

PACS: 05.70.Ln, 64.60.Bd, 64.70.Kd, 64.75.Op, 66.30.Fq, 81.10.Jt, 81.30.Kf

ISSN 1729-4428 (Print)  
ISSN 2309-8589 (Online)

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## Diffusion kinetics in a multicomponent thermodynamic system at small deviations from the equilibrium state

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The theory of diffusion processes in solids has achieved significant results in recent decades, but the development of methods for calculating diffusion in a multicomponent thermodynamic system is still an urgent task. Problems of diffusion in solid and liquid solutions with small deviations from the equilibrium state, or fluctuations, are of significant interest. The work develops a general methodology for calculating diffusion flows in a multicomponent thermodynamic system for small deviations from the equilibrium state. A connection has been established between the mechanical approach to the analysis of generalized systems and the phenomenological equations of nonequilibrium thermodynamics. Examples are given of the use of the developed methodology for the analysis of carbide transformations in chromium steel.

**Keywords:** non-equilibrium thermodynamics, variational principles, diffusion fluxes, equations of motion, carbide transformations, chromium steel.

Received 24 January 2024; Accepted 11 June 2024.

### Introduction

The mathematical apparatus of non-equilibrium thermodynamics and phase-field modeling is usually used to analyze diffusion processes in a complex thermodynamic system [1-3].

In general, the thermodynamic equations of motion have the form [1,3]:

$$J_i = \sum_{k=1}^N L_{ik} X_k \quad (i=1, \dots, N), \quad (1)$$

Where  $J_i$  are fluxes;  $X_k$  are thermodynamic forces;  $L_{ik} = L_{ki}$  are Onsager kinetic coefficients;  $i, k$  are numbers of charges (transfer substrates).

The main driving forces of diffusion in non-equilibrium thermodynamics are gradients of chemical potentials  $\mu_i$  system components [4-6]:

$$X_i = -\nabla \mu_i. \quad (2)$$

In accordance with the provisions developed in phase-

field modeling, chemical potentials, in turn, are related to the Gibbs energy  $G$  by equations [7]:

$$\mu_i = \frac{\partial G}{\partial c_i}, \quad (3)$$

The theory of diffusion in metal alloys with a vacancy mechanism of atomic migration was developed by Darken [4]. The main limitations of this theory are associated with the need for the diagonality of the Onsager matrix and the equilibrium condition for the concentration of vacancies [5, 6].

In [6], the kinetics of diffusion in a bimetallic system was considered taking into account the off-diagonal coefficients of the Onsager matrix. The thermodynamic potential in this work was presented as:

$$\mu_i = \mu_i^0 = RT \ln \ln (\gamma_i C_i), \quad (4)$$

Where  $C_i$  – concentration of the  $i$ -element;  $\gamma_i$  – activity coefficient of the  $i$ -th element, which is considered dependent on the same concentration  $C_i$ .

The equation for the diffusion fluxes of the system contains generally unknown activity coefficients of elements and vacancies and their derivatives with respect to concentrations, which makes it extremely difficult to find the values of direct and cross coefficients. In [6], expressions for the cross coefficients for an ideal solid solution were found.

Calculating fluxes in a system using the proposed method is a very labor-intensive task with a large number of unknown dependences of the activity coefficients of elements on concentration. Similar difficulties arise in the phase-field model [2, 7].

Very often in materials science there is a problem of finding flows of elements in time in interacting phases. At the same time, the distribution of concentrations in space can be neglected, and the systems are considered as composite [8-10]. When considering intermittent systems, that is, systems that contain several phases, between which flows of elements and vacancies pass, finite chemical potential differences can be used as thermodynamic forces ( $-\Delta\mu_i$ ) [8-10].

In [8], the values of diffusion fluxes in the Fe – C – Cr system were calculated taking into account cross coefficients at the initial time. In [9], equations were obtained that describe the kinetics of the diffusion process in a system consisting of two phases and three elements.

The theory of diffusion processes in solids continues to develop intensively in recent years, as can be seen from works [10-19], however, the development of methods for calculating diffusion in a multicomponent thermodynamic system is still an urgent task.

Of particular interest are problems of diffusion in solid and liquid solutions with small deviations from the equilibrium state, or fluctuations [19, 20]

The purpose of this work is to obtain kinetic diffusion equations for small deviations of a composite thermodynamic system from the equilibrium state and to use them to analyze the transformation of carbides in chromium steel.

## I. Kinetic equations of a multicomponent thermodynamic system

To describe our thermodynamic system, we use elements of the theory of small oscillations of a generalized mechanical system [21].

We define the equilibrium state of a thermodynamic system as a state described by a set of generalized coordinates  $q_k^{(0)}$ , for which

$$\dot{q}_k = 0 \text{ at } q_k = q_k^{(0)}, \quad (5)$$

Moreover, all higher derivatives vanish. In this state, entropy and Gibbs energy have extreme values.

This also means that if all coordinates of the system are equal to the generalized coordinates  $q_k = q_k^{(0)}$ , then the system is in equilibrium at given external parameters of temperature and pressure, i.e. fulfillment of condition (5) at  $t=t_0$  must result in respect for equalities  $q_k = q_k^{(0)}$  at

any subsequent time. It will also be assumed that generalized coordinates are related to concentrations as follows:

$$q_k = C_k - C_k^0, \quad (6)$$

Where  $C_k^0$  - equilibrium value of the concentration of the component in the selected part of the system.

The kinetics of diffusion in our multicomponent thermodynamic system can be described by a system of differential equations [2, 7, 11, 15]:

$$\dot{q}_i = -\nabla\left(\sum_{k=1}^N L_{ik}\nabla\left(\frac{\partial G}{\partial q_k}\right)\right), \quad (7)$$

where  $\nabla$  is the gradient.

When simplifying the system to a discontinuous one, we consider diffusion along one coordinate. Replacing gradients with finite differences along one coordinate axis  $\Delta$ , equation (7) can be represented in the form

$$\dot{q}_i = -\frac{1}{\Delta x \times \Delta X} \Delta j \left( \sum_{k=1}^N L_{ik} \frac{1}{\Delta x} \Delta \left( \frac{\partial G}{\partial q_k} \right) \right), \quad (8)$$

where  $\Delta$  is the chemical potential difference between two parts of the system,  $\Delta x$  is the distance between two parts of the system,  $\Delta j$  is the difference in fluxes between two points,  $\Delta X$  is the distance between two points of the system for fluxes. In the general case, we assume that the selected points for potentials and fluxes are different and, accordingly, different distances between the points (Fig. 1).

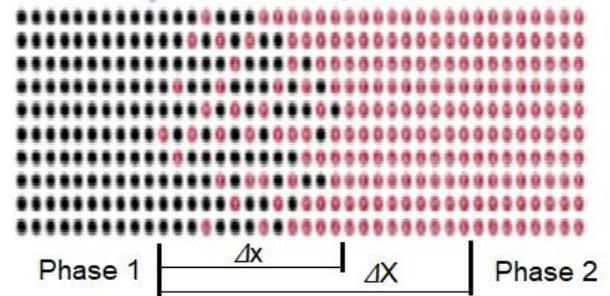


Fig. 1. Diagram of a two-phase system.

In equation (8), we will put the sign of the difference in chemical potentials in brackets, referring it to the thermodynamic potential, and we will omit the sign of the difference in fluxes, since the expression in brackets already determines the difference in particle fluxes between parts of the system.

From the equations of motion (8) we obtain the following system of first-order differential equations that describe the kinetics of a thermodynamic system for small deviations from the equilibrium position:

$$\dot{q}_i = -\frac{1}{\Delta x \times \Delta X} \sum_{k=1}^N L_{ik} \frac{\partial \Delta G}{\partial q_k}. \quad (9)$$

From conditions (8), which determine the conditions of equilibrium, and the equations of motion (9), it follows that the necessary conditions of equilibrium are the equalities:

$$\frac{\partial G}{\partial q_k} = 0, \text{ at } q_k = q_k^{(0)}, k=1, \dots, N. \quad (10)$$

For a mechanical system in a state of stable equilibrium, the value of the potential function has an absolute minimum [21]. For a thermodynamic system in a state of equilibrium, the value thermodynamic potential G

$$G(q_k) = G(q_{k0}) + \sum_k \left( \frac{\partial G}{\partial q_k} \right)_0 q_k + \frac{1}{2} \sum_{k,l} \left( \frac{\partial^2 G}{\partial q_k \partial q_l} \right)_0 q_k q_l + \dots \quad (11)$$

Taking into account equalities (10), and omitting all terms of the third order and higher, we obtain the following expression for the thermodynamic potential:

$$\Delta G = \frac{1}{2} b_{kl} q_k q_l, \quad (12)$$

$$\text{where } b_{kl} = \left( \frac{\partial^2 G}{\partial q_k \partial q_l} \right)_0 = \left( \frac{\partial \mu_k}{\partial q_l} \right)_0. \quad (13)$$

Equations (9), taking into account (15), lead to the following basic equations of motion of a multicomponent thermodynamic system for small deviations from the equilibrium position:

$$\dot{q}_i = - \frac{1}{\Delta x \times \Delta X} \sum_{k=1}^N \sum_{l=1}^N L_{ik} b_{kl} q_l, \quad i=1, \dots, N. \quad (14)$$

In equation (14) it is necessary to substitute the values of the kinetic conductivity coefficients  $L_{ik}$  and power coefficients  $b_{kl}$ .

As is known [1, 3], direct kinetic coefficients  $L_{ii}$  related to the diffusion coefficients of the elements  $D_i$  ratio:

$$L_{ii} = C_i D_i / RT, \quad (15)$$

Cross Onsager coefficients for a thermodynamic system tending to equilibrium are found using the formulas given in [8-10]:

$$L_{ik} = L_{ki} = \pm \sqrt{L_{ii} \times L_{kk}}, \quad i, k = 1 \dots N \quad (16)$$

Power coefficient values  $b_{ik}$  in the general case, it should be found using formula (13), taking into account the dependence of the thermodynamic potential on concentration of the form (4). This greatly complicates calculations and requires a large amount of experimental data to determine the dependence of activity coefficients on concentration. However, in a system state close to equilibrium, the following reasonable assumptions can be made.

Firstly, we will assume that the interaction between various elements of the system with a sufficient degree of accuracy near equilibrium is determined by cross coefficients (16), and the force coefficients

$$b_{ik} = \left( \frac{\partial \mu_i}{\partial q_k} \right)_0 = 0, \quad i \neq k. \quad (17)$$

This means that the dependence of chemical potentials  $\mu_i$  from the content of other elements in a state

has an extremum [2].

Further we will consider small deviations from the equilibrium state, then the values  $q_k$  will be small and we can use a series expansion in these quantities, limiting ourselves to the first few terms. Then the expression for the thermodynamic potential can be written as:

close to equilibrium is insignificant.

Secondly, the dependence of the chemical potential  $\mu_i$  from the element content near equilibrium is determined by its expression for an ideal solution, and the difference in chemical potentials is determined by the formula [1, 3]:

$$\mu_i = \mu_i^0(T) + RT \ln C_i, \quad (18)$$

Using (18) in equation (17), we find the values of the direct force coefficients:

$$b_{ii} = \frac{RT}{C_i^0}. \quad (19)$$

Now the problem of finding kinetic diffusion equations in a multicomponent system is completely defined. Substituting expressions (15) – (19) into the equation of motion (14), we obtain the following system of differential equations:

$$\dot{q}_i = - \frac{1}{\Delta x \times \Delta X} \sum_{k=1}^N \frac{\sqrt{D_i C_i^0 D_k C_k^0}}{C_i^0} q_k. \quad (20)$$

For a closed thermodynamic system, we must also take into account the completeness condition for concentrations:

$$\sum_{k=1}^N C_k = 1, \quad \text{or, what is the same,} \quad \sum_{k=1}^N q_k = 0. \quad (21)$$

One of the variables is not independent.

System of equations (20), taking into account condition (21), makes it possible to calculate the diffusion kinetics of elements of a composite multicomponent thermodynamic system for small deviations from the equilibrium state, primarily fluctuations or small external influences. The condition for small deviations can be written as an inequality:

$$q_i < C_i^0. \quad (22)$$

Below we will consider a non-trivial example of constructing kinetic equations for model steel.

## II. Kinetics of carbide transformation in a three-component system Fe – C – Cr

As an example, we will find solutions to the kinetic

equations for model steel Fe – C – Cr with 0.15% C and 5% Cr, previously used in [8, 9]. The initial state of this steel is chromium with a concentration  $C_{Cr}^{\alpha} = 0.05$  and carbon with concentration  $C_C^{\alpha} = 0.007$ , iron concentration  $C_{Fe}^{\alpha} = 0.943$ .

This steel is subjected to hardening from 900°C followed by high tempering at a temperature of 600°C. At the first stage, the formation of cementite-type carbides occurs as a result of the rapid diffusion of carbon from the solid solution; this process was described earlier in the work [9].

Let's calculate the kinetics carbide transformation  $(Fe_{3-x}, Cr_x)C \rightarrow (Fe_{3-x}, Cr_{4+x})C_3$  happening in such steel at a temperature of 600°C [9, 16, 22]. We will assume that in the solid  $\alpha$ -solution after the completion of the stage of rapid diffusion of carbon, chromium is found with a concentration  $C_{Cr}^{\alpha} = 0.05$  and carbon with concentration  $C_C^{\alpha} = 0.002$ , iron concentration is  $C_{Fe}^{\alpha} = 0.948$ . In cementite type carbide there is chromium with a mass fraction of ~5% (concentration 0.05) and carbon with a concentration  $C_C = 0.25$ , iron concentration in carbide

$C_{Fe} = 0.7$ . In total, 0.005 at. units carbon, the amount of cementite-type carbides was correspondingly 0.02 at. Units. This carbide at a temperature of 600°C gradually transforms into a special carbide  $(Fe_{3-x}, Cr_{4+x})C_3$  with concentration  $C_{Cr} \approx 0.4$  and carbon with  $C_C = 0.3$ , iron concentration in carbide is  $C_{Fe} \approx 0.3$  [9, 22]. In this case, the concentrations of elements in the solid solution change to their equilibrium value for chromium  $C_{Cr}^{\alpha 0} = 0.040$  ( $q_{Cr} = 0,01$ ),  $C_{Fe}^{\alpha 0} = 0.959$  ( $q_{Fe} = 0.011$ ) and carbon with concentration  $C_C^{\alpha 0} = 0.001$  ( $q_C = 0.001$ ).

Diffusion of iron in a solid solution occurs in the direction of increasing its concentration, i.e. forced [8, 9].

As you can see, the conditions for small deviations for our system (22) are satisfied for chromium and iron and are not satisfied for carbon. Therefore, we cannot construct a kinetic equation for carbon. Below we will show how to get around this difficulty.

The temperature dependences of the diffusion coefficients of chromium and carbon in chromium-alloyed ferrite are:  $m^2/s$ :

$$D_{Fe}^{\alpha} = 2.0 \times 10^{-4} \exp \left[ \frac{-251000}{RT} \right], \quad [23] \quad (23)$$

$$D_{Cr}^{\alpha} = 3.0 \times 10^{-4} \exp \exp \left[ \frac{-306400}{RT} \right], \quad [23] \quad (24)$$

$$D_C^{\alpha} = 8.0 \times 10^{-7} \exp \left[ \frac{-84000}{RT} \right] + 2.2 \times 10^{-4} \exp \left[ \frac{-123000}{RT} \right]. \quad [24] \quad (24)$$

For our thermodynamic system, we must also take into account the completeness condition for concentrations in the solid solution (21), which we write in the form (we neglect the change in vacancy concentration):

$$q_{Fe} + q_C + q_{Cr} = 0. \quad (25)$$

At the second stage of diffusion in our system, carbon can diffuse only when the concentration of chromium in the carbide increases simultaneously with it, i.e. slowly. We will assume, introducing one more additional condition, that the fluxes of carbon and chromium are consistent, and change carbon concentration in solid solution proportional to the change chromium concentrations:

$$\dot{q}_C = \frac{q_C^0}{q_{Cr}^0} \dot{q}_{Cr} \quad (26)$$

This is the second stage of diffusion in our system - the stage of slow diffusion of carbon, but fast diffusion of chromium and iron.

At this stage, the concentrations of carbon, chromium

and iron tend to their equilibrium concentrations in the carbide and solid solution.

The kinetic equations of our thermodynamic system take the form:

$$\dot{q}_{Fe} = \frac{D_{Fe}}{s} q_{Fe} + \frac{\sqrt{D_{Fe}C_{Fe}^0 D_{Cr}C_{Cr}^0}}{sC_{Fe}^0} q_{Cr} + \frac{\sqrt{D_{Fe}C_{Fe}^0 D_C C_C^0}}{sC_{Fe}^0} q_C, \quad (27)$$

$$\dot{q}_{Cr} = \frac{D_{Cr}}{s} q_{Cr} + \frac{\sqrt{D_{Fe}C_{Fe}^0 D_{Cr}C_{Cr}^0}}{sC_{Cr}^0} q_{Fe} + \frac{\sqrt{D_{Cr}C_{Cr}^0 D_C C_C^0}}{sC_{Cr}^0} q_C \quad (28)$$

The system of equations (27)-(28) is consistent and allows one to find the change in concentrations in steel over time.

At a temperature of 600°C:

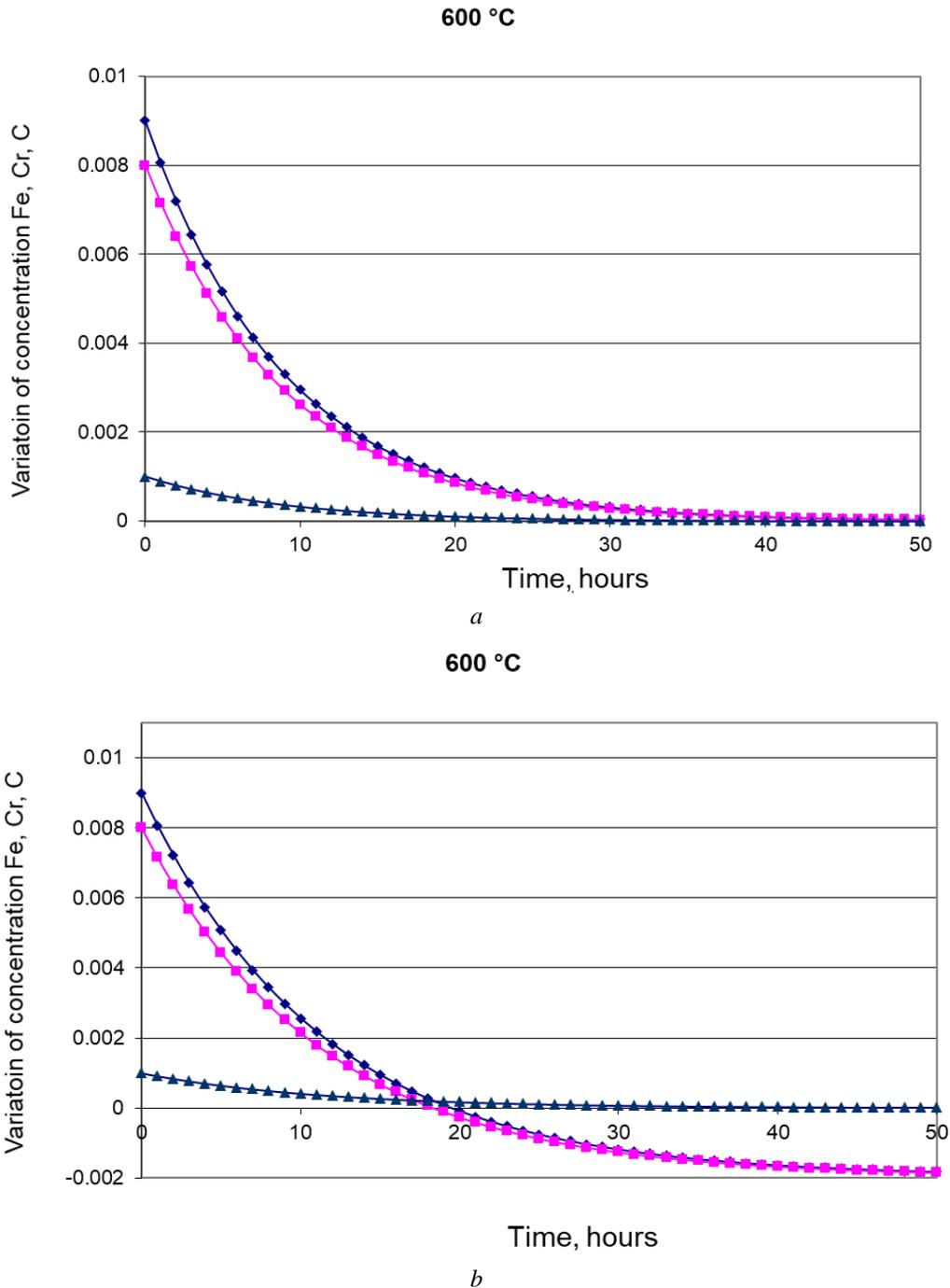
$$D_1 = D_{Fe}^{\alpha} \approx 1.0 \cdot 10^{-19} m^2/s; \quad D_2 = D_{Cr}^{\alpha} \approx 1.0 \cdot 10^{-23} m^2/s; \\ D_3 = D_C^{\alpha} \approx 2.0 \cdot 10^{-11} m^2/s.$$

For numerical assessment we also use the values  $\Delta X = \Delta x = 1.0 \times 10^{-7} m$ .

Finally, we get:

$$\dot{q}_{Fe} = -(1.0 \times 10^{-5} q_{Fe} + 2.0 \times 10^{-8} q_{Cr} + 4.5 \times 10^{-3} q_C), \quad (29)$$

$$\dot{q}_{Cr} = -(1.0 \times 10^{-9} q_{Cr} + 5.0 \times 10^{-7} q_{Fe} + 2.3 \times 10^{-4} q_C). \quad (30)$$



**Fig. 2.** Calculated change in the concentrations of elements in the solid solution:  
 a – at the value  $\dot{q}_C = 0.08\dot{q}_{Cr}$ , b – at the value  $\dot{q}_C = 0.1\dot{q}_{Cr}$ ,  
 Fe is represented blue diamonds, Cr is shown red squares, C is represented blue triangles.

Numerical calculations show that noticeable diffusion of chromium (63%  $q_0^{Cr}$ ) at a distance of  $1.0 \times 10^{-7}$  m with the size of the resulting carbide particles  $\sim 1.0 \times 10^{-7}$  m occurs in  $\sim 10$  hours (Fig. 2).

If relation (26) is not satisfied, but there is another proportionality coefficient, then this leads to equilibrium of the system with other parameters of component variations. Thus, variations in the concentrations of Fe and Cr at  $\dot{q}_C = 0.1\dot{q}_{Cr}$ , tend to values of -0.002, i.e. the initial variations of these concentrations acquire values of 0.011 for Fe and 0.09 for Cr. The diffusion of chromium is significantly accelerated in comparison with the diffusion

equation (24), due to the cross coefficient in equations (28) and (30), and is practically completed in about 50 hours. The diffusion of carbon in our case is slow, accompanying the diffusion of chromium, and the diffusion of iron, generally speaking, is forced, because it occurs in the direction of increasing iron concentration.

### Conclusions

1. A general method of calculating diffusion flows in a multicomponent thermodynamic system with small deviations from the equilibrium state has been developed.

2. The connection between the mechanical approach to the analysis of generalized systems and the phenomenological equations of non-equilibrium thermodynamics is established.

3. Examples of the use of the developed methodology for the analysis of carbide transformations in chromium steel are given.

4. Numerical calculations show that noticeable diffusion of chromium in steel at a temperature of 600°C with the size of the obtained carbide particles of 10 μm occurs in about 10 hours.

#### Acknowledgements

*This project was funded by the Swedish Foundation for Strategic Research (SSF), contract UKR22-0070. I want to thank profs. Annika Borgenstam and Liubov Belova for supporting this project.*

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## Кінетика дифузії в багатокомпонентній термодинамічній системі при малих відхиленнях від рівноважного стану

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Теорія дифузійних процесів у твердих тілах за останні десятиліття досягла значних результатів, але розробка методів розрахунку дифузії в багатокомпонентній термодинамічній системі залишається актуальною задачею. Значний інтерес представляють проблеми дифузії в твердих і рідких розчинах з малими відхиленнями від стану рівноваги, або флуктуаціями. У роботі розроблено загальну методику розрахунку дифузійних потоків у багатокомпонентній термодинамічній системі при малих відхиленнях від рівноважного стану. Встановлено зв'язок між механічним підходом до аналізу узагальнених систем і феноменологічними рівняннями нерівноважної термодинаміки. Наведено приклади використання розробленої методики для аналізу карбідних перетворень у хромистій сталі.

**Ключові слова:** нерівноважна термодинаміка, варіаційні принципи, дифузійні потоки, рівняння руху, карбідні перетворення, хромиста сталь.