

# Chapter 2

## Equilibrium Background of Processes Initiated by Heating and Ehrenfest's Classification of Phase Transitions

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### 2.1 Introduction

For a long time, transmutations, metamorphoses, and changes of substances (of fluid and solid bodies) have been the original subject of any investigation of alchemists as well as of more recent chemists. One of the oldest schemes of classification in chemistry was dividing chemical reactions into classes of decompositions (analyses), combinations (syntheses), substitutions (single replacements), and metatheses (double displacements). The invention of heat engines<sup>1</sup> turned the attention of scientists to transitions between liquid water and its steam and led to the first quantitative relationship (today known as the Clapeyron equation) in 1834 [1] describing the phase transformation and later to the foundation of thermodynamics as a new discipline of physics by William Thomson, later Lord Kelvin (1849) [2], and Clausius (1850) [3].

Simultaneously, by virtue of the results by Cagniard de la Tour (1822) [4], Andrews (1869) [5], and van der Waals (1873) [6], critical behavior of fluids and connections between the liquid and gaseous state of fluids were discovered. In the 1860s and 1870s, publications appeared concerning the application of the Clausius–Clapeyron equation to dissociation reactions (see Kipnis [7]), and two key works: on the mass action law by Guldberg and Waage [8] and on heterogeneous equilibria by Gibbs [9]. New knowledge on fluid and dissociation transitions as well as the results of thermochemical, electrochemical, and osmotic measurements led to the

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<sup>1</sup>The condenser as a substantial part of steam engine was patented by Watt in 1769.

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formation of a new chemical discipline, physical chemistry, which was presented by a new scientific periodical, *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre* (*Journal of Physical Chemistry, Stoichiometry and Affinity*) founded by Ostwald, van't Hoff, and Arrhenius in 1887. The following development of physical chemistry and thermodynamics was then accomplished by Gilbert Lewis (1907) by his “new system of thermodynamic chemistry” [10], which became after translation into German to be “neues System der chemischen Thermodynamik” [11] and which later resulted in an influential classical textbook of chemical thermodynamics by Lewis and Randall [12] in 1923.

Aside from chemical thermodynamics, mineralogists and metallurgists found the succession of changes of a substance state observed at heating (or cooling) a useful tool to identify the state of solid substances, and after the thermocouple was discovered and applied in laboratories the method of thermal analysis was established (for the history of thermal analysis: e.g., Šesták 2005 [13]).

Efforts to improve iron and steel products connected with studies of phase composition of metallic samples found an important support in the theory of phase diagrams developed by Roozeboom (1854–1907), who applied the Gibbs phase rule to alloys (1900) [14] and wrote a fundamental book on phase equilibria [15], which was finished after his death (in 1907) by his students. One of the students, Schreinemakers, continued to develop the theory of phase equilibria in multicomponent systems [16].

In 1882, Kamerlingh Onnes was appointed a professor of experimental physics and meteorology at Leiden University, and he reorganized the physical laboratory into a cryogenic laboratory, which enabled him to verify the law of corresponding states by his friend van der Waals. In 1892 his apparatus for liquefaction of air was constructed and in 1906 a large hydrogen liquefier was built. Using the evaporation of liquid hydrogen, he succeeded to liquefy helium (on 10 July 1908), and subsequently he discovered superconductivity on deeply cooled mercury (in 1911) [17]. In this laboratory, W.H. Keesom and his co-workers observed an unusual phase transition (lambda transition) in liquid helium [18]:

...that raised the issues of how many types of transition there were and how they could be classified. In 1933, Paul Ehrenfest, also working in Leiden, introduced the first comprehensive scheme for classifying phase transitions, which here will be referred to as the Ehrenfest classification [19]. The new helium transition was classified by the Ehrenfest scheme as a “second-order transition” and the ordinary phase transitions as “first-order transitions.”

as has been described by Jaeger (1998) [20]. The application of Ehrenfest's classification scheme was discussed without its author because Ehrenfest died shortly after its publication in September 1933.

The scheme of Ehrenfest's classification is based phenomenologically on temperature and pressure dependences of the Gibbs free energy  $G$ , the change of which at any phase equilibrium is equal to zero ( $\Delta G = 0$ ). Difference between the first-order and second-order transitions is hidden in the behavior of the first and second derivative of  $\Delta G$  with respect to temperature  $T$  and pressure  $P$ : in the case of first-order transition, the volume  $V = (\partial G / \partial P)_T$  as well as the entropy  $S = (\partial G / \partial T)_P$  are changed abruptly at the transition point exhibiting

the differences  $\Delta V \neq 0$  and  $\Delta S \neq 0$ . For the second-order transitions, these differences are zero ( $\Delta V = 0$  and  $\Delta S = 0$ ); however, the quantities that are the second derivatives of  $G$ , that is, heat capacity  $C_P = T(\partial^2 G/\partial T^2)_P$ , thermal expansion  $\alpha = (\partial^2 G/\partial P\partial T)/V$ , and isothermal compressibility  $\beta = (\partial^2 G/\partial P^2)_T/V$ , are changed stepwise at the transition point with differences  $\Delta C_P \neq 0$ ,  $\Delta\alpha \neq 0$ , and  $\Delta\beta \neq 0$ . This scheme seemed to be extendable in two directions: (1) to nonclassical thermodynamic systems where the first derivatives of  $G$  other than volume and entropy exist (e.g., magnetic induction  $\mathbf{B} = (\partial G/\partial \mathbf{H})_{T,P}$  where  $\mathbf{H}$  means the intensity of magnetic field); and (2) to the third-order (or higher-order) transitions for which the stepwise transition appears neither for a quantity that is the first derivative nor for a quantity being the second derivative but until at a quantity which is the third-order (or higher-order) derivative of the Gibbs free energy,  $G$ .

The first-order transitions obey the Clapeyron equation expressing the change of the transition temperature  $dT$  with the change of pressure  $dP$ :  $dT/dP = \Delta V/\Delta S = T\Delta V/\Delta H$  (where  $\Delta H$  means the change of enthalpy  $H$ ), which is derived according to rules of partial differentiation:

$$\frac{dP}{dT} = -\frac{\left(\frac{\partial \Delta G}{\partial T}\right)_P}{\left(\frac{\partial \Delta G}{\partial P}\right)_T} \quad (2.1)$$

For the first-order transitions at which a gaseous phase participates (boiling/condensation or sublimation/deposition), the Clausius [3] approximation  $\Delta V \approx RT/P$  is used and the Clausius–Clapeyron equation  $dT/dP = (RT^2/P)/\Delta H$  is found.

As Ehrenfest proposed, the second-order transitions should obey relationships derived from Eq. (2.1) using the l'Hôpital rule [21]:

$$\frac{dT}{dP} = -\frac{\left(\frac{\partial \Delta S}{\partial P}\right)}{\left(\frac{\partial \Delta S}{\partial T}\right)} = VT \frac{\Delta\alpha}{\Delta C_P} = -\frac{\left(\frac{\partial \Delta V}{\partial P}\right)}{\left(\frac{\partial \Delta V}{\partial T}\right)} = -\frac{\Delta\beta}{\Delta\alpha} \quad (2.2)$$

The equations analogous to the Ehrenfest relationships were derived and used by Rutgers for superconducting transitions [22].

Melting, freezing, boiling, condensation, sublimation, deposition, and classical phase transformations belong to a class of the first-order transitions. According to *The Great Soviet Encyclopedia* [23]: “Examples of the second-order phase transitions, which take place below a specific temperature in each case, include the occurrence of a magnetic dipole moment in a magnetic substance upon a transition from the paramagnetic to the ferromagnetic state, the occurrence of anti-ferromagnetic ordering upon a transition from the paramagnetic to the anti-ferromagnetic state, the occurrence of superconductivity in metals and alloys, the occurrence of superfluidity in  $^4\text{He}$  and  $^3\text{He}$ , the ordering of alloys, and the spontaneous polarization of a substance upon a transition from the para-electric to the ferro-electric phase.” Also, the glass transition was sometimes included into the class of second-order phase transitions.

The Ehrenfest classification was widely accepted after the classic book by A. Brian Pippard was published in 1957 [24] and remains an influence also after generalized thermodynamics was established by Tisza [25] and Callen (1960) [26], who found that from the point of view of their thermodynamics only two types of transitions are possible: the first-order transition and the transition occurring when the system passes through its critical point. At the end, as it was concluded by Jaeger [20]: “by the 1970s, a radically simplified binary classification of phase transitions into “first-order” and “continuous” transitions was increasingly adopted.”

Writing a chapter in a monograph on ceramic materials [27], the discrepancies I encountered in different approaches to phase transitions encouraged me to search for an “independent approach” overcoming the differences in education of physicists and chemists. It seemed to me that the discussions on classification of transitions had not a sufficiently defined conceptual framework in several aspects, which raised the following questions:

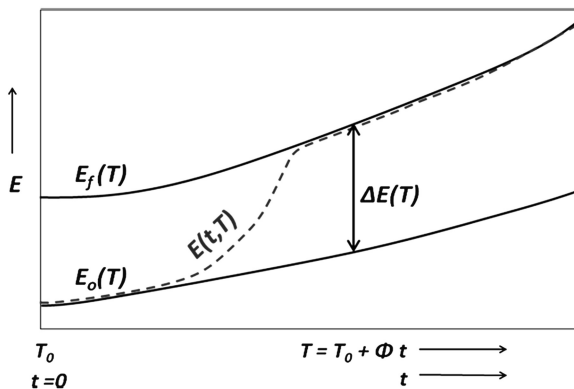
1. Where is the boundary between a chemical reaction and a phase transition? Besides the pure first-order transition in unary systems and simple homogeneous chemical reactions, there exist a series of changes known as decompositions, decays, incongruent melting, eutectic melting, partial dissolution (if not only unary systems are considered), etc., which are known in phase diagrams but yet are not considered as objects of classification.
2. Why is only the Gibbs free energy (which corresponds to equilibria of a closed isobaric isothermal system) used in assessing the class of transition, when transitions can be also observed under isochoric conditions or under conditions of partly open systems? [28].
3. Is the classification scheme valid also for the transitions where metastable or quasi-stable states are involved?
4. What is the relationship between a critical transition (a system passing through the critical point) and a second-order transition (relationship between Ehrenfest’s and Tisza’s approach)?

This work should be considered as an attempt to join the discussion on classification of transitions that was evoked by Ehrenfest’s proposal from 1933, with some aspects rooted in the theory and practice of thermal analysis and of phase equilibria.

## **2.2 Extent of Transition and Equilibrium Background of Processes**

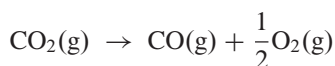
According to one of the recent books on thermal analysis (TA) [29], “TA is the study of the relation between sample property and its temperature as the sample is heated or cooled in a controlled manner,” when “A techniques exists for each property or physical quantity that is measured versus temperature . . .”

**Fig. 2.1** Dependence of state quantity  $E$  (full line) and course of process (dashed line)

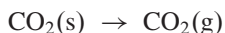


The behavior of a substance on heating or cooling is determined by two aspects: the thermodynamic (what is the state of stable equilibrium to which the sample should approach) and the kinetic (which way and at what rate the sample is approaching its stable equilibrium state). A TA curve generally represents a dependence of sample property  $E$  as a function of time  $t$  and temperature  $T$  at an adjusted regime of temperature change as a (linear in classical use) function of time  $T = T(t)$ . The sample response to the continuous temperature change is detected as a dependence of a sample property  $E = E(T(t), t)$ , which consists of two principally separable parts (see Fig. 2.1): (1) a *smooth monotonous behavior* caused by temperature change scaling the heat capacity without any change of chemical and/or phase composition and (2) *rapid or gradual behavior* caused by change of chemical and/or phase composition or, in other words, resulting from a process at which the identity of the substance is changed.

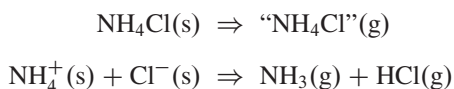
The processes in which sample identity is changed are commonly referred to as chemical reactions (when the chemical composition is changed) or phase transitions (without change of chemical composition). However, the term *chemical composition* has two different meanings: (1) *microscopic composition* (contents of microscopic species, e.g., molecules and ions) and (2) *macroscopic composition* (contents of macroscopic substances, e.g., elements and compounds). Under the conditions of a closed thermodynamic system the macroscopic composition of a homogeneous system must be constant while the microscopic composition can be changed by internal *homogeneous reactions*. For example, when considering a homogeneous gas with a macroscopic composition corresponding to the carbon to oxygen ratio  $C:O = 1:2$ , the microscopic composition at sufficiently low temperature corresponds to 100% of  $CO_2$  molecules, whereas at high temperatures a part of the  $CO_2$  molecules dissociates into  $CO$  and  $O_2$  molecules following the reaction



(so that the microscopic composition is changed) without any change of the macroscopic composition given by the ratio C:O = 1:2. On the other hand, the same substance (CO<sub>2</sub>) can change its identity by a phase transition, for example, by sublimation:



The difference between the chemical reaction and the phase transition can become unclear, for instance, in the case of ammonium chloride (salmiak) NH<sub>4</sub>Cl when its sublimation is realized by means of microscopic composition change:



This is the reason why it is useful to introduce a more general definition of (generalized) phase transition as a process (change of state) at which *phase composition* (content of individual chemical phases) is changed and to define the *transition point* as a point (on a temperature scale in TA) where a new phase (one or a set of new phases) in the sample is formed or where some (one or a set) of coexisting phases in the sample disappears.

Introducing the definition of “generalized phase transition,” also, *heterogeneous reactions* such as thermal decompositions, for example:



can be named and described as the phase transitions. The advance of any transition process at which a new phase is formed or any original phase disappeared can be called the *extent of transition*  $\xi$ . In the case of homogeneous reactions (where no new phase is formed and no original phase becomes extinct), the quantity *degree of conversion*  $\lambda$  will be used instead of  $\xi$ .

A typical object of study is a section of TA curve consisting of three parts: (1) the *initial stage*, expressing temperature dependence of a given property for the initial state of the sample, (2) the *transitional stage* at which a sample property depends on the extent of transition  $\xi$  (or degree of conversion  $\lambda$ ), and (3) a *final stage* expressing temperature dependence of a purely resulting state (Fig. 2.1).

The stages on TA curve can be characterized by the following features:

(i)	Initial stage:	$\xi = 0$	$E(T, t) = E_0(T)$
(ii)	Transitional stage:	$0 < \xi < 1$	$E(T, t) = E_0(T)(1 - \xi) + E_f(T)\xi$
(iii)	Final stage:	$\xi = 1$	$E(T, t) = E_f(T)$

where  $E_0$  and  $E_f$  are the properties of the initial and final state, respectively. The extent of transition can be defined phenomenologically as

$$\xi(T, t) = \frac{E(T, t) - E_0(T)}{E_f(T) - E_0(T)} \quad (2.3)$$

and if the integral change of property  $E$  connected with accomplishing the transition is introduced as  $\Delta E(T) = E_f(T) - E_0(T)$ , the value of property  $E(T)$  is given by

$$E(T, t) = E_0(T) + \xi(T, t)\Delta E(T) \quad (2.4)$$

In isothermal ( $T = \text{const}$ ) kinetic studies, the *isothermal degree of conversion*  $\alpha$  is defined as

$$\alpha(T, t) = \frac{E(T, t) - E(T, t = 0)}{E(T, t \rightarrow \infty) - E(T, t = 0)} \quad (2.5)$$

where quantity  $E(T, t \rightarrow \infty)$  has the meaning of the value of property  $E$  corresponding to equilibrium at temperature  $T$  and can be marked as  $E_{\text{eq}} = E(T, t \rightarrow \infty)$ . Then using Eq. (2.4) and assuming  $E(T, t = 0) \approx E_0(T)$ , the relationship for isothermal extent of transition<sup>2</sup>  $\alpha$  can be rewritten into

$$\alpha(T, t) = \frac{E(T, t) - E_0(T)}{E_{\text{eq}}(T) - E_0(T)} \quad (2.6)$$

where  $E_{\text{eq}}(T)$  is given by the equation

$$E_{\text{eq}}(T) = E_0(T) (1 - \xi_{\text{eq}}(T)) + \xi_{\text{eq}}(T)E_f(T) = E_0(T) + \xi_{\text{eq}}(T)\Delta E(T) \quad (2.7)$$

where  $\xi_{\text{eq}}(T)$  means equilibrium degree of conversion, which represents the temperature depending on the *equilibrium background of the process*, therefore defined as

$$\xi_{\text{eq}}(T) = \frac{E_{\text{eq}}(T) - E_0(T)}{E_f(T) - E_0(T)} \quad (2.8)$$

Comparing Eqs. (2.3), (2.6), and (2.8), the following simple relationship between the general ( $\xi$ ), isothermal ( $\alpha$ ), and equilibrium ( $\xi_{\text{eq}}$ ) extent of transition is found [30]:

$$\xi(T, t) = \alpha(T, t)\xi_{\text{eq}}(T) \quad (2.9)$$

and substituting Eq. (2.9) into Eq. (2.4) we obtain

$$E(T, t) = E_0(T) + \alpha(T, t)\xi_{\text{eq}}(T)\Delta E(T) \quad (2.10)$$

In the case of linear heating rate  $\Phi = dT/dt = \text{const}$  so that  $T = T_0 + \Phi(t - t_0)$ , the rate of quantity change  $dE/dt$  is given by

$$\frac{dE}{dt} = \left[ \frac{dE_0}{dT} + \alpha(T, t) \left( \frac{d\xi_{\text{eq}}}{dT} \Delta E(T) + \xi_{\text{eq}}(T) \frac{d\Delta E(T)}{dT} \right) \right] \Phi + \frac{d\alpha}{dt} \xi_{\text{eq}} \Delta E \quad (2.11)$$

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<sup>2</sup>*Degree of conversion* in the case of homogeneous reactions.

At the extremely slow heating rate  $\Phi \rightarrow 0$  we can assume the value of  $\alpha$  is reaching unity ( $\alpha \rightarrow 1$ ) and the rate of transition reaches zero ( $d\alpha/dt \rightarrow 0$ ). Then Eq. (2.11) is simplified into

$$\lim_{\Phi \rightarrow 0} \frac{dE}{dt} = \left[ \frac{dE_0}{dT} + \left( \frac{d\xi_{eq}}{dT} \Delta E + \xi_{eq} \frac{d\Delta E}{dT} \right) \right] \Phi = \left( \frac{dE}{dT} \right)_{eq} \Phi \quad (2.12)$$

where the quantity

$$\left( \frac{dE}{dT} \right)_{eq} = \frac{dE_0}{dT} + \left( \frac{d\xi_{eq}}{dT} \Delta E + \xi_{eq} \frac{d\Delta E}{dT} \right) \quad (2.13)$$

can be called the “equilibrium background” of the process under TA study.

At differential scanning calorimetry (DSC), the “equilibrium background” is found for enthalpy  $H$  substituted instead of quantity  $E$ , where it is clear that the derivative of enthalpy with respect to temperature is the heat capacity ( $dH_0/dT = C_{P0}$ ) and its change caused by transition ( $d\Delta H/dT = \Delta C_P$ ):

$$\left( \frac{dH}{dT} \right)_{eq} = C_{P0} + \left( \frac{d\xi_{eq}}{dT} \Delta H + \xi_{eq} \Delta C_P \right) \quad (2.14)$$

Similarly, at thermogravimetry (TG) we found for the content (mole amount) of free (shared between the sample and its gaseous surroundings) component  $N_f = W_f/M_f$  ( $W_f$ , weight amount;  $M_f$ , molar weight of free component  $f$ ) substituted instead of quantity  $E$ , where derivative of free component content with respect to temperature is the solubility coefficient  $\eta_f$ , slope on the temperature dependence of equilibrium solubility ( $dN_{f0}/dT = \eta_{f0}$ ) and its change caused by the transition ( $d\Delta N_f/dT = \Delta \eta_f$ ):

$$\frac{dN_f}{dT} = \eta_{f0} + \left( \frac{d\xi_{eq}}{dT} \Delta N_f + \xi_{eq} \Delta \eta_f \right) \quad (2.15)$$

In both cases the equilibrium background is determined mainly by the temperature dependences of  $\xi_{eq}(T)$  and  $(d\xi_{eq}(T)/dT)$ , which could be used to classify the processes studied by TA.

## 2.3 Types of Processes with Respect to Temperature Dependences of Equilibrium Extent of Transition

As was said, the process of transition or reaction at heating is resultant of both the thermodynamic (equilibrium) and kinetic factors. The equilibrium part of factors consists of (a) *initial state of sample*, (b) *character of contact between sample and surroundings*, and (c) *the state of surroundings*.



From the point of view of thermodynamics, there are two possible classes of the initial state of the sample: *stable equilibrium state* and *metastable state*. The processes of samples that are not in stable equilibrium are independent on the equilibrium background.

Contact between the sample and surroundings under TA conditions can be realized by (1) “isochoric” conditions: sample closed in a sealed tube (ampule); (2) “dynamic atmosphere:” sample in contact with flowing controlled atmosphere of a given pressure and given activities of volatile components; and (3) “static atmosphere:” sample is exposed to surrounding atmosphere (or vacuum) of a given pressure but of uncontrolled composition.

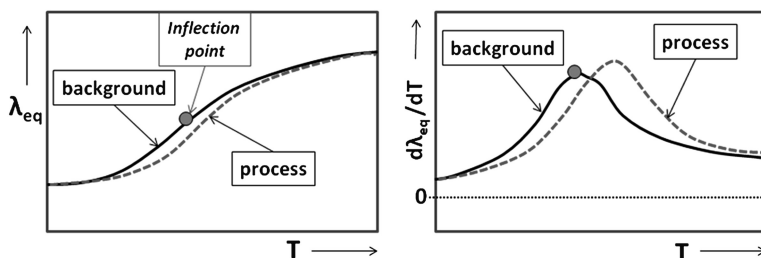
It should be noted that the state of complete stable thermodynamic equilibrium of a classical system (without influence of external fields and surface phenomena) includes several particular equilibria:

1. Homogeneous equilibria between the chemical species inside each phase of the system
2. Phase equilibrium (between the phases coexisting in the system) realized through
  - (a) Equality of pressure
  - (b) Equality of temperature
  - (c) Equality of chemical activity of all macroscopic components
3. Equilibrium between the system and its surroundings realized through
  - (a) Equality of pressure
  - (b) Equality of temperature
  - (c) Equality of chemical activity of free macroscopic components.

Some of the aforementioned particular equilibria are realized without a delay (e.g., equality of pressure); however, the reaching of particular equilibria introduced under points 1, 2c, and 3c require (mainly at the lower part of temperature range) a long time to be accomplished.

The maximum number of coexisting phases is limited by a number of independent macroscopic components of the system. The simplest phase relationships are exhibited by unary (one-component) systems and binary (two-component) systems. The processes occurring in unary and binary systems can be divided into the following classes:

1. *Monotropic process*, for which the initial state of sample is unstable (or metastable). The initial degree of transition is zero ( $\xi(T_0)=0$ ) and the equilibrium extent of transition equals to unity ( $\xi_{eq}(T)=1$ ) over the whole temperature range. The rate of monotropic processes is given only by the kinetic aspects without any influence of the equilibrium aspects. Monotropic phase transitions, oxidation processes, degradation of organic substances, and relaxation of frozen states (including glass transitions) are examples of this type of process.



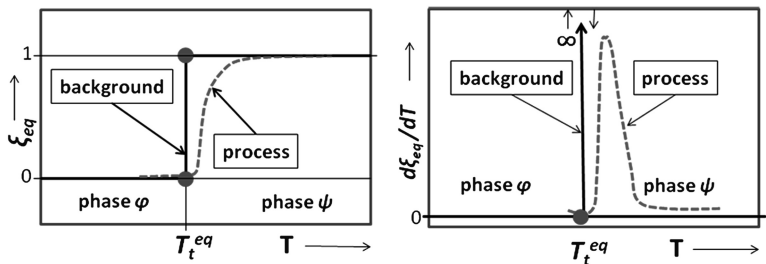
**Fig. 2.2** Equilibrium background  $\lambda_{eq}$  of a homogeneous reaction (full lines) and the course of the process (dashed lines)

2. *Homogeneous reaction*, for which the equilibrium degree of conversion  $\lambda_{eq}$  is a smooth function of temperature going from zero to unity through an inflection point but without any transition point. Derivative of equilibrium with respect to temperature shows one maximum corresponding to the mentioned inflection point. The temperature-dependent equilibrium of the nitrogen dioxide monomer and dimer is an example of such a process. Homogeneous reactions, as they have no transition point, are not included in transitions, and the impact of their behavior is considered as a reason for smooth temperature variation of heat capacity<sup>3</sup>  $C_P(T)$  and of free component solubility  $N_f(T)$  (Fig. 2.2).
3. *Sharp transition*,<sup>4</sup> for which the initial state of the sample has zero extent of transition and the equilibrium extent of transition jump at transition temperature  $T_t$  from zero to unity. The class corresponds fully to the first-order transition in Ehrenfest's classification (phase transitions including melting, boiling, and sublimation transitions in unary systems under isobaric–isothermal conditions), but it includes also decompositions such as  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$  or  $2\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O}$  or  $3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + \frac{1}{2}\text{O}_2$  and an eutectic melting (passage through the eutectic point). Derivative of the equilibrium degree ( $d\xi_{eq}/dT$ ) at the transition temperature jumps from zero to infinity and then (at the same temperature) jumps back to zero. Both transition points (one at which the new phase is formed and the other where the old phase disappears) are situated at the transition temperature  $T_t$  (Fig. 2.3).
4. *Gradual transition*,<sup>5</sup> where the initial state of the sample corresponds to zero extent of transition and the equilibrium extent of transition is zero but increases at the initial temperature  $T_{in}$  where the new phase is formed and reaches unity at the final temperature  $T_{fin}$  where the original phase has disappeared. The gradual transition corresponds to the passage of the system through a two-phase field of a phase diagram, for example, from solidus to liquidus curve at fusion or between solvus curves limiting the field of immiscibility of solid solutions.

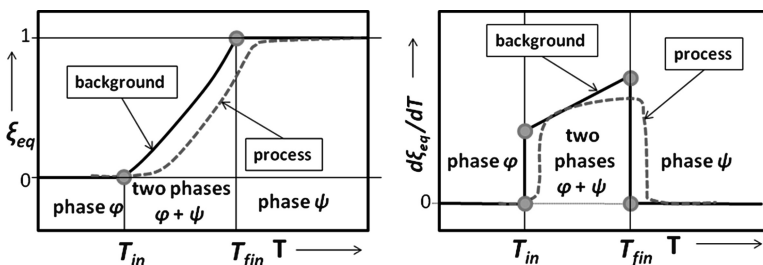
<sup>3</sup>See Chap. 3 in this book.

<sup>4</sup>The name is taken from Mats Hillert's book [31].

<sup>5</sup>The name is taken from Hillert [31].



**Fig. 2.3** Equilibrium background  $\xi_{eq}$  of the sharp transition (full lines) and the course of the process (dashed lines)

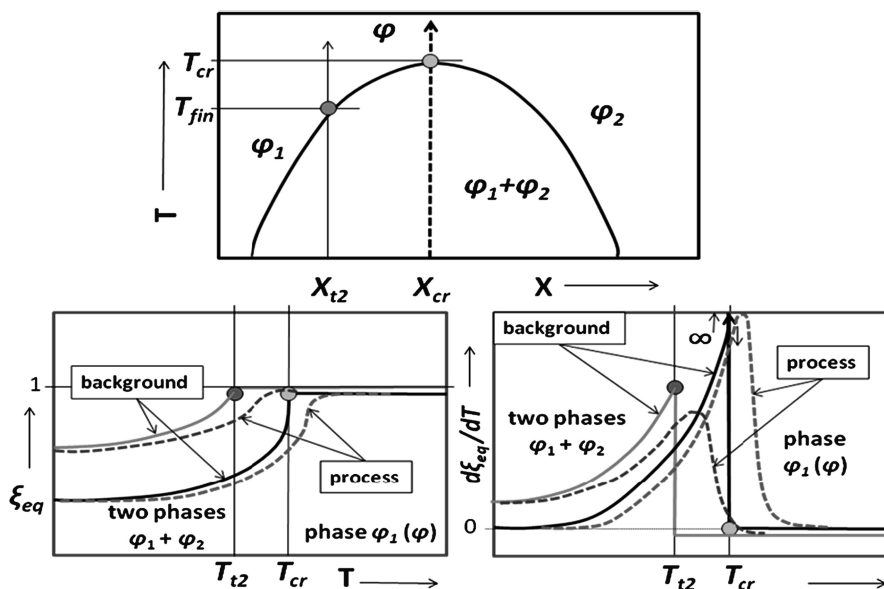


**Fig. 2.4** Equilibrium background  $\xi_{eq}$  of the gradual transition (full lines) and the course of the process (dashed lines)

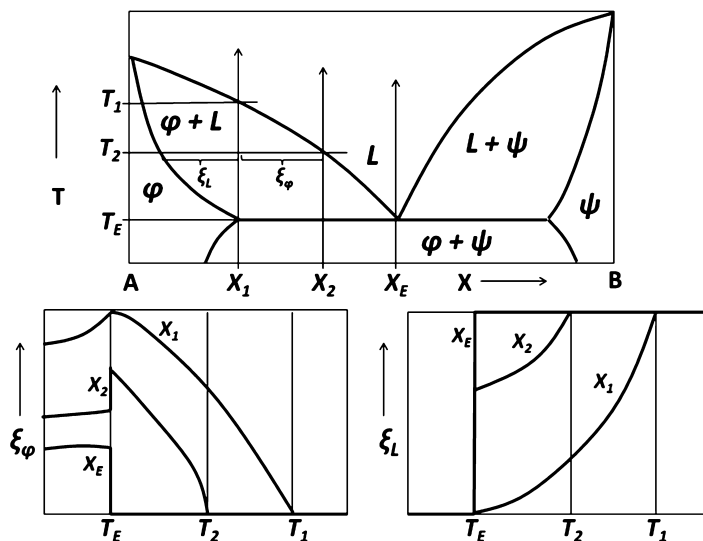
The dependences of derivative ( $d\xi_{eq}/dT$ ) jumps at temperature  $T_{in}$  from zero to a finite value that is changing until the temperature reaches  $T_{fin}$  when it jumps back to zero (Fig. 2.4).

5. *Semigradual transition*, for which the initial state of a sample corresponds to a two-phase state as it became in the equilibrium sample inside the miscibility gap. The initial value of the equilibrium extent of transition is nonzero and increases with temperature until reaches unity at temperature  $T_{fin}$ . At the semigradual transition, one of two original phases disappears at the final transition temperature  $T_{fin}$ . The derivative ( $d\xi_{eq}/dT$ ) rises to the mentioned temperature  $T_{fin}$  where it reaches its maximum and then jumps back to zero. In a special case—when the sample has a composition corresponding to the *critical point of miscibility*—the maximum of ( $d\xi_{eq}/dT$ ) at  $T_{fin} = T_{cr}$  reaches infinity. Behavior at the semigradual transition corresponds to the second-order transition in Ehrenfest's classification (Fig. 2.5).
6. *Combined transitions* are the processes at which two (or more) of the last three types are combined. At this transition the equilibrium background is expressed by two different extents of transition phase fractions (here  $\xi_\varphi$  and  $\xi_L$ ) (Fig. 2.6).

In the following sections, the examples of the last four types of transitions (sharp, gradual, semigradual, and combined) are introduced, and the thermodynamic relationships applicable for analysis of TA curves obtained for the course of the transitions are derived.



**Fig. 2.5** Miscibility gap in the binary  $T$ - $X$  diagram, the equilibrium background  $\xi_{eq}$  of the semigradual (full lines with the break at  $T_{t2}$ ) and critical (full lines with the break at  $T_{cr}$ ) transitions, and the courses of the corresponding processes (dashed lines)



**Fig. 2.6** Eutectic melting in  $X$ - $T$  diagram of binary A-B and equilibrium backgrounds  $\xi_\varphi$ ,  $\xi_L$  for compositions  $X_1$ ,  $X_2$ , and  $X_E$

## 2.4 Processes Under Conditions of Closed Isothermal Isobaric System

The conditions of closed isothermal isobaric system in TA studies cannot be strictly guaranteed; strict separation of the sample from the surroundings at high temperatures is possible only under conditions of an isochoric system. However, a large number of samples do not react with the surrounding atmosphere or decompose so that conditions of a closed isothermal isobaric system are fulfilled for these samples.

The most familiar relationship for sharp transitions in a closed system is the *Clapeyron equation* in the form  $dT/dP = T\Delta V/\Delta H$ , where  $T$  and  $P$  are temperature and pressure;  $\Delta V$  and  $\Delta H$  are integral change of volume and of enthalpy of the sharp transition. The equation after substituting  $d(\ln T) = dT/T$  can be rewritten into

$$\frac{d \ln T}{dP} = \frac{\Delta V}{\Delta H} \quad (2.16)$$

In the case of sublimation or boiling, the quantity  $\Delta V$  represents the difference between molar volume of the gaseous form and molar volume of the condensed form  $\Delta V = V_{\text{gas}} - V_{\text{cond}}$  where  $V_{\text{gas}} \gg V_{\text{cond}}$  so that  $\Delta V \approx V_{\text{gas}}$ . If  $V_{\text{gas}}$  is expressed from the state equation of a perfect gas as  $V_{\text{gas}} = RT/P$ , then the original Clapeyron equation can be transformed into the *Clausius–Clapeyron equation*:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H}{R} \quad (2.17)$$

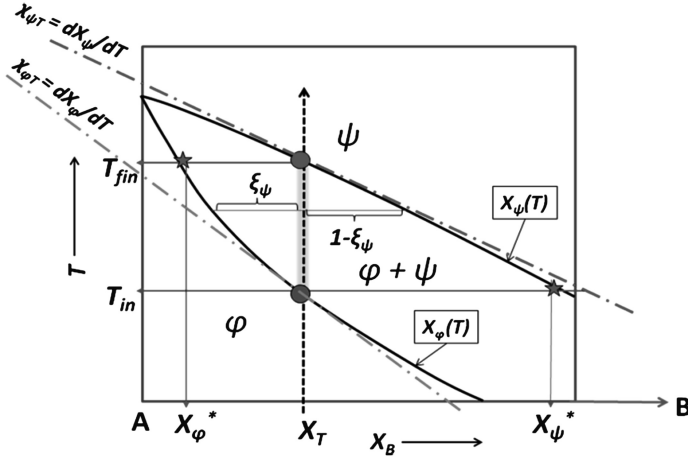
Considering the gradual transition in a binary system A–B, two transition points exist. The first of them (at temperature  $T_i$ ) corresponds to the boundary separating the initial single-phase  $\varphi$  field and the two-phase ( $\varphi + \psi$ ) field. At this point on the  $\varphi/(\varphi + \psi)$  boundary, no jumps in values of the system Gibbs free energy ( $G$ ) or of enthalpy ( $H$ ), entropy ( $S$ ), volume ( $V$ ), or the contents of macroscopic components ( $N_i$ ) occur, but the dependences of  $H(T, P)$ ,  $S(T, P)$ , and  $V(T, P)$  are changed.

In the one-phase  $\varphi$  and one-phase  $\psi$  fields, the *temperature dependence of enthalpy* of a sample with average (total) composition  $X_T$  (mole fraction of component B in system A–B) is given by  $H(T) = H_\varphi(X_T, T, P)$  and  $H(T) = H_\psi(X_T, T, P)$ , whereas in a two-phase field ( $\varphi + \psi$ ) the dependence  $H(T)$  is given by

$$H(T) = H_\varphi(X_\varphi, T, P)(1 - \xi_\psi) + H_\psi(X_\psi, T, P)\xi_\psi \quad (2.18)$$

where  $\xi_\psi$  is the phase fraction of phase  $\psi$  coexisting with phase  $\varphi$  determined through the lever rule by composition data  $X_T$ ,  $X_\varphi(T, P)$ ,  $X_\psi(T, P)$  as

$$\xi_\psi = \frac{X_T - X_\varphi}{X_\psi - X_\varphi} \quad (2.19)$$



**Fig. 2.7** Equilibrium relationships between mole fractions ( $X_\phi^*$ ,  $X_T$ ,  $X_\psi^*$ ), phase fractions ( $\xi_\psi$ ,  $1 - \xi_\psi$ ), and temperatures ( $T_{in}$ ,  $T_{fin}$ ) at the two-phase field of binary system A–B in  $T$ – $X$  diagram.  $X_{\phi T}$  and  $X_{\psi T}$  are values of tangents to curves  $X_\phi(T)$  and  $X_\psi(T)$  at  $X_\phi = X_T$  and  $X_\psi = X_T$ , respectively

The slope of temperature dependence in the one-phase fields  $\phi$  and  $\psi$  is then given by  $(\partial H_\phi / \partial T)_P = dH_\phi / dT = C_{P\phi}(X_T, T, P)$  and  $(\partial H_\psi / \partial T) = dH_\psi / dT = C_{P\psi}(X_T, T, P)$ , respectively, whereas in a two-phase field ( $\phi + \psi$ )

$$\left( \frac{\partial H_{\phi+\psi}}{\partial T} \right)_P = \frac{dH_\phi}{dT} + (H_\psi - H_\phi) \frac{d\xi_\psi}{dT} + \left( \frac{dH_\psi}{dT} - \frac{dH_\phi}{dT} \right) \xi_\psi \quad (2.20)$$

and after substituting  $\xi_\psi$  from Eq. (2.19) and

$$\begin{aligned} \left( \frac{\partial \xi_\psi}{\partial T} \right)_P &= \frac{-\frac{dX_\psi}{dT}(X_\psi - X_\phi) - (X_T - X_\phi) \left( \frac{dX_\psi}{dT} - \frac{dX_\phi}{dT} \right)}{(X_\psi - X_\phi)^2} \\ &= \frac{-\chi_{\phi T}}{X_\psi - X_\phi} - \frac{(X_T - X_\phi)(\chi_{\psi T} - \chi_{\phi T})}{(X_\psi - X_\phi)^2} \end{aligned} \quad (2.21)$$

where  $\chi_{\phi T} = (dX_\phi / dT)_P$ ,  $\chi_{\psi T} = (dX_\psi / dT)_P$  (see Fig. 2.7), and the following relationship is found:

$$\begin{aligned} \left( \frac{\partial H_{\phi+\psi}}{\partial T} \right)_P &= \frac{dH_\phi}{dT} + \frac{H_\psi - H_\phi}{X_\psi - X_\phi} \left( -\chi_{\phi T} - (\chi_{\psi T} - \chi_{\phi T}) \frac{X_T - X_\phi}{X_\psi - X_\phi} \right) + \\ &\quad + (C_{P\psi} - C_{P\phi}) \frac{X_T - X_\phi}{X_\psi - X_\phi} \end{aligned} \quad (2.22)$$

At the boundary  $\varphi/(\varphi + \psi)$  (at temperature  $T_{\text{in}}$ ), the equality  $X_T = X_\varphi$  is valid and the difference between  $(\partial H_\psi/dT)_P$  and  $(\partial H_{\varphi+\psi}/dT)_P$  is found in the form

$$\left(\frac{\partial H_{\varphi+\psi}}{\partial T}\right)_P - \left(\frac{\partial H_\varphi}{\partial T}\right)_P = -\chi_{\varphi T} \frac{H_\psi(X_\psi^*) - H_\varphi(X_T)}{X_\psi^* - X_T} = \Delta_{\text{in}} C_P \quad (2.23)$$

where  $X_\psi^*$  represents the composition (by mole fraction) of phase  $\psi$  coexisting with phase  $\varphi$  of which the composition is  $X_\varphi = X_T$ . Similarly, for boundary  $(\varphi + \psi)/\psi$  (at temperature  $T_{\text{fin}}$ ) with equality  $X_T = X_\psi$  we can find the difference:

$$\left(\frac{\partial H_\psi}{\partial T}\right)_P - \left(\frac{\partial H_{\varphi+\psi}}{\partial T}\right)_P = -\chi_{\psi T} \frac{H_\psi(X_T) - H_\varphi(X_\varphi^*)}{X_T - X_\varphi^*} = \Delta_{\text{fin}} C_P \quad (2.24)$$

Similarly, the difference between the slopes of *temperature dependence of entropy* can be derived from equations for single-phase fields  $\varphi$  and  $\psi$ :

$$\left(\frac{\partial S_\varphi}{\partial T}\right)_P = \frac{C_{P\varphi}(X_T, T, P)}{T}; \quad \left(\frac{\partial S_\psi}{\partial T}\right)_P = \frac{C_{P\psi}(X_T, T, P)}{T} \quad (2.25)$$

and for a two-phase field  $(\varphi + \psi)$  (where  $S_{\varphi+\psi} = S_\varphi(1 - \xi_\psi) + S_\psi \xi_\psi$ )

$$\left(\frac{\partial S_{\varphi+\psi}}{\partial T}\right)_P = \left(\frac{\partial S_\varphi}{\partial T}\right)_P + (S_\psi - S_\varphi) \left(\frac{\partial \xi_\psi}{\partial T}\right)_P + \left(\left(\frac{\partial S_\psi}{\partial T}\right)_P - \left(\frac{\partial S_\varphi}{\partial T}\right)_P\right) \xi_\psi \quad (2.26)$$

The difference at transition point with temperature  $T_{\text{in}}$  (boundary  $\varphi/(\varphi + \psi)$ ) is then given by

$$\Delta_{\text{in}} \left(\frac{\partial S}{\partial T}\right)_P = T_{\text{in}} \cdot \Delta_{\text{in}} C_P = -\chi_{\varphi T} \frac{S_\psi(X_\psi^*, T_{\text{in}}) - S_\varphi(X_T, T_{\text{in}})}{X_\psi^* - X_T} \quad (2.27)$$

and the difference at the transition point with temperature  $T_{\text{fin}}$  (boundary  $(\varphi + \psi)/\psi$ ) by

$$\Delta_{\text{fin}} \left(\frac{\partial S}{\partial T}\right)_P = T_{\text{fin}} \cdot \Delta_{\text{fin}} C_P = -\chi_{\psi T} \frac{S_\psi(X_T, T_{\text{fin}}) - S_\varphi(X_\varphi^*, T_{\text{fin}})}{X_T - X_\varphi^*} \quad (2.28)$$

Similarly, differences between slopes of *pressure dependences of entropy* can be derived from the following equations:

$$\left(\frac{\partial S_\varphi}{\partial P}\right)_T = -\left(\frac{\partial V_\varphi}{\partial T}\right)_P = -V_\varphi \alpha_\varphi; \quad \left(\frac{\partial S_\psi}{\partial P}\right)_T = -\left(\frac{\partial V_\psi}{\partial T}\right)_P = -V_\psi \alpha_\psi \quad (2.29)$$

$$\begin{aligned}
\left(\frac{\partial S_{\varphi+\psi}}{\partial P}\right)_T &= -\left(\frac{\partial V_{\varphi+\psi}}{\partial T}\right)_P = -\left(\frac{\partial [V_\varphi(1-\xi_\psi) + V_\psi\xi_\psi]}{\partial T}\right)_P \\
&= -V_\varphi\alpha_\varphi - (V_\psi - V_\varphi)\left(\frac{\partial \xi_\psi}{\partial T}\right)_P - \left(\left(\frac{\partial V_\psi}{\partial T}\right)_P - \left(\frac{\partial V_\varphi}{\partial T}\right)_P\right)\xi_\psi
\end{aligned} \quad (2.30)$$

where the Maxwell relationship  $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$  and isobaric expansion coefficients  $\alpha_\varphi$  and  $\alpha_\psi$  defined by  $\alpha_\varphi = (1/V_\varphi)(\partial V_\varphi/\partial T)_P$  and  $\alpha_\psi = (1/V_\psi)(\partial V_\psi/\partial T)_P$  are used.

Substituting for  $\xi_\psi$  and  $(\partial \xi_\psi/\partial T)$  from Eqs. (2.19) and (2.21), we then obtain for the boundary  $\varphi/(\varphi + \psi)$

$$\Delta_{\text{in}}\left(\frac{\partial V}{\partial T}\right)_P = V_\varphi(X_T, T_{\text{in}})\Delta_{\text{in}}\alpha = +\chi_{\varphi T} \cdot \frac{V_\psi(X_\psi^*, T_{\text{in}}) - V_\varphi(X_T, T_{\text{in}})}{X_\psi^* - X_T} \quad (2.31)$$

and for the boundary  $(\varphi + \psi)/\psi$

$$\Delta_{\text{fin}}\left(\frac{\partial V}{\partial T}\right)_P = V_\psi(X_T, T_{\text{fin}})\Delta_{\text{fin}}\alpha = +\chi_{\psi T} \cdot \frac{V_\psi(X_T, T_{\text{fin}}) - V_\varphi(X_\varphi^*, T_{\text{fin}})}{X_T - X_\varphi^*} \quad (2.32)$$

When entropy change  $\Delta_{\text{in}}S$  at the boundary  $\varphi/(\varphi + \psi)$  is equal to zero, then a shift of the boundary temperature  $T_{\text{in}}$  at composition  $X_T$  with a change of pressure  $P$  can be determined from

$$\frac{dT_{\text{in}}}{dP} = -\frac{\left(\frac{\partial \Delta_{\text{in}}S}{\partial P}\right)_T}{\left(\frac{\partial \Delta_{\text{in}}S}{\partial T}\right)_P} = +\frac{\left(\frac{\partial \Delta_{\text{in}}V}{\partial T}\right)_P}{\left(\frac{\partial \Delta_{\text{in}}S}{\partial T}\right)_P} \quad (2.33)$$

(where the Maxwell relationship is used), substituting from Eqs. (2.31) and (2.27):

$$\frac{dT_{\text{in}}}{dP} = -\frac{V_\psi(X_\psi^*, T_{\text{in}}) - V_\varphi(X_T, T_{\text{in}})}{S_\psi(X_\psi^*, T_{\text{in}}) - S_\varphi(X_T, T_{\text{in}})} \quad (2.34)$$

Similarly, an equation can be obtained for the shift of temperature  $T_{\text{fin}}$  resulting from a change in pressure  $P$  at boundary  $(\varphi + \psi)/\psi$  as fraction  $-\Delta_{\text{fin}}(\partial V/\partial T)_P/\Delta_{\text{fin}}(\partial S/\partial T)_P$  using Eqs. (2.28) and (2.32):

$$\frac{dT_{\text{fin}}}{dP} = -\frac{V_\psi(X_T, T_{\text{fin}}) - V_\varphi(X_\varphi^*, T_{\text{fin}})}{S_\psi(X_T, T_{\text{fin}}) - S_\varphi(X_\varphi^*, T_{\text{fin}})} \quad (2.35)$$

The last question of gradual transitions in a closed binary system is the quantitative relationship for difference of slopes of *pressure dependences of volume*



$V$  at composition  $X_T$ . The mentioned differences can be derived from the equations  $(\partial V_\varphi/\partial P)_T = -V_\varphi\beta_\varphi$  and  $(\partial V_\psi/\partial P)_T = -V_\psi\beta_\psi$  and

$$\begin{aligned} \left(\frac{\partial V_{\varphi+\psi}}{\partial P}\right)_T &= \left(\frac{\partial [V_\varphi(1-\xi_\psi) + V_\psi\xi_\psi]}{\partial P}\right)_T \\ &= -V_\varphi\beta_\varphi + (V_\psi - V_\varphi)\left(\frac{\partial \xi_\psi}{\partial P}\right)_T + \left(\left(\frac{\partial V_\psi}{\partial P}\right)_T - \left(\frac{\partial V_\varphi}{\partial P}\right)_T\right)\xi_\psi \end{aligned} \quad (2.36)$$

where the *isothermal compressibility coefficients*  $\beta_\varphi$  and  $\beta_\psi$  defined by  $\beta_\varphi = -(1/V_\varphi)(\partial V_\varphi/\partial P)_T$  and  $\beta_\psi = -(1/V_\psi)(\partial V_\psi/\partial P)_T$  are used. Substituting  $\xi_\psi$  from Eq. (2.19) and using derivative  $(\partial \xi_\psi/\partial P)_T$

$$\left(\frac{\partial \xi_\psi}{\partial P}\right)_T = \frac{-\chi_{\varphi P} - (\chi_{\psi P} - \chi_{\varphi P})(X_T - X_\varphi)/(X_\psi - X_\varphi)}{X_\psi - X_\varphi} \quad (2.37)$$

where  $\chi_{\varphi P} = (\partial X_\varphi/\partial P)_T$  and  $\chi_{\psi P} = (\partial X_\psi/\partial P)_T$ , the difference of  $(\partial V/\partial P)_T$  slopes at boundary  $\varphi/(\varphi + \psi)$  (for  $X_\varphi = X_T$ ) is found in the form:

$$\Delta_{\text{in}}\left(\frac{\partial V}{\partial P}\right)_T = -V_\varphi(X_T, T_{\text{in}})\Delta_{\text{in}}\beta = -\chi_{\varphi P}\frac{V_\psi(X_\psi^*, T_{\text{in}}) - V_\varphi(X_T, T_{\text{in}})}{X_\psi^* - X_T} \quad (2.38)$$

and at the boundary  $(\varphi + \psi)/\psi$  (for  $X_\psi = X_T$ ) we have

$$\Delta_{\text{fin}}\left(\frac{\partial V}{\partial P}\right)_T = -V_\psi(X_T, T_{\text{fin}})\Delta_{\text{fin}}\beta = -\chi_{\psi P}\frac{V_\psi(X_T, T_{\text{fin}}) - V_\varphi(X_\varphi^*, T_{\text{fin}})}{X_T - X_\varphi^*} \quad (2.39)$$

When the volume change at the boundary  $\varphi/(\varphi + \psi)$  is equal to zero  $\Delta_{\text{in}}V = 0$ , then a shift of the boundary temperature  $T_{\text{in}}$  at composition  $X_T$  with a change of pressure  $P$  can be determined from

$$\frac{dT_{\text{in}}}{dP} = -\frac{\left(\frac{\partial \Delta_{\text{in}}V}{\partial P}\right)_T}{\left(\frac{\partial \Delta_{\text{in}}V}{\partial T}\right)_P} \quad (2.40)$$

and similarly at the boundary  $(\varphi + \psi)/\psi$  where  $\Delta_{\text{fin}}V = 0$  for a shift of temperature  $T_{\text{fin}}$  with a change of pressure  $P$ , we can use

$$\frac{dT_{\text{fin}}}{dP} = \frac{-\left(\frac{\partial \Delta_{\text{fin}}V}{\partial P}\right)_T}{\left(\frac{\partial \Delta_{\text{fin}}V}{\partial T}\right)_P} \quad (2.41)$$

Substituting Eqs. (2.38) and (2.30) into Eq. (2.40) and Eqs. (2.39) and (2.31) into Eq. (2.41), we obtain

$$\frac{dT_{\text{in}}}{dP} = -\frac{\chi_{\varphi P} \left[ V_{\psi}(X_{\psi}^*, T_{\text{in}}) - V_{\varphi}(X_T, T_{\text{in}}) \right]}{\chi_{\varphi T} \left[ V_{\psi}(X_{\psi}^*, T_{\text{in}}) - V_{\varphi}(X_T, T_{\text{in}}) \right]} = -\frac{\chi_{\varphi P}(X_T, T_{\text{in}})}{\chi_{\varphi T}(X_T, T_{\text{in}})} \quad (2.42)$$

$$\frac{dT_{\text{fin}}}{dP} = -\frac{\chi_{\psi P} \left[ V_{\psi}(X_T, T_{\text{fin}}) - V_{\varphi}(X_{\varphi}^*, T_{\text{fin}}) \right]}{\chi_{\psi T} \left[ V_{\psi}(X_T, T_{\text{fin}}) - V_{\varphi}(X_{\varphi}^*, T_{\text{fin}}) \right]} = -\frac{\chi_{\psi P}(X_T, T_{\text{fin}})}{\chi_{\psi T}(X_T, T_{\text{fin}})} \quad (2.43)$$

## 2.5 Processes Under Conditions of a Partly Open Isothermal Isobaric System

A partly open system differs from a closed system by a different contact with surroundings. In a partly open system, the mole content  $N_f$  of free component  $f$  is not constant but variable as a result of equilibrium between the system (sample) and its surroundings, which is characterized by pressure  $P$ , temperature  $T$ , and *activity of free component*  $a_f$  [28, 32, 33]. Thus, as the Gibbs free energy  $G$  is not a corresponding characteristic (criterion) function for partly open systems, other thermodynamic potential appropriate to conditions of equilibrium of these systems should be used. For this reason the thermodynamic function called *hyperfree energy* is constructed as the Legendre transformation [34] of the Gibbs free energy  $G$  by

$$Z = G - N_f \mu_f = G - N_f (G_f^0 - RT \ln a_f) \quad (2.44)$$

where  $N_f$  is the mole amount,  $\mu_f$  is the chemical potential, and  $G_f^0 = \mu_f^0$  is the standard chemical potential of the free component. To understand the physical meaning of the hyperfree energy  $Z$ , consider the following illustration.

Assume a condensed system “c” containing three components A, B, and  $O_2$  in equilibrium with a gas “g” containing oxygen ( $O_2$ ) and some other components not reacting with the condensed system. If the gas forms a dynamic atmosphere with a constant activity of oxygen  $a_{O_2}^g$ , then the condensed system “c” tends to reach equilibrium with the surrounding gaseous atmosphere “g” to fulfill the following equilibrium condition:

$$\left( \frac{\partial G^c}{\partial N_{O_2}^c} \right)_{P, T, N_A, N_B} = \mu_{O_2}^g = \mu_{O_2}^0 + RT \ln a_{O_2}^g \quad (2.45)$$

where  $G^c$  and  $N_{O_2}^c$  mean the Gibbs free energy and the molar content of oxygen in the condensed system, respectively, and  $\mu_{O_2}^g$  is the chemical potential of oxygen in the surrounding gas. The last equation can be transformed as

$$[dG^c - \mu_{O_2}^g dN_{O_2}^c = 0]_{P,T,N_A,N_B} \quad (2.46)$$

and if  $T$  and  $a_{O_2}^g$  are kept constant then  $d\mu_{O_2}^g = 0$  so that

$$d(\mu_{O_2}^g N_{O_2}^c)_{T,a(O_2)} = \mu_{O_2}^g dN_{O_2}^c \quad (2.47)$$

and Eq. (2.46) can be rewritten as

$$[dG^c - d(\mu_{O_2}^g N_{O_2}^c) = 0]_{P,T,N_A,N_B,a(O_2)} \rightarrow d(G^c - \mu_{O_2}^g N_{O_2}^c) = dZ_{O_2}^c = 0 \quad (2.48)$$

where  $Z_{O_2}^c \equiv G^c - \mu_{O_2}^g N_{O_2}^c$  is called hyperfree energy of condensed system “c” with respect to constant activity of free component  $O_2$ .

The Clapeyron equation is then derived not from pressure and temperature dependence of the Gibbs free energy change  $\Delta G(T, P)$  but from the dependence of the hyperfree energy change:

$$\Delta Z(T, P, \ln a_f) = \Delta G(T, P) - \Delta N_f (G_f^0 + RT \ln a_f)$$

which is equal to zero at the transition point (see Appendix B in [28]):

$$\begin{aligned} \Delta Z &= \Delta G - \Delta N_f G_f^0 - \Delta N_f RT \ln a_f = \\ &= (\Delta H - \Delta N_f H_f^0) - T(\Delta S - \Delta N_f S_f^0 + \Delta N_f R \ln a_f) = 0 \end{aligned} \quad (2.49)$$

where  $\Delta H$ ,  $\Delta S$ , and  $\Delta N_f$  mean the changes of enthalpy, entropy, and free component content at the given transition and  $H_f^0$ ,  $S_f^0$ , mean the standard molar enthalpy and the standard molar entropy of the pure component  $f$ .

For thermal decomposition (dissociation) we then obtain the Clapeyron equation analogically to Eq. (2.1) but under the condition of constant free component activity  $a_f$

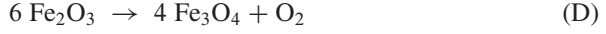
$$\left( \frac{\partial T}{\partial P} \right)_{a_f} = - \frac{\left( \frac{\partial \Delta Z}{\partial P} \right)_{T,a_f}}{\left( \frac{\partial \Delta Z}{\partial T} \right)_{P,a_f}} = \frac{(\Delta V - \Delta N_f V_f^0) \cdot T}{\Delta H - \Delta N_f H_f^0} \quad (2.50)$$

where equality

$$\Delta S - \Delta N_f S_f^0 + \Delta N_f R \ln a_f = \frac{\Delta H - \Delta N_f H_f^0}{T}$$

following from Eq. (2.49) is used,  $\Delta V$  means change of volume at given dissociation, and  $V_f^0$  mean values of standard molar volume of pure component  $f$  (in the case of gaseous components, behavior of perfect gas can be assumed  $V_f^0 = RT/P$ ).

For example, at dissociation (D) of hematite  $\text{Fe}_2\text{O}_3$  to magnetite  $\text{Fe}_3\text{O}_4$  according to the scheme



values of  $\Delta V$ ,  $\Delta H$  are determined from molar volumes  $V_m$  and molar enthalpies  $H_m$  of the participating substances:

$$\begin{aligned} \Delta V &= 4V_m(\text{Fe}_3\text{O}_4) + V_m^0(\text{O}_2) - 6V_m(\text{Fe}_2\text{O}_3) \\ \Delta H &= 4H_m(\text{Fe}_3\text{O}_4) + H_m^0(\text{O}_2) - 6H_m(\text{Fe}_2\text{O}_3) \end{aligned}$$

For free component  $\text{O}_2$  the value of  $\Delta N_f$  equals to unity ( $\Delta N_f = 1$ ) so that

$$\begin{aligned} \Delta V - \Delta N_f V_f^0 &= 4V_m(\text{Fe}_3\text{O}_4) - 6V_m(\text{Fe}_2\text{O}_3) \\ \Delta H - \Delta N_f H_f^0 &= 4H_m(\text{Fe}_3\text{O}_4) - 6H_m(\text{Fe}_2\text{O}_3) \end{aligned}$$

Equation (2.50) then gives

$$\left( \frac{\partial T}{\partial P} \right)_{a(\text{O}_2)} = \frac{(4V_m(\text{Fe}_3\text{O}_4) - 6V_m(\text{Fe}_2\text{O}_3)) \cdot T}{4H_m(\text{Fe}_3\text{O}_4) - 6H_m(\text{Fe}_2\text{O}_3)} \quad (2.51)$$

so that the shift of transition temperature caused by the change of pressure (under constant free component activity) is determined only by the change of volume and enthalpy of the condensed part of the sample.

Another Clapeyronian equation can be derived for the dependence between the equilibrium free component activity  $a_f$  (or its logarithm  $\ln a_f$ ) and temperature  $T$  at a constant pressure  $P$ , if we start from another analogy of Eq. (2.1) considering Eq. (2.49):

$$\frac{\left( \frac{\partial \Delta Z}{\partial T} \right)_{P, a_f}}{\left( \frac{\partial \Delta Z}{\partial \ln a_f} \right)_{T, P}} = \frac{\Delta H - \Delta N_f H_f^0}{\Delta N_f R T^2} = - \left( \frac{\partial \ln a_f}{\partial T} \right)_P \quad (2.52)$$

where by substituting  $d(1/T) = -(1/T^2)dT$  an alternative form is found:

$$\left( \frac{\partial \ln a_f}{\partial (1/T)} \right)_P = \frac{\Delta H - \Delta N_f H_f^0}{R \Delta N_f} \quad (2.53)$$

Phase relationships in system A–B–X (where X is the free component) can be drawn as a quasi-binary phase diagram  $\text{AX}_a - \text{BX}_b$  at constant activity  $a_X$ , if *quasi-molar fractions*  $Y \equiv Y_B$  determined from mole fractions  $X_A$  and  $X_B$  by  $Y \equiv Y_B = X_B/(X_A + X_B)$  are used for the  $Y$ – $T$  plot. The boundaries of two-phase

$(\varphi + \psi)$  field for sample of total composition  $Y_T$  are then given as  $T_{\text{in}}$  at  $\varphi/(\varphi + \psi)$  boundary and  $T_{\text{fin}}$  at  $(\varphi + \psi)/\psi$  boundary and the value of enthalpy inside the two-phase field is proportional to phase fraction  $\zeta_\psi$  determined for the sample with composition  $Y_T$  by an equation similar to Eq. (2.19):

$$\zeta_\psi = \frac{Y_T - Y_\varphi}{Y_\psi - Y_\varphi} \quad (2.54)$$

and in all following equations the quasi-molar ( $Y$ ) instead of molar ( $X$ ) fraction are used, phase fractions  $\zeta$  defined by Eq. (2.50) instead of  $\xi$  defined by Eq. (2.19) and for quantities  $\chi_{\varphi T}$ ,  $\chi_{\psi T}$  used first in Eq. (2.20) and for  $\chi_{\varphi P}$ ,  $\chi_{\psi P}$  used first in Eq. (2.37), the slopes of two-phase boundaries are expressed as derivatives of quasi-molar fractions  $Y$ :  $\chi_{\varphi T} = (dY_\varphi/dT)_P$ ;  $\chi_{\psi T} = (dY_\psi/dT)_P$ ;  $\chi_{\varphi P} = (\partial Y_\varphi/\partial P)_T$ ;  $\chi_{\psi P} = (\partial Y_\psi/\partial P)_T$ .

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