{T,P} + dG''\big|_{T,P} +...+,dG^\varphi =0 \tag{3.21}$$

or

$$\mu_1' dn_1' +\mu_2' dn_2'+...+\mu_k' dn_k' + \mu_1'' dn_1'' +\mu_2'' dn_2''+...+\mu_k'' dn_k''+$$
$$\mu_1''' dn_1'''+\mu_2''' dn_2'''+...+\mu_k''' dn_k'''+......+ \mu_1^\varphi dn_1^\varphi +\mu_2^\varphi dn_2^\varphi+...+\mu_k^\varphi dn_k^\varphi = 0 \tag{3.22}$$

If the system is isolated, the change in the number of particles of different components take place only internally due to phase changes, i.e. there is no exchange of matter (or number of atoms or molecules) with the environment, then

$$
\begin{aligned}
dn'_1 + dn''_1 + dn'''_1 + \ldots + dn^{\varphi}_1 &= 0 \\
dn'_2 + dn''_2 + dn'''_2 + \ldots + dn^{\varphi}_2 &= 0 \\
dn'_3 + dn''_3 + dn'''_3 + \ldots + dn^{\varphi}_3 &= 0 \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
dn'_k + dn''_k + dn'''_k + \ldots + dn^{\varphi}_k &= 0
\end{aligned}
\tag{3.23}
$$

Suppose now that the number of particles of all phases, except the first one, do not change. In other words, transitions between different phases occur only in the case of particles of the first component. Then (3.23) has the following form

$$
\begin{aligned}
dn'_1 + dn''_1 + dn'''_1 + \ldots + dn^{\varphi}_1 &= 0 \\
dn'_2 = dn''_2 = dn'''_2 = \ldots = dn^{\varphi}_2 &= 0 \\
dn'_3 = dn''_3 = dn'''_3 = \ldots = dn^{\varphi}_3 &= 0 \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
dn'_k = dn''_k = dn'''_k = \ldots = dn^{\varphi}_k &= 0
\end{aligned}
\tag{3.24}
$$

The top line in (3.24) can be written as

$$
\begin{aligned}
dn^{\varphi}_1 = -dn'_1 - dn''_1 - dn'''_1 = -\ldots - dn^{\varphi-1}_1 \\
dn'_2 = dn''_2 = dn'''_2 = \ldots = dn^{\varphi}_2 = 0 \\
dn'_3 = dn''_3 = dn'''_3 = \ldots = dn^{\varphi}_3 = 0 \\
\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
dn'_k = dn''_k = dn'''_k = \ldots = dn^{\varphi}_k = 0
\end{aligned}
\tag{3.25}
$$

Substituting (3.25) in (3.22)

$$
\mu'_1 dn'_1 + \mu''_1 dn''_1 + \mu'''_1 dn'''_1 + \ldots + \mu^{\varphi}_1(-dn'_1 - dn''_1 - dn'''_1 = -\ldots - dn^{\varphi-1}_1) = 0
$$

Thus,

$$
(\mu'_1 - \mu^{\varphi}_1)\, dn'_1 + (\mu''_1 - \mu^{\varphi}_1)dn''_1 + (\mu'''_1 - \mu^{\varphi}_1)dn'''_1 + \ldots + (\mu^{\varphi-1}_1 - \mu^{\varphi}_1)dn^{\varphi-1}_1 = 0 \tag{3.26}
$$

since according to the previous assumption, only particles from the first

component of the system are interchanged between phases,$' n_1$," n_1,''' n_1,...,n_1 are independent variables. As a consequence, dn_1, dn_1, " dn_1 ''' ,..., $dn_{1}^{\varphi-1}$,dn_{1}^{φ} are not equal to zero. That is why, the expression (3.26) is possible only if all coefficients of differentials are equal to zero, i.e.,

$$(\mu'_1 - \mu^{\varphi}_1) = 0, \ (\mu''_1 - \mu^{\varphi}_1) = 0, \ (\mu'''_1 - \mu^{\varphi}_1) = 0,...,(\mu^{\varphi-1}_1 - \mu^{\varphi}_1) = 0$$

or

$$\mu'_1 = \mu''_1 = \mu'''_1 = ... = \mu^{\varphi}_1$$

Thus, if two or more phases are in equilibrium, the chemical potentials of the components of these phases must be equal to each other. As a result, the equilibrium condition is as follows

$$\mu^l_i = \mu^s_i \tag{3.27}$$

This conclusion is quite obvious if we consider that, in an isolated system in thermodynamic equilibrium, the Gibbs energy is minimal. Let us imagine that the system is in equilibrium, but the chemical potentials (the Gibbs energy corresponding to a particle) of one component i in different phases are different. For clarity, assume that $\mu_i > \mu_i$. When component i transitions from the first phase to the second phase, the Gibbs energy of the whole system decreases, which contradicts our initial assumption or the fact that a minimum is reached only when the system is in equilibrium. In other words, any transition of components between phases is caused by an increase in energy which is possible only at unequal chemical potentials. If there are no such transactions in the system, the system is in equilibrium, that corresponds to the minimum of its energy, and hence to the equality of the chemical potentials in different phases of similar components.

An important conclusion can be derived from this: If the chemical potentials of the components of a multiphase system are different, then among all the phases, the one with the lowest value of μ is the stable one.

3.5 The Gibbs phase rules

Suppose that a thermodynamic system contains k components. The chemical composition of this system is determined by the concentrations, that can be represented, for example, by weight, atomic, molar and volume parts. Thus,

$$x_1 = \frac{m_1}{\sum m_i} \,, \; x_2 = \frac{m_2}{\sum m_i} \,, \; x_3 = \frac{m_3}{\sum m_i} \,,..., \; x_k = \frac{m_k}{\sum m_i} \qquad (3.28)$$

, where $m_1.\ m_2.\ m_3,\ ...,\ m_k$ are the masses of the component, and $\sum m_i$ is the sum of the masses of all components. If we speak about atomic concentrations, then the numerator of (3.28) will contain respectively the number of atoms of each component, and the denominator the total number of atoms. Obviously, in this case, the number of atoms of any atom i can be determined by dividing the mass of the component by its atomic mass.

Consider a heterogeneous equilibrium system composed of two phases, one of which is an aqueous solution saturated with salt (NaCl) and the other is a crystal of this salt. In this system, the concentration of NaCl in the solid phase is equal to *1* or *100%*, and in its liquid phase the salt concentration is naturally less than *1*. Note that at different temperatures the concentration of the salt in the water will be different, while in the solid phase it will remain unchanged. From the previous example, we can observe that in the general case when the number of components is greater than *1*, the chemical composition of the phases in equilibrium can be differentiated, and therefore each phase must be categorized by its concentrations. From (3.28) it derives that for each phase

$$x_1 + x_2 + x_3 + ... + x_k = 1 \qquad (3.29)$$

And so, for example, if three independent variables *x, y,* and *z* are linked by a system that contains three equations, then the three variables will have a fixed value; if there are only two linked variables then two variables will have a fixed values and the third can have arbitrary values. If there is only one equation for the three variables, then only one of the variable values is defined and the others are arbitrary.

The number of parameters that can take arbitrary values in thermodynamics is called: degrees of freedom in a thermodynamic system. This way, in the above

examples, the first case corresponds to zero degrees of freedom, the second to one degree of freedom, and to the third case to two degrees of freedom. Obviously, to find the number of degrees of freedom of any thermodynamic system of general form, it is necessary to have the number of variable parameters of the system, and then find the number of equations linking these parameters. The difference between these numbers determines the number of degrees of freedom of the thermodynamic system under consideration.

Assume that there are k components and φ phases in the system. The chemical composition of the system is determined by the concentrations $x_1, x_2, x_3, \ldots x_k$ and the sum of these concentrations is equal to one. It follows from (3.29) that $k-1$ concentrations can be independently varied in one phase, but the last remaining concentration is predetermined when they are chosen. Hence, we have $k-1$ variable concentration in one phase, and a total of $(k-1)$ independent variable concentrations in the φ phases, respectively. The variables are pressure and temperature, and for this reason in the φ phases we get

$$2 + (k\text{-}1)\ \varphi \tag{3.30}$$

independent variable values.

The equilibrium condition in a phase and multicomponent system is given by the equality of the chemical potentials of each component in all phases. As we have done so far, denoting the components by the lower index and the phase the upper index, so we write the equilibrium condition in the form of a system of equations

$$
\begin{aligned}
\mu_1' &= \mu_1'' = \mu_1''' \ldots = \mu_1^{\varphi} \\
\mu_2' &= \mu_2'' = \mu_2''' \ldots = \mu_2^{\varphi} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
\mu_k' &= \mu_k'' = \mu_k''' \ldots = \mu_k^{\varphi}
\end{aligned}
\tag{3.31}
$$

Each row in (3.31) contains $\varphi-1$ equations, and the number of rows is equal to k. Thus, the total number of equations in (3.31) is equal to

$$k(\varphi - 1) \tag{3.32}$$

When the number of variables in (3.30) is equal to the number of equations (3.32), then, as stated earlier, the system has a singular solution and their

variables have fixed values. If the number of variables is larger, the difference between this number and the number of equations determines the number of parameters that can be assigned completely arbitrary values. In other words, this difference will determine the number of degrees of freedom f of the thermodynamic system in equilibrium

$$f = [2 + (k - 1)\ \varphi] - [k\ (\varphi - 1)] = k - \varphi + 2 \tag{3.33}$$

Expression (3.33) is called the Gibbs Phase Rule. Naturally, if any of the parameters is constant, for example, pressure, the number of degrees of freedom of the system diminishes by one

$$f = k - \emptyset + 1$$

CHAPTER 4.

ONE COMPONENT SYSTEMS

4.1 Thermodynamic Equilibrium in a One Component System

The Gibbs phase rule for a one component system *(k=1)* is written as

$$f = 3 - \varphi$$

the possible number of degrees of freedom *k=1* can be equal to *2*, *1*, or *0*, which corresponds to the equilibrium of one phase (vapor, liquid or solid), two phases (vapor-liquid, vapor-solid and liquid-solid), or three phases (vapor-liquid-solid). We are going to consider the equilibrium in a one component system, analyzing the behavior of the Gibbs energy, since, as pointed out before, this thermodynamic function is characteristic when temperature and pressure are chosen as parameters.

We first consider a simple case. Assume that ice, water, and vapor are in equilibrium. If we add more ice or water in the same state as the equilibrium phases, i.e. at *T=0°C* and *P=1 atm*, the system will remain in equilibrium. Likewise, the total Gibbs energy of the whole system will also increase because the total number of particles in the system has increased. So, the Gibbs energy is extensive or dependent on the number of particles in the system. Therefore, when studying the equilibrium of phases, it is necessary to consider its specific value $\bar{G} = \dfrac{G}{n}$. Furthermore, in order to simplify, we shall eliminate the horizontal line over *G*, remembering that the Gibbs energy, like all other thermodynamic functions, is an extensive function. There is no need to keep this sign when analyzing the chemical potentials determined by other corresponding partial differential equations in regards to the number of particles, for example, from the Gibbs energy itself.
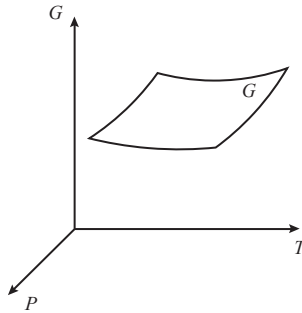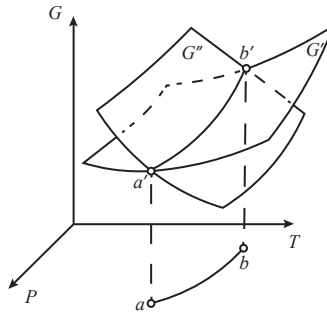
**Fig. 4.1. Representation of the energy Gibbs in dependence on temperature T
and pressure P for a one-component system of one phase.**

It should be kept in mind that the condition $dG<0$ means that at constant temperature and pressure only the changes possible in the system are those for which the Gibbs free energy decreases. The state of equilibrium in the system occurs when $dG=0$ and the Gibbs energy reaches its minimum value. Let us consider the possible cases of phase equilibrium in a one component system.

1. Suppose that the system is one phase, and therefore, has two degrees of freedom.

   Since the Gibbs energy is a function of temperature and pressure, then

   $$G=G(T,P). \qquad (4.1)$$

   For the case of phase equilibrium in the coordinate system G, T, P, equation (4.1) represents a certain area shown in Fig. 4.1. Each state in the single-phase system, at which all three coordinates (G, T, P) are assigned certain values, is characterized by one point in this area.

   Thus, the area or the field of the points in the space of three coordinates G, T, P is a geometric image of a system with two degrees of freedom. Such system, with $f=2$, is called divariante system. In a bivariant equilibrium, i.e., in the presence of one phase, T and P can vary within certain limits, which corresponds to two degrees of freedom.

2. In the case of a one-component system, when there are two phases and, respectivly, $f=1$, then equation (4.1) is applied for each of these phases

$$G' = G'(T,P)$$
$$G'' = G''(T,P) \qquad\qquad (4.2)$$

Let us define the relation in which the values G' and G'' are in the case when the analyzed two-phase system is in equilibrium. Assume, that G' and G'' are different values, and for definiteness we will consider $G' > G''$. Then a transition of a certain amount of substance from the first phase to the second phase decreases the value of the Gibbs energy in the whole system decreases. Since any system tends to minimize the Gibbs energy, such a transition will proceed until the first phase is completely transformed into the second phase. In the opposite case, i.e, when $G' < G''$, the entire second phase will turn into the first phase. Hence, if $G' \neq G''$, an irreversible phase transition occurs in the system, starting with a large value of Gibbs energy and evolving towards a phase with a smaller value Gibbs energy.
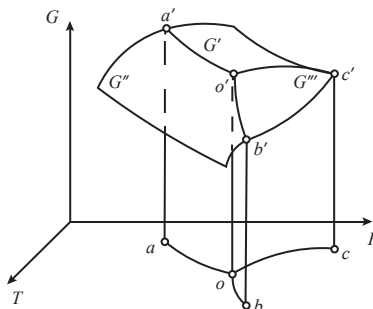

Fig. 4.2. Representation of the energy Gibbs in dependence on temperature T and pressure P for a one-component system of two phases.

Thus, the thermodynamic system under consideration turns out to be nonequilibrium, since there is an arbitrary transformation from one phase to another. Consequently, the assumption of inequality of the Gibbs energy for both analyzed phases leads us to a contradiction with the initial affirmation about equilibrium of the system.

Consequently, the equilibrium condition of both phases consists in the equivalence of G' and G''. The equililbrium state of a two-phase system is described simultaneously by two equations (4.2) with three variables G, T, and P, of which only one is independent. Equations (4.2) define in the space of three coordinates G, T, P two areas intersecting each other along the line $a'b'$ (Fig. 4.2), which meets the equilibrium condition of phases $G' = G''$.

Therefore, a' b' is a geometric image or place of the points of the system with one degree of freedom, since the line is a one-dimension geometric object. When the thermodynamic system is characterized by one point located on the line of any of the two variables parameters, it can be arbitrarily changed, but provided that the parameter left must have a definite, well defined and unique value.

So, if the temperature is specified, the vapor pressure or vice versa can be determined, which exactly corresponds to a system of degrees of freedom. A system having one degree of freedom is called singular or monovariant.

3. In conclusion, let us analyze the case of coexistence of three phases in a one-component system. An example of such system we can consider the case of three phases in equilibrium: gas, liquid and solid. For each one of these phases, as it was shown earlier, the equation (4.1) is fulfilled in such a way that the state is now determined by a system of three equations

$$
\begin{aligned}
G' &= G' \,(T,P) \\
G'' &= G'' \,(T,P) \\
G''' &= G''' \,(T,P)
\end{aligned}
\qquad (4.3)
$$

According to the previous reasoning about both phases, the whole system will be in equilibrium only if $G'=G''=G'''$. In this case, if, for example, the Gibbs energy of the first and second phases is greater than G''', then both phases will transform into the third one. From this, we can draw a simple but extremely important conclusion: of the three analyzed phases, the one with the lowest Gibbs energy will be stable.

Fig. 4.3. Representation of the energy Gibbs in dependence on temperature T and pressure P for a one-component system of three phases.

The three equations (4.3) with the three variables *G, T* and *P* define the three-phase state of a one-component thermodynamic system. None of these three components is independent, since the system has one single solution. Such a solution in the spatial system of three coordinates *G, T, P* is represented by a single point. This point is located at the intersection of the three areas (Fig. 4.3), that define the state of each of the three phases of the system and that are described by equations (4.3). The coexistence in equilibrium of the three phases of a one-component system is possible only in a particular state, under quite specific conditions, or, in other words, when the temperature and pressure have unique values. If one single parameter changes, there will be at least one phase change. This is why a system that does not have a single degree of freedom is called an invariant system. One example of such system is: ice, water and vapor, which exist in equilibrium only at *T=0 °C* and *P=1 atm*. Note that the invariability of this one-component three phase system has long been used to determine the reference point or point of zero in the Celsius temperature scale (there is a slight shift relative to zero in the Celsius scale of the temperature of coexistence in thermodynamic equilibrium of the three phases: ice, liquid and vapor, a state of coexistence known as the "triple temperature point of water" that occurs at a temperature of *0.01°C*.

It is important to note that in a one-component system several solid phases can be formed (polymorphism). Each variant of the solid phase has its own crystal structure. The physical and chemical properties of the phases are also different and they will be located in different regions on the state diagram. Two well-known forms of carbon can be considered as an example: diamond and graphite.

4.2 The Clausius Equation – Clapeyron and the Thermodynamics of Phase Transformations in a One Component System

Let it be a case of two phases of a one-component system in equilibrium. Using the concept of the Gibbs energy, we derive a thermodynamic equation known as the Clausius–Clapeyron equation, that describes the equilibrium between the two phases. When *P* and *T* are equal, both phases are in equilibrium, then

$$G_1 = G_2.$$

As a consequence

$$d\ (G_1 - G_2) = 0$$

On the basis of this definition of the G differential, we

write
$$d(G_1 - G_2) = \frac{\partial(G_1 - G_2)}{\partial T}\bigg|_P dT + \frac{\partial(G_1 - G_2)}{\partial P}\bigg|_T dP$$

Hence

$$\frac{\partial G}{\partial T}\bigg|_P = -S, \quad \frac{\partial G}{\partial P}\bigg|_T = V$$

we have

$$\frac{\partial(G_1 - G_2)}{\partial T}\bigg|_P dT + \frac{\partial(G_1 - G_2)}{\partial P}\bigg|_T dP = -(S_1 - S_2)\ dT + (V_1 - V_2)\ dP = 0$$

By definition

$$Q = TS \ \text{ y } \ \Delta Q = \Delta H \ \text{ when } P = constant,$$

From this we obtain

$$\Delta H = H_1 - H_2 = T(S_1 - S_2)$$

Thus

$$-(S_1 - S_2)\ dT + (V_1 - V_2)\ dP = -\frac{\Delta H}{T}\ dT + (V_1 - V_2)\ dP = -\frac{\Delta H}{T}\ dT + \Delta V dP = 0$$

Finally,

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{4.4}$$

Equation (4.4) is called the Clausius–Clapeyron equation. Let us analyze, using this equation, some particularities of the phase transformations or transitions that can occur in a one-component system.

Two types of phase transition are distinguished: first and second order transitions. The first order transitions are accompanied by discrete changes in internal energy and density. The first order transitions are always associated with the emission or absorption of heat, which is called a phase transition of latent heat. Examples of first order transitions are evaporation, fusion, crystallization, sublimation and distillation, transitions of a solid from one crystalline modification, and others.

Second orger phase transitions are transitions in which no discrete changes in internal energy and density occure. The heat of the second order phase transitions is zero, however, discrete changes in heat capacity and dilation and compression coefficients occure during these transitions. Examples of the second order phase transitions are the transition of liquid helium into a superfluid state, the transition at the Curie point (Curie temperature) of a ferromagnetic substance into a paramagnetic substance.

Let us consider the phase transitions of the first order. At the absolute temperature $T=0$ the entropy of the solid phase is also zero. At a higher temperature and constant pressure, entropy can be calculated using the expression

$$đQ = TdS \quad y \quad dS = \frac{đQ}{T}$$
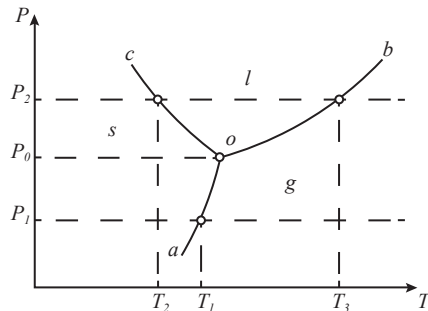
Fig. 4.4. Projection of the energy Gibbs of a one-component system of three phases on the P-T plane.

Just like the heat capacity of a solid c_P^{sol} varies slightly with temperature, it can be argued that the entropy of a solid is practically a function of temperature alone. Thus

$$S_{sol} = \int_0^T \frac{c_p^{sol}}{T} \; dT \tag{4.5}$$

A phase diagram of a single phase thermodynamic system is shown in Fig. 4.4. This diagram was obtained by projecting the dependences of the three phases of the Gibbs energy – solid, liquid and gas relative to temperature and pressure (Fig. 4.3) onto the horizontal plane P–T. The solid phase is located on the left area of this diagram marked with the letter s, and the liquid and gas phases are in the area marked with the letters l and g. In the three coordinate space $G, T, P,$ as seen in Fig. 4.3, for each one of these Gibbs energy dominions, the area corresponding to the phase is located (smaller) under the Gibbs energy regions of the two remaining phases (Fig. 4.3). In other words, the phase located in the s, l or g dominion will be stable compared to the other two, since their Gibbs energy is lower inside such dominions.

Suppose, as shown in Fig. 4.4 that the pressure P_1 is less than the pressure P_0 at point O. Then horizontal line drawn through point P_1 in the region $0 < T < T_1$ is located on the area of the solid phase, and the region $T > T_1$ is in the area of the gas phase. Being in the region of the solid phase, that is, at relatively low temperatures, we will increase the temperature of the system. If the pressure is maintained constant as the temperature rises, then when temperature T_1 is reached (the entry point of the horizontal P_1 into the ao curve), the solid phase will begin to sublimate, i.e., the number of phases will become $\varphi = 2$.

In this case, the system has a degree of freedom equal to zero, since P is constant, the process will continue and finish without changing the temperature T_1. At the end of the sublimation process, the solid phase disappears and the system acquires an additional degree of freedom. After the system reaches a certain temperature T and begins to cool, then when the horizontal P_1 is introduced again with the ao curve, the gas phase will crystallize into a solid one. Therefore, the ao curve is called the sublimation-crystallization curve.

Passing along the ao curve from left to right, there is a discrete change in entropy equal to the heat absorption by the body (or enthalpy, since the pressure is constant) divided by the sublimation temperature

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}} \tag{4.6}$$

The magnitude $\Delta H_{sub} = \Delta Q_{sub}$ in expression (4.6) is called the latent enthalpy or heat of sublimation. This heat is consumed on breaking the interatomic bonds of the solid. Adding this magnitude, referred to the sublimation temperature, to the entropy of the solid (4.5) that corresponds to the region to the left of the transition line ao and to the entropy of vapor at $T > T_1 = T_{sub}$, we obtain the entropy of vapor at any temperature T

$$S_{vap} = \int_0^{T_{Sub}} \frac{c_p^{sol}}{T} \, dT + \frac{\Delta H_{sub}}{T_{sub}} + \int_{T_{Sub}}^{T} \frac{c_p^{vap}}{T} \, dT \qquad (4.7)$$

If the pressure P_2 is higher than the pressure corresponding to the point P_0, then the solid melts and then evaporates as the temperature rises. The fusion occurs at the point of intersection of the horizontal line at pressure P_2 with the curve co. If this curve is crossed from right to left, then at temperature T_2 the liquid phase or the molten material crystallizes into a solid. Therefore, the line co is called the fusion-crystallization curve. Melt evaporation occurs at temperature T_3 at the point of intersection of the horizontal line with the bo curve, that corresponds to the equilibrium of two phases (liquid–gas). When crossing this line from right to left, the gas phase condenses. As a result, the bo line is an evaporation–condensation line.

Let us determine the change in the entropy of the system that occures in the process of increasing the temperature with a change in pressure P_2. During a fusion, the entropy rises by a magnitude which is then called the fusion entropy

$$\Delta S^M = \frac{\Delta H^M}{T^M}$$

The entropy of the liquid at $T > T_{mel}$

$$S_{liq} = \int_0^{T^M} \frac{c_p^{sol}}{T} \, dT + \frac{\Delta H^M}{T^M} + \int_{T^M}^{T} \frac{c_p^{liq}}{T} \, dT$$

As the temperature rises, the liquid evaporates, and the entropy increases discretely in the direction of the evaporation entropy. The entropy of the vapor at $T > T_{evap}$

$$S_{vap} = \int_0^{T_{mel}} \frac{c_p^{sol}}{T} \, dT + \frac{\Delta H_{mel}}{T_{mel}} + \int_{T_{mel}}^{T_{evap}} \frac{c_p^{liq}}{T} \, dT + \frac{\Delta H_{evap}}{T_{evap}} + \int_{T_{evap}}^{T} \frac{c_p^{vap}}{T} \, dT \qquad (4.8)$$

Imagine that P_1 and P_2 are approaching P_0. In this case, from equations (4.7) and (4.8), we derive that at the triple point the equality $\Delta H_{sub} = \Delta H_{mel} + \Delta H_{evap}$ takes place, since P_1, P_2 tend to P_0, therefore, S_{liq} tends to zero.

Let us compare the curves of evaporation–condensation (*bo*) and sublimation–crystallization (*ao*). For evaporation from the Clausius–Clapeyron equation, we have

$$\left.\frac{dP}{dT}\right|_{evap} = \frac{\Delta H_{evap}}{T\Delta V_{evap}}$$

For sublimation we have

$$\left.\frac{dP}{dT}\right|_{sub} = \frac{\Delta H_{sub}}{T\Delta V_{sub}}$$

During evaporation $\Delta V_{evap}=V_{vap}-V_{liq}$, and during sublimation $\Delta V_{sub}=V_{vap}-V_{sol}$. Since V_{liq} and V_{sol} among them are almost equal and, accordingly, $\Delta V_{evap}\approx V_{sub}$, then at the same temperature $\frac{dP}{dT}$ is larger, the numerator is higher. Since $\Delta H_{sub}=\Delta H_{mel}+\Delta H_{evap}$, then $\Delta H_{sub}>\Delta H_{evap}$ and

$$\left.\frac{dP}{dT}\right|_{sub} > \left.\frac{dP}{dT}\right|_{evap} \tag{4.9}$$

In the expression (4.9) $\frac{dP}{dT}$ are the slopes of the sublimation and evaporation curves, respectively. From this expression we derive that the sublimation curve *ao* is steeper than the evaporation curve *bo*. The sublimation and evaporation curves intersect at the point of the fusion, since at this point the vapor pressure of the liquid must be equal to the vapor pressure of the solid. In reality, at this temperature, the liquid and solid phases are in equilibrium, and if the phases of a given substance are in equilibrium, then they must have the same vapor pressure. To demonstrate this, we shall mentally separate these two phases from one another and place them in a vacuum that will eventually be filled with the vapor of the substance in question. If both phases did not have the same vapor pressure, then the phase having a higher pressure would begin to evaporate until the corresponding vapor became saturated, but then it would be

supersaturated with respect to the other phase would therefore condense. When this happens, the vapor pressure tends to diminish and so, the first phase will continue to evaporate. This process will end only when the first phase has evaporated, and then we will have a system consisting of the second phase and saturated vapor in relation to it. However, we will not be able to talk about two phases in equilibrium, since one of them, arbitrarily (without external influence), turns into the other. On the other hand, if two phases of a given substance are in equilibrium, they must certainly have the same vapor pressure. From this, we conclude that the most stable phase has a lower vapor pressure.

CHAPTER 5.

TWO COMPONENT SYSTEMS

5.1 The Component Chemical Potential in the Mixture of an Ideal Gas and no Ideal System.

The chemical potential of a pure substance is the specific Gibbs energy $\mu=\bar{G}$. It is known that at a constant temperature the volume can be expressed as the partial derivative of the Gibbs energy with respect to pressure $\frac{\partial G}{\partial P}\big|_T=V$. Using the equation of state for one mole of the ideal gas is $PV=RT$, where R is the universal gas constant, we derive

$$V=\frac{RT}{P}$$

and

$$\frac{\partial G}{\partial P}\bigg|_T=\frac{RT}{P} \tag{5.1}$$

Integrating the equation (5.1) within one atmosphere to a given pressure P, we have

$$\mu^0-\mu^\Theta = \bar{G}^0 - \bar{G}^{\,\Theta} = RT\ln P,$$

where μ^Θ is the chemical potential of an ideal gas at the pressure equal to one, defined as the corresponding pressure of one atmosphere, and G^Θ is the specific Gibbs energy at $P=1$. As a result

$$\mu^0 = \mu^\Theta + RT\ln P \tag{5.2}$$

Equation (5.2) is the chemical potential of an ideal gas. To apply this equation to mixtures of ideal gases, we use Dalton's law, that states that if two or more gases are mixed at equal temperature and pressure, then in the absence of chemical reactions, the volume of the mixture is equal to the sum of the volumes of its constituent gases, and the temperature of the mixture remains unchanged.

This means that the pressure of an ideal mixture of gases is the sum of the partial pressures of its components, i.e., it is the pressure that each component would exert in the absence of the others. Thus, the partial pressure P_i, of the i–th gas in a mixture is the pressure that this gas would encounter if the remaining gases were withdrawn from the mixture while maintaining a constant volume and temperature. Thus,

$$P_{com} = P_1 + P_2 + \cdots = \sum P_i$$

In other words, the components of an ideal gas mixture behave independently of each other, without interaction. The partial pressure of one component is determined by the total pressure of the mixture P_{com} and the concentration of the component

$$P_i = P_{com} \frac{n_i}{\sum n_i} = Px_i \tag{5.3}$$

where n_i is the number of the particles of the considered component, x_i denotes the concentration and we take $P_{com} = P$.

Due to the absence of interaction between the components of the mixture and their independent behavior, for the mixture of ideal gases (by analogy with the chemical potentials of the ideal gas)

$$\mu_i = \mu_i^{\ominus} + RT \ln P_i$$
$$\bar{G}_i = \bar{G}_i^{\ominus} + RT \ln P_i \tag{5.4}$$

Substituting equation (5.3) into (5.4), we have

$$\mu_i = \mu_i^{\ominus} + RT \ln P_i = \mu_i^{\ominus} + RT \ln P + RT \ln x_i$$
$$\bar{G}_i = \bar{G}_i^{\ominus} + RT \ln P_i = \bar{G}_i^{\ominus} + RT \ln P + RT \ln x_i$$

, where $\mu_i^{\ominus} + RT \ln P$ is the chemical potential of the pure substance at temperature T and pressure P. Let us denote $\mu_i^{\ominus} + RT \ln P = \mu_i^0$. Then

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{5.5}$$

is the chemical potential of the i–th component of the mixture of ideal gases. Let's analize one simple case when the chemical potentials of any of the system

components have the form (5.5), where $\mu_i^0(T,P)$ depends only on T and P. Systems, in which the chemical potential is described using the above expression, have simple properties and are called the ideal systems.

In thermodynamics, it is often found that certain thermodynamic magnitudes with intensity J in a homogeneous system are represented as a sum of two functions, one of which depends only on T and P, and the second also on the concentration

$$J = J^0 \ (T,P) + J^M \ (T,P,x_1,x_2,...,x_k)$$

The first term $J^0(T,P)$ in the first part of this expression is known as the standart function, and the second $J^M \ (T,P,x_1,x_2,...,x_k \ )$ reflecting the influence of the composition is known as the mixture function (for example: the heat of the mixture, entropy of the mixture). As a consequence, in (5.5) μ_i^0 is the standard chemical potential of i-th component of an ideal gas mixture, and $RTln(x_i)$ is the function of the mixture showing how the chemical potential μ is affected by the fact that the component i is in mixture with other gases, not in its pure form.

5.2 Ideal Solutions

Solutions are homogeneous systems or phases of variable composition. Solutions can be solid, liquid or gaseous. The latter refers to gas mixtures. The question of the theory of solutions is posed as a problem related to the discovery of the properties of solutions depending on the properties of their constituent atoms or molecules and on their concentration.

The concentrations x_i of the components composing the solution can be determined by various methods, which we analyze below:

   1.- The molecular mass fraction

$$\varpi i = \frac{q_i}{\Sigma q_i}$$

, where q_i is the mass of the component in solution, $100 \cdot \varpi_i$ is the mass percentage of the component in solution.

2.-The mole fraction

$$N_i = x_i = \frac{n_i}{\Sigma n_i}$$

, where n_i is the number of moles of component i, $100 \cdot N_i$ is the molar percentage.

3.- The atomic fraction

$$A_i = x_i = \frac{n_i}{\Sigma n_i}$$

, where n_i is the number of atoms of component i, $100 \cdot A_i$ is the atomic percentage.

4.- The volume fraction

$$\varphi_i = \frac{V_i}{V}$$

, where V_i is the volume of component i in a solution with volume V. $100 \cdot \varphi_i$ is the percentage of the volume that is the same as the molar and atomic percentages for ideal systems.

The value of each of these fractions can vary only from 0 to 1. To analyze the main properties of ideal solutions, we write an expression for the Gibbs energy, considering one mole of a mixture containing two components. Suppose that in the general case, in one mole of a mixture, the concentration of the first component is x_1, and the concentration of the second component is x_2. As a result, the Gibbs energy corresponding to one mole of the mixture is denoted as

$$G = x_1\mu_1 + x_2\mu_2 = x_1(\mu_1{}^0 + RT \ln x_1) + x_2(\mu_2{}^0 + RT \ln x_2) =$$
$$= x_1\mu_1{}^0 + x_2\mu_2{}^0 + x_1 RT \ln x_1 + x_2 RT \ln x_2 = G^0 + G^m \qquad (5.6)$$

In the expression (5.6)

$$G^0 = x_1\mu_1{}^0 + x_2\mu_2{}^0$$

is called the standard function (standard Gibbs energy corresponding to the Gibbs energy of one mole), determined by the chemical potentials of the pure components 1 and 2, while

$$G^m = x_1 \, RT \ln x_1 + x_2 \, RT \ln x_2 \qquad\qquad (5.7)$$

is called the mixture function, that shows how the specific Gibbs energy changes during the formation process of a solid solution from pure components.

Assume that the mixing of two components forming an ideal solution occurs without changing the enthalpy. This means that if the components are mixed at constant temperature and pressure, no heat is released or absorbed, since at $P=const$ the heat Q is equal to the enthalpy H.

Considering that $\dfrac{\partial G^m}{\partial P} = V^m = 0$ in the case where there is no pressure dependence expressed in (5.7), the volume of the system does not change during the formation of an ideal solution, i.e., the mixing process is not accompanied by either compression or expansion.

The energy of the mixture

$$u^m = h^m - Pv^m$$

Consequently, it is also to zero.

If we differentiate the mixture function g^m by temperature, we find the entropy of the mixture

$$S^m = -\frac{\partial G^m}{\partial T} = x_1 \, R\ln x_1 - x_2 \, R\ln x_2 \qquad\qquad (5.8)$$

In the last expression, we see that s^m is always positive, since the natural logarithms $\ln x_j$ are negative for any $x_j<1$, and the plot of this function is symmetrical about the point $x_1 = x_2 = 0.5$ with the maximum value of s^m.

The analyzed properties allow us to formulate some assumptions regarding the conditions that must be met for the atoms of both mixed systems to form a solution. First, the change in the volume of the mixture is zero, since the sizes of the atoms of the mixing components remain unchanged. The internal energy in a solution is closely related to the interaction of atoms. The change in energy in the mixture is zero, in other words, the internal energy does not change

during the mixing process, since the interaction between different atoms in a solution must be equal to the arithmetic mean of the interacting energies of the atoms of both pure substances.

5.3 The Laws of Raoult and Henry

According to the condition of thermodynamic equilibrium, the chemical potentials of the components of the equilibrium liquid μ_i^L and gaseous μ_i^{Vap} phases must be equal. For an ideal system, we have the following expressions for chemical potentials

$$\mu_i^L = \mu_i^{L0} + RT \ln x_i^L$$
$$\mu_i^{Vap} = \mu_i^{Vap\Theta} + RT \ln P_i$$

Applying the equilibrium condition, we obtain that

$$\mu_i^{L0} + RT \ln x_i^L = \mu_i^{Vap\Theta} + RT \ln P_i$$

or

$$RT \ln \frac{P_i}{x_i^L} = \mu_i^{L0} - \mu_i^{Vap\Theta}$$

And we can express the pressure as

$$P_i = x_i^L e^{\frac{\mu_i^{L0} - \mu_i^{Vap\Theta}}{RT}} \tag{5.9}$$

When $x_i^{liq} = 1$ (5.9) corresponds to the vapor pressure or elasticity of the pure component i

$$P_i^O = e^{\frac{\mu_i^{L0} - \mu_i^{Vap\Theta}}{RT}}$$

Therefore

$$P_i = P_i^0 x_i^L \tag{5.10}$$

Thus, the vapor pressure of component i of the solution is directly proportional to the product of the vapor pressure of the pure component and its concentration

x_i^L in the solution. This formulation of the law was experimentally established by Raoult in *1882-1883*. This law is also valid for the equilibrium solid- and gaseous-phases. In this case, in expression (5.9), the concentration of component x_i^L in the liquid is simply replaced by the concentration of component in the solid phase x_i^S. The derivation of the same law for liquid and gaseous phases in equilibrium is achieved in exactly the same way as the previous one.

If we consider a gas dissolved in some liquid, then from (5.9) it follows that

$$x_i^L = P_i\, e^{\dfrac{\mu_i^{LO} - \mu_i^{Vap\theta}}{RT}}$$

At a constant temperature, the exponential coefficient is independent on concentration. Therefore, it can be denoted as a constant by the letter K

$$x_i^L = KP_i \qquad\qquad\qquad (5.11)$$

This shows that the concentration of dissolved gas (component *i*) in an ideal solution is directly proportional to the pressure of on the solution. This law is called Henry's law.

5.4 General Properties of Gibbs Energy

Consider a hypothetical case when a system can simultaneously exist in two phases at constant temperature and pressure, for example, in the form of solutions or mechanical mixtures. To answer the question which of these states will be stable, it is necessary to compare the Gibbs energies of these phases. As it was established earlier, the stable state corresponds to the one with the minimum Gibbs energy.

Suppose, for example, that the Gibbs energy of a system in the form of a solution is higher than that of a system consisting of a simple mechanical mixture. In this case, the solution eventually arbitrarily transforms to the mixture state. If the Gibbs energy of the solution is less than the Gibbs energy of the mechanical mixture, then the solution is stable.

Let us demonstrate that the Gibbs energy is additive at *P=const* and *T=const*. Now, we will analyze two systems forming a mechanical mixture representing

the values of the Gibbs energy, internal energies, entropies and volumes of these two systems through G_1, G_2, U_1, U_2, S_1, S_2, V_1, V_2, respectively. Mixing the systems *I* and *II*, we obtain the sum of the systems for which the above values will be represented by *G, U, S, V*. Since in the analyzed process the systems form a mechanical mixture, the components in the initial systems *I* and *II* do not interact when mixed, therefore the internal energy, entropy and volume of the newly formed system are additive

$$U = U_1 + U_2;\; S = S_1 + S_2;\; V = V_1 + V_2 \qquad (5.12)$$

By definition, the Gibbs energy of the analyzed systems can be represented as follows

$$G_1 = U_1 - TS_1 + PV_1;\; G_2 = U_2 - TS_2 + PV_2;\; G = U - TS + PV \qquad (5.13)$$

Adding G_1 and G_2

$$G_1 + G_2 = U_1 + U_2 - T(S_1 + S_2) + P(V_1 + V_2)$$

If we follow (5.12) and (5.13) then we have

$$G_1 + G_2 = U - TS + PV = G \qquad (5.14)$$

Thus, we have confirmed that the Gibbs energy of a mechanical system is simply equal to the sum of the Gibbs energies of the parts that compose the mixture. And in the general case, this statement is also true, if we take into account that the forces of interaction between the components of the mixture are discarded.

However, if the mixing of the systems *I* and *II* is accompanied by an interaction of components, for example, by dissolution or alloy formation, then the Gibbs energy is no longer additive. From the expression (5.13) we also conclude that the Gibbs energy depends on the mass of the substance of the system, just as the internal energy, entropy and volume depend on this mass. In other words, as noted in Section 4.1, for a one-component system, the value of the Gibbs energy is extensive. Therefore, to solve the question of the stability of one of these two states of the system, it is necessary to equate the value of $\bar{G}$ per mass unit (Gibbs specific energy) or per mole (Gibbs molar energy). However, in accordance with

the simplification adopted in Section 4.1, we will omit the horizontal line over the letter G, but always remember that for different phases, the specific or molar Gibbs energy must be exactly equal in a thermodynamic equilibrium condition. Since the Gibbs energy of a two-component mixture is an additive value, the dependence of G on the composition in this case is represented by a straight line $G_A G_B$ that joins the points corresponding to the Gibbs energies for components A and B. This is illustrated in Fig.5.1, are graph for a two-component mixture of substances A and B, where the Gibbs energy is a function of their concentration x.

Now assume that a two-component system is a homogeneous solid, liquid, or gaseous solution and exists over the full range of concentrations.
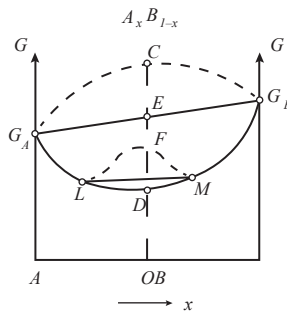
Fig. 5.1. The Gibbs energy for the two-component solid solution with complete mutual solubility (line $G_A DG_B$), the mechanical mixture (line $G_A G_B$) and the system with a partial solubility (line $G_A LFMG_B$).

Let us represent the chemical composition of such a system through the formula $A_x B_{1-x}$. If components A and B have infinite solubility among themselves in the solid, liquid, and gaseous phases, then the parameter x or the composition of the system can continuously change form 0 to 1, i.e., complete solubility between two substances is possible. In this case, the dependence of the Gibbs energy on concentration is represented by the curve passing under the additive line $G_A G_B$.

Now suppose that for the solution, the line of the Gibbs energy curve $G_A CG_B$ is above the dashed line $G_A G_B$ in Fig. 5.1. In this case the Gibbs energy of the solution, represented by the vertical segment OC is higher than G for a mechanical mixture of the same composition (segment OE), so the mechanical mixture must

have a stable state. However, we initially assumed that there is a continuous series of solutions between *A* and *B*, that is possible if and only if the Gibbs energy curve of the solution is below the $G_A G_B$ line, which would represent the case of a simple mechanical mixture.

It is easy to see that the curve in Fig. 5.1, labeled as $G_A D G_B$ to illustrate the Gibbs energy of the solution, should be a concave curve. Assume, on the contrary, that the isobaric potential curve has a convex segment *LFM* for the Gibbs energy of the solution. Then one can draw a straight line *LM* tangent to the line $G_A L F M G_B$, which will characterize the dependence of *G* on the composition of the mechanical mixture by the segment *LM*. In this case, in the concentration range *LM*, the Gibbs energy for the solution is higher than for the mixture. As a result, the solution in the *LM* range spontaneously transforms into a mechanical mixture, which contradicts the initial assumption about the mutual complete solubility of components *A* and *B* as thermodynamically stable state.

Thus, if the components have a complete mutual solubility, the Gibbs energy curve cannot contain segments similar to the *LFM*. In general, this curve must lie completely under the chord connecting its extreme points, and must be concave throughout its its entire length. If the curve contains any convex segment (for example, *LFM*), then the composition of the system is divided into a mixture of two limited solutions, the compositions of wich are determined by the positions of the tangent points *L* and *M*.

To analyze the behavior of the Gibbs energy near the pure components *A* and *B*, we annotate the expressions for the chemical potentials. Assuming that the system is ideal, then

$$\mu_A = \mu_A{}^0 + RT \ln x, \; \mu_B = \mu_B{}^0 + RT \ln (1{-}x), \; \text{y} \; G = \mu_A x + \mu_B (1{-}x)$$
$$G = \mu_A{}^O x + RTx \ln x + \mu_B{}^0 (1{-}x) + RT(1{-}x) \ln(1{-}x)$$
$$\frac{\partial G}{\partial x} = \mu_A{}^0 - \mu_B{}^0 + RT \ln x - RT \ln(1{-}x)$$

If in the last expression, *x* tends to *0* or to *1*, then

$$x \to 0, \frac{\partial G}{\partial x} \to -\infty$$

$$x \to 1, \frac{\partial G}{\partial x} \to +\infty$$
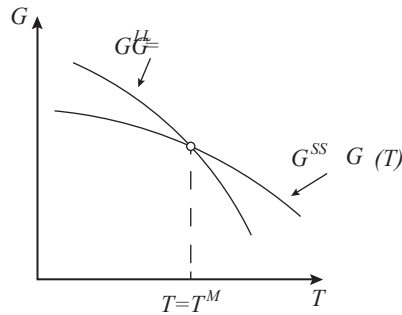
Fig.5.2. The dependences of the Gibbs energies of the liquid G^L and the solid G^S on temperature for the one-component system.

The curve characterizing the dependence of the Gibbs energy on the composition is tangent to the vertical lines corresponding to the pure components A and B, i.e., the compositions $x=0$ and $x=1$.

We can determine the dependence of the Gibbs energy for a phase of constant composition (e.g., a solid, liquid, or gaseous phase of a pure component) as a function of temperature

$$G = U - TS + PV = H - TS$$

Assume, that the thermodynamic system under consideration is a closed system. But first, note that the entropy term TS is always positive, because entropy is positive and T is absolute temperature. We can simplify the problem by assuming that the value of the enthalpy H is also positive. Then, considering the sign (–) in front of TS, we can say that with increasing temperature, the value of the Gibbs energy will decrease and the curve $G = G(T)$ will approach the T axis, for which the concavity of this curve directed downward. The slopes of the function $G = G(T)$ for different phases will be different due to differences in entropies.

According to the Boltzmann formula (2.38), the entropy S^L of the liquid phase is greater than S^S of the solid phase. For this reason, as shown in Fig. 5.2, the curve $G = G(T)$ for the liquid phase has a more pronounced slope than for the solid phase as the temperature increases. The point of intersection of these two curves corresponds to the equilibrium point between the two phases. Below and above these temperatures, phases with lower G values are stable. As seen in Fig.19, when

$T > T^M$, $G^L < G^S$, means that there is only one liquid phase in the system. When $T < T^M$, $G^S < G^L$, the solid phase is stable. The temperature T^M at which $G^L = G^S$ determines the condition of simultaneous existence of liquid and solid phases and is called the fusion temperature.

5.5 Classification of the Diagrams of State of Two Component Systems

When analyzing binary systems, i.e., those consisting of two elements or components, it is assumed that external pressure is constant. In this case, the number of degrees of freedom is equal to

$$f = k - \varphi + 1 = 3 - \varphi$$

where, as in Section 3.4, k denotes the number of components, in this case 2, and φ the number of phases.

Consider that components A and B of any binary system are completely mutually soluble in the liquid state. In other words, A and B, at least at temperatures above the fusion point, form liquid solutions of any concentration. It is important to note that this assumption is true for vast majority of diverse systems of semiconductor materials.

Solid phases, in general, can be formed by single component substances, alloys or compounds, or solid solutions. Remember that solid solutions, like liquid and gaseous ones, differ from pure substances or from alloys in the fact that their composition can be changed. If we write down in general terms the chemical formula of a binary alloy such as $A_m B_n$, then m and n are integers. This formula shows that the components A and B forming the alloy are in multiple proportions, and that is how alloys differ from solutions.

In addition to these variants, the solid phase can also be formed by a mechanical mixture, where components A and B do not interact, i.e., do not form solid solutions or alloys.

Thus, the following situations are possible in the solid phase:
1. A and B are not soluble between themselves and do not form alloys. In such case, when in the solid state there is no solubility between A and B, the binary system is characterized by a state diagram called a eutectic.

2. Components A and B in the solid state are infinitely soluble with each other, it is said to be a system with infinite mutual solubility.
3. Components A and B are partially soluble with each other and do not form alloys.
4. Components A and B form an alloy in the solid state.

Almost all types of state diagrams of a binary system lead to any of the above mentioned cases or their combinations. We will analyze in detail the first two types of phase diagrams, starting from two different points of view.

The first view is based on the fact that the liquid and solid phases are in equilibrium and, therefore, the partial pressure components forming these phases should be equal. In this case, Raoult's law is used to analyze the state diagram, as well as the fact that the derivative of pressure over temperature for the sublimation curve is higher than for the evaporation curve, as shown in section 4.2, and equation (4.9).

The second point of view is based on the plotting of the specific Gibbs energy as a function of concentration and temperature for liquid G^L and solid G^S phases. Between curves $G^L=G^L(x^L)$ and $G^S=G^S(x^S)$, plotted for different temperatures, a common tangent is drawn, which actually means finding the conditions under which the differential equations of the Gibbs energy as a function of concentration of the chemical potentials are equal to $\mu_i^L=\mu_i^S$. The point of the tangent line will indicate the composition of phases in equilibrium.

5.6 Binary Systems with Simple Eutectic

As suggested above, we consider a liquid phase containing components A and B infinitely soluble in each other. At the same time, if A and B are soluble in the solid phase, the same phase can be formed either by pure components A and B or by their mechanical mixture. Thus, in binary systems with simple eutectic the following variants of the equilibrium phase are possible

$$AB^L \leftrightarrow A^S,\ AB^L \leftrightarrow B^S,\ AB^L \leftrightarrow A^S + B^S \qquad (5.15)$$
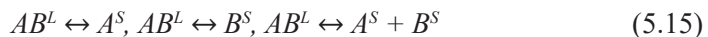
where in (5.14) AB^L is the liquid, A^S, B^S and are solid phases of A, B and A^S+B^S is their mechanical mixture, respectively.

I. First, we analyze the phase diagram on the example of a simple eutectic. Assume that if phases (AB^L) and (A^S o B^S) are in equilibrium, then the partial pressures of corresponding components of the system (P_A in the first case and P_B in the second case) must be equal. If components A and B form ideal liquid solutions with each other, it means that they fulfill Raoult's law in the whole interval of concentrations

$$P_A = P_A^O x_A,$$
$$P_B = P_B^O x_B,$$

where, respectively, P_A^O and P_B^O are the vapor pressures of the components on pure liquids A and B at a certain temperature, where P_A and P_B are their partial pressures on the solution at the same temperature, x_A and x_B are the respective concentrations of A and B in the liquid phase. As was shown in Section 4.2 (equation 4.9), for a one-component system, the solid phase sublimation curve ao is more pronounced than the pure liquid evaporation curve oc (Fig.5.3).
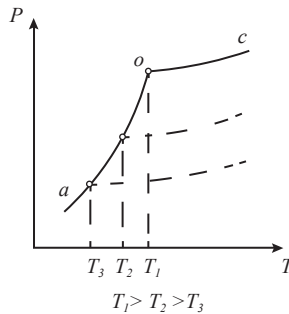
Fig. 5.3. The curves of sublimation of the solid phase (line ao) and
the liquid phase (line oc) in the one-component system.

In the case of $AB^L \leftrightarrow A^S$ equilibrium, the pressure on the pure solid phase A^S is still characterized by the curve ao. In this case, the partial pressure A on the liquid phase represented by the solution $A–B$ is smaller according to Raoult's law, since $0 \leq x_A \leq 1$. As a result, the partial pressure curve of A on the liquid phase $A–B$ will shift downward with regard to oc as the concentration of A in the liquid increases, as shown by the dotted lines in Fig. 5.3. Thus, when component B is introduced into the liquid AB^L as its concentration increases, the intersection point of the sublimation curve of pure solid phase A^S with the curve characterizing the pressure A on the liquid $A–B$ will shift toward lower temperatures, as illustrated in Figs. 5.3 and 5.4a.
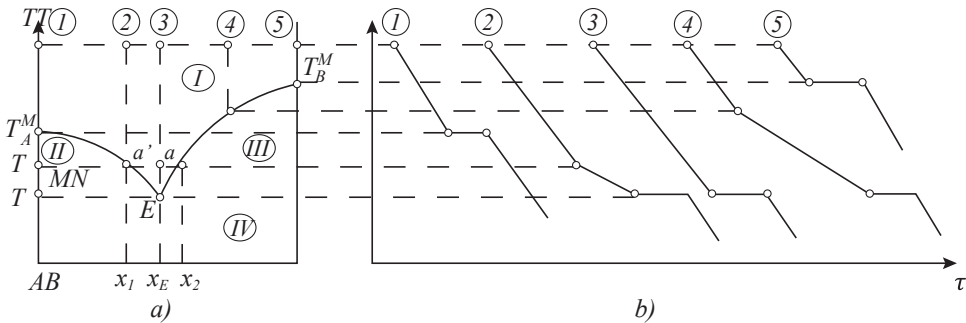
Fig. 5.4. The state diagrams of the two-component system without solubility in the solid phase (simple eutectic).

This point, as indicated previously, corresponds to the state of equilibrium, since it is the point where the pressure on the analyzed phases is equal. Therefore, the solid phase A^S and the liquid A–B will be in equilibrium at a temperature that is lower than the equilibrium temperature T_1 (Fig.5.3) for the liquid phases, A^L and the solid phase A^S. Naturally, the difference between temperatures T_1 y T_2 will be larger in the liquid with a lower concentration of A.

Now, if a large dose of component B is added to the liquid phase A^L, the equilibrium temperature of the system A–B (líquido) –A (solid) will decrease (in Fig.5.3 $T_1 > T_2 > T_3$). This means that, in the temperature-composition coordinates, the curve corresponding to the $AB^L \leftrightarrow A^S$ equilibrium begins at the fusion point TA since the concentration of B slopes downward with increasing concentration. Similarly, the curve that corresponds to the $AB^L \leftrightarrow A^S$ equilibrium will also decline, starting at point T_B, as the concentration of component A in the liquid increases. Since each of these curves is formed by points characterizing the compositions of the liquid phases (which are in equilibrium with the solid phases A or B), they together form what is known as liquidus line. Both curves intersect at point E, which is called eutectic. The meaning of this name is explained below. The composition of the liquid is non-equilibrium with both solid phases simultaneously at temperature T_E, and its composition x_E is determind at point E, located simultaneously on the curves T_AE and T_BE. Correspondingly, the line characterizing the compositions of the solid phases A^S and B^S is called solidus. Obviously, this line is formed by the segments of vertical lines y, since it is here that the points corresponding to the solid pure phases A^S y B^S are located. To find the compositions of the liquid and solid phases in equilibrium at certain temperature T, it is enough to draw a horizontal line through this temperature.

The segment of this line between the points of intersection with the liquidus and solidus curves allows us to determine the unknown compositions of the phases in equilibrium. This segment is called *conode* and we shall use this term when discussing this topic in the following figures. For example, Fig. 21 shows that at temperature *T*, composition x_1 is in equilibrium with A^S and x_2 is in equilibrium with B^S. The plane of the analyzed *T–x* diagram is divided by the liquidus lines T_AE and T_BE a horizontal eutectic passing through the point T_E, and the vertical solidus lines into four regions. Region *I*, limited from below by the liquidus curve, is a single-phase region, and at its boundaries there is only the liquid AB^L, the composition of which can vary from *A* to *B*. Between the liquidus curve and the horizontal eutectic there are two two-phase regions *II* and *III*, at the boundaries of which the liquid phase of changing composition is in equilibrium with the solid phase of constant composition with crystals *A* in region *II* and with crystals *B* in region *III*. Below the horizontal eutectic is located in region *IV*, in which two solid phases of constant composition (crystals *A* and crystals *B*) coexist, forming a mechanical mixture.

According to the phase rule, the liquid in region *I* has two degrees of freedom, $f=k–\varphi +1=3–\varphi=2$, since $\varphi=1$ is the number of phases, which in this region is only that of the liquid, and *k* is the number of components, in this example 2. Thus, in the first region, the temperature and composition can vary independently of each other, which in turn means that the point that characterizes the state of the system is called the figurative point, and can be located anywhere in region *I*. In the remaining three regions *II*, *III* and *IV* the system is a two-phase system and therefore has only one degree of freedom, i.e. it is univalent. This means that in these three regions only one of the parameters (either composition or temperature) can vary independently and the remaining parameters will have a well-defined value. Therefore, the figurative point characterizing the state of the system in the second, third and fourth regions must be found on the lines that are geometric representation of the univalent system. Therefore, for regions *II* and *III*, the liquid phase point can only be found on the liquidus line, and for the solid phase only on the solidus line. In region *IV*, the two-phase region, the figurative point is located on the solidus lines T_AA and T_AB. Note again that the figurative point cannot be located inside the two-phase region and is always located on the dividing lines between these regions. It follows that when the temperature decreases, the figurative points in regions *II* and *III* will scroll down along the corresponding liquidus and solidus lines, and in region *IV* - only along the solidus line. Suppose that the state of the liquid phase is characterized by the figurative point (*a*). Since this point is in a region with two degrees of freedom,

the composition of the liquid can be changed independently on the temperature, e.g. by increasing the concentration of component *A*. Such a change is represented in Fig. 21 by a shift to the left on the horizontal line. This point can only be shifted to the intersection of the horizontal with the liquidus line, i.e., up to position (*a′*) since no figurative point can be located in region *II*. Since at position (*a′*) the concentration x_1 of component *A* is the maximum at a given temperature, the liquidus line is also called as the saturated liquid phase interface line. Therefore, T_AE is the point line that corresponds to the liquid saturated with component *A*, and T_BE with component *B*. Similarly, as the concentration of component *B* increases, the initial figurative point (a) shifts to the right to the position (*a″*).

Next, we analyze the processes that occur during the cooling of the liquid phase *AB*. First, consider the pure components of *AB*. If the temperature of the system exceeds the fusion temperature of *A* and *B*, that corresponds, for example, to figurative points *1* and *5* in Fig. 5.4.*b*, then the single-phase system has one phase and one component, and the number of degrees of freedom is $f=k–\varphi+1=1$. This means that in those cases considered at constant pressure and concentration, the only variable independent parameter is temperature. Thus, as the temperature is decreased, the figurative point characterizing the system simply moves down the fusion temperature $T=T^M$ of the corresponding component. In the process of decreasing the temperature, there should already be two phases in equilibrium: liquid and solid. In this case, the only degree of freedom of the system is lost. Therefore, in the one-component systems, the crystallization occurs only at constant temperature if the pressure is constant.

These processes can be illustrated using the cooling curves, which show how the temperature *T* in the system changes over time *τ*. Clearly, in a one-component system with one phase, naturally having only one degree of freedom, the cooling curve is represented by a sloping segment as the temperature decreases. At temperature $T=T^M$ this segment, as shown in Fig. 21.*b*, changes in the horizontal direction. The temperature constancy at $T=T^M$ is due to the latent heat of the solid-liquid phase transition. After solidification of the entire liquid, only one solid phase remains in the system - the solid, and the number of degrees of freedom becomes again equal to one. The subsequent cooling of the system is characterized by the second sloping segment of curves *1* and *5*, shown in Fig.5.4.*b*.

The cooling curve of an alloy with eutectic composition (point *3*) has the same form. First, as the system cools, the temperature goes down the sloping line, as shown

in Fig.5.4.*b*. When the system is cooled to the eutectic temperature, the liquid phase is saturated with both components *A* and *B*, which simultaneously begin to crystallize. Crystallization occurs in any infinitesimal volume of liquid, so at the end of this process the solid phase is a very well-mixed mixture of *A* and *B* crystals. It can be seen that the eutectic point is at a lowest temperature. This determines the name of this type of state diagrams, since the word "eutectos" translates as "easily melted".

At point *E* the liquid phase of the eutectic composition X_E is in equilibrium with the two solid phases S_A and S_B. According to the rule of phases, the number of degrees of freedom of a two-component regulatory system with three phases is equal to zero *f=k–φ+1=2–3+1=0*. As a result, the eutectic will crystallize at a constant temperature, which is demonstrated by the horizontal segment of the cooling curve *3*.After the eutectic crystallization is completed, the cooling curve turns downward.

Let us analyze the processes that occur in the system during cooling of the liquid phase, the composition of which is distributed between points *1* and *3*. While figurative point *2* remains in the region of the liquid phase, the system maintains two degrees of freedom, so no changes occur in it when the temperature decreases, and this process is characterized by a vertical line in the diagram (Fig.5.4.*a*). When the liquid cools to the temperature of crystallization onset, the figurative point is localized on the liquidus $T_A E$ (point *a′*), the liquid is saturated with reference to the component *A*. It is at this point that the first crystal of the solid phase with pure composition of component *A* bursts out the liquid. This is accompanied by the release of heat during crystallization, which leads to an increase in the cooling rate: the cooling curve in Fig. 5.4.*b* changes its slope $\dfrac{dT}{d\tau}$ and a narrowing appears that corresponds to the temperature at which the first crystal of component *A* drops out. At further cooling the number of crystals of *A* increases, and the remaining liquid phase is enriched with component *B*, i.e. in Fig.5.4.*a*, the figurative point slides down the liquidus line to the eutectic. We draw the isothermal line $T_2(Aa′)$ connecting the figurative points that are in phase equilibrium.

The extreme left point of this line T_2 shows the composition of the solid phase (pure component *A*) and the extreme right point (*a′*) shows the composition x_1 of the equilibrium liquid phase. When the system is cooled to the eutectic temperature, the extreme right point of the allied line ends at point *E*, i.e., the composition of the

liquid phase will correspond to the eutectic composition. In addition to A, component B will also crystallize from the liquid of such composition. The eutectic crystallization occurs at constant temperature, so a horizontal section appears on the cooling curve, corresponding to the invariant process. After eutectic crystallization is complete, the system transforms into a monovariant system, as one of the phases (liquid phase) disappears and the cooling curve turns downward again. Thus, the crystallization of solutions, that conditionally can be called eutectic, begins with the release of component A from the liquid phase and ends with the eutectic crystallization, i.e. occurs in a certain temperature interval. The upper limit of the interval is determined by the temperature at the beginning of crystallization of A and depends on the composition of the solution, and the lower limit is located at the temperature of eutectic crystallization.
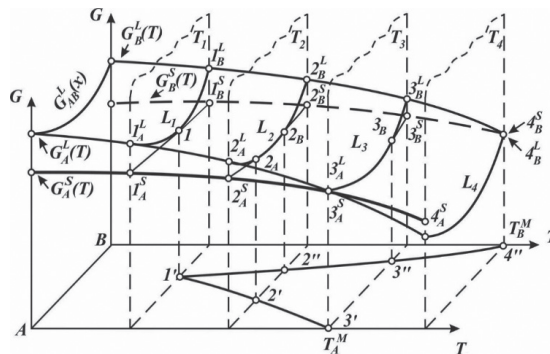
Fig. 5.5. The state diagram of the system with simple eutectic.

The crystallization of the liquid phases whose composition is distributed between the eutectic and pure component B, i.e., post-eutectic phases, according to the common terminology, for example, in point *4*, occurs in the same way as in the case discussed above.

Since the solidus lines on the state diagrams of binary systems with eutectics are simple vertical lines, only the liquidus lines and saturation curves should be constructed in the experimental study of such diagrams. Since these lines represent temperature parameters–composition dependences, their construction can be performed by two different methods. In each of these methods, one of the parameters is constant and the other is determined experimentally. Thus, for example, it is possible to determine the temperature at which the last crystal disappears when various liquid phases of known composition are heated. The

second method consists in determining the composition of the liquid phases in relation to the solid phase at different temperatures. Both methods allow us to plot the function between the composition of system and the temperature at which the liquid and solid phases are in equilibrium. It is important to note that the above state diagrams are idealizations, since in real systems the solid phases always have mutual solubility of their constituent elements. Often this mutual solubility is extremely small and cannot be determined experimentally, because the existing measuring equipment is not sensitive enough. For simplicity, the cooling curves plotted in Fig.5.4.*b* also represent an idealization. In practice, these dependences can often differ significantly from those analyzed.

II. Let us look at the diagram of state of the system with simple eutectic using the dependency of the Gibbs energy on temperature and concentration. Such dependence is represented in a tridimensional system of coordinates in Fig. 5.5.

Under the condition that there is a series of continuous solutions between *A* and *B* in the liquid phase, the Gibbs energy for the liquid will depend on concentration to the same extent as on temperature. In other words, in the tridimensional space *G, T, x*, this dependence can be represented by a convex region and limited by the curves $G^L = G^L_{AB}(x)$, $G^L_A = G^L_A(T)$ and $G^L_B = G^L_B(T)$. Since *A* and *B* in the solid phase form neither alloys nor solid solutions with each other, G^S will not be a function of concentration. For this reason, for the solid phase, G^S can be represented by the curves $G^S = G^S_A(T)$ and $G^S = G^S_B(T)$ located in the *GAT* and *GBT* planes. Plotting a set of vertical planes for constant temperatures T_1, T_2, T_3, T_4, we obtan the points of intersection of these planes with the curves G^S_A and $G^S_B(1^S_A, 1^S_B, 2^S_A, 2^S_B)$. The vertical planes T_1, T_2, T_3, T_4, will intersect with the surface of the Gibbs energy for the liquid phase by lines L_1, L_2, L_3, L_4.

Consider the plane T_1. The points $1^S_A, 1^S_B$ of the solid phases and the curve L_1 for the liquid are located in this plane. The equilibrium condition for the liquid and solid phases is the equality of their respective chemical potentials. Since by definition the chemical potential is a differential equation of the Gibbs energy in regards to the concentration passing through the points 1^S_A and 1^S_B that characterize the Gibbs energy for the solid phase, it necessary to draw the tangent lines to the curve L_1. It is in this case that the differential equations of G^L and G^S will be equal. Thus, tangen point *1* corresponds to the composition of the liquid phase being at temperature T_1 in simultaneous equilibrium with the solid phases *A* and *B*. In other words, the temperature T_1 is the eutectic temperature.

As we can see, from points 2^S_A and 2^S_B in the vertical plane T_2 two tangents to the line L_2 can be drawn. The tangent points 2_A and 2_B define the composition of liquid A–B that is in equilibrium at temperature T_2 with the pure solid phases A and B. At the temperature of the fusion point of pure element A, the pure phases, liquid and solid A, are in equlibrium at the combined points 3^L_A and 3^S_A. As can be seen in Fig. 5.5, at this temperature a tangential line L_3 can be drawn through point 3^S_B. The position of the tangent point 3_B will determine the composition of the liquid phase A-B, which at temperature T_3 will be in equilibrium with solid phase B. Therefore, the temperature T_4 corresponds to the fusion temperature of B, at which the solid and liquid phases coexist in equilibrium.
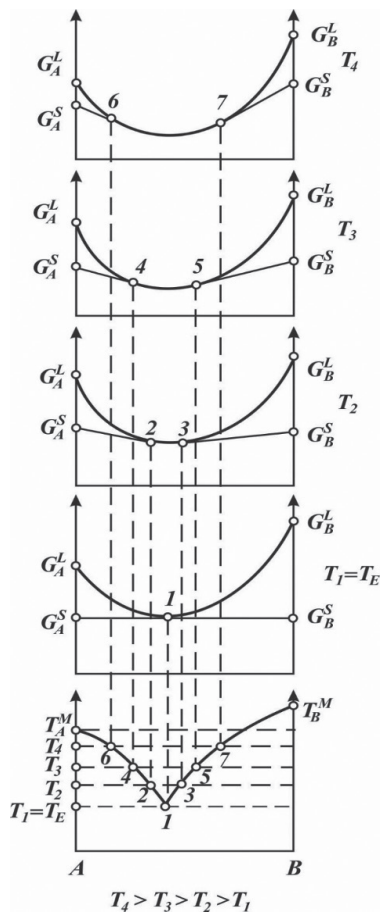
Fig. 5.6. Construction of the state diagram with simple eutectic.

Finally, the state diagram of a system with simple eutectic can be built if the points *(1,2A,2B,3A,...)* obtained to determine the compositions of the liquid phases are in equilibrium with the solid phases A^S y B^S at various temperatures and projected onto the *TABT* plane as shown in Fig. 5.6.

The Gibbs free energy G^L curves will be convex curves for the liquid phases at each of these sites. As the temperature rises, these curves slope downward. Since there is no interaction between *A* and *B* in the solid phase, for each temperature the Gibbs energy for the solid phase is represented by the points in sections G^S_A and G^S_B. These points also slide downwards with the increasing temperature. Since the rate of downward sliding of the curve corresponding to the solid phase is less than for the liquid phase, the distance between points G^L and G^S decreases with increasing temperature due to the ratio of the entropy ($S^L > S^S$) and $\quad S = \left. \dfrac{\partial G}{\partial T} \right|_P$.

As shown in Fig. 5.6, in the temperature interval T_1–T_4, tangents can be drawn to the G^L curve through the G^S points. The tangent points indicate the composition of the liquid in equilibrium with solid phase *A* or *B*, or with their eutectic mixture. Points 1–10 thus obtained are transferred to a new system of coordinates temperature–composition, as shown at the bottom of Fig. 5.6.

5.7. Binary Systems with Unlimited Solubility in the Solid Phase

In this case, if the components of a binary system have a reciprocal solubility in the solid state,
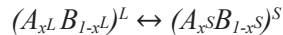
$$(A_{xL} B_{1-xL})^L \leftrightarrow (A_{xS} B_{1-xS})^S$$

then a maximum of two phases can be found in that system, where $(A_{xL} B_{1-xL})^L$ is a liquid solution of composition x^L y $(A_{xS}B_{1-xS})^S$ is the solid solution of composition x^S. Note that unlimited solubility of the components of the solid phase is possible if they belong to the same type of crystal structure and if the sizes of their atoms and molecules are similar.

At the extreme points corresponding to the two pure components *A* and *B* or to two one component systems, the liquid- and solid-phases have the same compositions. Naturally, if the temperature of the components exceeds the corresponding fusion temperatures (T^M_A or T^M_B), the liquid phases are stable and

the one-component systems are monovariant, i.e., have only one degree of freedom. When these systems have the temperatures below T^M_A or T^M_B, corresponding solid pure phases exist. At the fusion point of the pure components of the system A and B, there are no degrees of freedom and the liquid and solid phases are in equilibrium.

If the compositions of the phases in equilibrium are different from 1, the binary system AB will have only one degree of freedom. This means, in particular, that to any value of temperature corresponds one value of liquid and solid compositions, and vice versa. For this reason, as the temperature decreases, the compositions of the liquid and solid compositions slide along the liquidus and the solidus lines, that, as we have already mentioned, define the geometry of the monovariant system. It follows that in a binary system with unlimited solubility in the liquid and solid phases there are temperatures of the beginning and end of the crystallization process. The temperature of the beginning of crystallization is naturally located at the liquidus line, where the liquid phase is saturated. The temperature of the end of crystallization is located on the solidus line.

As in the previous section, we use two methods to study the state diagrams of binary systems with unlimited solubility in the solid phase:
  I. The partial pressures of the components of the system on the phases in equilibrium are equal.
 II. In order to find the equilibrium conditions between the liquid and solid phases at a given temperature, it is necessary to draw a tangent common to the dependence of the Gibbs energy on the composition. The points on the tangent line will indicate the compositions of the phases in equilibrium at a given temperature, since at these points the differential Gibbs energy equations, taking into account the number of particles and chemical potentials, should be equal.

I. Let us consider the first method. Fig. 5.7 shows the curves of pressure as a function of temperature for the liquid and solid phases of a one component system, where (co) is the evaporation curve, and (ao) is the sublimation curve of the pure component A. At the intersection of these curves at temperature T_0, the pure phases, liquid A^L and solid A^S, are in equilibrium, since the pressures of their corresponding vapors are equal. The transition from a one component system to a binary system by adding component B to the pure liquid and solid phases of component A will cause the evaporation and sublimation curves to slide downward relative to co and ao. This is in agreement with Raoult's law that the

pressure on the vapor on the liquid and solid solutions is always lower than that on the liquid or solid phase of a one component. The vapor pressure of component A is proportional to its concentration. Therefore, as more and more component B is added to the liquid or solid phase of component A, i.e., as the concentration of A decreases, the point of intersection of the evaporization curves may slide toward higher and lower temperatures relative to the temperature T, as shown in Fig. 5.7.
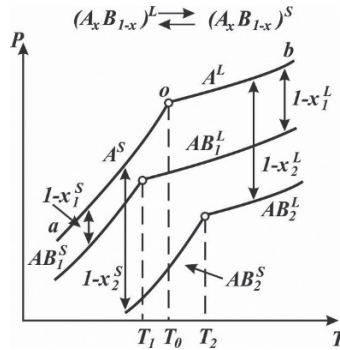

Fig. 5.7. The curves of sublimation for the binary system at different temperatures.

It follows that components A and B form a continuous series of solid solutions, in which case three liquidus curves are possible:
1. As the concentration of one the components increases, the crystallization onset temperature or liquidus temperature increases continuously.
2. When one component is added to another, the temperature of the beginning of crystallization becomes higher, but there is a maximum on the liquidus line.
3. When one component is addede to another, the temperature of the beginning of crystallization becomes lower and a minimum is observed on the liquidus line.

Fig. 5.8 shows three types of liquidus curves forming a continuous series of solid solutions of the system. Let us analyze the state diagram of the system in which the liquidus is a curve of the first type. As noted earlier, any liquid phase represented by any point on the liquidus curve must correspond a definite and single point characterizing the composition of the solid phase in equilibrium, i.e., a point on the solidus line. Therefore, the liquidus and solidus curves are often called conjugate curves.
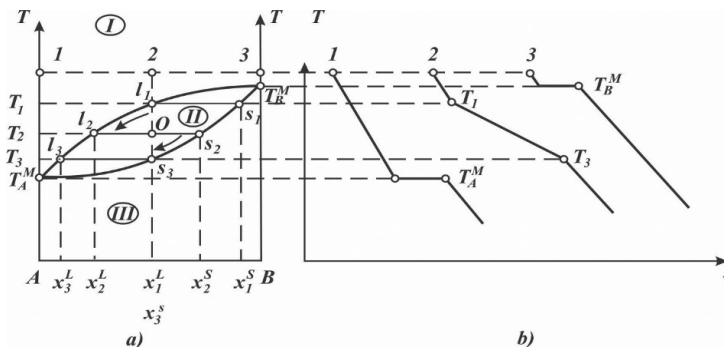
Fig. 5.9.*a* shows the liquidus and solidus lines for a simple system with unlimited mutual solubility in the liquid and solid phases. Such diagrams of state are often called "cigarette" or "lens" type diagrams. The liquidus and solidus lines divide the diagram into three parts or regions (*I*, *II*, *III*). Regions *I* and *III* correspond to the liquid and solid phases, which represent the liquid and solid one phase solutions that exist due to unlimited solubility of any concentration. In this case, the system is homogeneous and has two degrees of freedom, and the figurative points can be located anywhere in the regions *I* and *III*. The second region is heterogeneous and the two phases are in equilibrium. For this reason, it is a monovariant system and the figurative point cannot be located inside this region, but only on the liquidus and solidus lines. To find the compositions of the phases that are in equilibrium in the state diagram, it is sufficient to draw a horizontal line from the point T (in Fig. 5.9.*a* conodus *ls*), intersecting the liquidus and solidus curves at constant temperature. The abscissa of the intersection point indicates the composition of the equilibrium liquid x^L and solid x^S phases.
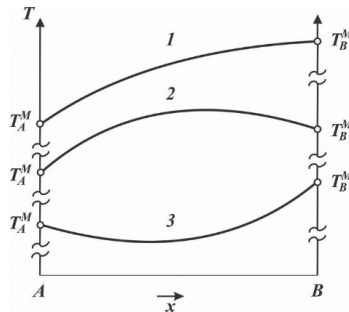
Fig. 5.8. Possible positions of the liquidus line in the case of the unlimited solubility.

Fig. 5.9. The liquidus and solidus lines for the binary system with an unlimited mutual solubility in the liquid and solid phases.

Observing the diagram, we can see that the solid solution will always be enriched in the concentration of the element B relative to the equilibrium liquid, so that the liquidus temperature increases as the concentration of B in the liquid.

Suppose that the crystallization of a solid solution begins from the liquid phase whose the concentrations is x^L_1. Assume that the temperature is such that in the diagram under consideration the figurative point characterizings the system (or the liquid phase) is located in position 2, i.e., in region I. As the temperature decreases, point 2 will fall down the straight line because the system has two degrees of freedom and a change in one parameter (temperature) does not result in a change in the other (concentration). At the moment when the vertical line crosses the liquidus line at point l_1, the first crystal with the composition determined by the point s_1 should appear. The emergence of the second phase reduces the number of degrees of freedom and the system becomes monovariant. Therefore, the subsequent decrease in temperature leads to a change in concentration. The composition of the liquid phase will change along the solidus line. For example, at temperature T_3, the composition of the liquid phase is represented by the abscissa of the point s_2. Obviously, the previously separated solid solution s_1 is no longer in equilibrium with the liquid phase l_2. To reach equilibrium, the whole composition of this solid solution must change so that it corresponds to the abscissa of point s_2, that means enrichment with component A. In principle, such enrichment can occur, for example, by diffusion. However, these processes are very slow because the diffusion coefficients of the elements in the solid phase are very small. In this connection, the composition of the liquid phase corresponds to the whole composition of the crystal growth, which would be achievable when s_2 corresponds the composition of the liquid phase l_2, is not achieved in practice, and therefore the real crystallization processes do not coincide with the equilibrium state diagrams.

From the previous analysis of crystallization processes in a system with a cigarette-shaped state diagram, simple conclusions can be drawn as follows:
- In the crystallization process, the solid phase, in comparison to the liquid phase, turns out to be enriched with the component that has a higher fusion temperature (in the previous case, component B);
- As this component rapidly passes into the solid phase, its concentration diminishes in the liquid phase ;
- This in turn leads to a decrease in the content of this component in the solid phase, and therefore the growing crystal will always have a gradient

of the composition, in particular, the first formed volumes of the crystal will be enriched with the component with the higher fusion temperature in relation to the subsequent volumes.

As the temperature decreases to the point T_3, the volume of the solid phase increases and that of the liquid one decreases, and as seen in Fig. 5.9.a, the last traces of the liquid phase will have the composition of point l_3. As a result, on the cooling curve drawn for the initial point 2, which has the composition $x^L{}_1$, in Fig. 5.9.b, two changes in the slope $\dfrac{dT}{dt}$ will be observed, one of which determines the beginning and the other, the end of the crystallization process. The shape of the cooling curves for figurative points 1 and 3 is similar to the previously shown dependences for pure components in the state diagram of the system with one single eutectic. As we have already noted, the cooling curves in practice may differ significantly from those shown in Fig. 5.9.b, which are presented in idealized form for simplification purposes.

The ratio between the number of liquid and solid phases in the crystallization process is determined by the lever rule. According to this rule, for instance, at temperature T_2, the ratio of volumes of the liquid and solid phases in the system is determined by the ratio of the distances between the segments Os_2 y Ol_2. To derive this rule, we will assume that at the time of the beginning of crystallization, that means, at temperature T_1, the system had N particles. After some time in the process of cooling the system to temperature T_2, the particles remained in the liquid phase $N^L{}_2$ and the rest remained in the solid phase $N^S{}_2 = N - N^L{}_2$. Let us write the expression for the mass balance for component B. At the beginning in the liquid phase of the composition $x^L{}_1$ (at point l_1) is the amount of B, which is equal to $Nx^L{}_1$. At temperature T_2 in the solid phase, it is equal to $N^S{}_2 x^S{}_2$ and, corresponingly, in the liquid phase to $N^L{}_2 x^L{}_2$. Naturally, $N = N^L{}_2 + N^S{}_2$ and $Nx^L{}_1 = N^L x^L{}_2 + N^S x^S{}_2$ since the total number of particles has not changed during the process. Hence, $(N^L + N^S)x^L{}_1 = N^L x^L{}_2 + N^S x^S{}_2$. It is from this that we infer what we intended to demonstrate.

$$N^S \left(x^S_2 - x^L_1\right) = N^L \left(x^L_1 - x^L_2\right) \quad \text{or} \quad \frac{N^L}{N^S} = \frac{x^S_2 - x^L_1}{x^L_1 - x^L_2} = \frac{Os_2}{Ol_2}$$

Now analyze the state diagram of a two component system with unlimited solubility in the solid phase, departing from the laws that regulate the change of the Gibbs energy as a function of concentration and temperature.

For simplicity, as in the first part of this section, we will first study the "cigarette" shaped diagram. In a three-dimensional space G–T–x, the Gibbs energy for the liquid phase, as well as for the solid phase, is represented by concave region (a curve whose second derivative in this case with a G positive; the opposite case we will call it a convex, that means it has a negative second derivative) (Figs. 5.10 and 5.11). These regions will slide downward, reaching the x–T plane due to the temperatures increase, with the downward sliding $G^L=G^L(T,x^L)$ being faster for the liquid phase than for the solid phase.

We shall draw, as shown in Fig. 5.10, a set of isothermal cross sections representing perpendicular planes to x–T. Obviously, in each cross section, the intersection of the vertical isothermal planes will result in two Gibbs energy curves, one for the liquid phase G^L and the one for the solid G^S. In such case, if the cross-sections are at temperatures below the fusion temperature of the component with the lowest fusion temperature in the system (in Fig. 11 it is component A), then the Gibbs energy curve in the concentration region for the solid phase will be located under the corresponding curve for the liquid. Therefore, other things being equal, it is impossible to draw a common tangent, i.e., there is no composition in which these phases could be in equilibrium. The only stable phase under these conditions is the solid phase, since its Gibbs energy for any composition is lower than that for the liquid phase. Likewise, for temperatures $T>T_B$, the curves $G^L=G^L(T,x^L)$ or $G^S=G^S(T,X^S)$ also do not intersect. In Fig. 5.11 the liquid phase is stable, since the composition-dependent Gibbs energy function below the isothermal sections is in the temperature intervals $T_A \leq T \leq T_B$, in each of these sections the curves $G^L=G^L(x^L)$ or $G^S=G^S(X^S)$ will intersect as shown in Figs. 5.10 and 5.11. Consequently, it is possible to draw a straight common tangential line whose points of tangency will indicate the lines $G^L=G^L(x^L)$ or $G^S=G^S(X^S)$ of the phase compositions in equilibrium at a given temperature.

For a more graphic illustration of the method of state diagram construction, previously shown in Fig. 5.11, four isothermal sections T_1, T_2, T_3, T_4 located in the interval of $T_A \leq T \leq T_B$ are presented separately. The points denoting the compositions of the equilibrium liquid and solid phases for different temperatures are transferred to the temperature–composition coordinate plane, i.e., to the state diagram shown at the bottom part of Fig. 5.11.
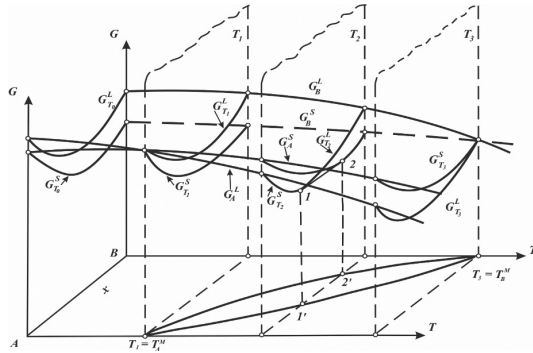
Fig. 5.10. Construction of the state diagram for the binary system with the unlimited mutual solubility.
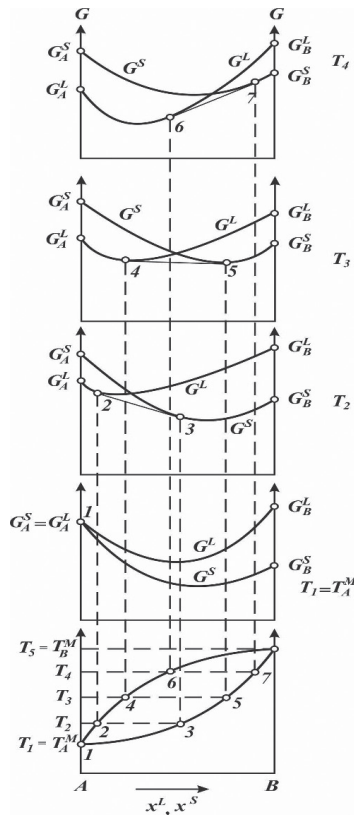
Fig. 5.11. Construction of the state diagram of the system with unlimited solubility with tangents to the Gibbs energy.
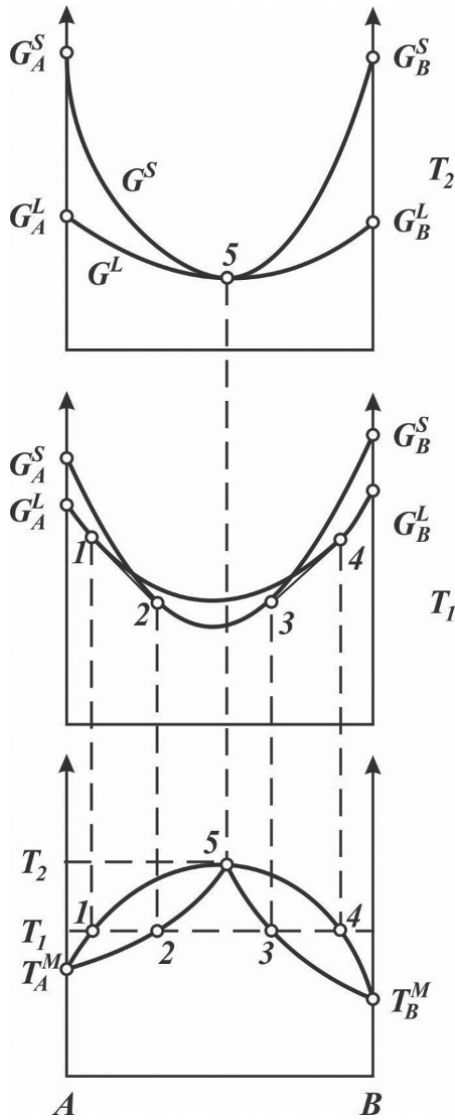
Fig. 5.12. Various types of the state diagrams in the solutions with unlimited mutual solubility.
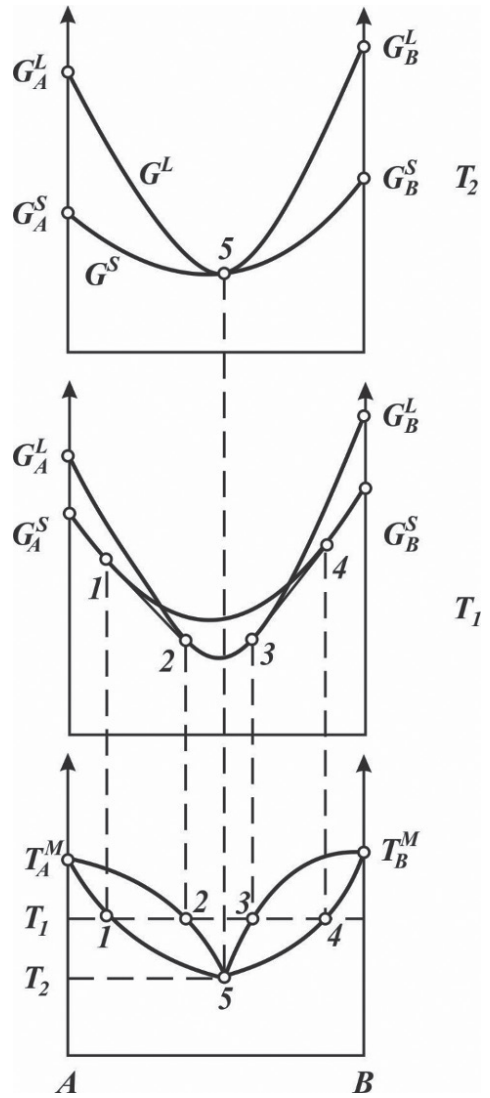
Fig. 5.13. Various types of the state diagrams in the solutions with unlimited mutual solubility.

The example considered earlier rerers to one of the cases when the state diagram turns into a cigarette- or lens-type diagram, and the liquidus and solidus temperatures refer to the fusion points of components *A* and *B*. These diagrams are formed when the curvature of lines $G^L=G^L(x^L)$ or $G^S=G^S(X^S)$ does not differ much. Examples of systems that have similar diagrams are *Cu–Ni, Ag–Au, Ge–Si, AlAs–GaAs* and some others.

Nevertheless, in various cases on the state diagrams of systems forming a series of continuous solid solutions, intermediate maxima and minima are observed, which correspond to the second and third types of liquidus curves what was indicated at the beginning of this section. These types of liquidus curves, and correspondingly the diagrams with maxima or minima, are formed when the curvature of the lines $G^L=G^L(x^L)$ or $G^S=G^S(X^S)$ differ significantly from each other. If the G^S curve has greater curvature than the G^L curve, as shown in Fig. 5.12, then the diagram has an intermediate maximum. On the contrary, there is a state diagram with an intermediate temperature minimum, as shown in Fig. 5.13. In the latter case, the state diagram of the *Ag–Cu* system is shown as an example.

Note that at the maximum or minimum points, the system should be considered as a one component system, since both phases, solid and liquid, coincide in their composition. Thus, the degree of freedom is zero.

5.8 Real Systems and the Coefficients of Segregation

As shown previously, the chemical potential of an ideal system has the form

$$\mu_i = \mu^O_i\,(T,P) + RT \ln x_i \qquad (5.15)$$

Where the first term is the chemical standard potential and the second term is a mixture function. Note that the described model using the equation (5.15) has not only a theoretical meaning, allowing us to study the properties of the ideal systems, but is also successfully applied in very specific calculations of the state diagrams. Of course, in such calculations, the criterion for the validity of using the model, in particular, the model of ideal systems, is the coincidence of theoretical and experimental data. It turns out that, for example, the *Ge–Si* system can be considered close to the ideal case, since the calculated data obtained for this system in the models of ideal solutions generally coincide with experimental data, as can be seen in Fig. 5.14. This figure shows the results of the study of the *Ge–Si* system given in the book of Richard A. Swalin *"Thermodynamics of Solids"* (John Wiley and Sons 1972), first published in the works of C.D. Thurmond, J. Phys. Chem. 57, p.827 (1953).

Another example of close to ideal systems that can be mentioned is the *GaAs-AlAs* system. The state diagram of this system has been theoretically studies using the method of the chemical equilibrium constant. In this method, widely described in the following chapter 6, approximations corresponding to the solid solutions were used. The validity of the application of this model is confirmed by a good coincidence of the calculated and experimental data. The method of the chemical equilibrium constant for the *GaAs–AlAs* system was developed by Dimitriy Nikolaievich Tretyakov in the book "The liquid phase epitaxy in the technology of semiconductor devices", V. M. Andreev, L. M. Dolginov, D. N. Tretyakov, Moscow, Soviet-radio, 1975. 621.382:621.315.592 (Available in Russian only). It should be noted that the most of the state diagrams cannot be accurately described by means by the ideal solution models. That is why a special method is used for ideal systems, which we will analyze below.

Suppose that the chemical potential of some real system μ_i^{real} is represented in the same way as it is done for an ideal system, but to account for the deviations from

ideal behavior, the concentration in (5.15) is changed by one parameter a_i, which we shall call "activity". Thus, the activity can be defined as the corrected or "effective" concentration that allows the equation for the ideal systems to be applied. The degree or magnitude of deviation of the system with respect to concentration is called the activity coefficient

$$\gamma_i = \frac{a_i}{x_i}$$

It is clear that in the ideal systems $\gamma=1$.

Using these definitions, the chemical potential of a real system is written as follows

$$\mu_i{}^{real} = \mu_i{}^O + RT\ln a_i = \mu_i{}^O + RT\ln\gamma_i + RT\ln x_i = \mu_i{}^{real} + RT\ln\gamma_i \qquad (5.16)$$

That is why, in a general, the calculation of the phases in equilibrium involves solving a system of equations in which part of the equations relates temperature and concentration through the activity coefficient and the thermodynamic constants that characterize the interaction of the particles in solid solutions.

The first group of equations is written on the basis of chemical potentials of components in different phases. The second group of equations is derived in correspondence with the models of solutions in the liquid and solid phases. Let us give the equilibrium condition for the *i-th* component of the two phase system: (*L*) liquid and (*S*) solid.

$$\mu_i^L = \mu_i^S,$$
$$\mu_i^l = \mu_i^{l0} + RT\ln a_i^l = \mu_i^{l0} + RT\ln\gamma_i^l + RT\ln x_i^l,$$
$$\mu_i^{l0} + RT\ln\gamma_i^L + RT\ln x_i^L = \mu_i^{0S} + RT\ln\gamma_i^S + RT\ln x_i^S,$$
$$RT\ln \frac{x_i^S}{x_i^L} = (\mu_i^{0L} - \mu_i^{0S}) + RT\ln \frac{\gamma_i^L}{\gamma_i^S},$$
$$\frac{x_i^S}{x_i^L} = \frac{\gamma_i^L}{\gamma_i^S} \, exp\left(\frac{\mu_i^{0L} - \mu_i^{0S}}{RT}\right)$$
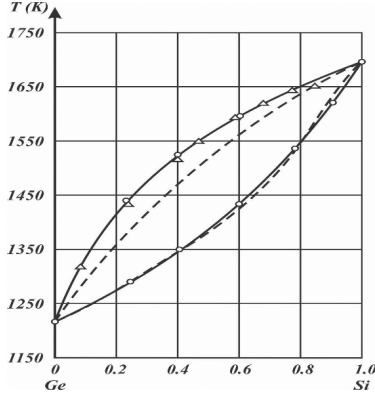
Fig. 5.14. The phase diagram Ge-Si.

Let us transform the exponent. It is known that

$$\bar{G}_i = \mu_i = \bar{H}_i - \bar{S}_i T$$

As a result

$$\frac{\mu_i^{0L} - \mu_i^{0S}}{RT} = \frac{\bar{H}_i^{0L} - \bar{S}_i^{0L}T - \bar{H}_i^{0S} + \bar{S}_i^{0S}T}{RT} = \frac{\Delta H_i^0}{RT} - \frac{\Delta S_i^0}{R} \tag{5.17}$$

In the expression (5.17) $\Delta H^0{}_i$ and $\Delta S^0{}_i$ refer to the enthalpy and the entropy differences in the liquid and solid phases at an arbitrary temperature. The magnitudes of $\Delta H^0{}_i$ and $\Delta S^0{}_i$ also change with the temperature, but only slightly. That is why we substitute the magnitudes of $\Delta H^0{}_i$ and $\Delta S^0{}_i$ calculated at a given temperature T with ΔH_i^M and ΔS_i^M at the fusion temperature T_i^M of component i. The resulting error from this substitution is so small that it can be neglected in the further calculations. Thus,

$$\frac{\Delta H_i^0}{RT} - \frac{\Delta S_i^0}{R} = \frac{\Delta H_i^M}{RT} - \frac{\Delta S_i^M}{R} = \frac{\Delta H_i^M T_i^M}{RTT_i^M} - \frac{\Delta S_i^M}{R} = \frac{\Delta S_i^M}{R}\left(\frac{T_i^M}{T} - 1\right)$$

Therefore,

$$k_i = \frac{x_i^S}{x_i^L} = \frac{\gamma_i^L}{\gamma_i^S} exp\left[\frac{\Delta S_i^M}{R}\left(\frac{T_i^M}{T} - 1\right)\right] \tag{5.18}$$

The resulting equation relates the concentration of component i in the liquid and solid phases to the temperature and thermodynamic parameters ΔH_i^M and ΔS_i^M. The factor in front of the exponent characterizes the interaction $\dfrac{\gamma_i^L}{\gamma_i^S}$ of the particles in the liquid and solid phases and is determined by the solutions model. In the model of the ideal solutions $\gamma_i^S = \gamma_i^L = 1$. That is why, for the ideal case we have

$$k_i = \frac{x_i^S}{x_i^L} = exp\left[\frac{\Delta S_i^M}{R}\left(\frac{T_i^M}{T} - 1\right)\right] \tag{5.19}$$

The magnitude k_i in (5.18) and (5.19) is called the segregation coefficient or distribution coefficient. This coefficient is one of the most important technological parameters in the crystal growth processes. If $k_i > 1$, the solid phase is enriched in component i in comparison to the liquid phase at a given T. Consequently, in the crystal growth process, the concentration i in the liquid phase x_i^L decreases, which, in turn, causes a decrease in the concentration of this component in the solid phase x_i^S. If, on the contrary, $k_i < 1$, then x_i^L increases with the growth, which leads to an increase x_i^S in the depth profile along the crystal growth direction.

Suppose that the binary system A–B is ideal, i.e., it is described by expression (5.19). Let us imagine a hypothetical case when

$$T_A^M = T_B^M = T \tag{5.20}$$

Then it follows from (5.19) that $x_i^L = x_i^S$. However, since no two different elements with the same melting point exist in nature, (5.20) cannot be fulfilled, so in any system containing more than one component, the composition of the liquid phase does not coincide with the composition of the crystal. Suppose that in a binary system, as shown in Fig. 27, $T_A^M < T_B^M$. In this case, for component A we have $T_A^M < T$ and, as can be seen from (5.19), $k_A < 1$.

Similarly, for component B, we have $B - T_B^M > T$ and $k_B > 1$. In this way, the component that passes into the liquid phase at increasing liquidus temperature will always have a segregation coefficient higher than 1, and its concentration, as indicated above, will decrease from the beginning to the end

of the crystal. And vice versa, for a component that, when introduced into the liquid phase, lowers the liquidus temperature, the segregation coefficient will be less than *1*. Therefore, its concentration will increase along the crystal.

5.9 The Regular Solution Model

Consider two liquid phases formed by pure components *A* and *B*. Certain bonding or interacting energies act between the atoms of the different phases, which we denote as φ_{AA} and φ_{BB}. Suppose that *A* and *B* in the liquid phase are soluble in each other, i.e., when mixed they form a continuous series of liquid solutions. Then, when two liquids are mixed, the properties of the solutions should depend on the ratio of the interaction energies between equal and unequal atoms, that is, be a function of φ_{AA} and φ_{BB}. Thus three different cases are possible: all interaction energies are equal

$$\varphi_{AA} = \varphi_{BB} = \varphi_{AB}$$

- The interaction energies among different atoms are stronger than among identical atoms

$$\varphi_{AB} > \varphi_{AA} \, (or \; \varphi_{BB})$$

- The interaction energies among different atoms are weaker than among identical atoms

$$\varphi_{AB} < \varphi_{AA} \, (or \; \varphi_{BB})$$

Each type of bond correponds to a different type of enthalpy H_{AA}, H_{BB}, and H_{AB}. If in one gram-atom of a solution contains η_{AA} of bonds *A–A*, η_{BB} of bonds *B–B*, and η_{AB} of bonds *A–B*, then the common enthalpy of the solution is written as follows

$$H = \eta_{AA} H_{AA} + \eta_{BB} H_{BB} + \eta_{AB} H_{AB}$$

When the enthalpy composition of solution changes, other properties or parameters will also change. Thus, the properties of the solutions depend on the magnitude of the interaction energies of different atoms, their distribution and

concentration. Therefore, finding analytical functions of the properties of the solutions depending on their composition can only be achieved with the help of an adequate molecular kinetic model.

Likewise, in the case of equality of all inter-atomic interactions, the thermal effect should not appear, since the formation of new bonds A–B is equivalent to the breaking of the bonds A–A and B–B. In this case

$$H_{AB} = \frac{1}{2} (H_{AA} + H_{BB})$$

and therefore the properties of the solutions must be a linear function with regards to the concentration as was shown previously for ideal solutions. In section 5.2 it is shown that for ideal systems

$$h^m = 0, v^m = 0, q^m = 0, u^m = h^m - Pv^m = 0, s^m = -Rx_1 \ln x_1 - Rx_2 \ln x_2 \quad (5.21)$$

If at least one of the conditions in (5.21) is not met, the system deviates from tthe ideal system. One of the parameters of such models in which one of the idealization conditions is not satisfied is the so-called regular solution model, which is successfully used to describe the properties of many systems based on various semiconductors. In this model, all functions of the mixture are assumed to be equal to the corresponding functions for ideal solutions, except for the enthalpy, which is different from zero. As the volume of the mixture is $v^m(reg) = v^m(id)$, since $U = H - PV$, is treated as one of the regular solutions in the model. It is known that $\mu = \bar{G} = \bar{H} - T\bar{S}$. From where

$$\mu^{reg} - \mu^{id} = h^m = u^m = RT \ln \gamma \quad (5.22)$$

Thus, to find an expression for the activity coefficient in the regular solution model, it is necessary to calculate the internal energy of the system, which is the sum of the potential energies of the atoms forming it. After that, it is necessary to choose from the obtained expression the energy or enthalpy of the mixture, which, accordaning to (5.22), will determine the studied magnitude of the activity coefficient.

To simplify the calculations, we make the following assumption under which the solutions under consideration are called strictly regular:

1. The atoms of components A and B analyzed in the system do not differ in size and shape significantly.
2. In the calculation, we will consider only the interaction of neighboring atoms, disregarding the action of those that are farther away from this immediate vicinity. It is assumed that the interaction energy attributable to the neighboring single- or adjacent atoms φ_{AA}, φ_{BB} and φ_{AB} is constant.

Based on the first assumption, we consider that the atom distribution in the solid phase is random. The second statement is equivalent to the fact that the internal energy of the system is the sum of the interaction energies of the neighboring atoms.

Now suppose that each atom is surrounded by z neighbors, i.e., z is the coordination number of N_A atoms of one type and N_B of another type. So, around one atom of component A there will be $z \dfrac{N_A}{N_A + N_B}$ atoms of the same type and $z \dfrac{N_B}{N_A + N_B}$ atoms type B.

The interaction energy of atom A with its neighbors is a consequence of the limit 2 for the energy of its interaction with the whole system and it is written in the form

$$\frac{N_A}{N_A + N_B}\, z\varphi_{AA} + \frac{N_B}{N_A + N_B}\, z\varphi_{AB} \tag{5.23}$$

Similarly, as we have N_A atoms of the first type, their total interaction energy with the whole system is

$$\frac{N_A^2}{N_A + N_B}\, z\varphi_{AA} + \frac{N_A N_B}{N_A + N_B}\, z\varphi_{AB} \tag{5.24}$$

Analyzing the atoms of the second type, we obtain a similar expression

$$\frac{N_B^2}{N_A + N_B}\, z\varphi_{BB} + \frac{N_A N_B}{N_A + N_B}\, z\varphi_{AB} \tag{5.25}$$

The total energy of the system is equal to half of the sum of expressions (5.24) and (5.25), since no double counting should be done for each pair.

$$U = \frac{N_A^2}{N_A + N_B} \left(\frac{1}{2} z\varphi_{AA}\right) + \frac{N_B^2}{N_A + N_B} \left(\frac{1}{2} z\varphi_{BB}\right) + \frac{N_A N_B}{N_A + N_B} \left(z\varphi_{AB}\right) \qquad (5.26)$$

In (5.26) we will carry on elementary transformations:

$$U = \frac{N_A^2}{N_A + N_B} \left(\frac{1}{2} z\varphi_{AA}\right) + \frac{N_B^2}{N_A + N_B} \left(\frac{1}{2} z\varphi_{BB}\right) + \frac{N_A N_B}{N_A + N_B} \left(z\varphi_{AB}\right) =$$

$$= \frac{N_A^2 + N_A N_B - N_A N_B}{N_A + N_B} \left(\frac{1}{2} z\varphi_{AA}\right) + \frac{N_B^2 + N_A N_B - N_A N_B}{N_A + N_B} \left(\frac{1}{2} z\varphi_{BB}\right) +$$

$$+ \frac{N_A N_B}{N_A + N_B} \left(z\varphi_{AB}\right) = \frac{N_A (N_A + N_B)}{N_A + N_B} \left(\frac{1}{2} z\varphi_{AA}\right) - \frac{N_A N_B}{N_A + N_B} \left(\frac{1}{2} z\varphi_{AA}\right) +$$

$$+ \frac{N_B (N_A + N_B)}{N_A + N_B} \left(\frac{1}{2} z\varphi_{BB}\right) - \frac{N_A N_B}{N_A + N_B} \left(\frac{1}{2} z\varphi_{BB}\right) + \frac{N_A N_B}{N_A + N_B} \left(z\varphi_{AB}\right) =$$

$$= N_A \left(\frac{1}{2}\right) z\varphi_{AA} + N_B \left(\frac{1}{2} z\varphi_{BB}\right) + \frac{N_A N_B}{N_A + N_B} \, z \left[\varphi_{AB} - \frac{1}{2} \left(\varphi_{AA} + \varphi_{AA}\right)\right].$$

As a consequence, the internal energy of the system in the frame of regular solutions is written as follows

$$U = N_A \left(\frac{1}{2} z\varphi_{AA}\right) + N_B \left(\frac{1}{2} z\varphi_{BB}\right) + \frac{N_A N_B}{N_A + N_B} \, z \left[\varphi_{AB} - \frac{1}{2} \left(\varphi_{AA} + \varphi_{AA}\right)\right]. \quad (5.27)$$

If $N_A = 0$, then

$$U = N_B \frac{1}{2} z\varphi_{BB}$$

Consequently $\frac{1}{2} z\varphi_{BB}$ is the average energy of a B atom in a pure solid or liquid solution. Likewise, when $N_B = 0$

$$U = N_A \frac{1}{2} z\varphi_{AA},$$

where $\frac{1}{2} z\varphi_{AA}$ is the average energy of an A atom.

Suppose that we have two pairs $AA(\circ\circ)$ and $BB(\bullet\bullet)$. If two mixed pairs A–A and B–B are formed from two identical pairs, the energy change of the system is equal to $2\varphi_{AB}-\varphi_{AA}-\varphi_{BB}$. Therefore, the energy increase during pair formation is expressed as

$$\varphi_{AB}-\frac{1}{2}\left(\varphi_{AA}+\varphi_{BB}\right) \qquad (5.28)$$

The physical sense of this formula can be understood from Fig. 5.15, in the upper part of which two mixtures A–B are represented, and in the lower part two equal pairs A–A and B–B. Here it can be seen that expression (5.28) represents half of the energy difference of the two configurations of atoms deplected in the upper and the lower parts of Fig. 5.15.
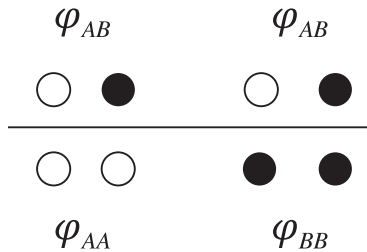
Fig. 5.15. To the definition of the interaction parameter.

For this reason, expression $\varphi_{AB}-\frac{1}{2}\left(\varphi_{AA}+\varphi_{BB}\right)$ is called exchange energy since it characterizes the average increase in the energy of an atom of any type when all its neighbors are replaced by atoms of opposite type. If, for example, the coordination number z is equal to 6, the sense of the exchange energy can be illustrated by Fig. 5.16.
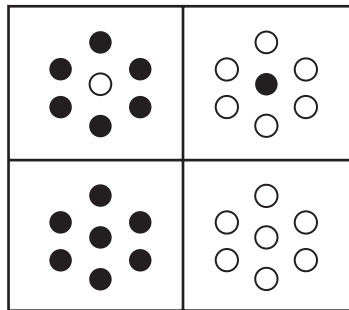
Fig. 33. To the definition of the interaction parameter (z=6)

In (5.27) we indicated $\dfrac{1}{2} z\varphi_{AA}$ through α_A, and $\dfrac{1}{2} z\varphi_{BB}$ through α_B, and $z\left(\varphi_{AB} - \dfrac{1}{2} \varphi_{AA} - \dfrac{1}{2} \varphi_{BB}\right)$ through α_{AB}. The magnitude α_{AB} is called interaction parameter. This parameter is equivalent to the exchange of energy in the calculation for one mole.

Once we have introduced these notations in (5.27) we have

$$U = N_A\alpha_A + N_B\alpha_B + \frac{N_A N_B}{N_A + N_B} \alpha_{AB} \qquad (5.29)$$

Since the expression (5.29) represents the total energy of the system, the energy per atom of each type is equal to

$$\left.\frac{\partial U}{\partial N_A}\right| = \alpha_A + \left(\frac{N_B}{N_A + N_B}\right)^2 \alpha_{AB} = \alpha_A + x_B^2\alpha_{AB} = \alpha_A + (1-x_A)^2\alpha_{AB} \qquad (5.30)$$

$$\left.\frac{\partial U}{\partial N_B}\right|_{N_A} = \alpha_B + \left(\frac{N_A}{N_A + N_B}\right)^2 \alpha_{AB} = \alpha_B + x_A^2\alpha_{AB} = \alpha_B + (1-x_B)^2\alpha_{AB} \qquad (5.31)$$

As can be seen from expressions (5.30) and (5.31), the mixture energy (or residual term) for atom A is equal to $U^m{}_A = x^2{}_B\, \alpha_{AB}$ and for atom B is equal to $U^m{}_B = x^2{}_A\, \alpha_{AB}$.

Therefore, for the system containing atoms A and B and obeying the approximation of regular solutions, we have

$$RT\ln\gamma_A = \alpha_{AB}x^2{}_B = \alpha_{AB}(1 - x_A)^2, \qquad (5.32)$$
$$RT\ln\gamma_B = \alpha_{AB}x^2{}_A = \alpha_{AB}(1 - x_B)^2, \qquad (5.33)$$

where α_{AB} in the frame of regular solutions is a constant magnitude.

For the solutions in which "a strict regularity" is observed, in many cases a good agreement between experimental and calculated data is achieved by using a linear dependence of the interaction parameter on temperature

$$\alpha = a + bT$$

In this expression, a and b are parameters independent of temperature and concentration. The values of these parameters in each particulate case, i.e., for any specific diagram, are determined by substituting the experimentally found data between temperature and concentration into the corresponding equations for calculation of the equilibrium phases. The dependence of α on temperature indirectly accounts for the fact that the difference in interaction energies between homogeneous and heterogeneous pairs leads to a deviation of the statistical distribution in the solution. Therefore, the ratio of the number of homogeneous and heterogeneous pairs will depend on temperature. This approximation, often used in the calculation of state diagrams in various semiconductor systems, is called quasiregular approximation or quasiregular model.

5.10 Disintegration of Solid Solutions

Analyze the disintegration processes in the framework of regular solution models. As it was shown earlier, the entropy of the mixture in this model is equal to

$$\Delta S^m = -Rx_1 - Rx_2 \ln x_2$$

Since the concentrations x_1 or x_2 can take values between 0 to 1, the value of the ΔS^m is always positive, as discussed earlier in section 5.2, equation (5.8). In addition, the function ΔS^m is symmetric with respect to the composition $x_1 = x_2 = 0.5$, for the maximum value of the entropy of the mixture. Since the absolute temperature T is also positive, the entropy term $-T\Delta S^m$ in the Gibbs energy expression

$$\Delta G^m = \Delta H^m - T\Delta S^m \tag{5.34}$$

will be negative and the curvature of the function $T\Delta S^m$ with respect to the concentration will always be directed downward. As shown in the previous paragraph, the total energy of the regular solution is equal to

$$U = N_A \left(\frac{1}{2} z\varphi_{AA} \right) + N_B \left(\frac{1}{2} z\varphi_{BB} \right) + \frac{N_A N_B}{N_A + N_B} \ z \left[\varphi_{AB} - \frac{1}{2} \ (\varphi_{AA} + \varphi_{BB}) \right]$$

The symbol x will indicate the concentration of element A. Thus, the concentration of element B will be expressed as $1-x$. Suppose that the total number of particles in the system is N. It is clear that $N_A = Nx$, $N_B = N(1-x)$, $N_A + N_B = N$, and

$$\frac{N_A N_B}{N_A + N_B} = \frac{NxN \ (1\text{-}x)}{N} = Nx(1\text{-}x)$$

Hence the inference that

$$U = Nx\left(\frac{1}{2}\ z\varphi_{AA}\right) + N(1\text{-}x)\left(\frac{1}{2}\ z\varphi_{BB}\right) + Nx(1\text{-}x)z\left[\varphi_{AB} - \frac{1}{2}\ (\varphi_{AA} + \varphi_{BB})\right] \quad (5.35)$$

In the expression (5.35), the first two terms determine the energy of the system consisting of the mixture of the pure components A and B, which, in turn, depends linearly on their concentration. The last term in (5.35) represents the energy of the mixture, which in the model of regular solutions is equal to the enthalpy of the mixture and has the following form

$$\Delta U^m = \Delta H^m = Nx(1\text{-}x)\ z\left[\varphi_{AB} - \frac{1}{2}\ (\varphi_{AA} + \varphi_{BB})\right] \quad (5.36)$$

where φ_{AB}, φ_{AA}, φ_{BB}, determined in section 5.9, are called the interaction energies of the corresponding pairs of atoms. As seen in (5.36), the enthalpy of the mixture is a parabolic function of the concentration and, like ΔS^m, is symmetric about the point $x=0.5$. Nevertheless, unlike the entropy term, the term ΔH^m can be either positive or negative depending on the sign of the interchange energy term $\varphi_{AB} - \frac{1}{2}\ (\varphi_{AA} + \varphi_{BB})$. Let us analyze in detail these two cases, since the sign of ΔH^m significantly affects the process of formation or disintegration of solid solutions. It is known that the atoms of the solid, located in the nodes of the crystal lattice, experience the interactions of both attractive and repulsive forces. The equilibrium state of the atoms is determined by the balance of these forces.
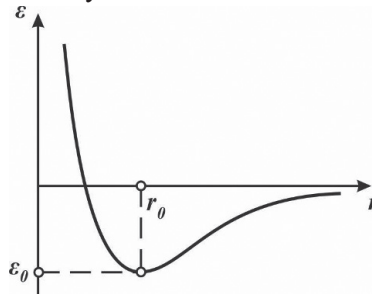
Fig. 5.17. The interaction energy between the atoms in dependence of distance.

Analyze the dependence of the interaction energy between the atoms in a solid ε as a function of the distance r between them in Fig. 5.17. At first, when the distance between the atoms is large, the energy is close to zero, but as r decreases, ε increases continuously in absolute value. Suppose that in this section the atom interaction is due to the attraction forces and that the attraction energy is negative and proportional to $\dfrac{1}{r}$.

The forces of repulsion prevent atoms from coming closer together. The energy of repulsion is considered positive and is proportional to $\dfrac{1}{r^n}$, where n is a constant magnitude. Thus, at $r=r_0$ the function curve passes through the minimum, and the distance r_0 is equal to the distance between the atoms of the solid or the period of the crystall lattice parameter. In the periodical crystal lattice, the energies φ_{AA}, φ_{BB} and φ_{AB} are negative. Let us return to the Gibbs energy for the mixture for regular solutions, which is represented by expression (5.36). In this case, if the value $\Delta H^m=\Delta U^m$ is negative, the function ΔG^m, equal to the sum of ΔH^m and $-T\Delta S^m$, the curvature of ΔG^m as a function of composition is concave with respect to the composition axis of the solid solution. Such a function ΔG^m is shown in Fig. 5.18 and corresponds to the unlimited solubility in the solid phase. As seen in expression (5.36), the limited solubility will take place when $\Delta H^m<0$, as demanded, and thus, since all φ are negative, when

$$\left|\varphi_{AB}\right|>\left|\frac{1}{2}\ (\varphi_{AA}+\varphi_{BB})\right| \tag{5.37}$$
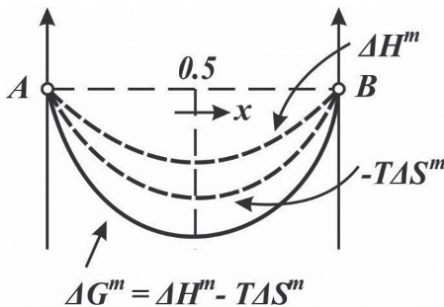
Fig. 5.18. The Gibbs energy in dependence on composition in the system with unlimited mutual solubility for
$\left|\varphi_{AB}\right|>\left|\dfrac{1}{2}\ (\varphi_{AA}+\varphi_{BB})\right|$
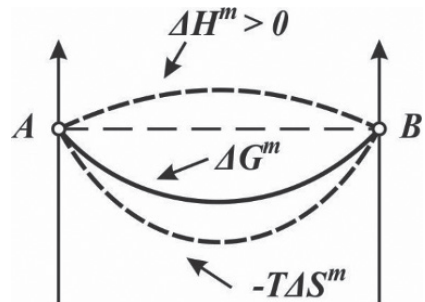
Fig. 5.19. The Gibbs energy in dependence on composition in the system with unlimited mutual solubility for
$\left|\varphi_{AB}\right|<\left|\dfrac{1}{2}\ (\varphi_{AA}+\varphi_{BB})\right|$

In other words, if for the interaction energy between atoms of different types φ_{AB}, so it happens that its absolute value is higher than the average of the energies for atoms of the same type; φ_{AA} and φ_{BB}. Then the enthalpy of the mixture is negative, which in turn accounts the existence of solid solutions.
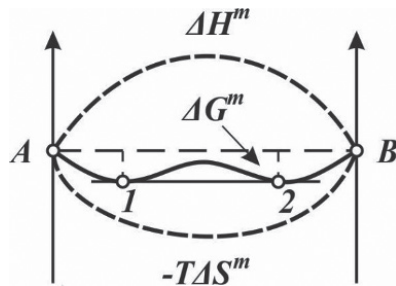

Fig. 5.20. The Gibbs energy in dependence on composition in the system with espinodal decomposition
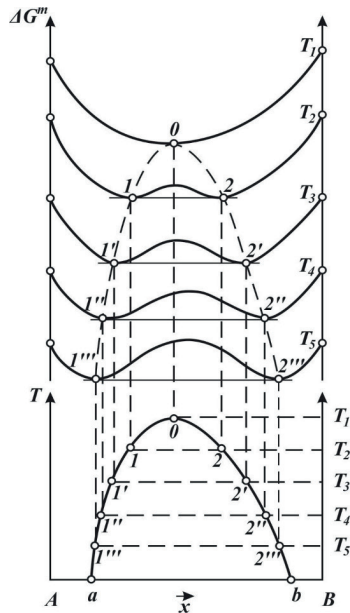

Fig. 5.21. Formation of the area with limited solubility in the solid solution.

On the contrary, if

$$\left| \varphi_{AB} \right| < \left| \frac{1}{2} \left(\varphi_{AA} + \varphi_{BB} \right) \right| \tag{5.38}$$

then the value of ΔH^m becomes positive, as shown in Fig. 5.19. If ΔH^m is a small magnitude, the bonding energy of atoms of onetype and atoms of another type is not much different, then $\Delta G^m = \Delta H^m - T\Delta S^m$ will continue to be concave (Fig. 5.19). Let us indicate that this is possible at very high temperatures when the mixing energy (Fig. 5.21) leads to the formation of the area with limited solubility in the solid solution. ΔG^m is related to the part containing the entropy ($-T\Delta S^m$). Nevertheless, as the temperature drops, this part also decreases, and gradually the ΔH^m becomes the main term. Therefore, at relatively low temperatures, the relationship between functions ΔH^m and $-T\Delta S^m$ can be such that ΔG^m changes its curvature from concave to convex over some concentration interval, as illustrated in Fig. 5.20.

If ΔH^m is negative, the Gibbs energy of the mixture always has a U-shape with a minimum. If, on the contrary, the average of the interaction energies between atoms of one type exceeds the absolute value of the interaction energy between atoms of different types φ_{AB}, then, at relatively high temperatures, the ΔG^m curve can have a W-shape with two minima, as shown in Fig. 5.20. In such case, a tangent to the ΔG^m curve can be drawn at points *1-2*. Therefore, as was shown in Section 5.4, the solid solution in the concentration range determined by segment *1–2* decomposes into two solid solutions, one near component A (point 1) and the other near component B (point 2). Often in the literature, the solutions rich in component A, i.e., the corner A of the state diagram, are called α and, accordingly, the corner B is called β.

Consider the possible behavior of ΔG^m as a function of temperature and composition for a given binary system $A–B$ in which the enthalpy of the mixture ΔH^m is positive. Suppose that at sufficiently high temperatures the absolute value of the entropy term ($-T\Delta S^m$) exceeds ΔH^m. In this case, the curve $\Delta G^m = \Delta G^m (x)$ will have a U-shape similar to that shown in Figs. 5.18 and 5.19. When T diminishes, as a consequence of the decreasing the magnitude $T\Delta S^m$, the curve with the U-shape of the function ΔG^m changes to a W-shape. In the upper part of Fig. 5.21, which shows the function ΔG^m in dependence on composition for five different temperatures, the change in the shape of the ΔG^m curve occurred at temperature T_2. A tangent can be drawn between the minima of the curve ΔG^m for temperature T_2, as is done in Fig. 5.21. The points obtained along tangent *1* and *2* allow us to determine the compositions of the solid solutions in which the initial solid phase will first decompose. As seen in the figure, these points diverge in the

process of temperature decrease due to decreasing $T\Delta S^m$. The positions of these points for different isothermal sections $T_1{>}T_2{>}T_3{>}T_4{>}T_5$ are marked by the numbers 1 and 2 with different numbers of apostrophes. This is how the compositions of the solutions are determined by the limit at which the system decomposes when lowering the temperature. By referring points 1 and 2 to the graph representing the $T–x$ function, the decomposition curve is shown as $a0b$ in the bottom part of Fig. 5.21.

For this reason, at relatively high temperatures, unlimited solubility can exist between elements A and B in the solid phase, which in some cases will be characterized by cigarette shaped diagrams of state. If the U-shaped curve of the function ΔG_m transforms into a W-shaped curve as the temperature decreases, the solid phase decomposition curve appears on the state diagram shown in Fig. 5.21 as line $a0b$.

Suppose that in the analyzed system the temperature in the liquid phase T_1, the composition of which is determined by the position of point 1. In the process of lowering the crystallization temperature, something similar to what we described in section 5.7, will happen to the system. Immediately after crystallization is complete at temperature T_2, the system will consist of single phase, representing the solid phase in fig. 5.22, whose composition x will be the same as the initial composition of the liquid phase (point 1). If the temperature continues to decrease, there will be no change in the state of the system until the figurative point is found on the decomposition curve. Naturally, the figurative point characterizing the state of the system in the temperature interval $T_2–T_3$ slides down the vertical line, since the single-phase system with two components at constant temperature has two degrees of freedom. At temperature T_3, the solid solution of composition x_S (point a_1) must decompose to form a solid solution of composition characterized by point b_1. The appearance of the second phase at temperature $T_3–\beta$ of the solid solution reduces the number of degrees of freedom of the system to 1. In this case, the state of the system during the process of continuous temperature decrease will be characterized by its displacement along the curved lines.

These curved lines correspond to segments a_1a and b_1b of the solid solution decomposition curve. Thus, the decomposition of the solid phases α and β occurs simultaneously when the system is cooled. This process will be characterized by a displacement of point a_1 along the decomposition curve Oa in the direction of point

a, and *b₁* by a displacement along *Ob* in the direction of point *b*. We analyze the decomposition processes in the framework of the regular solution model when the functions ΔH^m and $T\Delta S^m$ are symmetric aound the point *x=0.5*.
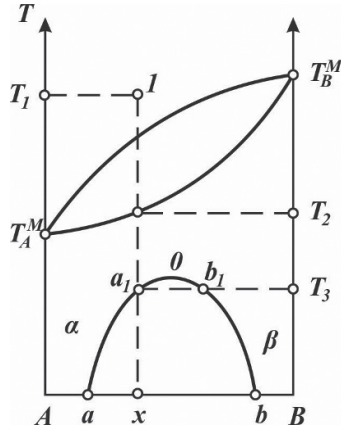

Fig. 5.22. The phase diagram with limited solubility in the solid phases at low temperatures.

Nevertheless, in practice, there are many systems not described by the regular solution model in which functions ΔH^m and $T\Delta S^m$ are not simple functions and are not symmetric with respect to the concentration point *x=0.5*. Although, regardless of the shape of the functions ΔH^m and $T\Delta S^m$, the solid solution decomposition processes should be observed when the shape of the curve of the function $\Delta G^m = \Delta H^m - T\Delta S^m$, which has a concave curvature, transforms into the *W*-shape. In this case, a tangent can always be drawn between the two minima of the *W*-shaped curve from ΔG^m, which will determine the corresponding decomposition process.

5.11 Systems with Limited Solubility in the Solid State

In different systems, the positions of the solidus curve and the decomposition curve of the solid solutions may differ significantly. In some cases, when the interaction energy between atoms of the same type φ_{AA} and φ_{BB} they barely exceed φ_{AB}, the decomposition of the solid solutions will happen at sufficiently high temperatures. As the temperature rises from the onset of decomposition, the decomposition curve will move upward. At some point, this curve can reach and intersect the solidus line, resulting in a state diagram of a specific type: with eutectic and peritectic* equilibrium* (from the Greek periteko=melting).

The subsequent transformation of the state diagram that occurs as the decomposition curve moves upward, as shown in Fig. 5.23. This figure shows how the eutectic and peritectic phase diagrams unfold.

Now in two-component systems with unlimited solubility in the solid state three equilibrium phases can be found: one liquid L and two solid solutions α and β. This statement also follows from the Gibbs rule for phases. In reality, a thermodynamic system cannot have a negative number of degrees of freedom. Therefore, the minimum value of f is zero, which means that in any binary system, the number of phases in equilibrium at constant pressure cannot exceed 3. Therefore, the eutectic and peritectic equilibria take place at constant temperature (Fig. 5.23), and the equilibrium of the liquid phase and solid solutions α and β is represented by a horizontal line, since the binary system is invariant at the equilibrium of all three phases.
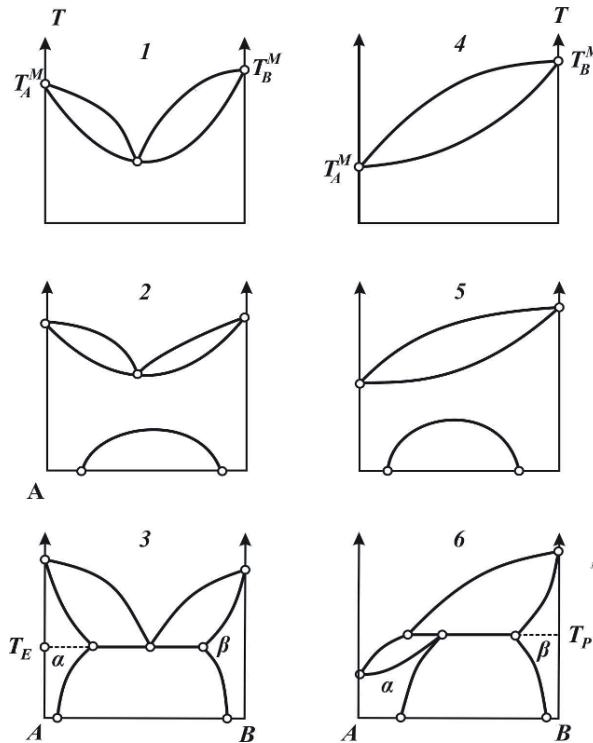
Fig. 5.23. Transformation of a state diagram with limited solubility in the liquid phase into a state diagram with limited solubility in the liquid and solid phases.

It follows that the points of intersection of the segments of the decomposition curve and the corresponding solidus lines with the eutectic or peritectic horizontal line must coincide. Otherwise there would be more than three phases in equilibrium, and therefore such a mutual arrangement of the solidus and liquidus lines of the decomposition and eutectic (or peritectic) curves, as shown in Fig. 5.24, where 5 phases would be in equilibrium, which contradicts the Gibbs rule of phases, is impossible.

ae – eutectic curve
aa' y *ee'* – decomposition curves
bb' y *dd'* – solidus lines
cc' y *cc''* – liquidus lines
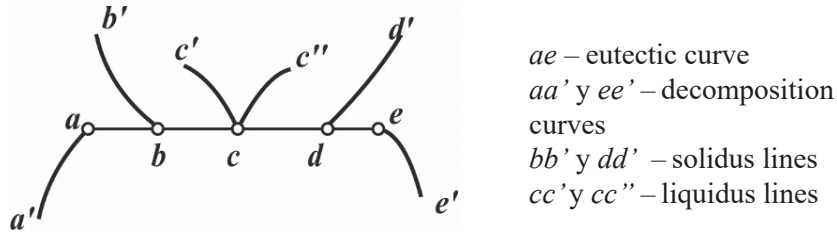
Fig. 5.24. Example of impossible positions of points on the state diagram for the solutions with limited solubility.

In the general case of a very complicated system, when the equilibrium is displaced, transformations from some phases into others occur. Suppose that the total number of phases is φ. Then as a result of the displacements, one phase is transformed into $\varphi - 1$, two phases into $\varphi - 2$, three phases into $\varphi - 3$, etc. The maximum number of transformed phases does not exceed $\varphi - 1$. Thus, the transformation processes can be written in the following form

$$\varphi_1 \to \varphi_2 + \varphi_3 + \varphi_4 + ... + \varphi_\varphi$$
$$\varphi_1 + \varphi_2 \to \varphi_3 + \varphi_4 + ... + \varphi_\varphi$$
$$..$$
$$\varphi_1 + \varphi_2 + \varphi_3 + ... + \varphi_{\varphi-2} \to \varphi_{\varphi-1} + \varphi_\varphi$$
$$\varphi_1 + \varphi_2 + \varphi_3 + ... + \varphi_{\varphi-2} + \varphi_{\varphi-1} \to \varphi_\varphi$$

As a consequence, if three phases exist in the system, one or two can be transformed. This, in turn, means that two types of transformations are possible in systems with limited solubility in the solid state. In the first case, the liquid phase *L* transforms into two solid solutions α and β

$$L \leftrightarrow \alpha + \beta$$
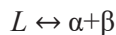
In the second case, the liquid phase and one of the solid phases, for example α, are transformed into another solid phase, that is

$$L + \alpha \leftrightarrow \beta$$
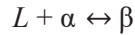
The first type of equilibrium corresponds to the eutectic and the second to the peritectic equilibrium.

When analyzing diagrams of state with one simple eutectic, it is seen that if two solid phases composed of pure components can crystallize, the liquidus curve consists of two branches. Each one of these branches is the geometric location of the crystallization temperatures of the pure solid phases, A or B. Each branch of the liquidus corresponds to one conjugated vertical line from the solidus to it.

If there is a continuous series of solid solutions in the system, the liquidus is a continuous curve, which is the geometric location of the crystallization onset temperatures of one of the solid phases of the solid solution. As a result, the number of branches of the liquidus curve is equal to the number of solid phases crystallizing from the liquid. On the state diagram, each solid phase will correspond to an initial crystallization temperature, which should be on the same line as the solidus. In other words, for each branching of the liquidus curve, there will be a corresponding branching of the solidus curve. For this reason, on the diagram of state with limited solubility in the solid phase it is always possible to distinguish regions of coexisting equilibrium of the liquid phase with solid solutions α or β.

5.12 Eutectic State Diagram of a System with Limited Solubility in the Solid Phase

The eutectic equilibrium of the state diagrams of the systems with limited solubility in the solid phase is denoted as

$$L \rightleftarrows \alpha + \beta \tag{5.39}$$
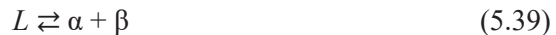
Naturally, the equilibrium described by expression (5.39) can be preceded by two types of transformations: $L \rightleftarrows \alpha$ and $L \rightleftarrows \beta$. To each of these processes on the diagram of state will correspond two curves - liquidus and solidus, characterizing

monovariant equilibrium between liquid and solid solutions. A general view of the state diagram with limited solubility in the solid phase with a eutectic is shown in Fig. 25.a. In this figure, the solidus curves $T^M_B F$ and $T^M_A D$ and the liquidus curves $T^M_A E$ and $T^M_B E$ begin at the fusion points of pure components A and B. The liquidus lines intersect at the eutectic point E. Points D and F on the solidus lines indicate the composition of solid solutions α and β in equilibrium with the liquid solution of eutectic composition.

The state diagram is divided by the decomposition, liquidus, and solidus curves as well as the eutectic horizon into six different regions. The regions I, II, and III corresponds to single phase solutions. Region I contains the liquid phase, region II contains the α solid solution, and region III contains the β solid solution. Regions IV, V, and VI are two-phase regions. Region IV corresponds to the equilibrium between the liquid phase and the $L \rightleftarrows \alpha$ solid solution, region V to the $L \rightleftarrows \beta$ equilibrium, and region VI to the equilibrium of the two $\alpha \rightleftarrows \beta$ solid solutions. In the single-phase regions the system is coinvariant and in the two phase regions it is monovariant. At the eutectic point, the three phases $L \rightleftarrows \alpha + \beta$ are in invariant equilibrium.
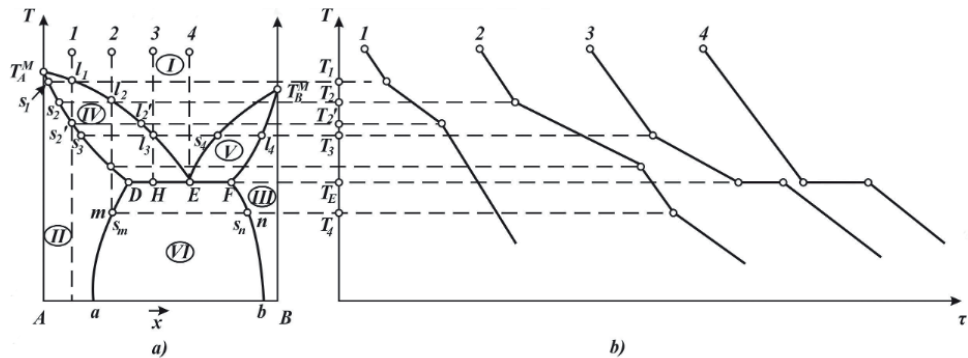
Fig. 5.25. State diagram and cooling curves for a system with limited solubility in the solid phase.

Consider the crystallization processes in a system with eutectic for solutions of different composition. Suppose the composition of the initial liquid phase is determined by point 1 (Fig. 5.25.a). If the temperature of the system is reduced, this point will move along the vertical line, since there are two degrees of freedom in the system. When the figurative point appears on the liquidus line l_1, a solid solution starts to emerge from the liquid, whose composition can be found

by means of a conode beginning at the point l_1 and extending to the point of its intersection s_1 with the solidus line. Naturally, when a new phase appears, the system loses one degree of freedom. During the subsequent cooling process, the right end of the conode will move along the liquidus segment $l_1 l_2$, and the left end will move along the solidus segment $s_1 s_2$. As the system cools down, the α crystals move out of the liquid, and the liquid is enriched component B, which is characterized by the displacement of point l_1 along the liquidus in the direction of point E. In accordance with the lever rule, the entire liquid phase crystallizes at the moment of reaching the temperature T'_2, the composition of the formed solid phase is determined by point s'_2 and corresponds to the initial composition of the liquid phase. After that, the system becomes covariant, i.e., acquires an additional degree of freedom, and in the process of temperature decrease, the figurative point slides down the vertical line. Three segments will be observed on the cooling line (Fig. 5.25b): the first one corresponds to the process of liquid cooling, the second one is determined by the process of solid solution α crystallization, and the third one is the cooling of the solid phase. The moderate slope of the second segment in comparison to the first one is related to the transformation process $L \leftrightarrow \alpha$, where the heat is released by the crystallization phase intrinsic to the transition stage, that slows down the cooling rate of the system naturally. Thus, if the figurative point characterizing the initial composition of the liquid is located between points A and a on the horizontal line of compositions, the crystallization process is completely analogous to the case we previously considered for the systems with unlimited solubility in the solid phase. If the figurative point is farther to the right of point a, then certain particularities appear in the cooling process. Let us analyze the crystallization of the liquid phase, its composition and the temperature that is characterized by point 2.in this case, without waiting for the temperature to decrease to the value of T_4, all the transfoematios in the system occur according to the previous case for point 1. Nevertheless, at temperature T_4, when the figurative point moves vertically during cooling, it arrives the segment of the decomposition curve aD, and the solid solutions α of composition s_m must be in equilibrium with the solid solution β of composition s_n. Therefore, at temperature T_4, the decomposition of the solid solution α results in the appearence of a second phase in the system and, thus a certain degree of freedom is lost. If the temperature continues to decrease, then the ends of the isothermal segment of the m_n or conode line will slide along the curves aD and bF that characterize the decomposition of the α and β solid solutions, respectively. In principle, when this happens in the cooling curve, there should be a discontinuity due to the transition from the

phase $\alpha \rightleftarrows \beta$. Nevertheless, in practice, this discontinuity is often not observed due to the negligible heat effect of the decomposition and the long duration of the process.

At point 3, when the eutectic temperature is reached, the liquid phase of the composition determined by point E will exist in equilibrium with the solid solution α of the composition determined by point D. According to the lever rule, the relationship between the volumes of the liquid and solid phases will be determined by the relationship between the DH and HE segments. In accordance with the diagram of state, point E belongs simultaneously to the liquidus lines T_AE and T_BE. That is why the liquid phase of the eutectic composition at temperature T_E is in equilibrium simultaneously with both solid solutions α and β, and their compositions are determined by the position of points D and F. When the remaining liquid reaches the eutectic temperature, two more solid solutions crystallize. This process occurs at constant temperature, since with the emergence of a new phase the system under consideration becomes invariant. Therefore, on the cooling line after the breaking caused by the formation of solid α phases, there appears a horizontal segment corresponding to the crystallization of the eutectic. The dimension of this segment will depend on the volume of eutectic liquid remaining in the system after the crystallization process of the solid solution α. In other words, the time required for the complete decomposition of the liquid eutectic phase into solid solutions α and β is determined by the initial position of the figurative point. For example, if the initial composition of the liquid corresponds to point D, at the moment the system reaches the eutectic temperature, the entire liquid will crystallize. Therefore, the subsequent process will be determined only by the decomposition and there will be no horizontal segment on the cooling curve. If the eutectic liquid undergoes cooling, the dimension of the horizontal segment corresponding to the transformation, $L \rightleftarrows \alpha + \beta$, will not be long. The previous reasoning is fully justified for the right part of the state diagram.

In principle, the phase equilibrium diagram for an eutectic system with limited solubility in the solid phase can be obtained, like any other phase diagram, by graphing isothermal sections for the functions $G^L=G(T,x)$ and $G^S=G(T,x)$. By drawing common tangents to the functions and, at each isothermal section, the composition of the phases in equilibrium can be determined. This diagram of the principle of state construction is illustrated in Fig. 5.26.
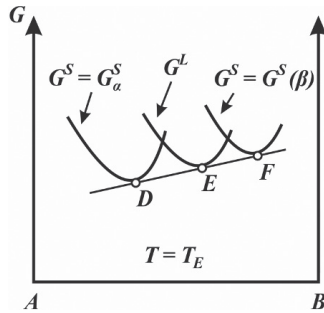
Fig. 5.26. Determination of compositions of phases in equilibrium using a common tangent drawn to their Gibbs energies.

For instance, it can be seen that at the temperature $T = T_E$, a common tangent can be drawn for the G^L, G^S_α and G^S_β curves.

This corresponds to the equivalence of the chemical potentials of the liquid phase of eutectic composition, determined by point E, and the two solid solutions α and β, whose compositions corresponding to points D and F. Whereas in the graphs of the Gibbs energy functions as dependence on composition the equilibrium conditions are determined using a common tangent to the curves of the liquid and solid phases, in the state diagram the equilibrium points can be found by means of a conode. For example, in Fig. 5.25.a at temperature T_2, the conode is the horizontal segment s_2–l_2.

The state diagrams of the type discussed previously are characteristic of the systems $Cr - Ni$, $Al - Si$, $Pb - Sb$, $NaNO_3 - KNO_3$, $CdCl_2 - CdJ_2$, etc. In general, it should to be emphasized that the state diagrams of simple eutectics presented in section 5.6 are, to some extent, idealizations. The reality is that, in nature, there is always a small solubility between components A and B in the solid phase. For that reason, if a system is described by a simple eutectic diagram, as in Section 5.6, it is most probably due to inaccuracy of the experimental determination of the solid phase compositions, which do not allow to identify the regions of mutual solubility of the components. Likewise, in a number of important practical cases, the existence of mutual solubility of the components in the solid phase may simply be underestimated.

5.13 Peritectic Type Systems

As shown in Section 5.11, in addition to the eutectic equilibrium discussed earlier, the equilibrium $L+\alpha \rightleftarrows \beta$, called peritectic equilibrium, is also possible. In this case, the transforming phases are the liquid and one of the solid solutions, and, as a result of this transformation crystals appear from another solid solution. Naturally, the peritectic transformation occurs at constant temperature T_P, since the two-component system containing three phases has no degrees of freedom. Remember that peritectic transformation requires the existence of at least two phases: the liquid phase and one solid solution α. In other words, the peritectic transformation must be preceded by the two-phase process $L \leftrightarrow \alpha$. Depending on the quantitative ratio between the liquid phase and the solid solution α, the peritectic transformation process $L+\alpha \rightleftarrows \beta$ can end in three ways.

1. First, the process may exhaust all α crystals. As a consequence, a two-phase process $L \rightleftarrows \beta$ ensues after the peritectic process.

2. Second, all the liquid may be consumed after the peritectic transformation. In this case, the solid phase decomposition occurs according to the $\alpha \rightleftarrows \beta$ reaction.

3. Last, a third variant of the unique compositions of the liquid L and the solid phase α is also possible, when both phases are completely consumed at the end of the transformation. In other words, in this case the liquid and the solid phase α are in such a proportion that neither L nor α remains after the formation of the solid solution β.

It is clear that as the temperature of the system that forms the solid solution β decreases, it will disintegrate in accordance with the next $\alpha \rightleftarrows \beta$. reaction. In this way, based on the previous discussion, a conclusion can be reached, that the process $L \rightleftarrows \alpha$ must occur at higher temperatures than the peritectic, and the processes $L \rightleftarrows \beta$ and $\alpha \rightleftarrows \beta$ at a lower temperature. These conditions are met in the state diagram represented in Fig. 5.27. The diagram of state of this type, as a rule, is formed between components A and B with very different fusion temperatures. In this diagram the liquidus curves T^M_A and T^M_B cross at the peritectic point P, between the fusion temperatures of the components.
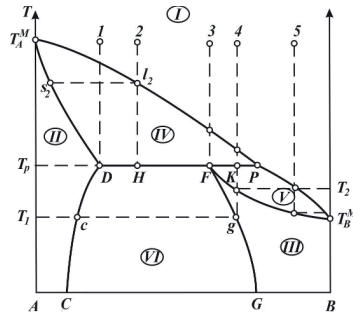
Fig. 5.27. Peritectic diagram of state.

Since increasing the component *A* in *B* raises the liquidus and solidus temperatures, the corresponding T^M_BP and T^M_BF curves run above the fusion point of component *B*. Correspondingly, the liquidus T^M_AP and of the solidus T^M_AD curves are directed downward, below the fusion point of *A*. The decomposition curves of the solid solutions *α* and *β* are *CD* and *GF*. The intersection points *D* and *F* of these curves with the corresponding solidus curves lie on the same horizontal line at point *P*, that corresponds to the peritectic composition of the liquid. This horizontal, located at the peritectic temperature T_P, characterizes the invariant equilibrium between the liquid (whose composition is determined by point *P*) and its corresponding solid solutions *α* (the composition of point *D*) and *β* (the composition of point *F*). As in the eutectic case, the liquidus lines, solidus lines, *DFP* isothermal straight lines, and the curves of the solid solutions divide the state diagram into 6 regions. Three of these regions are homogeneous or consist of only one phase: Region *I* corresponds to the liquid, region *II* to the solid solution *α*, and *III* to the solid solution *β*. Regions *IV, V*, and *VI* respectively characterize the equilibrium of two phases *L⇄α*, *L⇄β* and *α⇄β*. Let us analyze the crystallization processes in the peritectic type state diagram system. If the figurative point characterizing the initial composition and temperature of the system is located to the left of point *1*, the crystallization processes do not differ from the previously analyzed diagrams of the eutectic type. As the liquid with the composition at point *1* cools down, in accordance with the lever rule, the whole liquid phase will crystallize as a solid solution *α* at the moment the peritectic temperature is reached.

Now consider the crystallization of the liquid of an initial composition, which is determined by point *2*. As the temperature decreases, point *2* moves

along the liquidus curve and a solid phase α is formed from the liquid phase, the composition of which can again be found with the help of conode l_2s_2. During the process of temperature decrease, the composition of the liquid phase will change along the liquidus curve l_2P, and equilibrium with a point horizontally connected to the conodes at one point of the solidus curve s_2D. At the peritectic temperature T_P, the liquid phase will have the composition of point P and the solid phase α of point D. Since at temperature T_P the peritectic solid solutions α_D and β_F are in equilibrium with the liquid, the interaction in the system should proceed as follows: $L + \alpha \rightleftarrows \beta$.

In this manner, a third phase appears in the system - the solid solution β with a composition at point F. Since the equilibrium is invariant, the cooling curve at temperature T_P should show a horizontal segment corresponding to the equilibrium between the *3* phases.

The only composition at which the solid solution α_D and the liquid solution L_P are completely consumed in the process of peritectic transformation is determined by point F or otherwise by point *3*. At this point the ratio between the amounts of the liquid and solid phases will be proportional to the ratio of the segments DF and FP. Since point *2* is located to the left of point *3*, at the moment when the system reaches the peritectic temperature, in accordance with the lever rule, the amount of liquid will be proportional to the segment DH, and the amount of solid phase to segment HP.

Let us indicate for the point H the mass of the liquid as $m_L{}^H$ and the mass of the solid solution α as $m_\alpha{}^H$. If for point F we have respectively $m_L{}^F$ and $m_\alpha{}^F$, then, based on the lever rule

$$\frac{m_L^H}{m_\alpha^H} = \frac{DH}{HP} < \frac{DF}{FP} = \frac{m_L^F}{m_\alpha^F}$$

This way, for the initial liquid phase with a composition determined by point 2, at the moment the peritectic transformation concludes, all of the liquid will have been consumed, since it had a lower mass than $m_L{}^F$. In the system, two phases will remain: the solid solutions α and β with their respective compositions determined by points D and F. With the subsequent cooling of the system, the solid solutions will disintegrate and, for example, at temperature T_1 their compositions may be found with the help of the conode cg.

As already noted, upon cooling of the liquid phase with the composition determined at point *3*, solutions α and *L* are completely consumed as a result of the peritectic transformation. Therefore, during cooling, the solid solution β_F decomposes according to the scheme $\alpha \rightleftarrows \beta$. If the figurative point is located to the right of point *3* (point *4*, for instance), when the temperature reaches the point T_P, the mass of the liquid is proportional to the length of segment *DK*, and the mass of the solid phase is proportional to the length of segment *KP*. Since in this case

$$\frac{m_L^K}{m_\alpha^K} = \frac{DK}{KP} > \frac{DF}{FP} = \frac{m_L^F}{m_\alpha^F},$$

then after the peritectic transformation in the system there remains a residue of the liquid and the solid solution β. At further temperature decrease, the composition of the liquid phase will change along the curve $PT^M{}_B$, and β will change along the curve $FT^M{}_B$. In other words, the crystallization process of the solid solution β will begin in the system and will end at temperature T_2. At this moment, the system turns into a single-phase β-system, and as the temperature diminishes, the figurative point moves along the vertical line. When this line is intersected with the decomposition curve (point *g*) of the solid solution, the second phase appears (point *c* of the solid solution), and changes in the system will be determined by the decomposition processes.

The crystallization processes of the liquid phases with the compositions determined by points located to the right of point *P* (point *5*, for instance) do not differ at all from those earlier analyzed in the systems with unlimited solubility in the solid phase.

From the previous analysis we conclude that the duration of the peritectic point should be the longest, its composition is determined by point *F*, and the number of degrees of freedom is zero when considering the compositions characterized by points *D* and *P*. It should be noted that the real crystallization processes often do not correspond described ones, which are possible only at very low cooling rates and sufficiently high diffusion rates.

The analyzed phase system can be obtained by constructing isothermal cross sections for the functions $G^L = G(T,x)$ and $G^S = G(T,x)$, drawing common tangents to the functions G^L and G^S in each of these sections.

5.14 Diagrams of State of Systems with Chemical Compounds

Systems with chemical compounds, depending on the particularities of the fusion processes of the same alloy, can be divided into two different types. The first type includes those that coexist in equilibrium at the fusion temperature of the compound, and whose liquid and solid phases have the same composition.

$$S \rightleftarrows L$$

Let us first analyze the simplest case: when components A and B form a chemical alloy A_mB_n, that fuses congruently, and there are no solid solutions. In the absence of solubility in the solid phase, as in the previous case with simple eutectic, the solidus of components A and B and of the alloy A_mB_n will be represented as vertical lines that end at the fusion temperatures T^M_A, T^M_B and T^M_{AB}, respectively. Similar to the simple eutectic systems, the crystallization temperature of the pure components A or B should decrease when components A or B are added to the liquid A_mB_n. As a consequence, the liquidus curve of the system under consideration should exhibit three maxima located on the fusion points of A, B and A_mB_n, respectively, as shown in Fig. 45. Such a system can be represented as a set of two diagrams of state of two components with simple eutectics

$$A + A_mB_n \text{ and } A_mB_n + B.$$

These diagrams of two components have a common ordinate in which the chemical compound is located, and the right and left parts of the composition diagram can be analyzed independently of each other. It is obvious that the crystallization processes occur in the same way as in simple eutectic systems, with the only difference that in the left part of the diagram there are the solid phases of the pure component A and of the pure compound A_mB_n, and in the right part of the diagram are solid phases of the pure compound A_mB_n and pure component B.

Before proceeding to the study of other, more complicated types of diagrams, it is necessary to clearly formulate the concept of stoichiometry. This term comes from two greek words: "stoicheion" meaning basis, and "metred" meaning measurement. Stoichiometric relations are understood as relations between atoms that correspond to the chemical formula of a certain alloy formed by these atoms. So, for example, if an alloy has the formula A_mB_n and the concentration A is determined by the number m, and that of β by the number n, then such alloy is called stoichiometric.

In the stoichiometric compound A_mB_n, the elements A and B are insoluble, i.e. there are no solid solutions between A and A_mB_n and between B and A_mB_n. For this reason, the solidus of a stoichiometric compound is a vertical line. It should then be clear that the compound in Fig. 5.28 is stoichiometric. Likewise, the real composition of the compound may differ noticeably from its chemical formula, or, in other words, it is possible for solid solutions to form between the compound and its components.
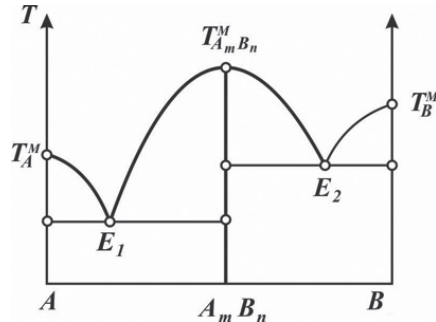
Fig. 5.28. State diagram of a system with the formation of a chemical compound between its components.

The solidus of a compound that is not stoichiometric is represented not by a single line, but by a region, the size of which may be determined by the solubility of the components in the compound. Often such a region is called the region of homogeneity. In general, in all chemical compounds there are always deviations from the stoichiometric composition. Nevertheless, in a set of systems such deviations are insignificant.

Some possible state diagrams for the systems of components that melt congruently and form solid solutions with their components A and B are shown in Fig. 5.29.

Let us now focus on a typical state diagram of a compound that melts incongruently. Suppose for simplicity that the solid solutions, based on their components and compounds, can be separated. Furthermore, suppose that the compound A_mB_n at the fusion point decomposes into a liquid of composition L_P and a solid phase S_B.

$$A_m B_n \rightleftarrows L_P + S_B$$
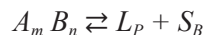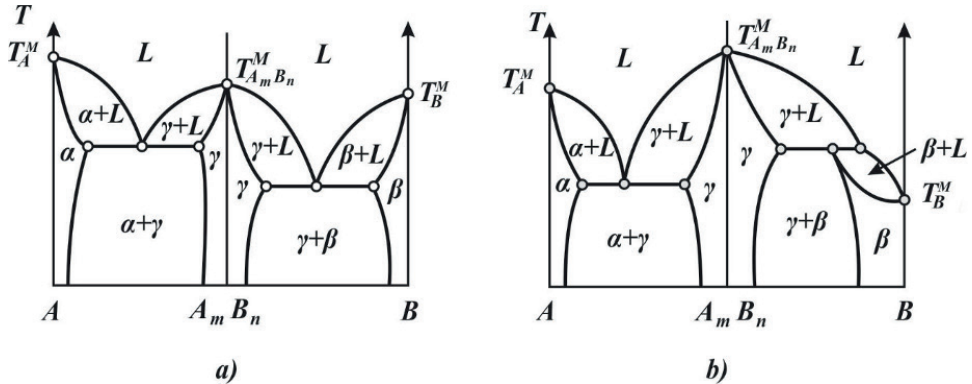
Fig. 5.29. State diagrams of different types containing chemical compounds.

The general view of this state diagram is shown in Fig. 5.30. Consider the crystallization processes occuring in this system of liquid phases of different compositions. If the composition of the liquid phase is between points T_A and E, then at the beginning of the liquid cooling process, crystals will emerge from component A. As the crystallization proceeds, the figurative point characterizing the state of the system will move along the liquidus curve $T_A E$. At the eutectic point E, another phase appears of the composition $A_m B_n$, and the system becomes invariant. At this point at temperature T_E the crystallization ends with the formation of the eutectic having the composition $A + A_m B_n$.
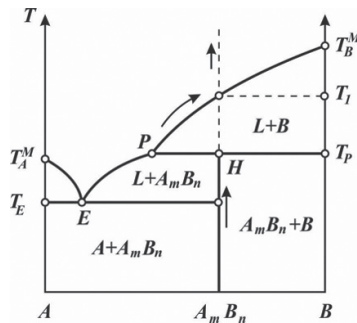
Fig. 5.30. State diagram with chemical compounds that fuse incongruently.

From the liquid phases with compositions between points E and P, the crystallization commences with the formation of the compound $A_m B_n$ and ends at the eutectic point. The crystallization of the liquid phases with composition between points P and T_B has certain particularities. In order to clarify these particularities, let us

— 147 —

first imagine that the pure compound A_mB_n is heated. If during the heating process the peritectic temperature T_P, is reached, then at this temperature the compound decomposes in the liquid phase with composition at point P and the solid phase S_B with composition equal to that of the pure component B. The decomposition process is an invariant process (with one degree of freedom). At the moment the decomposition of the compound is completed, the number of phases is reduced to two (liquid L_P and solid component B), and this system acquires one degree of freedom. With further heating, the liquid is enriched with component B due to the dissolution of small crystals of component B, which is caused by the increase in solubility with rising temperature. At this moment, the figurative point moves along the liquidus curve PT_B and when the temperature T_1 is reached, the last crystal disappears. After that, the covariance of the system is exactly the same as the composition of the compound. Terefore, during the heating process, the figurative point will move up the vertical line as shown in Fig. 5.30.

If now the liquid of A_mB_n composition, which is at temperature $T > T_1$, will be cooled down, crystals of pure component B will appear when it first reaches the temperature T_1. As the crystallization process of the pure component B develops, the composition of the liquid phase will change along the liquidus line T_B, and when the point P is reached, the crystallization of the compound A_mB_n will commence. The alloy is formed at temperature T_P from the liquid phase of composition L_P and the crystals of component B

$$L_P + S_B \rightleftarrows A_m B_n \qquad\qquad (5.40)$$

At the moment of the end of this transformation all the liquid L_P and all the crystals B are consumed, and one phase remains in the system - the crystals of the compound A_mB_n.

If now the composition is determind between points A_mB_n and P, crystallization begins with the separation of B. At temperature T_P, the volume of the separated crystals will be consumed to form the compound A_mB_n, since in this case the liquid in the process of diffusion of the component B starts with a negligible amount, compared to the amount of liquid at point H. In this case, there remains a liquid residue with a composition corresponding to point P, and the system becomes invariant. In the process of the temperature decrease of this liquid, the crystals of A_mB_n will separate and the figurative point will move along the segment PE of the liquidus curve. When point E is reached, an eutectic crystallization will occur with the formation of crystals A and A_mB_n.

If the composition of the liquid phase is between points B and A_mB_n, then by the time the transformation by reaction (5.40) is completed, all the liquid L_P will have been consumed and the system will be a mechanical mixture of B and A_mB_n crystals.

In many component systems, some intermediate phases may exist between the initial substances A and B, such as compounds or solid solutions based on them. For the analysis of more complicated state diagrams, it is convenient to divide them into elementary diagrams, limited, for example, by two compounds or one compound and one component, and further analyze the crystallization processes of each of them separately.

5.15 Diagrams of State of the Binary Systems A^3-B^5

Today, binary compounds of elements of groups *3* and *5* of the periodic table and solid solutions based on them occupy a very important place among various semiconductor materials. The most of modern devices used in optoelectronics, such as laser and light diodes operating in spectral regions from infrared to ultraviolet range, nowadays are fabricated on the basis of A^3B^5 solid solutions. Indeed, to grow bulk crystals as well as various device structures based on these materials, it is necessary to know their corresponding state digrams.

In this paragraph we focus on the A^3–B^5 state diagrams a of binary systems such as *Ga–P, Ga–As, Ga–Sb, In–P, In–As, In–Sb* (the systems containing N and B are not considered). Each of these systems contains a compound that melts congruently, and their state diagrams have a similar form, differing only in the fusion temperatures corresponding to the elements and compounds. The elements of group *3* are often reffered to as metals and those of group *5* as nonmetals. Each of these two types of elements must occupy a certain place in the crystal lattice of the compound, so two sublatticess can be distinguished in the lattice: metallic and non-metallic. A common particularity of the state diagrams of A^3–B^5 systems is that they have a very limited region of homogeneity of compounds and a significant vapor pressure of the nonmetals.

In the sequence of the fifth group elements *Sb–As–P*, the vapor pressure increases rapidly for the lighter components from left to right. For example, the vapor

pressure of *Sb* is about *10⁻⁶* bar at the fusion temperature of *GaSb* at *712°C*, the vapor pressure of *As* is *0.976* bar for *GaAs* fused at *1240°C*, and the vapor pressure of *P* reaches 32 bar at the fusion point of *GaP* at *1465°C*.

We shall analyze the solubility of the elements of groups *3* and *5* in A^3B^5 compounds, which, as already mentioned, have a very limited area of homogeneity. Note that the experimental study of homogeneity is very complicated due to the limited sensibility of existing methods of composition measuring. Various theoretical estimations show that the average size of homogeneity areas of A^3B^5 compounds is of the order of $10^{18} - 10^{19}$ cm⁻³. Because of this, in diagrams of ordinary binary systems, in which the horizontal axis corresponds to the interval from $0 \leq x \leq 1$ (from de *0* to *100* %), the areas of homogeneity simply cannot be shown on an adequate scale. It follows that in the state diagrams between *0* to *1*, the solidus of the various A^3–B^5 systems will be represented as a vertical line starting at *0.5* from the horizontal axes. Since solubility in the solid phase de facto also does not exist between pure elements A^3 and B^5 and their corresponding compounds A^3B^5, the general phase diagrams have the form of diagrams with simple eutectic. In the A^3–A^3B^5 systems presented in the left part of the diagrams, the eutectic points are located in the vicinity of the vertical axis corresponding to a pure element of group *3* (e.g., *Ga*, *In*), i.e., the eutectic degenerates next to the metals. In real crystal growth processes, the areas of phase diagrams in the vicinity of the element of group *3* are not used, and therefore the shape or character of these areas are of no practical meaning. In connection to this, in the majority of cases analyzed, diagrams are represented without eutectic points in the vicinity of the metallic area, as shown in Fig. 5.31. The location of the eutectic point in the vicinity of element A^3 is schematically presented in a separate frame of Fig. 5.31.
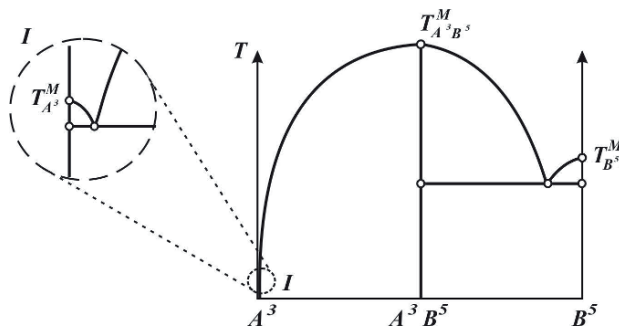

Fig. 5.31. State diagram III-V.

In A^3B^5 compounds, the presence of homogeneous areas is often emphasized because to their small size (up to the minute scale of their average length in the diagrams where they appear). Nevertheless, in a number of cases it is necessary to consider the deviation of the stoichiometric ratio in the concentrations in which the elements of A^3B^5 alloys are found. As an example is the well-known case of Gallium Antimonide (*GaSb*), that without intentionally introducing impurities during crystallization (this happens due to liquid epitaxis) has a *p*-type conductivity with a gap concentration of about 10^{17} cm^{-3}. In contrast, all other A^3B^5 alloys (ignoring nitrides and borides as originally conditioned) always grow with *n*-type conductivity due to uncontrolled introduction of donors. The previously mentioned particularity of *GaSb* is related to the stoichiometric deviation of the components or to the emergence of stoichiometric defects, which in this alloy are electrically active, i.e., form electrical inductions from acceptors in the bandgap.

One of the important technological characteristics of A^3B^5 systems is the vapor pressure function in dependence on temperature for all possible components of the gaseous phase formed above the solutions corresponding to the liquidus curve. Such a function for the *Ga–As* system is presented in Fig. 5.32 as one of the most studied and important from the practical point of view.

Arsenic is present in the gaseous phase in equilibrium with the *GaAs* solid phase, forming As_2 and As_4 molecules. At low temperatures, the vapor pressure of the two-atom molecules exceeds that of As_4. It is known experimentally that at temperatures around *660*°C (*1/T = 1.145x10³ K⁻¹*), the vapor pressure of Arsenic is determined mainly by As_2, which is comparable in value to the vapor pressure of Gallium. At this temperature, *GaAs* evaporates congruently. It should be noted that the precision of determination of the position of the point of congruent evaporation is small. This is primarily due to the difficulties that arise in the measurement of small changes in pressure, which can be as low as 10^{10} atmospheres. If *GaAs* is heated above the temperature of its congruent evaporation, drops of liquid Gallium saturated with Arsenic will form on the crystal surface, and the gaseous phase will be mainly composed of As_2 and As_4 molecules, whose fraction will be determined by temperature, as shown in Fig. 5.32.

While the total Arsenic vapor pressure at the fusion point of Gallium Arsenide is about *1* atmosphere (Fig. 5.32), for the binary phosphide systems such

as *Ga–P* and *In–P*, the Phosphorus vapor pressure at the corresponding fusion temperatures reaches several tens of atmospheres. Hence, the crystallization processes in Phosphide and Arsenide systems in a number of cases (in particular when there is no need for a large crystalline volume) are viable in the metallic corners of state diagrams, i.e., on the basis of liquid solutions rich in Gallium and Indium. Under these conditions, the vapor pressure of elements of group *5* of the periodic table can be significantly reduced. On the contrary, the vapor pressure of Antimonium at the corresponding fusion temperatures of its binary alloys is considerably low. Therefore, antimonides of various metals from group *3* of the periodic table can be grown from both metallic solvents and Antimonium-rich solvents. In other words, in *Sb* systems, the crystallization processes can be carried out both in the metallic corner of the state diagram and in the non-metallic one. In the latter case, the replacement of metallic solvents by *Sb* may show advantages that will simplify a number technical problems in the crystallization process, as well as to improve the quality of the grown material.
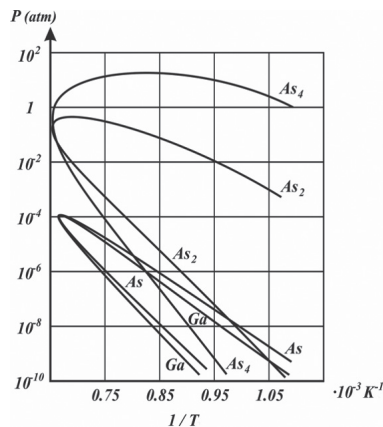
Fig. 5.32. Dependence of As vapor pressure on temperature.

Note that the sections of the state diagram describing the behavior of the system in the coordinates pressure *(P)* – temperature *(T),* similar to those shown in Fig. 5.32, turn out to be very important for the molecular-beam and gas epitaxy technologies. In the liquid phase epitaxy, as a rule, relatively low crystallization temperatures are used at which the vapors pressure of volatile elements is negligible, so the function of *P*–pressure with respect to *T*–temperature can be neglected.

When analyzing the state diagrams of the systems with simple eutectics (Section 5.6), the Gibbs energy G^S for the pure solid phases was represented by a single point on the corresponding axis, as can be seen in Figs. 5.5 and 5.6. Likewise, areas of homogeneity exist in all semiconductor alloys. In other words, there are deviations of stoichiometric composition in alloys, conditioned by the formation of solid solutions between its compounds and its components. In the presence of solid phase solubility, the dependence of the Gibbs energy on the composition $G^S=G^S(x)$, as demonstrated in Section 5.4, should be represented as a curve whose convexity is directed downward. If the homogeneity area of the compound is sufficiently narrow, the Gibbs energy increases rapidly with deviation from the stoichiometric relationship, or, in other words, is a curve with a narrow minimum, as seen in Fig. 5.33.
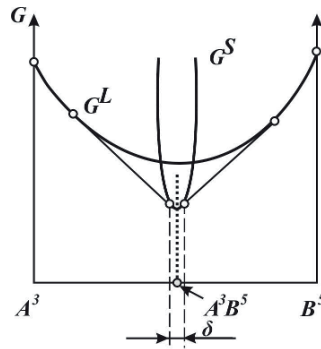
Fig. 5.33. A region of homogeneity of solid solutions based on the binary
A^3B^5 system and its components.

This figure shows the dependence of Gibbs energy on composition $G^L=G^L(x)$ for the liquid phase. This function has a much smaller curvature than $G^S=G^S(x)$ since, in accordance with the assumption made earlier (Section 5.5), components A and B form liquid solutions at any concentration, i.e., they are mutually soluble over the whole range of composition. If we again draw tangents to the curves $G^S(x)$ and $G^L(x)$, we will find the compositions that are in equilibrium in the liquid and solid phases, i.e., we build the region of homogeneity, or the region of existence of solid solutions based on the binary compounds A^3B^5 and their components A^3 and B^5. This region in Fig. 5.33 is labeled by letter δ. For clarity, Fig. 5.33 is not scale. It is only a schematic illustration. As stated before, the length of the homogeneous region is too small to be seen in detail on a horizontal scale of concentrations in the interval from 0 to 1.

In the general case, the formation of the region δ can be due not only to the dissolution in the alloy of any of its components, but also to the formation of vacancies. The energy of vacancy formation at the sites of A^3B^5 elements is always differentiated according to which site of the considered A^3 or B^5 elements is vacant, and hence these vacancies in the metallic and nonmetallic sublattices are also different. Therefore, the homogeneity region of the alloy is not symmetric respect to the stoichiometrical composition, as illustrated by Fig. 5.34 (Morozov A.N., Bublik B.T. *Journal of Crystall Growth 1986*, v. 75, #3, p. 497-503) where calculated solidus curves for some A^3B^5 compounds are shown.

If we ignore the existence of the homogeneity region due to its short extension, the solidus in any A^3-B^5 system is a vertical line, and the solid phase composition corresponds to *0.5*. Therefore, both experimental and theoretical studies of state diagrams in A^3-B^5 systems are reduced only to the construction of the liquidus line. Only the section of the line located near the group *3* element (in the metallic corner) is of practical interest. In this corner, the pure A^3B^5 solid compound is in equilibrium with liquid phase, which at relatively low temperatures is a solution with the group *5* element strongly dissolved in the metal (Fig. 5.31). It is this region of the state diagram that is typically used in the liquid phase epitaxy and widely applied to grow the most important semiconductor crystals, including A^3B^5 compounds. The use of lower crystallization temperatures in comparison to the fusion temperatures of the corresponding alloys or the transition of stoichiometrically alloyed materials into solutions, as can be seen from the state diagram in Fig. 5.32, makes it possible to significantly reduce the vapor pressure of the group *5* element.
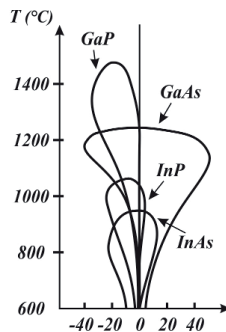

**Fig. 5.34. Horizontal axis: excess of atoms by 10^{18} cm^{-3}.
Left: atoms of group III; right: atoms of group V.**

The attempt to carry on the growth processes of the binary alloys A^3B^5 from the liquid phases located in the corner B^5 in the corresponding state diagrams, is inappropriate, and in many cases technically impossible. The exception, as already noted, are Sb-based systems in which the pressure of Antimony vapor on the liquid phases in the nonmetallic corner is insignificant.

A number of scientific articles have been published on the processes of crystallization of alloys and solid solutions based on antimonides from the liquid phases enriched with Sb, i.e., the processes carried out in the nonmetal corner of the state diagrams.

Let us pay attention to calculations of the phase equilibria in the binary systems A^3–B^5. In general, the equilibrium between the liquid phase that is a non-metal solution B^L in the melting of metal A^L, and the solid phase AB^S is written in the form of a simple chemical reaction
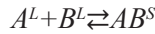
$$A^L + B^L \rightleftarrows AB^S$$

At equilibrium, the chemical potentials of the solid and liquid phases should be equal

$$\mu^L_A + \mu^L_B = \mu^S_{AB} \tag{5.41}$$

As seen above, the chemical potentials of components A and B in the liquid phase are of the form:

$$\mu^L_A = \mu^0_A + RT\ln\gamma^L_A + RT\ln x^L_A$$
$$\mu^L_B = \mu^0_B + RT\ln\gamma^L_B + RT\ln x^L_B \tag{5.42}$$

Where $\mu^0_{A,B}$, $\gamma^L_{A,B}$ and $x^L_{A,B}$ are, respectively, the chemical potentials of the pure components A and B, their activity coefficients and concentration in the liquid phase. In the model of quasiregular solution, successfully used to calculate the equilibrium of the phases in various A^3–B^5 systems, as shown in paragraph 5.9, the activity coefficients are described by the expressions

$$RT\ln\gamma_A = \alpha_{AB}x^2_B = \alpha_{AB}(1-X_A)^2$$
$$RT\ln\gamma_B = \alpha_{AB}x^2_A = \alpha_{AB}(1-X_B)^2 \tag{5.43}$$

Where $\alpha^L_{AB} = a+bT$ is the interaction parameter between the components in the liquid phase, in which a and b are constant and T is the temperature.

In expression (5.41) the chemical potential for the pure solid phase can be annotated as follows

$$\mu^S_{III\text{-}V} = \mu^0_{III\text{-}V} \tag{5.44}$$

Since x^S_{AB}, and the solid phase AB^S is assumed to be ideal, the activity for it is also equivalent to unity. Substituting (5.42) and (5.44) into (5.41) we obtain

$$\mu^0_A + RT\ln(\gamma^L_A x^L_A) + \mu^0_B + RT\ln(\gamma^L_B x^L_B) - \mu^0_{AB} = 0 \tag{5.45}$$

If we write the equation (5.45) for different temperatures T_2 and T_1 $(T_2 > T_1)$, and then perform the subtraction of these two equations, we obtain the following result

$$\mu^0_A(T_2) - \mu^0_A(T_1) + \mu^0_B(T_2) - \mu^0_B(T_1) - \mu^0_{AB}(T_2) + \mu^0_{AB}(T_1) =$$
$$= -RT_2\ln [\ \gamma^L_A(T_2)\ \gamma^L_B(T_2)\ x^L_A(T_2)\ x^L_B(T_2)\ ]+$$
$$+ RT_1\ln [\ \gamma^L_A(T_1)\ \gamma^L_B(T_1)\ x^L_A(T_1)\ x^L_B(T_1)\ ]$$

Since the left part of this expression refers only to the pure components A, B, and AB, we shall label it as $\Delta\mu^0$

$$\mu^0_A(T_2) - \mu^0_A(T_1) + \mu^0_B(T_2) - \mu^0_B(T_1) - \mu^0_{AB}(T_2) + \mu^0_{AB}(T_1) = \Delta\mu^0 \tag{5.46}$$

Starting with the already known relationship

$$\frac{\partial\bar{G}}{\partial T} = \frac{\partial\mu}{\partial T} = -S,$$

the difference can be calculated $\mu^0_i(T_2) - \mu^0_i(T_1)$

$$\mu^0_i(T_2) - \mu^0_i(T_1) = -\int_{T_1}^{T_2} S^0_i(T)dt \tag{5.47}$$

Using the expression for the differential of the entropy shown in Section 4.2, we have

$$dS = \frac{c_P}{T}\ dT,$$

where $S^0_i(T)$ for the pure component i

$$\int_{T_2}^{T} dS^0_i = \int_{T_2}^{T} \frac{c^0_P}{T}\, dT, \qquad S^0_i(T) = S^0_i(T_2) + \int_{T_1}^{T_2} \frac{c^0_{P,i}}{T}\, dT \qquad (5.48)$$

Substituting (5.48) into (5.47) we obtain

$$\mu^0_i(T_2) - \mu^0_i(T_1) = -\int_{T_1}^{T_2} S^0_i(T)dt - \int_{T_1}^{T} \left[S^0_i(T_2) + \int_{T_2}^{T} \frac{c^0_{P,i}}{T}\, dT \right] dT' \qquad (5.49)$$

$$= S^0_i(T_2)(T_1 - T_2) - \int_{T_1}^{T_2}\int_{T_2}^{T} \frac{c^0_{P,i}}{T'}\, dT'\, dT.$$

After, considering (5.49) and the used notation (5.46) it can be written in the following form

$$\Delta\mu^0 = \Delta S^0(T_2)(T_1 - T_2) - \int_{T_1}^{T_2}\int_{T_2}^{T} \frac{\Delta c^0_P}{T'}\, dT'\, dT. \qquad (5.50)$$

In the expression (5.50), $\Delta S^0(T_2) = S^0_A(T_2) + S^0_B(T_2) - S^0_{AB}(T_2)$ and $\Delta c^0_P = c^0_{P,B} - c^0_{P,AB}$. Since the sum of the heat capacities $c^0_{P,A} + c^0_{P,B}$ and the heat capacity of the solid phase $c^0_{P,AB}$ differ slightly from each other, the value Δc^0_P turns out to be small in comparison with other values in (5.50). For this reason, the double integral in this expression can be neglected. Additionally, by replacing T_2 by the fusion temperature T^M, and T_1 by the current temperature T, and noting that the fusion temperature T^M, $x^M_A(T^M) = x^M_B(T^M) = 0.5$ we finally obtain

$$RT\ln[\gamma^L_A(T)\, \gamma^L_B(T)\, x^L_A(T)\, x^L_B(T)] - \qquad (5.51)$$
$$-RT^M\ln[0.25\gamma^L_A(T^M)\, \gamma^L_B(T^M) +$$
$$\Delta S0(T^M)(T^M - T) = 0$$

In the expression (5.51), i.e. the liquidus equation, the elements for calculating $\Delta S^0(T^M)$ can be found in reference books on the thermodynamic constants available in scientific literature, as well as the fusion temperature of the T^M alloy and its corresponding activity coefficients γ. In this equation, the liquidus line contains three unknown values: temperature T, concentration of components A and B in the liquid phase (x^L_A y x^L_B). The number of the unknown concentrations can be reduced to one if we consider the equation of the liquid phase balance that allows any of the concentrations to be expressed through the other one.

$$x^L_A + x^L_B = 1.$$

After that, two values or unknown/free variables remain in the liquidus equation (5.51). If one of them, e.g., temperature, is given different values, the corresponding compositions of the liquid phases at these temperatures can be found from the resulting equation, or, in other words, the liquidus curve, i.e., the whole state diagram can be calculated. In the theoretical method analyzed for the study of state diagrams, the values of the thermodynamic parameters ΔS^M and T^M are not known exactly, and therefore the state diagrams calculated in this way are not very precise.

In the calculation method of state diagrams using the chemical equilibrium constant is devoid of this disadvantage, but, nevertheless, it cannot be applied to all systems. This method will be analyzed in the next chapter on the example of ternary systems A^3–B^5. Knowledge of the ΔS^M y T^M values are not required when using the method of calculating state diagrams from the chemical equilibrium constant. A complete treatment of this method is given in the book "Heterostructure lasers" H.C.Casey, Jr. M.B.Panish. Part B. Materials and Operating Caracteristics. Academic Press, INC. 1978, Orlando San Diego New York Austin Boston London Sydney Tokyo Toronto.

CHAPTER 6.

MULTIPLE COMPONENT SYSTEM

6.1 General Points About Three Component Systems

In each phase of any thermodynamic system, the sum of concentrations of the components is equal to 1. Therefore, in any binary system it is sufficient to know the concentration of one of the components to determine its composition. Thus, when representing the axis of the compositions in a two-component system, the length of an arbitrarily chosen straight line segment should be taken as an unit, as we did before in the analysis of various binary systems. The position of each dot on the horizontal axis corresponds to one unique composition that is determined by the values of the line segments on either side of the selected point. Since, at constant pressure, the temperature becomes the second variable parameter along with the composition, the two-dimensional phase diagram of any binary system is represented in a surface.

In a three-component system we have

$$x_A + x_B + x_C = 1, \tag{6.1}$$

where x_A, x_B and x_C are, respectively, the concentrations of the components A, B, and C, expressed in atomic mass or volume units. Thus, the one-dimensional axis of the compositions of the two-component system turns into a surface for a three component system. In this case, we use an equilateral triangle (called the *concentration triangle*) as a geometric image reflecting the composition of the system. The vertices of this triangle correspond to the pure components A, B, and C. The points on the sides of the triangle correspond to the composition of each two-component system: A–B, B–C, and A–C. The points *inside* the concentration triangle determine the composition of the three-component system. One of the geometrical properties of an equilateral triangle can be used to quantitatively characterize the composition of this system:
 – If we draw lines parallel to the sides through any point of the triangle, then the sum of the lengths of the segments intersected by the lines on each side is independent on the position of the point and it is equal to the length of one side of the triangle.

   – If *perpendicular* lines are drawn from any point of the triangle to each side, then the sum of the lengths of these lines is independent of the position of the point and is equal to the height of the triangle.

Thus, condition (6.1) in the concentration triangle can be satisfied in two different methods:

1. The unit (or 100% if the concentration is expressed as a percentage rather than a fraction) is the length of one side of the triangle. The concentration values x_A, x_B and x_C are related to the length of the intersected segments on the sides of the triangle along the parallel lines passing through the point characterizing the composition of the ternary system. This method of representing the concentrations in a three-component system is called the *Roseboom triangle*. Fig. 6.1*a* illustrates this method.
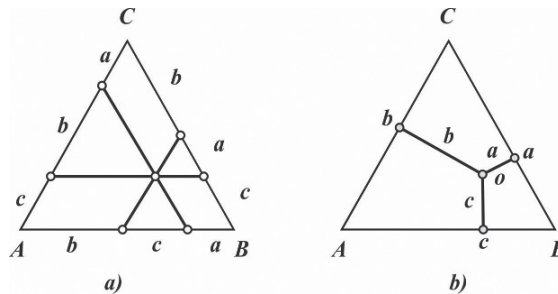
Fig. 6.1. a) Roseboom triangle; b) Gibbs triangle.

2. The height of the triangle is taken as the unit of measurement. The relative lengths of the perpendiculars drawn to each side of the triangle from any point inside correspond to the concentration of the component realative to the vertex from which the perpendicular is directed. This method, shown in Fig. 6.1*b*, is called the *Gibbs triangle*.
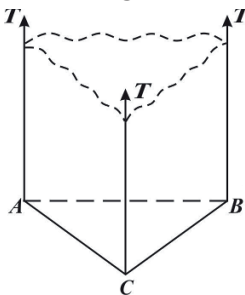
Fig. 6.2. Coordinate volume space for constructing three-dimensional phase diagram.

The Roseboom triangle method is often used to build phase diagrams of ternary systems. In this method, the compositions determined by points on a line parallel to one side of the triangle contain a constant concentration of the component at the vertex opposed to the side.

When studying the state diagrams of a ternary system, i.e., its behavior as a function of its composition and temperature, the latter is represented by the vertical axis. In comparison to the binary case, the system is three dimensional, and therefore it transforms into a straight prism (Fig. 6.2). The three vertical planes of this prism contain the binary diagrams A–B, A–C, and B–C. As an example of a ternary state diagram, first consider a system with unlimited solubility of component in the solid phase. Such a diagram is usually found in systems formed by pure metals (for instance: Nb–Mo–W, Ag–Au–Pt) or semiconductor alloys of the A^3B^5, A^2B^6, $A^5_2B^6_3$ type (for example: AlP–GaP–InP, Bi_2Te_3–Bi_2Se_3–Sb_2Te_3).

For clarity, consider three binary diagrams: A–B, A–C and B–C, in which solid solutions exist in the whole range of compositions. If we "unfold" the lateral planes of the prism, as in Fig. 6.3, we can visualize the binary concentration diagrams. In the planes, the vertical axes of the prism correspond to the temperatures. Note that the triangle in the center is the concentrations triangle.
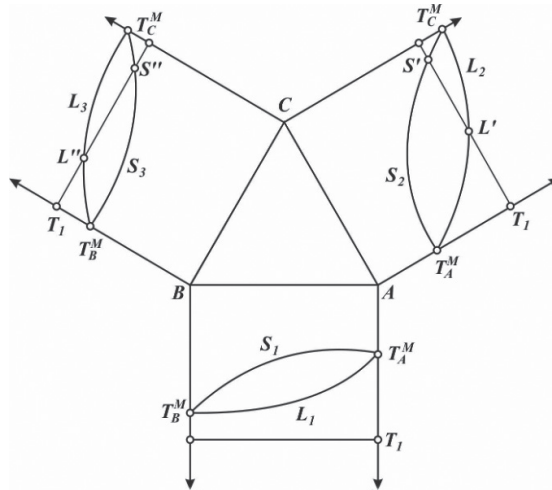

Fig. 6.3. The diagram of state for a three-component system with unlimited mutual solubility represented as unfolding planes of binary concentration diagrams.

The three-dimensional ternary diagram is obtained by unfolding the planes with repeated prism formation. In them, the solid solutions exist in the whole range of compositions. In the volume diagram thus obtained (Fig. 6.4), the liquidus is a surface with the convex curvature and limited by the lateral planes, on wich the corresponding binary systems are located.
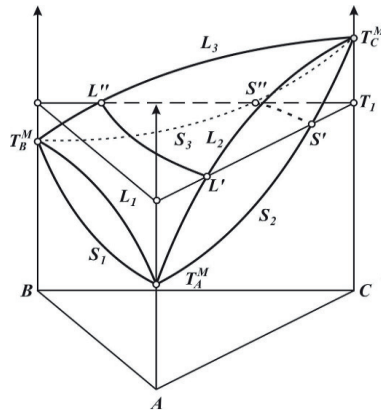

Fig. 6.4. The volumetric diagrams of state for a three-component system with unlimited mutual solubility represented as folding planes of binary concentration diagrams.

In Fig 6.4, the liquidus lines of these binary systems are labeled as $T^M_A L_1 T^M_B$, $T^M_B L_3 TMC$ and $T^M_C L_2 T^M_A$. The solidus of a ternary system is a surface whose curvature faces down. The lateral vertical planes intersect this surface along the solidus lines labeled as $T^M_A S_1 T^M_B$, $T^M_B S_3 T^M_C$ and $T^M_C S_2 T^M_A$, respectively.
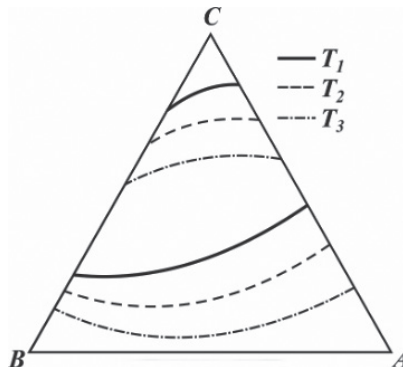
Fig. 6.5. Projections of liquidus and solidus isotherms on the plane of the concentration triangle.

The liquidus and solidus surfaces are intersected by the horizontal planes of the constant temperature and the isotherms of the liquidus and solidus, as can be seen in Figs. 6.5 and 6.7. The points characterizing the compositions of the liquid and solid phases in equilibrium at a given temperature are located on the isothermal lines.

It should be noted that, on the state diagram of a ternary system, unlike a two-component system, it is impossible to find the equilibrium compositions of the liquid (x^L) and solid (x^S) phases. If in a two-component system there is a chord (i.e., a segment of a horizontal straight line) whose extreme points are the compositions of the phases in equilibrium, then for a three-component system we can only say that the chord lies in the horizontal plane where the liquidus and solidus isotherms are located.
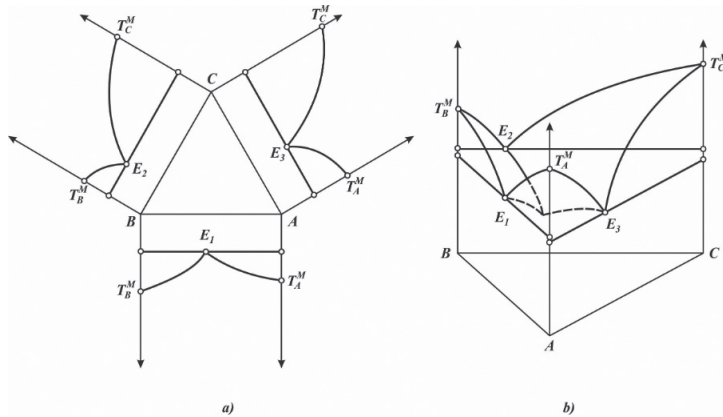
Fig. 6.6. The diagrams of state for a three-component system without solubility in the solid phase as unfolding (a) and folding (b) planes of binary concentration diagrams.

To determine the position of the chord in this plane, or, in other words, to find the equilibrium compositions of the liquid and solid phases in the diagram of the ternary system, it is necessary to know the dependence between x^L and x^S at the considered temperature. In fact, such dependences found for a given temperature show how the segregation coefficient changes with the concentration. As an example, Figs. 6.6.*a* and *b* show a diagram of an eutectic system in which there is no solubility between the components of the solid phase.

6.2 Diagrams of State in Ternary Systems A^3B^5

Let us analyze the state diagram a ternary system representing solid solutions of two semiconductor binary compounds of the A^3B^5 type. As noted in the previous chapter, such state diagrams are very important from a practical point of view, since a large number of optoelectronic devices are produced on the basis of various ternary and quaternary systems of A^3B^5 solid solutions.

All ternary systems of this type are similar, except that in some cases there are immiscibility gaps. The main differences between such diagrams are the fusion temperatures of their components and the positions of eutectics.

As we have already mentioned in Chapter 5.15, we shall not analyze the systems containing Boron and Nitrogen. Among the remaining ternary systems, two types can be distinguished. The first is the solid solutions with two elements of group A^3 and one of group B^5, such as, for example, the well-known $Al_xGa_{1-x}As$, $Al_xGa_{1-x}P$, $Ga_xIn_{1-x}As$ and others. The second group includes solutions with the metallic element A^3 and two different elements from the fifth group of the periodic table. An example of such a system is the $GaAs_xP_{1-x}$ solid solution.
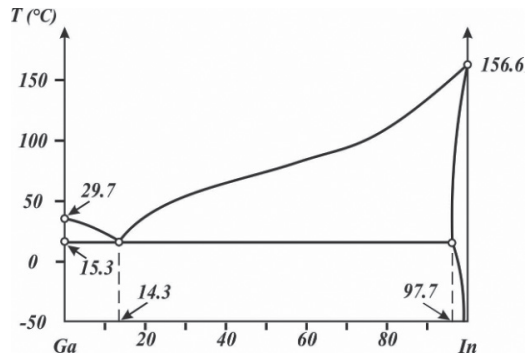

Fig. 6.7. Ga-In system diagram of state.

Let us consider the first type of diagrams. In the system $A^3_1A^3_2B^5$ the component parts are the double diagrams $A^3_1–B^5$, $A^3_2–B^5$ and $A^3_1–A^3_2$. The first two diagrams are similar, and they were analyzed, in a general way, in Chapter 5.15 (Fig. 5.32). As mentioned there, in them we only pay attention to metal corners. The third component part $A^3_1–A^3_2$ is formed by binary combinations of metals Al, Ga and In. As a characteristic example, Fig. 6.7 shows a diagram of the $Ga–In$ system.

The two remaining diagrams, namely *Al–Ga* and *Al–In*, are shown in Fig. 6.7. In the vicinity of these diagrams, i.e., in the liquid phases enriched with metals, at low temperatures (the maximum temperature in the liquidus line is *156.6* °C, as in the example in Fig. 6.7) the solubility of the elements of the fifth group is negligible. Therefore, in the processes of the crystal growth these parts of the ternary diagram are not used, and the binary diagrams based on the metals A^3_1–A^3_2 are simply not taken into consideration. In the future, diagrams of the A^3_1–A^3_2 type should be presented only in the form of straight lines emphasizing the particularities of the liquidus lines. Note that in a ternary system such a simplification is not a change, since the liquidus line can be approximated as a straight line (see Fig. 6.7).

Besides the three given diagrams A^3_1–B^5, A^3_2–B^5 and A^3_1–A^3_2, another component of the considered ternary system is the quasi-binary system $A^3_1B^5$–$A^3_2B^5$. In all ternary systems of this type (except for the *AlSb–AlAs* systems) in the solid phases there is unlimited solubility in the whole range of compositions. Therefore, in such systems there exist either liquid- A^3_1–A^3_2–B^5, solid- $A^3_xA^3_{1-x}B^5$, or both solution phases simultaneously. Solid solutions of A^3B^5 as well as its alloys are stoichiometric, that is, the content of element B^5 in the solid phase is equal to *0.5*, and of course, stoichiometric deviations do not matter. As a result, in the concentrations triangle as shown in Fig. 6.8, the $A^3_xA^3_{1-x}B^5$ solid solutions will be located on the median parallel to the A^3_1–A^3_2 side. The composition of the solid solution $A^3_xA^3_{1-x}B^5$ can change when the ratio of its components A^3 and A^3_2 changes or, in other words, when the ratio between the binary alloys $A^3_1B^5$ and $A^3_2B^5$ changes.
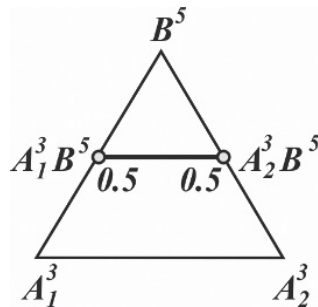

Fig. 6.8. Drawing a stoichiometric section in the Gibbs triangle.

This is why any $A^3_1B^5$–$A^3_2B^5$ system is called quasi-binary, as is the $A^3_xA^3_{1-x}B^5$ alloy, which is formed from three components. In principle, the solid solution can be considered as a $A'_xB'_{1-x}$ binary phase in which the composition varies in the range

$0{\leq}x{\leq}1$, where A' is $A^3_1B^5$ and B' is $A^3_2B^5$. In the liquid phase, the concentration of an element from group five in the quasi-binary system is constant and equal to 0.5.
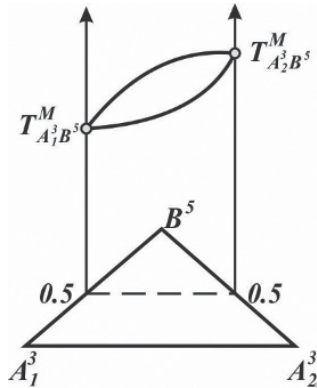

Fig. 6.9. Drawing a stoichiometric section in the Gibbs triangle.

The quasi-binary diagram of the system $A^3_1B^5$–$A^3_2B^5$, located on the vertical plane and resting on the median of the concentration triangle, is cigar-shaped, as shown in Fig. 6.10. Above the liquidus line is the liquid phase with a stoichiometric composition A^3_1–A^3_2–B^5 and below the solidus line is the solid phase of composition $A^3_xA^3_{1-x}B^5$. Between these lines, as in any binary diagram with unlimited solubility, both phases are in equilibrium.
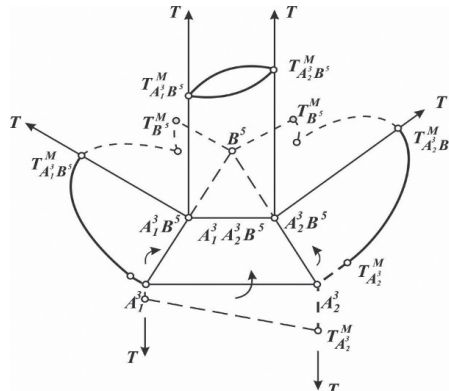

Fig. 6.10. Plotting a diagram of state for three-component A3-B5 system

In Fig. 6.10, the horizontal plane shows the diagrams, $A^3_1B^5$, $A^3_2B^5$ and A^3_1–A^3_2 on the sides of the concentration triangle, and the vertical plane shows the

quasi-binary diagram $A^3_1B^5$–$A^3_2B^5$. In this drawing, considering the restrictions mentioned above, the dashed lines show those parts that we will neglected further (the non-metal corner B^5 and the system A^3_1–A^3_2). According to these constraints, the concentration triangle transforms into an equilateral trapezium.
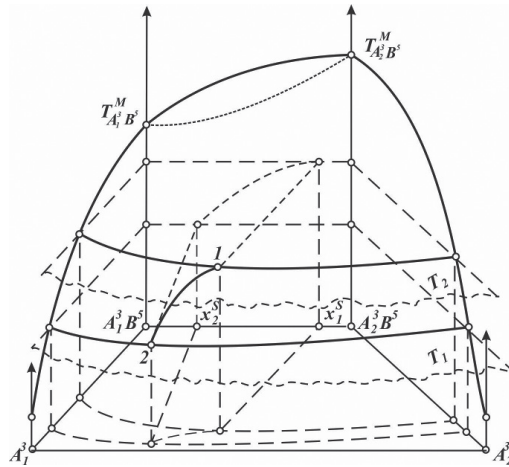

Fig. 6.11. General view of the diagram of state for the A3-B5 ternary system.

To obtain the volume diagram of the ternary system $A^3_1A^3_2B^5$, we rotate the binary diagrams A^3_1–A^3_2, A^3_1–B^5 and A^3_2–B^5 in Fig. 6.11 around the sides of the trapezium to the vertical position as indicated by the arrows. Then the solidus lines of these systems and the vertical axes corresponding to the pure alloys in the quasi-binary system $A^3_1B^5$–$A^3_2B^5$ will coincide. In the phase diagram thus obtained, shown in Fig. 6.12, the liquidus is a surface with a convex curvature towards any composition (remember that diagram A^3_1–A^3_2 is not considered). The surface of the liquidus is intersected by the vertical planes in which the binary systems A^3_1–$A^3_1B^5$ and A^3_2–$A^3_2B^5$ are located, and the quasi-binary diagram $A^3_1B^5$–$A^3_2B^5$ is intersected by the corresponding liquidus lines of these systems. The solidus of the ternary system $A^3_1A^3_2B^5$ is formed by a segment of the vertical plane located between the solidus of the systems A^3_1–$A^3_1B^5$, A^3_2–B^5, and $A^3_1B^5$–$A^3_2B^5$ and the bottom line, that is the upper base of the concentration trapezium in which the compositions of the solid solutions $A^3_1A^3_2B^5$ are placed.

The resulting diagram will be crossed by the horizontal planes T_1 and T_2, (planes denoting constant temperature). The liquidus surface lines formed by

intersection with these planes (T_1 and T_2) are called *liquidus isotherms*. In addition to these isotherms presented in Fig. 6.11 for temperatures T_1 and T_2 in the three-dimensional space of the diagram A^3_1–A^3_2–B^5, this figure shows projections of the isothermals on the plane of the concentration triangle plane (trapezium). Such projections are more convenient to use in practice.
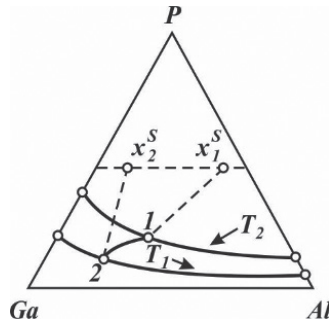

Fig. 6.12. Liquidus isotherms in the Al-Ga-P system.

On the liquidus isotherms, there are points corresponding to the liquid phases A^3_1–A^3_2–B^5, containing different concentrations A^3_1 and A^3_2, and saturated with the element B^5 at a given temperature. Since at a constant temperature and with an established concentration in a saturated ternary liquid phase, the concentration B^5 is a maximum, the liquidus isotherms are also often called *saturation* or *solubility curves*.
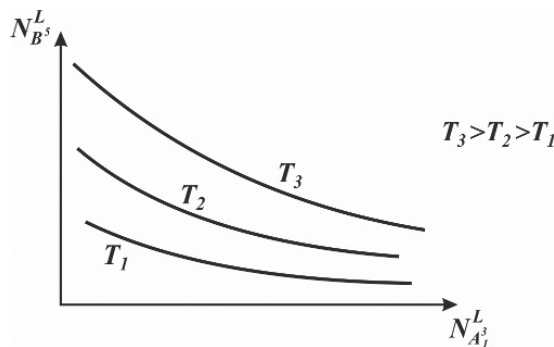

Fig. 6.13. Liquidus isotherms for various temperatures.

Consider the specific system *Al–Ga–P*. In this system, the solubility of phosphorus in pure *Ga* is noticeable higher than in *Al*. Therefore, an increase in the

concentration of this component in the liquid ternary phase leads to a decrease in the concentration of Phosphorus. Thus, any isotherms, as can be seen in Figs. 6.11 and 6.12, decrease as one moves from the gallium corner towards the aluminium corner in the diagram, i.e., as the concentration of element A_3 (Al, in the case of the considered system Al–Ga–P) in the liquid phase increases. Each of the saturated phases Al–Ga–P is in equilibrium with one unique solid phase, the composition of which is determined by the position of certain point located on the line of intersection of the horizontal isometric plane with the vertical solidus plane. Therefore, any point on the liquidus isotherm can be connected by a straight line segment (called a *conode*) to the corresponding point characterizing the composition of the equilibrium solid phase, as will be shown in Figs. 6.12 and 6.13.

Nevertheless, as already mentioned, there is no rule or law in a ternary diagram that allows to draw a chord across, or, in other words, to connect the points characterizing the equilibrium compositions of the liquid and solid phases. Additionally, it is necessary to know the dependence between the equilibrium compositions of the liquid and solid phases. These dependences are shown in Fig. 6.14 and are commonly called *distribution isotherms* for Al–Ga–P, Al–Ga–As, Ga–In–As, and other similar systems. Thus, when developing solid ternary solution growth processes of a certain composition, it is first necessary to construct two families of curves. One of them is the family of the liquidus isotherms, which characterizes the compositions of saturated liquid phases at different temperatures. The second is a family of the isothermal distribution curves that help to find the relationship between the compositions in equilibrium in the liquid and solid phases. In other words, those that describe the composition of the extreme points of the conode in the isothermal plane. As an illustration, let us examine by an example how these families are used to find the composition of the liquid phase required for the epitaxial growth of an $Al_xGa_{1-x}P$ film with a given value for the width of the bandgap energy E_g. First, the composition of the solid phase x^S is determined in accordance with the required value of the bandgap energy E_g. These dependences are well studied and widely presented in the literature for almost all ternary systems. Then, the crystallization temperature T is chosen with respect to the desired epitaxial coating thickness. After that, following the distribution curve (Fig. 6.14), it is possible to determine the concentration of A^3_1 for the already determined composition of the solid phase (for the considered case - Al) in the liquid phase, and then to find the solubility of element B^5 (P) at fusing of A^3_1 and A^3_2 (Al and Ga) using the liquidus line (Fig. 6.13).

As shown in Section 5.8 (equations 5.18 and 5.19), the segregation coefficient is one of the most important technological parameters in the crystal growth process. This coefficient for any component i is determined by the ratio of the concentration of this component in the solid phase x^S_i to its concentration in the liquid phase x^L_i.
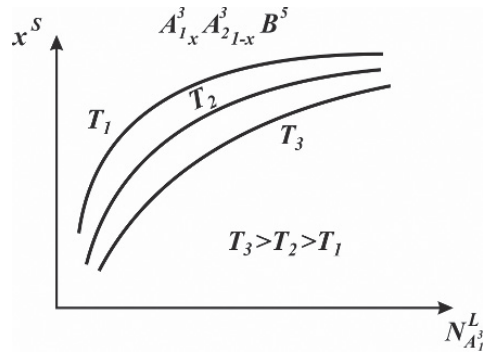

Fig. 6.14. Solidus isotherms for various temperatures.

Ignoring the borides and nitrides, which are rather difficult or practically impossible to grow from a liquid solution, then for from the remaining A^3B^5 materials the segregation coefficients of metals among themselves rise in the sequence $In \rightarrow Ga \rightarrow Al$ and for nonmetals $Sb \rightarrow As \rightarrow P$. In the Al–Ga–P system, the segregation coefficient for Al has a value of 10^2 (for relatively low temperatures, such as those used in the liquid phase epitaxy). In a similar system such as Al–Ga–As, the segregation coefficient of Al reaches a similar value. In another system, such as Ga–In–P, the Ga segregation coefficient is well above the unit (30 to 60) and is a function of composition and temperature.

Thus, it can be concluded from the previous examples that it is necessary to grow ternary solid solutions in various A^3B^5 systems from the solid phases located in the corner of the state diagram, where there is a component with a segregation coefficient below 1. For example, in the Al–Ga–P system, since solid solutions grow over almost the whole composition range, the liquid phases must contain Al in small proportions (0-1% atom concentration), so they must be prepared strongly enriched in gallium. Similarly, the solubility of P in melting Ga with Al at higher temperatures is in the range of 0.1–3% for temperatures between $900°C$ and $1100°C$, which are often used in real growth processes of these materials. Thus, in the analized case, the liquid phases can be considered as dilute solutions

of *P* in the fusions of *Ga* with *Al*, where *Ga* is the solvent. Likewise, for *Ga–In–P* and *Ga–In–As* systems at *Ga* concentrations and solubilities of *P* and *As* in the liquid phases at commonly used temperatures, the solvent is *In*. It follows that these families of the liquidus isotherms and the distribution curves need only be investigated in a limited range of concentrations close to the corner on the state diagram corresponding to the solvent. The liquidus isotherm family can be represented in the triangle coordinates, as shown in Fig. 6.12, and in the rectangular coordinates (Fig. 6.13). Various constraints or simplifications are introduced to represent the state diagrams of the systems that contain more than three components. In one method, the concentrations of some components are assumed to be constant, which in turn allows the system to be represented in two- or three-dimensional form. In addition, the state diagrams of many components can be represented in the form of a graph in which the compositions in equilibrium, in liquid and solid phases, are filled in at constant temperatures. Let us note that in practice, it is almost never necessary to use the diagram of state for the entire range of compositions of the system. For instance, in the solid quaternary solutions *GaInAsP*, widely used in the fabrication of a large number of devices of the fiber optics systems, only in a few cases it is necessary to know the state diagram and only for some ranges of compositions where the solid phase has a lattice parameter close to that of the binary compounds *GaAs* and *InP*. This is because the latter are used as the substrates to grow multilayer structures of semiconductor devices, such as laser diodes, photodiodes, photosensors, etc. The regions of the compositions of the state diagrams in which the lattice constant of the solid phase is close or equal to that of one of the binary compounds are called *isoperiodic sections*. Latter receive special attention, when drawing state diagrams of multicomponent systems.

6.3 Experimental Studies of Diagrams of State of Multi-component Systems

For the crystal growth of multicomponent solid solutions of a given composition, it is necessary to build a family of liquidus isotherms and distribution curves. Both families can be found theoretically or experimentally. Let us first analyze how this problem can be solved experimentally.

The liquidus curves show how the composition of saturated liquid phases changes at different temperatures. Therefore, two different methods can be used in the experimental study of these curves, in which one of the above parameters is fixed and the other is calculated. Thus, in the study of the liquidus curves it is possible:

1. To determine the composition of the saturated liquid phase at constant temperature. This method is called the s*olubility method* and can be carried out, for example, with the help of the determination of mass loss of a solid phase introduced into an unsaturated solvent.
2. To determine the complete disappearance of the solid phase in the liquid of a known composition. This method is performed by visual observation of the surface of the liquid phase during slow gradual heating and is called *"in situ"* (the Latin term which in this case means simultaneous observation during the process).

There are other methods of plotting diagrams of state. For example, differential thermoanalysis can be used in the study of the liquidus curves. Nevertheless, we shall analyze only these two methods in detail, since the accuracy of thermoanalysis is not very high. Each one of these methods of drawing liquidus isotherms has its own advantages and disadvantages.

The solubility method is characterized by high precision, limited only by the precision of the scales, which is currently very high. This also applies to the measurement of temperature. This method is used in the liquid phase epitaxy in the experimental study of various binary state diagrams in the A^3B^5 and some other systems. In this case, the mass loss of the substrate of any of the A^3B^5 binary compounds that have been in contact with an unsaturated liquid solution for some time is determined. The typical size of the substrate in the liquid phase epitaxial is usually about one square centimeter with a thickness of about *0.5* mm and is determined by thechnical specifications or the simplicity of the process. For experimental study of the liquidus isotherms, it is important to count on the availability of commercially available monocrystals from which substrates in the required sizes can be prepared. Currently, the substrates are made from A^3B^5 binary compounds such as *GaP*, *GaAs*, *GaSb*, *InP, InAs* and *InSb* are currently produced.

Likewise, in more complicated cases, such as ternary or quaternary solid solution systems, the solubility method cannot be applied. This is because the liquid phase

of a ternary or quaternary system is in equilibrium only with its corresponding ternary or quaternary solid solution. In view of this, when studying the liquidus isotherms in multicomponent systems, when their solid phases are introduced into the unsaturated liquid, in principle the multicomponent crystals should be used. Unfortunately, multicomponent crystals cannot be grown due to the difficulties of many fundamental reasons. Therefore, in the absence of multicomponent substrates, in some cases in the study of complex systems, the binary substrates are used as a simplification for experimental study of their liquidus isotherms.

As an example, we analyze the ternary system *Al–Ga–As*, on the basis of which the superiority of heterounions over homounions was first shown. In this system the initial binary alloys are *GaAs* and *AlAs*. *GaAs* substrates are produced commercially for use in the growth processes, while *AlAs* substrates are not produced, mainly due to their high corrosivity in air. Due to the high chemical activity of *Al*, this alloy quickly decomposes when interacting with water vapor according to the following reaction

$$AlAs + H_2O \leftrightarrow AsH_3 + Al_2O_3. \tag{6.2}$$
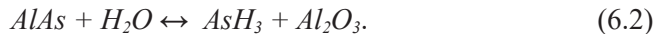
The only way to study the liquidus isotherms by the solubility method in the *Al–Ga–As* system is that the *GaAs* substrate at a certain constant temperature comes in contact with the *Ga+Al* liquid phase. Upon contact, a certain amount of *GaAs*, which of course depends on the temperature and concentration of *Al*, dissolves in the liquid phase due to *As* saturation. If the substrate is accurately weighed before and after the process, the mass loss can be determined. This means finding the concentration of *As* and *Ga* in the saturated liquid. The desired composition of the *Al–Ga–As* liquid phase can be defined considering the initial amount of *Al* in the *Ga* solvent and the amounts of *Ga* and *As* introduced during the substrate dissolution. This method is successfully used in various A^3B^5 systems. In particular, this method was used to study the state diagram in the *Al–Ga–P* system, which resembles the previously analyzed *Al–Ga–As*. Moreover, there are publications with the results of using this method in the *Ga–In–As–P* quaternary systems upon contact of the *InP* substrate with an unsaturated *Ga–In–As* solution.

As noted earlier, the method described above for studying the liquid and solid phases can be successfully applied to various A^3B^5 binary systems, since the liquid

and solid phases are able to find thermodynamic equilibrium. However, in the case of more complicated systems, problems arise, mainly related to nonequilibrium. In order to analyze these problems, we will first see some of the particularities of the process, such as what happens in the system when the compositions of the liquid and solid phases do not correspond. Assume that the solid phase of the system is a substrate prepared from the binary compound $A^3_1 B^5_1$, and the liquid phase is a solution saturated with the B^5_2 element in melts of the A^3_1 and A^3_2 metals. As examples of such a situation, we can name the processes of growing a structure by liquid phase epitaxia, in which *GaInP* and *GaInAs* solid solutions are grown on *GaAs* and *InP* substrates, respectively. In the first example, the liquid phase is a solution saturated with phosphorus in the *Ga-In* melts, and the solid phase is the *GaAs* substrate. In the second, the liquid is a solution saturated with *As* in the melts of the same metals, and the solid is the *InP* substrate. These systems are referred in the literature as *GaAs/GaInP* and, respectively, *InP/GaInAs*.

In real epitaxial processes, initially, the solid phase (the substrate) and the saturated liquid have the same temperature, and are isolated from each other. If at some moment these phases come in contact, the heterogeneous system of liquid and solid will be in nonequilibrium, since the Gibbs energy corresponding to a particle in the liquid ($\bar{G}^L$) and solid ($\bar{G}^S$) phases is different. There are two possible options. Either the Gibbs energy for one particle in the liquid phase is greater than the Gibbs energy for a particle in the solid phase $\bar{G}^L > \bar{G}^S$, or vice versa $\bar{G}^L < \bar{G}^S$. After the contact of the liquid phase and the substrate, the processes of reducing the Gibbs energy of the system will begin to establish equilibrium. Note that *equilibrium* in this case is not strictly true, since in thermodynamics the concept of equilibrium is understood as the correspondence of the composition of the whole volume of the solid phase to the composition of the liquid phase. In this case, between the substrate and the liquid phase, a transition coating of intermediate composition of finite thickness will be formed, containing all the elements of both phases. After the formation of this coating, the liquid in contact with the coating does not "feel" the material of the substrate. Thus, the process occuring between the liquid and solid phases, whose compositions do not correspond to either of them, is more correctly called the process of establishing *quasi-equilibrium*.

The formation of a transitional coating between the liquid phase and the substrate occurs due to the exchange of particles between them, and such an exchange is

performed on account of two processes occuring simultaneously. One of these processes is the dissolution of the substrate and, as a result, the elements that are not present in the liquid or whose presence is insufficient pass to it from the solid phase. For example, in the case of the *GaAs/GaInP* system, during the dissolution of the substrate, equal amounts of *As* and *Ga* atoms are passed into the liquid phase, which previously did not contain *As*.

Due to this, the solid phase, in comparison to the liquid phase, does not have the elements A^3_2 and B^5_2. In particular, *In* and *P* in the first case, and *Ga* and *As* in the second. In the second process, due to the establishment of quasi-equilibrium, these elements must partially rise to the surface of the substrate, which takes place through crystallization. A transition layer is formed on this surface containing elements that are not present in the substrate. In the general case, the transition layer may have a variable composition, due to diffusion processes in the liquid phase and segregation phenomena. In the solid phase, the diffusion velocity of atoms is very slow due to very small diffusion coefficients and, therefore, the diffusion processes can be neglected.

Thus, quasi-equilibrium in a heterogeneous system should be achieved as a result of two processes occuring simultaneously: the dissolution of the solid phase and the crystallization of transition layer of variable compositionon on the surface of the substrate. It is worth saying that although the term dissolution is often used in literature, as a rule, it does not describe precisely one of the processes that occurs when quasi-equilibrium between the substrate and the liquid is established, when the compositions do not correspond to each other. Initially, we assumed that when the substrate contacts the $A^3_1 A^3_2 B^5_2$ ternary liquid phase, it will be saturated with the B^5_2 element. That is why the process associated with the transition of a number of components from the solid phase to the liquid phase is more correctly called the *dissociation of the substrate due to the nonequilibrium of the system*.

In general, the process of establishing a quasi-equilibrium between the liquid phase and solid phasse is much more complicated than is shown in the elementary example illustrated above. Before anything else, we recall that the Gibbs energy of a particle in the liquid and solid phases is different when they are not in equilibrium. We suppose that the energy of the liquid phase is higher than of the solid phase. In this case, the tendency of the system to minimize its

total energy will lead to the prevalence of the crystallization process over the process of substrate dissociation during the formation of quasi-equilibrium between the liquid and solid phases. This happens because the Gibbs energy of one separate phase is equal to the chemical potential of one particle multiplied by the number of particles. Since the chemical potential depends on the concentration x and the temperature T, if the latter is constant, the total Gibbs energy G can be reduced only by decreasing x, that is, through an isothermal crystallization.

Assume that in a certain ternary system $A^3_1A^3_2B^5_2$, the lattice constants of the binary compounds $A^3_1B^5_2$ and $A^3_2B^5_2$ coincide, as, for example, in the systems $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}P$. In such cases it is advisable to use any of the binary compounds $A^3_1B^5_2$ or $A^3_2B^5_2$ as a susbstrate. For the above-mentioned cases of solid solutions $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}P$, the corresponding substrates are $GaAs$ and GaP, respectively. If the saturated liquid phases Al–Ga–As and Al–Ga–P at constant temperature contact $GaAs$ and GaP substrates, respectively, then a thin transition layer corresponding to a solid solution rapidly forms on the surfaces of the latter. The presence of such a layer was demonstrated in a series of research works on the establishment of quasi-equilibrium in the $GaAs/AlGaAs$ and $GaP/AlGaP$ systems. We note a very important circumstance: since the lattice constants of binary compounds $GaAs$ and $AlAs$, as well as GaP and AlP are practically the same, a monocrystal transition layer is formed on the corresponding substrate. The ternary liquid phase and the binary substrate are completely isolated by this layer ensuring the quasi-equilibrium in the system.

Suppose that the Gibbs energy of one particle of the solid phase is higher than that of the liquid phase. In this case, the tendency of the system to minimize the total energy will lead to one of the two processes participating in the establishment of quasi-equilibrium between the liquid and solid phases, to prevail over the other, i.e., the crystallization will occur on the substrate. If the liquid phase is saturated prior contact with the solid phase, the disassociation of the substrate, in other words, the entry of constituent elements, will lead to supersaturation of the liquid phase, promoting the crystallization process. All these events occur in the immediate vicinity of the substrate, and the process of establishing quasi-equilibrium ends when the formation of the transition layer consisting of all the elements contained in both phases is completed. Nevertheless, if the lattice parameters of the substrate and the transition layer are

different, this layer often does not crystallize as a monocrystal, but is absorbed in the $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}P$ systems mentioned earlier in the form of separated polycrystals. In the spaces between the polycrystals, the liquid phase, still in contact with the substrate, continues to interact with it. As a result, the liquid phase often fails to regenerate crystals in the growth process, and a part of them remains outside the surface of the substrate. Thus, the simultaneous processes of polycrystal growth and their dissociation from the substrate can lead to the formation of a transition heterogeneous and nonuniform layer.

Leaving both phases in contact for some time at a constant temperature is necessary to isolate them from each other. However, since the substrate surfaces are not completely flat due to the processes of establishing equilibrium in a number of systems, it is rarely possible to completely remove the residual liquid phase from the substrate surface. Therefore, when the reactor is cooled to room temperature, a polycrystalline layer is formed from these residues. This, as well as the presence of solvent residue on the surface of this layer, prevents an precise determination of mass loss of the substrate. That is why the solubility method for the experimental determination of the liquidus isotherms cannot not be used in systems where processes similar to those discussed above occur. The well-known case of the $GaSb/GaInAsSb$ system, which is extremely important for practical applications in infrared optoelectronics, can be cited as an example. In this system, the $GaSb$ substrate decomposes markedly upon contact with the saturated $Ga–In–As–Sb$ liquid phase, and Sb entering the liquid strongly conditions crystallization. Because of this, the substrate in contact with the liquid is often said to be unstable. Another example of a system with unstable interfaces between the liquid and solid phases is the $InP/GaInAsP$ system, that is currenlty used to create active elements (laser diodes, LED diodes, photodetectors for optical communication. As the composition of this system moves toward $GaInAs$ along the isoperiodic section with InP, i.e., as the bandgap of the solid solution narrows, the degree of nonequilibrium at the interface between the quaternary solid phase (in extreme cases, the ternary $GaInAs$ and the saturated liquid $In–P$ increases in the same proportion. Therefore, the growth of InP on the quaternary $GaInAsP$ solid slution enriched with As (i.e., with a composition close to that of $GaInAs$ or on the ternary $GaInAs$ leads to a surface that is not perfectly planar. Therefore, the instability of the interface between the solid solution and the binary $In – P$ saturated phase will affect the fundamental parameters of the device such as its degradation resistance and optical properties, and thus should

be minimized. For example, when growing *InP/GaInAsP* heterostructures for feedback distribution diode lasers, it is the best when the diffraction grating is placed directly over the quaternary solution layer and then the *InP* is grown on top of it. If the interface instability over which the Bragg diffraction grating is deposited cannot be eliminated, it will not be possible to fabricate the desired device.

In the liquid phase epitaxy, immediately after the crystallization process ends, the substrate with the layers grown below the last liquid phase must be mechanically moved away from contact with the liquid phase. It is also necessary that during the process of cooling the reactor to room temperature, all residual solvent is completely removed from the surface of the newly grown structure. Otherwise, when the furnace cools down to room temperature, a process of crystallization of the remaining residues, which will notably reduce the quality of the last layer. This effect, in turn, may complicate the so-called post-growth processes. Among the post-growth standard procedures, photolotography or chemical reactions are used to fabricate various devices. The quality of the top layer largely determines the parameters of any device made using these technological processes. This is why it is necessary that after finishing the growth of the structure, the top layer should be completely cleaned from solvent residues. However, in practice, the mechanical displacement of the substrate under the liquid phase does not always satisfy this requirement, and it is practically impossible to fulfill it.

For the *AlGaAs* and *AlGaP* systems there is a solution of this problem. The essence of this solution is that after the growth of the last layer, the structure is in contact with the liquid phase from which the auxiliary AlB^5 layer, or the $Al_xGa_{1-x}B^5$ solid solution enriched with *Al* (*x≥0.8*) crystallizes. For the arsenide systems it is understood that element B^5 is *As*, and for the phosphides, respectively, *P*. After the completion of this process, the auxiliary layer is easily removed from the surface of the structure together with the residual solvent, in accordance with the reaction (6.2), by simple boiling in water. As a result, the structure will have an ideal plane and a mirror-like surface. At first sight, the *AlGaSb* system is very similar to *AlGaAs* and *AlGaP*. Nevertheless, the attempts to apply the above method to *GaAsSb* when the top layer is a *GaSb* layer, and when trying to grow *AlSb* on the structure with a total thickness of *5* microns and then contacting the liquid saturated *Al-Sb* phase, all lost because of the thermodynamic nonequilibrium. It is considered that the chemical coating of the

surface is conditioned by thermodynamic nonequilibrium between the liquid phase *Al–Sb* and the solid phase *GaSb*, and the degree of this nonequilibrium increases as the concentration of *Al* in the liquid phase increases. In other words, in the example given earlier, the Gibbs energy in the solid phase (*GaSb*) of the system under consideration exceeds the Gibbs energy of the liquid phase *Al–Sb*.

The solubility method is not applicable in various systems as a consequence of the particularities of the processes of establishing quasi-equilibrium between the liquid and solid phases, that do not have the same composition. For such systems in the study their liquidus curves is used the method "in situ", in which during the slow heating of the liquid phase is determined by the temperature at which the solid phase completely disappears. The temperature thus determined corresponds to the liquidus temperature. If the components forming the liquid phase are carefully weighed before starting the experiment, the composition of the liquid phase at the moment of dissolution can be calculated. The liquidus temperature and composition of the liquid phase found in this manner allow us to obtain a given point on the liquidus curve. By repeating this experiment for other compositions, the families of the liquidus isotherms can be plotted. The method is accomplished in a vertical reactor by observing the liquid surface with the mirror systems through an optical microscope or using a video camera. It should be noted that although the advantage of this method is that it can be applied to any system, its main disadvantage is that it is rather inaccurate due to the lack of precision in measuring the liquidus temperature (approximately +/- *2*°C) and the subjective perception of the moment of complete disappearance of the solid phase on the surface of the solvent.

Both methods allow us to find the dependence between the composition of the liquid phase and the temperature at which the liquid is saturated. This liquid at a fixed temperature is in equilibrium with one unique solid phase. To find the composition of this equilibrium solid phase, it must first be grown from a liquid phase whose composition and temperature have been found by one of the methods previously described. The composition of the solid phase is then determined by any method of measuring the chemical composition, such as X-rays. In this way, the isothermal liquidus families and distribution curves can be found experimentally.

6.4 Calculation Methods of the Diagrams of State of Multi-component Systems of Group A^3B^5

Let us now analyze how we can theoretically study the state diagrams of the solid solutions of the ternary systems A^3B^5. Suppose that we have a pseudobinary system of alloys AC and BC that form solid solutions $A_xB_{1-x}C$.

Firstly, let us pass on to the method of the chemical equilibrium constant, which as we have already mentioned, is sufficiently simple and has certain advantages over other methods. It is important, however, to remember that it cannot be applied to all cases.

The state of equilibrium between the $A_xB_{1-x}C$ solid solutions and the liquid ternary phase can be described as a heterogeneous reversible reaction, where L and S are the indexes denoting the liquid and solid phases, respectively

$$A^L + B^L + C^L \rightleftarrows A_x B_{1-x} C^S \tag{6.3}$$

Formally, this expression can be represented as two chemical reactions for molecules AC and BC

$$A^L + C^L \rightleftarrows AC^S \tag{6.4}$$
$$B^L + C^L \rightleftarrows BC^S \tag{6.5}$$

Although the above mentioned molecules AC and BC do not exist in the real system, from the mathematical point of view, due to the stoichiometricity of the A^3B^5 compounds and the solid solutions based on them, this representation is valid. In (6.4) and (6.5) the concentrations of the AC and BC molecules define the composition of the solid phase as x^S and $1-x^S$, respectively.

It is known that the rate of a chemical reaction is proportional to the concentrations of the substances involved in it. Therefore, the reaction rate in (6.4) and (6.5) from left to right, can be written as follows:

$$
\begin{aligned}
V_1 &= \gamma^L_A x^L_A \times \gamma^L_C x^L_C \\
V_2 &= \gamma^L_B x^L_B \times \gamma^L_C x^L_C,
\end{aligned}
\tag{6.6}
$$

The rate of the reactions from right to left in (6.4) and (6.5)

$$V'_1 = \gamma^S_{AC} x^S_{AC}$$
$$V_2 = \gamma^S_{BC} x^S_{BC},$$
(6.7)

where γ_i and γ_{ij} are the activity coefficients of the components and molecules, respectively, involved in the reactions and x, as before, corresponds to the concentration of the elements and compounds in the liquid and solid phases.

The state of equilibrium in the system is established at equality of rates of the reactions proceeding from left to right (6.6) and from right to left (6.7) and is characterized by the equilibrium constants

$$k_{AC} = \frac{(\gamma^L_A x^L_A)\,(\gamma^L_C x^L_C)}{(\gamma^S_{AC} x^S_{AC})},$$
(6.8)

$$k_{BC} = \frac{(\gamma^L_B x^L_B)\,(\gamma^L_C x^L_C)}{(\gamma^S_{BC} x^S_{BC})}.$$
(6.9)

From here, we can obtain the relationship between x^L_A, x^L_B and x^L_C,

$$x^L_A + x^L_B + x^L_C = 1.$$
(6.10)

For the solid phase

$$x^S_{AC} + x^S_{BC} = 1$$
(6.11)

For practical objectives in the ternary systems $A_x B_{1-x} C$ it is important to study only one of its metal corners of the state diagram. To explain that particularity of the ternary systems $A^3 B^5$, we shall analyze the magnitude of the coefficients of segregation $k_i = \dfrac{x^S_A}{x^L_A}$ in the series of metals Al, Ga, In. The segregation coefficient of Al in the Al–Ga systems as a rule are higher than 100. In the Ga–In systems the segregation coefficientof of Ga is also around 100. In the Al–In systems k_{Al} is determined by the values of about 10^3. At typical temperatures used in the growth processes of various $A^3 B^5$ solid solutions from the solutions–melts, and in particular in the liquid phase epitaxy, the solubility of the fifth group in the A^3 melts is very low. Therefore, a large part of the liquid phase consists of metals, and the segregation coefficients are less than the unit, and because of this circumstance, they are called solvents. Therefore, the solvents in systems

A^3B^5 can be *Ga* or *In*, and the concentration of these elements in the liquid phase can be equal to *100*% without significant error.

Based on these considerations, we assume that equation (6.3) describes a heterogeneous reaction and the solvent is component *B*, i.e.

$$x^L_B = 1 \tag{6.12}$$

If we ignore the interaction between the liquid and solid phases, or in other words, study the system *A–B–C* as an ideal system, then the activity coefficients of all participants in the reaction can be equal to the one.

$$\gamma^L_A = \gamma^L_B = \gamma^L_C = 1$$
$$\gamma^S_{AC} = \gamma^S_{BC} = 1 \tag{6.13}$$

That is why (6.8) and (6.9) in consideration with (6.10, 6.11, 6.12 y 6.3)

$$k_{AC} = \frac{x^L_A \, x^L_C}{x^S_{AC}}$$
$$k_{BC} = \frac{x^L_C}{x^S_{BC}} \tag{6.14}$$

Considering that for the binary system *B–C*, taking into account the simplifications and assumptions, $k_{BC} = x^B_C = x^0_C$, where x^0_C is the solubility of component *C* in pure component *B*, and resolving the system of equation written above, we obtain simple expressions for the liquidus isotherms and distribution curves at constant temperature

$$x^L_C = x^0_C - \frac{\dfrac{k_{AC}}{k_{BC}}}{\dfrac{k_{AC}}{k_{BC}} + x^L_A}$$
$$x^S_{AC} = \frac{x^L_A}{x^L_A + \dfrac{k_{AC}}{k_{BC}}} \tag{6.15}$$

The expressions (6.15) establish the dependence of the solubility of the element *C* from the fifth group in the liquid phase on the concentration of element *A* and

the dependence of the composition of the solid phase on the composition of the liquid phase. That is, they permit the calculation of the diagram of state if the equilibrium constants k_{AC} and k_{BC} are known. This expression can be further simplified if the relation $\dfrac{k_{AC}}{k_{BC}}$ is denoted as k, called the *equilibrium constant*. Its value, as seen from (6.14), can be found from the experimental data on solubility and solid phase composition. Thus, using the analyzed method, the state diagrams can be calculated without using thermodynamic parameters as entropy and fusion temperature, which as already noted, are known with low accuracy only for some substances. In this method, these parameters are included automatically in their corresponding equilibrium constants, that are determined from experimental data, which is indeed an advantage of this method over other methods of calculation of the diagram of state. Perhaps the method of equilibrium constants was first used in semiconductor materials in the study of the liquidus isotherms in the *Ga–As–Cu* system. As a consequence, the equilibrium constants began to be used to interpolate and extrapolate experimental data for the systems such as *Ga–As–Si*, for example, and *A²B⁶–Si*. A notorious disadvantage of this method is that it can be successfully applied only to a limited number of near-ideal systems, such as $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}P$. The majority of the systems that are important from a practical point of view, since they can also be used to create various devices, cannot be considered ideal. Therefore, the method of chemical equilibrium constant cannot be applied to calculate the state diagram of such systems. In this case, the state diagrams are calculated using the classic method described in the equality of the chemical potentials in different equilibrium phases.

First consider this method in the system $A_xB_{1-x}C$ system. In this method, we shall also use the reactions (6.4) and (6.5) to construct the state diagram to find the chemical equilibrium constants. The equilibrium conditions of the phases of these reactions can be represented on the basis of equality of their respective chemical potentials, i.e.

$$\mu^L_A + \mu^L_C = \mu^S_{AC}$$
$$\mu^L_B + \mu^L_C = \mu^S_{BC} \tag{6.16}$$

Similar to the binary system described in Section 5.15, the chemical potentials in (6.16) for the components of the liquid phase are annotated as follows

$$\mu^L_A = \mu^0_A + RT\ln \gamma^L_A + RT\ln x^L_A$$
$$\mu^L_B = \mu^0_B + RT\ln \gamma^L_B + RT\ln x^L_B \qquad (6.17)$$
$$\mu^L_C = \mu^0_C + RT\ln \gamma^L_C + RT\ln x^L_C$$

And respectively for the solid phase

$$\mu^S_{AC} = \mu^0_{AC} + RT\ln \gamma^S_{AC} + RT\ln x^S$$
$$\mu^S_{BC} = \mu^0_{BC} + RT\ln \gamma^S_{BC} + RT\ln (1-x^S). \qquad (6.18)$$

As shown in chapter 5.15, (6.17) and (6.18) are substituted into (6.16)

$$\mu^0_A + RT\ln(\gamma^L_A x^L_A) + \mu^0_C + RT\ln(\gamma^L_C x^L_C) - \mu^0_{AC} - RT\ln (\gamma^L_{AC} x^S) = 0$$
$$\mu^0_B + RT\ln(\gamma^L_B x^L_B) + \mu^0_C + RT\ln(\gamma^L_C x^L_C) - \mu^0_{BC} - RT\ln [\gamma^L_{BC}(1-x^S)] = 0 \qquad (6.19)$$

After similar transformations made in Section 5.15 for a binary system, an arbitrary temperature can be written

$$RT\ln = \left[\frac{\gamma^L_A(T)\gamma^L_C(T)x^L_A(T)x^L_C(T)}{\gamma^S_{AC}(T)x^S(T)} \right] - RT_{AC}\ln \left[\frac{\gamma^L_A(T^M_{AC})\gamma^L_C(T^M_{AC})}{4\gamma^S_{AC}(T^M_{AC})x^S(T^M_{AC})} \right] +$$

$$+ \Delta S^0_{AC} (T^M_{AC}) (T^M_{AC} - T) = 0$$

$$(6.20)$$

$$RT\ln = \left\{ \frac{\gamma^L_B(T)\gamma^L_C(T)x^L_B(T)x^L_C(T)}{\gamma^S_{BC}(T)[1-x^S(T)]} \right\} - RT^M_{BC}\ln \left\{ \frac{\gamma^L_B(T^M_{BC})\gamma^L_C(T^M_{BC})}{4\gamma^S_{BC}(T^M_{BC})[1-x^S(T^M_{AC})]} \right\} +$$

$$+ \Delta S^0_{BC} (T^M_{BC}) (T^M_{BC} - T) = 0.$$

To calculate of the state diagrams based on (6.20), or, in other words, to determine the compositions of equilibrium liquid and solid phases, it is necessary to express the activity coefficients through interaction parameters. As a rule, for the majority of the A^3B^5 systems, the dependences of the activity coefficients on the composition and the binary interaction parameters are calculated on the basis of a regular approximation. These functions published in the literature are summarized below in (6.21)

$$RT\ln\gamma^L_A = \alpha^L_{AB}(x^L_B)^2 + \alpha^L_{AC}(x^L_C)^2 + x^L_B x^L_C(\alpha^L_{AB} - \alpha^L_{BC} + \alpha^L_{AC})$$
$$RT\ln\gamma^L_B = \alpha^L_{BC}(x^L_C)^2 + \alpha^L_{AB}(x^L_A)^2 + x^L_C x^L_A(\alpha^L_{BC} - \alpha^L_{AC} + \alpha^L_{AB}) \qquad (6.21)$$
$$RT\ln\gamma^L_C = \alpha^L_{AC}(x^L_A)^2 + \alpha^L_{BC}(x^L_B)^2 + x^L_A x^L_B(\alpha^L_{AC} - \alpha^L_{AB} + \alpha^L_{BC})$$

The activity coefficients for the solid phase using the regular solutions model are annotated as follows

$$RT\ln\gamma^S_{AC} = \alpha^S_{AC-BC}(x^S)^2$$
$$RT\ln\gamma^S_{BC} = \alpha^S_{AC-BC}(1-x^S)^2 \qquad (6.22)$$

To calculate the ternary phase diagram, three interaction parameters are needed: the temperature and the fusion entropies of the binary alloys AC and BC. This data can be found in the literature. Considering the law of conservation of mass

$$x^L_A + x^L_B + x^L_C = 1, \qquad (6.23)$$

that permits to reduce the number of unknown variables, to calculate the state diagrams by expressions (6.20), (6.21), (6.22), and (6.23), as well as the necessary thermodynamic data. The description of this method is discussed in more detail in various books, articles, and, in particular, in the second volume of the book "Heterostructure Lasers" by H. Casey and M. Panish , published by Academic Press, 1978.

When calculating the diagrams of state in the $A_xB_yC_{1-x-y}D$ quaternary systems, where A, B, and C are elements from the third group of the periodic table, and D is of the fifth group, the calculation method is similar to the method for ternary systems, since the interchange of atoms in the solid phase takes place only in the metallic sublattice. However, in the case of $A_xB_yC_{1-x-y}D$, when the atoms A and B are substituted in the metallic sublattice and the atoms of C and D are substituted in the nonmetallic sublattice, the calculations of the phase diagrams become more complicated. In such systems, the equilibrium equations are formally annotated as chemical potentials in the form of equations

$$\mu^L_A + \mu^L_C = \mu^S_{AC}$$
$$\mu^L_B + \mu^L_C = \mu^S_{BC}$$
$$\mu^L_A + \mu^L_D = \mu^S_{AD}$$
$$\mu^L_B + \mu^L_D = \mu^S_{BD} \qquad (6.24)$$

Without going into details, we note that, in the case of the quaternary system of the $A_xB_yC_{1-x-y}D$ type, the following additional conditions on the chemical potentials of the components of the solid phase arise

$$\mu^S_{AC} + \mu^S_{AD} = \mu^S_{BC} + \mu^S_{BD} \tag{6.25}$$

Using the mass balance equation for the liquid and solid phases, equations (6.24), (6.25) and the expressions for the activity coefficients, and the required values of the thermodynamic parameters such as the entropy, enthalpy, and fusion temperature of the respective components of the system, the desired state diagram can be calculated. A more detailed information concerning these calculations can be found, for example, in the books: "Liquid Phase Epitaxy of Electronic, Optical and Optoelectronic Material", edited by Peter Capper and Michael Mauk. Wiley series in Material for Electronic & Optoelectronic Application, 2007, and in the scientific literature relevant to this field.

BIBLIOGRAPHY

I realize that many students or teachers of thermodynamics and/or phase diagrams would prefer to have additional literature to improve their knowledge of thermodynamics as a science or as an engineering tool. Below, there is a list of articles that review the basic concepts of thermodynamics and phase diagrams.

The references numbered 1-33 in the list contain extensive additional discussion of the material presented in Chapters 1, 2, and 3. Among them, we would highlight the works of Lev Landau and E.N. Lifshitz, an extensive and very comprehensive text on the concepts and topics of thermodynamics, and a brief classic work by Max Planck (references 16 and 29, respectively).

Topics on phase diagrams are very important for students of materials science, metallurgy, and other sciences. The references listed 34 through 44 are an excellent and comprehensive series of reference books that provide extensive information on the concepts of the coexistence of different phases in materials.

1. M. W. Zemansky y Richard H. Dittman, *Heat and Thermodynamics*, 7th ed., McGraw-Hill Inc., USA, 1996.
2. Leopoldo García-Colín Scherer, *Introducción a la Termodinámica* Clásica, Trillas, México, 1990.
3. Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatics*, 2nd ed., New York: John Wiley & Sons, USA, 1985.
4. P. S. Epstein, *Textbook of Thermodynamics*, New York: John Wiley & Sons, USA, 1949.
5. W. Gibbs, *The collected Works of J. Willard Gibbs*, vol. I, Thermodynamics, Yale University Press, USA, 1948.
6. E. A. Guggenheim, *Thermodynamics: an advanced treatment for chemists and physicists*, 8th ed., North Holland Publishing, 1986.
7. A. B. Pippard, *The Efoments of Classical Thermodynamics*, Cambridge University Press, UK, 1957.
8. N. K. Adam. *The Physics and Chcmistry of Surfaces*, 3rd ed., Oxford University Press, UK, 1941.
9. Arthur W. Adamson, Alice P. Gast., *Physical Chemistry of Surface*, 6th ed.,]ohn Wiley, EUA, 1997.

10. Mihael Binnewies, E. Milke, *Thermochemical Data of Elements and Compounds*, 2nd, rev. and extended ed., Wiley-VCH, 2002.
11. P. W. Atkins, *Molecular Quantum Mechanics*, 5th. ed., Oxford University Press, USA, 2010.
12. Ihsan Barin, *Thermochemical Data of Pure Substances*, 3rd ed., VCH Verlagsgesellschaft mbH, 1995.
13. Duane E. Roller, *The Early Development of the Concepts of Temperature and Heat*, Harvard University Press, UK, 1961.
14. Gilbert W. Castellan, *Physical Chemistry*, 3rd. ed., Addison-Wesley, USA. 1983.
15. *Temperature, its Measurement and Control in Science and Industry*, vol. 2, edited by H. C. Wolfe, New York and London, 1955.
16. L. D. Landau y E. M. Lifshitz, *Statistical Physics*, 3a. ed., Elsevier, UK, 1975.
17. J. R. Waldram, *The Theory of Thermodynamics*, Cambridge University Press, UK, 1985.
18. H. Ted Davis, *Statistical Mechanics of Phases. Interfaces and Thin Films*, Wiley-VCH, USA, 1996.
19. Kenneth G. Denbigh, *The Principles of Chemical* Equilibrium, 4th ed., Cambridge University Press, UK, 2012.
20. Ralph Fowler, E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge University Press, UK, 1965.
21. M. L. McGlashan, *Chemical Thermodynamics*, London; New York: Academic Press, 1979.
22. W.J. Moore, *Basic Physical Chemistry*, Prentice-Hall, New York, 1983.
23. I. Müller, T. Ruggeri, *Extended Thermodynamics,* Springer-Verlag New York, USA, 1993.
24. Terrell L. Hill, *An Introduction to Statistical Thermodynamics*, 2nd ed., Addison-Wesley Pub Co, USA, 1962.
25. David Jou, George Lebon, *Extended Irreversible Thermodynamics*, 4th ed., Springer Dordrecht, 2010.
26. Charles Kittel, Herbert Kroemer, *Thermal Physics*, 2nd. ed., W. H. Freeman, USA, 1980.
27. Eldon L. Knuth, *Introduction to Statistical Thermodynamics*, McGraw-Hill, USA, 1966.
28. O. K. Rice, *Critical Phenomena in Thermodynamics and Physics of Matter*, Rossini, F.D., Oxford University Press, London, UK, 1955.
29. M. Planck, *Treatise on Thermodynamics*, 3rd revised ed., Dover Publications, EUA, 2010.

30. F. H. MacDougall, *Thermodynamics and Chemistry*, 3rd ed., John Wiley & Sons, USA, 1939.
31. I. Prigogine y R. Defay, *Chemical Thermodynamics*, Longmans Green, London, 1954.
32. S. R. De Grott *Thermodynamics of Irreversible Process*, North-Holland Publishing Comp., Amsterdam. 1951.
33. I. Prigogine, *Introduction to Thermodynamics of irreversible Processes*, Charles C Thomas Publishing, Springfield, IL, 1955
34. D. A. Porter, K. E. Easterling and M. Y. Sherif, *Phase Transformation in Metals and Allays*, 3rd ed., CRC Press, 2009.
35. M.F. Ashby y D. R. H. Jones, *Engineering Malerials*, 5th ed., Elsevier, 2018.
36. Sir Alan Cottrell, *An Introduction to Metallurgy*, 2nd ed., CRC Press, 1997.
37. Y. K. Rao, "Thermodynamics of Phase Diagrams", en A. M. Alper (ed.), *Phase Diagrams: Materials Science and Technology,* vol. l. Theory, Principles and Techniques of Phase Diagrams, Academic Press, USA, 1970.
38. N. Saundes y A. P. Miodownik, CALPHAD: *Calculation of Phase Diagrams: A Comprehensive Guide*, Pergamon Materials Series Volume I, Pergamon, UK, 1998.
39. R. A. *Swalin, Thermodynamics of Solid*s, 2nd ed., Wiley-VCH, USA, 1972.
40. Albert G. Guy, *Introduction to Materials Science*, McGraw-Hill, USA, 1972.
41. T. B. Massalski, *Phase Diagrams in Materials Science*, Metallurgical and Materials Transactions A., vol. 20, 1295-1323 (1989)
42. I. Barin, O. Knacke y O. Kubaschewski, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag Berlin Heidelberg, 1977.
43. O. Kubaschewski, C. B. Alcock y P.J. Spencer, *Metallurgical Thermochemistry,* 6th ed., Pergamon Press, UK, Oxford, New York, 1993.
44. A. Prince, *Alloy Phase Equilibrium*, Elsevier Publishing, Amsterdam, London and New York, 1966.

The presented book is written by Dr. Viatcheslav Andreevich Mishurnyi, a specialist in the field of semiconductor physics and technology of epitaxial crystal growth by liquid-phase epitaxy. A significant part of his activity, in addition to scientific work, was teaching. This book is the product of several years of teaching students in the physical engineering and optoelectronics programs at the Autonomous University of San Luis Potosí (UASLP). It deals with an important area of materials science and technology such as thermodynamics related to various phase diagrams. Special attention is paid to phase diagrams of III-V systems and solid solutions based on them, as well as methods of their experimental and theoretical study. The material is presented in a simple and accessible form for students of different levels of background.