Conditions of thermodynamic equilibrium and stability as a basis for the practical calculation of vapour–liquid equilibria

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Abstract

Some main aspects of the thermodynamics of vapour–liquid equilibrium are considered together with a brief review of classical thermodynamic methods. The general thermodynamic–topological singularities of the structure of phase diagrams are discussed, as are the possible use of differential and integral thermodynamic relationships for the analysis and verification of phase equilibria. Special attention is given to results from the work of Russian researchers. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of methods to calculate vapour–liquid equilibria is determined mainly by practical demands. Among the latter, calculating engineering separation processes (distillation, rectification, etc.) is the key problem. Certainly, the practical tasks are always related to the necessity of finding specific solutions, which is not always consistent with a rigorous approach based on fundamental research. The example of the theory of vapour–liquid equilibrium can be taken to illustrate that finding empirical regularities of a particular, narrow sense very often becomes an alternative to the fundamental approach. Obviously, it becomes very useful for practical purposes when, having analysed the experimental data, a researcher generalises an adequate empirical equation that can be used, in particular, to calculate vapour–liquid equilibrium parameters for ternary systems from the data for the binary subsystems even for a narrow class of compounds, e.g., for the systems composed of homologues. Meanwhile, can this approach be of any use for the development of fundamental theory? Moreover, does it make any sense from the practical viewpoint to forget about the capabilities of a universal and rigorous approach and thus to invest money and spend time to obtain particular results that can be useful in some cases but of no use in others?

The idea behind this paper is to remind its readers of the capabilities of the thermodynamic approach, to point out novel and remarkable results from vapour–liquid equilibrium studies, and, above all, to provide for the development of new calculation methods based on the assumptions of fundamental research rather than specific, though useful, correlations. We found it necessary also to refer specifically to results obtained by Russian researchers and thus not generally known to the English-speaking readership.

A sequential account of thermodynamic methods as well as all existing approaches to the investigation of heterogeneous equilibria is not within the scope of this paper. Particular attention is paid to specific problems of interest for the proper development of thermodynamic methods of research.

2. Principles of equilibrium and stability criteria for heterogeneous systems

A universal approach to the study and calculation of phase equilibria is in minimising the energy of the heterogeneous system (e.g., the Gibbs energy, G). In fact, the essence of this method is the direct use of the Gibbs relationships [1] expressing the principles of equilibrium. Thus for the internal energy we have

$$(\delta U)_{S,V,m_1,m_2,\dots,m_n} \geq 0, \tag{1}$$

where S is the entropy, V the volume, m_i the amount of the substance i (e.g., the number of moles). The principles

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Nomenclature

A	chemical affinity ($J\,mol^{-1}$)
C	heat capacity ($J\,mol^{-1}\,K^{-1}$)
f	fugacity of a component (–)
f	degrees of freedom in the phase rule (–)
g	molar Gibbs energy or function ($J\,mol^{-1}$)
K	volatility or K-value (–)
L	partial molar heat of vaporisation of a component ($J\,mol^{-1}$)
n	number of components (–)
n	number of components in the phase rule (–)
p	partial pressure of component (Pa)
P	pressure (Pa)
Q	differential molar heat for a phase transition ($J\,mol^{-1}$)
r	number of phases (–)
r	number of phases in the phase rule (–)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
R	species taking part in a chemical reaction (–)
s	molar entropy ($J\,mol^{-1}\,K^{-1}$)
S	entropy ($J\,K^{-1}$)
T	thermodynamic temperature (K)
u	molar internal energy ($J\,mol^{-1}$)
U	internal energy (J)
v	molar volume ($m^3\,mol^{-1}$)
V	volume (m^3)
x	mole fraction of a component (–)
x	mole fraction of a component in liquid phase, Eq. (71) (–)
X	generalised form of intensive thermodynamic property (–)
y	mole fraction of a component in vapour phase, Eq. (71) (–)
Y	generalised form of extensive thermodynamic property (–)
Z	generalised thermodynamic property (–)

Greek letters

α	composition parameter defined in Eq. (38) (–)
α	relative volatility (–)
α, β	labels denoting ends of a tie-line (–)
γ	activity coefficient of a component (–)
μ	chemical potential of a component ($J\,mol^{-1}$)
ν	stoichiometric number or coefficient for a reacting component (–)

Indices

Az	relates to an azeotrope (–)
i, j, k	indicate specific components in a mixture (–)

Subscripts

i	component in a system (or mixture) (–)
P	at constant pressure (–)
V	at constant volume (–)
$1, 2, n$	components in a system (or mixture) (–)

Superscripts

E	excess function (–)
r	denotes a phase (–)
$'$	relates to kth component subsystem (or sub-mixture) of an n-component multicomponent system (or mixture) (–)
$*$	limiting value, for example of temperature (–)

of equilibrium lead to the following particular conditions of phase equilibrium in a multicomponent multiphase system:

$$
\begin{aligned}
T^{(1)} &= T^{(2)} = \cdots = T^{(r)}, \\
P^{(1)} &= P^{(2)} = \cdots = P^{(r)}, \\
\mu_1^{(1)} &= \mu_1^{(2)} = \cdots = \mu_1^{(r)}, \\
\mu_2^{(1)} &= \mu_2^{(2)} = \cdots = \mu_2^{(r)}, \\
&\quad\vdots \\
\mu_n^{(1)} &= \mu_n^{(2)} = \cdots = \mu_n^{(r)},
\end{aligned} \tag{2}
$$

where T is the absolute temperature, P the pressure, μ_i the chemical potential of the component i, n the number of components, r the number of phases. The upper index refers to a phase.

The entropy form of the principle of equilibrium is as follows:

$$
(\delta S)_{U,V,m_1,m_2,\dots,m_n} \leq 0. \tag{3}
$$

Thus "for the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative" [1]. It should be noted that defining the principle of equilibrium in the form of Eqs. (1) or (3) does not clarify the type of the U or S extreme. In Eqs. (1) and (3), δ means a first-order change of state and corresponds to the virtual displacement in terms of analytical mechanics, i.e., an imaginable change of state. The inequality sign in Eqs. (1) and (3) determines conditions for a sharp extreme that can occur in the case of unidirectional shifts from the equilibrium state [2–4]. Therefore, in the rigorous approach relationships (1) and (3) cannot be interpreted as stability conditions for the equilibrium state. It should be noted that most monographs on thermodynamics present relations expressing principles of equilibrium as having only the equality sign. The inequality sign is considered to be of less importance for the solution of practical problems and of significance only in specific cases. In particular, the full form of the equilibrium principle (equality–inequality) becomes useful in studies of chemical equilibrium [2] and in the application of numerical methods to calculate equilibria [5,6].

The type of the extreme (maximum or minimum), as well as the type of equilibrium (stable, metastable, neutral), determines the criteria of thermodynamic stability:

$$(\Delta S)_{U,V,m_1,m_2,\ldots,m_n} \leq 0, \tag{4}$$

$$(\Delta U)_{S,V,m_1,m_2,\ldots,m_n} \geq 0. \tag{5}$$

According to Gibbs the symbol Δ in Eqs. (4) and (5) signifies an infinitesimal, although definite, increment of a function. This means that when the function is expanded into a Taylor series the infinitesimal members of higher orders have to be taken into account. For both stable and metastable equilibrium, the $<$ sign stays in Eq. (4) ($>$ in Eq. (5)). Gibbs notes that in both cases Δ can mean not only an infinitesimal increment, but also a finite difference in U and S values due to a disturbance of the equilibrium state. The difference between the stable and metastable states means that for the first one both Eqs. (4) and (5) are always valid for any finite difference. In the second case of a metastable state at least one finite displacement (perturbation) exists that does not obey either of the conditions expressed by Eqs. (4) or (5). Therefore, the analysis of stability contains in itself the problem formulated by Gibbs himself (when he discussed one of the form of stability conditions—the inequality $\delta U > T\delta S - P\delta V + \delta_1 m_1 + \cdots + \delta_n m_n$): "it must be possible to assign limits within which it shall hold true of finite differences" [1]. To solve this problem one needs to know the phase diagram of a system [2]; thus classical works on the thermodynamic stability of equilibrium states consider the general case combining both stability and metastability, which means using an infinitesimal Δ in Eqs. (4) or (5).

The equality sign refers to a neutral, or indifferent, equilibrium [1,7]. All other states differing from the equilibrium ones (stable, metastable, and neutral) are non-equilibrium states, Eqs. (4) and (5) are not valid for them, the states corresponding to the unstable range of the phase diagram.

In analysing the stability of phases one can express the stability criteria using variables drawn from the fundamental equations. The condition

$$\Delta T \Delta S - \Delta P \Delta V + \sum_{i=1}^{n} \Delta \mu_i \Delta m_i > 0 \tag{6}$$

is the necessary and sufficient stability criterion of a phase with regard to continuous changes of state. This inequality leads to the condition of convexity for the surface of internal energy,

$$\delta^2 U \geq 0, \tag{7}$$

widely used in the theoretical analysis of stability for specific systems.

In this section, we restrict ourselves to setting out these general and basic notes on deriving conditions of equilibrium and stability in thermodynamics.

3. Differential equations describing phase equilibria

If under changes of state the phase equilibrium is maintained, the equation set of Eq. (2) has to be valid not only for T, P, and μ_i but for the differentials of these parameters too:

$$\begin{aligned} \mathrm{d}T^{(1)} &= \mathrm{d}T^{(2)} = \cdots = \mathrm{d}T^{(r)}, \\ \mathrm{d}P^{(1)} &= \mathrm{d}P^{(2)} = \cdots = \mathrm{d}P^{(r)}, \\ \mathrm{d}\mu_i^{(1)} &= \mathrm{d}\mu_i^{(2)} = \cdots = \mathrm{d}\mu_i^{(r)}. \end{aligned} \tag{8}$$

In addition, the conditions of equilibrium shifts, i.e., the Gibbs fundamental equations, must be valid for each phase

$$\begin{aligned} S^{(1)}\,\mathrm{d}T - V^{(1)}\,\mathrm{d}P + \sum_{i=1}^{n} m_i^{(1)}\,\mathrm{d}\mu_i &= 0, \\ S^{(2)}\,\mathrm{d}T - V^{(2)}\,\mathrm{d}P + \sum_{i=1}^{n} m_i^{(2)}\,\mathrm{d}\mu_i &= 0, \\ &\vdots \\ S^{(r)}\,\mathrm{d}T - V^{(r)}\,\mathrm{d}P + \sum_{i=1}^{n} m_i^{(r)}\,\mathrm{d}\mu_i &= 0, \end{aligned} \tag{9}$$

where $S^{(k)}$, $V^{(k)}$, and $m_i^{(k)}$ are entropy, volume, and the number of moles of component i in the phase k. The upper indices are omitted for the intensive parameters T, P, and μ_i since in the coexisting phases these quantities are equal, due to Eqs. (2) and (8). Thus, Eq. (9) already includes conditions imposed by Eq. (8). If the number of variables T, P, μ_i ($n + 2$) in the set of Eq. (9) equals the number of equations in Eq. (9) then the set has the null solution. This corresponds to the Gibbs phase rule

$$f = n + 2 - r, \tag{10}$$

that defines such a state as invariant with the number of the degrees of freedom, f, equal to 0. It should be noted that it was the equation set of Eq. (9) that Gibbs himself used in deriving the phase rule [1]. For the case where $f > 0$ the variance of the set allows for the equilibrium state to shift along the curves or surfaces (hyper-surfaces) of phase coexistence. Two-phase equilibrium is the simplest case. The solution of the equation set of Eq. (9) for two coexisting phases can be set out as

$$\begin{aligned} (S^{(2)} - S^{(1)})\,\mathrm{d}T &- (V^{(2)} - V^{(1)})\,\mathrm{d}P \\ &+ \sum_{i=1}^{n} (m_i^{(2)} - m_i^{(1)})\,\mathrm{d}\mu_i = 0, \end{aligned} \tag{11}$$

or, replacing the number of moles by concentrations (mole fractions),

$$\begin{aligned} (s^{(2)} - s^{(1)})\,\mathrm{d}T &- (v^{(2)} - v^{(1)})\,\mathrm{d}P \\ &+ \sum_{i=1}^{n} (x_i^{(2)} - x_i^{(1)})\,\mathrm{d}\mu_i = 0, \end{aligned} \tag{12}$$

where $s^{(r)}$ and $v^{(r)}$ are the molar quantities and x_i^r are the mole fractions of a substance i. The use of mole fractions is not obligatory: one can equally use, e.g., weight fractions in writing Eq. (12) with a corresponding change in the meaning

of S, V and μ_i. The equation for the two-phase multicomponent system in the forms of Eq. (11) or (12) includes parameters that characterise changes in entropy, volume and masses of the substances under transition from phase (1) to phase (2). For example, when phase (2) is a vapour and phase (1) is a liquid the difference $S^{(2)} - S^{(1)}$ is the entropy of evaporation. For a single-component system the Clausius–Clapeyron equation for a two-phase single-component system follows directly from Eq. (12)

$$\frac{dP}{dT} = \frac{s^{(2)} - s^{(1)}}{v^{(2)} - v^{(1)}}. \tag{13}$$

We will return to this equation in the next section. Obviously, Eqs. (11) and (12) are rather convenient for the theoretical analysis of two-phase equilibria. In particular, the mathematical treatment is significantly simplified by the fact that all the independent variables in Eq. (11), i.e., the differentiated quantities T, P and μ_i, are intensive parameters that are equal in all coexisting phases. But Eqs. (11) and (12) include as variables the chemical potentials of components which are in general very difficult to both set and determine in practice, i.e., by experiment.

One of the major problems that was solved in the thermodynamics of heterogeneous systems is the transformation of the equations describing the phase equilibrium into the form having concentrations of components as variables rather than μ_i. The works of Van der Waals were the major achievement in this field [8]. He derived his famous differential equation for a two-phase binary system:

$$\left[v^{(2)} - v^{(1)} - (x_1^{(2)} - x_1^{(1)})\frac{\partial v}{\partial x_1}\right] dP$$
$$= \left[s^{(2)} - s^{(1)} - (x_1^{(2)} - x_1^{(1)})\frac{\partial s}{\partial x_1}\right] dT$$
$$+ \frac{\partial^2 g}{\partial x_1^2}(x_1^{(2)} - x_1^{(1)}) dx_1, \tag{14}$$

where g is the molar Gibbs energy. The derivatives in Eq. (14)

$$\frac{\partial V}{\partial x_1}, \qquad \frac{\partial S}{\partial x_1}, \qquad \frac{\partial^2 g}{\partial x_1^2}$$

as well as the dx_1 differential must refer to either phase (1) or phase (2). Deriving Eq. (14) together with its analysis and practical applications are the central point of the book [8] and present the basis of the thermodynamic theory of two-phase binary systems. Meanwhile, one can easily see that now the coefficients at dT and dP gain a different sense. We will consider this in detail when discussing the generalised equation for the multicomponent systems.

Eq. (14) was generalised for ternary systems by Schreinemakers [9]. Unlike Van der Waals' studies this work was almost unrecognised. In 1948, Storonkin [10] published his monograph "On the conditions of thermodynamic equilibrium of heterogeneous systems", where

he described the theory of phase equilibrium based on the differential equations derived by himself and, first of all, the differential equation describing the phase equilibrium in two-phase multicomponent systems. He called this equation the 'generalised Van der Waals differential equation'. His book appeared as a result of studies he had already started at the end of the 1930s. This work, and the subsequent studies of Storonkin and the school in thermodynamics that he founded in Leningrad University, initiated widespread fundamental research in the field of chemical thermodynamics and the theory of phase equilibria in different types of physico-chemical systems, including vapour–liquid equilibria. The significant factor determining the success of this research was the rigorous approach based on the works of Gibbs and Van der Waals. Meanwhile, research at the Department in St. Petersburg (Leningrad) University headed by Storonkin (formerly the Chair of Solution Theory, now the Department of Chemical Thermodynamics and Kinetics) genetically followed the works of the St. Petersburg thermodynamic school presented by such eminent scientists as Mendeleev, Konovalov, and Vrevskii. In most aspects these works meant an upheaval in both the methodology of thermodynamic studies of phase equilibria and the consciousness of physico-chemists in the Soviet Union and other countries. Unfortunately, due to the known barriers between the East and the West, the majority of publications in this area seem to be unknown to western researchers. Most of the works are published in Russian, though; e.g., one of the first and principal works of Storonkin [11] was published in German in 1940 when he was 23 years old. The full system of differential equations of Storonkin–Van der Waals for two-phase multicomponent systems includes the two equations which Storonkin called the generalised Van der Waals differential equations

$$\left[v^{(2)} - v^{(1)} - \sum_{i=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial v}{\partial x_i}\right)^{(1)}\right] dP$$
$$= \left[s^{(2)} - s^{(1)} - \sum_{i=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial s}{\partial x_i}\right)^{(1)}\right] dT$$
$$+ \sum_{i=1}^{n-1}\sum_{k=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial^2 g}{\partial x_i \partial x_k}\right)^{(1)} dx_k^{(1)}, \tag{15}$$

$$\left[v^{(2)} - v^{(1)} - \sum_{i=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial v}{\partial x_i}\right)^{(2)}\right] dP$$
$$= \left[s^{(2)} - s^{(1)} - \sum_{i=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial s}{\partial x_i}\right)^{(2)}\right] dT$$
$$+ \sum_{i=1}^{n-1}\sum_{k=1}^{n-1}(x_i^{(2)} - x_i^{(1)})\left(\frac{\partial^2 g}{\partial x_i \partial x_k}\right)^{(2)} dx_k^{(2)}, \tag{16}$$

and the additional conditions of equilibrium

$$\frac{L_i - L_n}{T} \, dT + (\Delta v_n - \Delta v_i) \, dP - D \left(\frac{\partial g}{\partial x_i} \right)^{(2)}$$

$$+ D \left(\frac{\partial g}{\partial x_i} \right)^{(2)} = 0,$$

$$i = 1, 2, \ldots, s-1, s+1, \ldots, n-1. \qquad (17)$$

The coefficients on the differentials of T and P in Eqs. (15) and (16) are the differential molar entropy and volume effects of the phase transitions. These effects are defined as the differential molar effects of the formation of phases, i.e., the corresponding changes of entropy and volume of a two-phase system under isothermal–isobaric formation of one mole of the phase (2) from the infinite amount of the phase (1) (Eq. (15)) or of one mole of the phase (1) from the infinite amount of the phase (2) (corresponding coefficients in Eq. (16) taken with the opposite sign) [7]. We will denote the volume effects as $v^{(12)}$ and $v^{(21)}$ and the entropy effects as $s^{(12)}$ and $s^{(21)}$. Where phase (1) is a liquid and phase (2) is a vapour, these effects are the differential molar effects of evaporation. The entropy effects in Eqs. (15) and (16) can be expressed through the differential heats $Q^{(12)}$ and $Q^{(21)}$ as given by

$$Q^{(kr)} = Ts^{(kr)}.$$

The derivatives of the type

$$\left(\frac{\partial^2 g}{\partial x_i \partial x_k} \right)$$

directly characterise the thermodynamic stability of a system. L_i in Eq. (17) is the partial molar heat of vaporisation of component i. With $n = 2$ Eqs. (15) and (16) transform into the Van der Waals equation (14) while with $n = 1$ they transform into the Clausius–Clapeyron equation (13).

Undoubtedly, it is not possible in this paper to give even a brief review of all the consequences that have been obtained from Eqs. (15)–(17). The majority of these results as obtained by the mid-1960s were published in monographs [7,12]. We will describe some of the results for vapour–liquid equilibria in the following section.

It should be noted that recently relationships similar to the generalised Storonkin–Van der Waals equation have been widely discussed in the literature (see, e.g., [13]), though it was the research started in St. Petersburg University that led to a very wide range of novel thermodynamic results in this area. In particular, Rusanov [14,15] derived the generalised differential equation for phase equilibria accounting for surface phenomena. Filippov worked out the thermodynamics of phase equilibria within the metrics of the Gibbs energy (see, e.g., [16–18]). According to the latter approach the generalised differential equation of Storonkin–Van der Waals takes the following compact form:

$$(\vec{x}_\beta - \vec{x}_\alpha)\hat{G}_\alpha \, d\vec{x}_\alpha = s(\alpha|\beta) \, dT - v(\alpha|\beta) \, dP, \qquad (18)$$

which simplifies both the use of the equation in some applications and deriving several new consequences. In Eq. (18) $\vec{x}_\beta - \vec{x}_\alpha$ and $d\vec{x}_\alpha$ are, respectively, the vectors of the $\alpha\beta$ tie-line and the shift of the α-phase composition ($\vec{x}_\beta - \vec{x}_\alpha)\hat{G}_\alpha \, d\vec{x}_\alpha$ is their scalar product in the metric of the Gibbs energy, $v(\alpha|\beta)$ and $s(\alpha|\beta)$ are the coefficients on the differentials of T and P in Eq. (14). For example, it follows directly from Eq. (18) that for $T, P =$ const the vectors $\vec{x}_\beta - \vec{x}_\alpha$ and $d\vec{x}_\alpha$ should be orthogonal, i.e., tie-lines and isotherms–isobars of coexistent phases can only cross but not touch each other.

Differential equations for multiphase multicomponent systems together with the results of their investigation are published in the monograph [12].

One would expect that the development of the thermodynamic theory on the base of rigorous differential equations describing phase equilibria might lead to the development of applied calculation methods on the base of these equations. It was Van der Waals who was the first to note that to do this one needs to know the equation of state for the phases [8]. Though Van der Waals himself was the author of a widely known equation of state, in his time the possibilities of such synthesis of the thermodynamic phenomenology and molecular-statistical approach were very restricted. This was due to the then insufficient development of the kinetic theory and of the molecular theory of solutions, and, naturally, to the lack of the calculation capabilities that we have nowadays.

Unfortunately, modern methods of phase equilibria calculation do not use the achievements of the thermodynamic theory to their full extent. Sometimes one gets the impression that thermodynamics and the calculation methods in the theory of equilibrium exist independently, being close but not closely related fields of science. The problem to be solved when putting together empirical equations of state and rigorous differential equations of the thermodynamic theory is the problem of integrating the differential equations. In doing this, even integrating such an important thermodynamic relationship as the Gibbs–Duhem equation becomes only a special case since it leaves open the question about the type of dependence of chemical potentials on temperature and pressure. Therefore, the universal approach would be in integrating a general relationship like, e.g., the generalised Storonkin–Van der Waals equation. Unfortunately, this problem is not yet solved.

4. Rules of Konovalov and Vrevskii

Numerous aspects of thermodynamics of equilibrium between liquid phases and vapour are widely described in the literature. There is no need in this brief review to either derive the main equations or to review all literature sources treating this problem. We will concentrate on describing only several important problems of the theory.

The main goal of the theory of phase equilibria is to establish a correlation between the compositions of the coexisting phases, temperature, pressure, and other thermodynamic properties (surface, electrical, magnetic and other properties).

Usually, the following problems are solved in the theory of vapour–liquid equilibria:

- the problem of the correlation between the composition of the phases, temperature, and pressure (under isobaric or isothermal conditions, respectively);
- the problem of the influence of temperature and pressure on the phase equilibrium under some additional conditions imposed by changes in the composition of the phases.

The first group of problems is the subject of the rules (laws) of Konovalov, the second that of the rules (laws) of Vrevskii. Both researchers gave their original thermodynamic inferences of several fundamental laws for vapour–liquid equilibria in binary systems. The further thermodynamic analysis showed that all these rules may be formulated on the base of a single approach, i.e., with the help of the Van der Waals differential equation [19].

Let us consider just three rules of Konovalov and three rules of Vrevskii. The first rule of Konovalov can be derived from the combination of the differential equations of Eq. (14) written with the variables for the liquid and vapour phases, which gives [7]

$$\left(\frac{\mathrm{d}P}{\mathrm{d}x^{(1)}}\right)_T = \left(\frac{\partial^2 g}{\partial x^2}\right)^{(1)} \frac{x^{(2)} - x^{(1)}}{v^{(12)}}, \tag{19}$$

$$\left(\frac{\mathrm{d}P}{\mathrm{d}x^{(2)}}\right)_T = \left(\frac{\partial^2 g}{\partial x^2}\right)^{(2)} \frac{x^{(1)} - x^{(2)}}{v^{(21)}}, \tag{20}$$

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x^{(1)}}\right)_P = -\left(\frac{\partial^2 g}{\partial x^2}\right)^{(1)} T \frac{x^{(2)} - x^{(1)}}{Q^{(12)}}, \tag{21}$$

$$\left(\frac{\mathrm{d}T}{\mathrm{d}x^{(2)}}\right)_P = -\left(\frac{\partial^2 g}{\partial x^2}\right)^{(2)} T \frac{x^{(1)} - x^{(2)}}{Q^{(21)}}. \tag{22}$$

One can easily see that Eqs. (19)–(22) directly determine the influence of changes in composition on pressure (T constant) or temperature (P constant). Under normal conditions far from the critical conditions, we have

$$V^{12} > 0, \qquad Q^{12} > 0, \tag{23}$$

and

$$V^{21} < 0, \qquad Q^{21} < 0. \tag{24}$$

The derivatives $\partial^2 g / \partial x^2$ in these relationships are positive due to the stability criteria. Therefore, the sign of the derivatives is fully determined by the difference in the liquid and vapour compositions. Hence we obtain the rules which express the well-known first rule of Konovalov:

- The pressure of the vapour over a solution increases (decreases) with the increase of the amount of the component whose concentration in the vapour is larger (lower) than in the solution.
- The boiling temperature of a solution increases (decreases) with the increase of the amount of the component whose concentration in the vapour is lower (larger) than in the solution.

Exceptions from these rules are due to the conditions of Eqs. (23) and (24). In fact, for the states close to the critical point the signs of the volume and heat effects can change to the opposite, which will result in the violation of the above rules. Figs. 1 and 2 present diagrams for binary systems
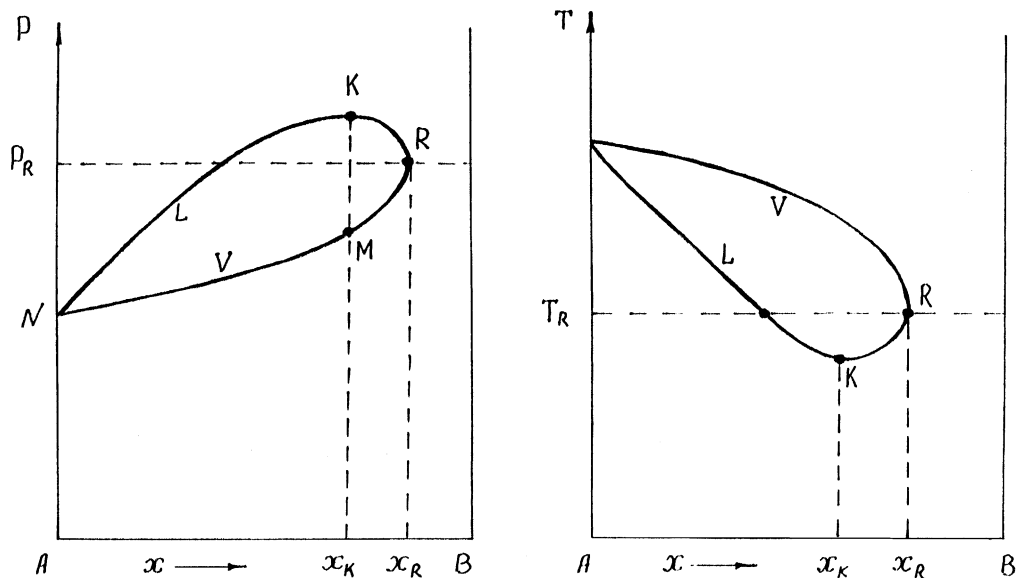

Fig. 1. Equilibrium diagrams of binary vapour–liquid systems under isothermal and isobaric conditions with critical points. K is the critical point, P_R and T_R the borders of the performance of Konovalov's first rule.
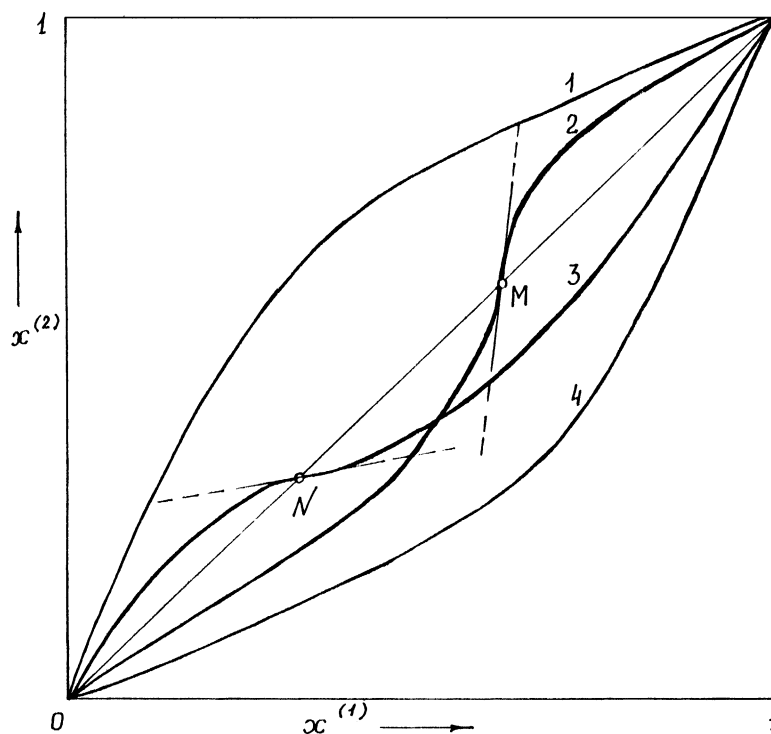
Fig. 2. Dependence of vapour composition on the liquid composition in binary systems. Dotted lines are tangents to the curve $x^{(2)} = f(x^{(1)})$ at the azeotropic points (M is the minimum of pressure or maximum of temperature, N the maximum of pressure or minimum of temperature). Curves 2 and 3 with azeotropic points, 1 and 4 with non-azeotropic systems.

with critical points in the vapour–liquid equilibrium. It is evident that at pressures higher than P_R and temperatures lower than T_R the first rule of Konovalov is not obeyed. At $P = P_R$ and $T = T_R$ the values of V^{12} and V^{21} or Q^{12} and Q^{21} become equal to zero.

The second rule of Konovalov refers not to the full vapour–liquid equilibrium diagram, but to the extreme points of the boiling temperature or vapour pressure. Therefore, it is a particular consequence following from Eq. (14):

- In the extreme points of temperature or pressure the compositions of the coexisting phases are equal.

This is a condition for azeotropy and it is the essence of the second rule of Konovalov. It should be noted that the second rule has a general thermodynamic meaning, i.e., it is not restricted to binary vapour–liquid systems but can be extended to two-phase multicomponent systems of any physico-chemical type, e.g., liquid–solid systems. In the world literature this rule (law) is called the Gibbs–Konovalov theorem since the analogous conclusion can be found already in the work of Gibbs [1].

If one combines Eqs. (19) and (20) or (21) and (22) for different phases the following equations are obtained:

$$\left(\frac{\mathrm{d}x^{(2)}}{\mathrm{d}x^{(1)}}\right)_T = -\frac{(\partial^2 g/\partial x^2)^{(1)}}{(\partial^2 g/\partial x^2)^{(2)}}\frac{v^{(21)}}{v^{(12)}}, \tag{25}$$

$$\left(\frac{\mathrm{d}x^{(2)}}{\mathrm{d}x^{(1)}}\right)_P = -\frac{(\partial^2 g/\partial x^2)^{(1)}}{(\partial^2 g/\partial x^2)^{(2)}}\frac{Q^{(21)}}{Q^{(12)}}. \tag{26}$$

When the inequalities given in Eqs. (23) and (24) are fulfilled one obtains the following rule:

- Under isothermal and isobaric conditions the compositions of the coexisting phases of a binary vapour–liquid system change in a similar direction.

This rule is referred to as the third rule of Konovalov. Now we will consider the rules of Vrevskii. For the sake of brevity we will give the rules without deriving them thermodynamically. According to the first rule [7],

- On increasing the boiling temperature of a solution with given composition the vapour becomes enriched with the component whose partial molar evaporation heat is larger.

Again, this rule may not be obeyed in the vicinity of critical points. Besides, it is supposed that one may neglect the non-ideality of the vapour.

The second rule of Vrevskii determines the direction of changes in the composition of the azeotrope with the changes in temperature [4,7,20]:

- If the vapour pressure of the vapour–liquid system has a maximum (minimum) value, then on increasing temperature the azeotrope mixture witnesses the increase of

concentration of the component whose partial molar evaporation heat is higher (lower).

Analogous rules occur in the case of varying pressure. The limitations with regard to the validity of the second rule are the same as for the first one. If one takes into account that the volume of the vapour significantly exceeds the volume of the condensed phases then the second rule of Vrevskii can be expressed by the following relationship:

$$\left(\frac{dx}{dT}\right)_{Az} \approx \frac{x_{Az}(1 - x_{Az})}{1 - (\partial x^{(2)}/\partial x^{(1)})_{P,T}} \frac{L_1 - L_2}{RT^2}, \tag{27}$$

where the index Az means that the respective quantity refers to the azeotrope, and L_1 and L_2 are the partial molar evaporation heats of components 1 and 2.

It follows from Eq. (27) that several qualitative consequences can be deduced with regard to the temperature shifts of the azeotropes [7]. For example, the intensity of the temperature shift of the azeotrope composition will be larger which

- the difference of partial molar evaporation heats of the components is higher;
- the difference in vapour and liquid compositions is lower;

- the composition of the azeotrope to 0.5 mol fraction is closer.

It should be noted that Eq. (27) can be used for the direct quantitative calculations of the shifts of the azeotrope composition with temperature. The value of the derivative

$$\left(\frac{\partial x^{(2)}}{\partial x^{(1)}}\right)_{P,T}^{Az}$$

can be calculated as the inclination tangent of the curve $x^{(2)} = f(x^{(1)})$ (Fig. 2). Fig. 3 presents the dependencies of azeotrope composition on temperature for various binary systems [7]. Difficulties in using Eq. (27) for practical calculations are due to the determination of values of partial molar evaporation heats of components, L_i. Though it is often noted in the literature that partial molar evaporation heats can be replaced by evaporation heats of pure components, in practice such replacement turns out to be incorrect.

The third rule of Vrevskii enables one to compare the influence of temperature changes on the composition of the azeotrope and vapour (with fixing the composition of the solution) [7].
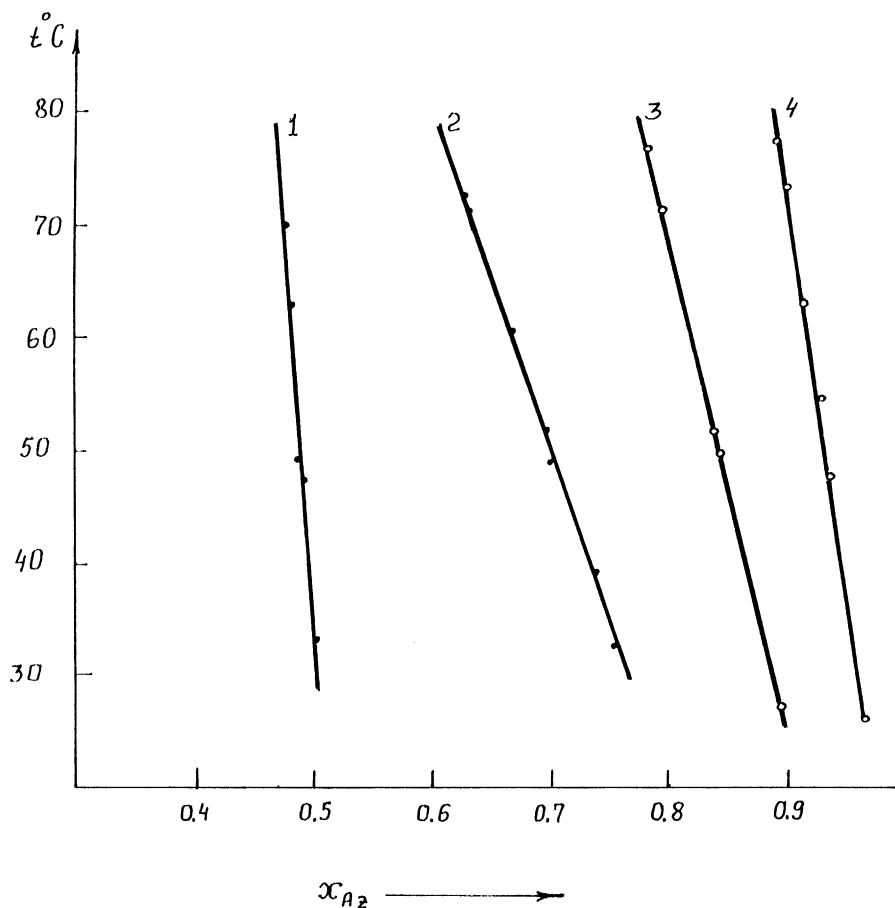

Fig. 3. Dependencies of binary azeotropic compositions on temperature in the systems: (1) cyclohexane (x)–benzene; (2) benzene (x)–propanol-2; (3) benzene (x)–propanol; (4) benzene (x)–2-methylpropanol-1 [7].
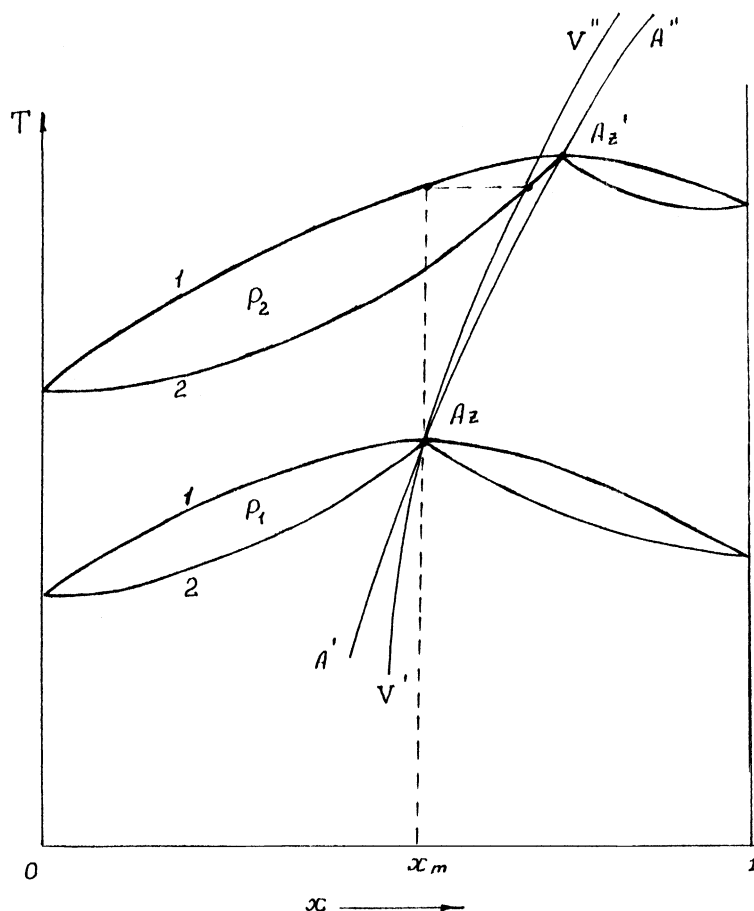
Fig. 4. Displacement of vapour composition and binary azeotropic composition relative to the initial composition of a solution with change of temperature. V′–V″ and A′–A″ curves for displacement of the vapour and solution compositions, respectively.

- On changing the temperature of the solution whose curve of the vapour pressure passes through the maximum (minimum) the composition of the vapour over the solution as well as the composition of the azeotrope mixture change in the same direction (in opposite directions).

Obviously, this rule can be considered the combination of the first and second rules of Vrevskii. Fig. 4 illustrates one of the variants of the system's behaviour. On increasing temperature, the composition of the azeotrope is enriched with the component 2. The vapour corresponding to the composition x^0 is also enriched with the component 2, which means that in this case the compositions of the azeotrope and the vapour change in the same direction. The analogous regularities occur in the case of dependence on pressure. It should be noted that the formulation of the third rule follows from the rigorous thermodynamic relationship

$$\left(\frac{dx_{Az}}{dT}\right)_{x^0} = \frac{(\partial^2 g/\partial x^2)^{(2)}}{(\partial^2 g/\partial x^2)^{(2)} - (\partial^2 g/\partial x^2)^{(1)}}\left(\frac{dx^{(2)}}{dT}\right)_{x^0},$$

(28)

where the symbol x^0 indicates that the derivatives are taken in the same point of the composition of the solution.

Therefore, the third rule is free from limitations similar to those for the first and second rules of Vrevskii. In particular, this rule is valid for the systems consisting only of condensed phases.

Expansion of the rules of Konovalov and Vrevskii to multicomponent systems can also be performed on the base of the differential equations of coexistence of phases, i.e., the system of generalised equations (15)–(17). However, even for ternary systems the fulfilment of the rules as expressed for binary systems depends on the way the composition is changed. For example, on adding one of the components to a ternary mixture, that is on shifting the composition of the solution along the secants of the concentration triangle, the first rule of Konovalov may not be fulfilled in the above formulation.

The book [7] gives the conditions under which this rule is violated (see Fig. 5). At the point M the secant of the concentration triangle touches the isotherm–isobar of the solution, i.e., the following condition holds:

$$\left(\frac{\partial P}{\partial x_3^{(1)}}\right)_{x_1/x_2=\text{const}} = 0, \quad \text{or} \quad \left(\frac{\partial T}{\partial x_3^{(1)}}\right)_{x_1/x_2=\text{const}} = 0.$$
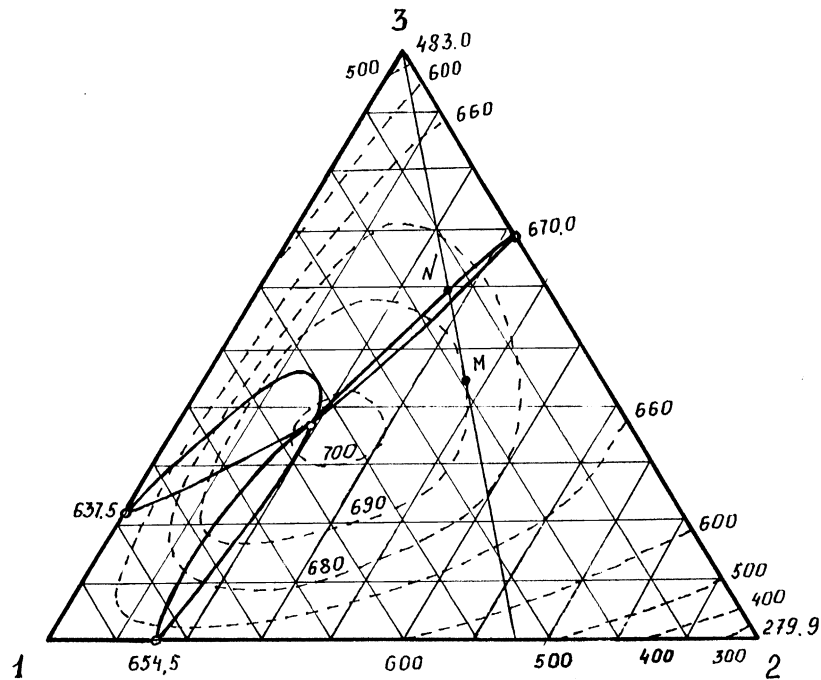
(29)

Fig. 5. Isotherms–isobars, the line x_1/x_2 = const and the region where Konovalov's first rule is not valid the segment MN (the chloroform(1)–ethanol(2)–hexane(3) ternary at 328.15 K [105]).

The condition that has to be fulfilled for the point N is

$$x_3^{(1)} = x_3^{(2)}. \tag{30}$$

Meanwhile, we can point to the only way of changing the composition when the first rule of Konovalov becomes valid for all components. This is the case of open evaporation curves, i.e., the curves along which the composition of the solution changes in the course of evaporation (simple distillation lines). It is well known that the differential equation of a simple distillation line is

$$\left(\frac{\mathrm{d}x_i}{\mathrm{d}x_k}\right)_D = \frac{x_i^{(2)} - x_i^{(1)}}{x_k^{(2)} - x_k^{(1)}}. \tag{31}$$

Combining this relationship with the generalised Storonkin–Van der Waals equation (15) and keeping in mind the criteria of stability for the phases we can show that the first rule of Konovalov is fulfilled along the curves described by Eq. (31). Obviously, the general regularities of the dependence of changes in T or P on the shift of the composition of a multicomponent system are not necessarily related to the classical formulation of the first rule of Konovalov for binary systems. For example, using the vector form of the generalised differential equation (18) one can show that when the composition of a liquid shifts infinitesimally from the isotherm–isobar in the direction of the vapour–liquid tie-line vector ($L \rightarrow V$) (in other words, from the isotherm–isobar of liquid to the isotherm–isobar of vapour in the concentration triangle), the pressure increases (the temperature decreases). This conclusion seems to be rather natural and self-evident.

In this paper, we will not consider in detail the generalisation of other rules of Konovalov and Vrevskii for multicomponent systems. It should be noted, e.g., that some qualitative rules for shifting the composition of azeotrope mixtures with temperature [21] can be treated as the generalisation of the respective rules of Vrevskii. Besides, we recall that the second rule of Konovalov (the Gibbs–Konovalov theorem) is of a general thermodynamic nature and has no limitations with regard to either the physico-chemical type of the systems or the number of components. Some peculiarities of the correlation between T, P and the composition of multicomponent systems including several liquid phases are also outside the scope of this paper. We only note that they can be treated on the base of the system of generalised Storonkin–Van der Waals differential equations for multiphase systems [10].

5. Systems with chemical reactions

In this section, we will discuss several peculiarities of the thermodynamic analysis of systems with chemical reactions. Nowadays these systems attract increasing attention of the researchers (see, e.g., [22–26]). The practical reason for this interest can be explained mostly by the intensive development of new technologies involving mass exchange processes in reactive systems.

Investigation of the correlation between chemical affinity, rate of chemical reactions, and other parameters characterising the state of a reactive system based on the thermodynamics of irreversible processes was carried out thoroughly

by the school of Prigogine. For relatively low reaction rates a reactive liquid mixture together with the coexisting vapour can be treated as a two-phase system in a state of partial (phase but not chemical) equilibrium. In this case, the investigation of the regularities of changes in the characteristics of the phases with the changes in composition can be performed in the way similar to that of the regularities for the common systems without reaction. Meanwhile, the reactive systems prohibit some peculiarities that differentiate them from the systems without reaction.

We will consider the ultimate instance of the chemical equilibrium in a multicomponent solution. In this case, the conditions of phase equilibrium or the fundamental equations for the phases must be taken together with the conditions of chemical equilibrium

$$\sum v_j \mu_j = 0, \tag{32}$$

where v_j is the stoichiometric coefficient of a substance i participating in the reaction

$$\sum v_j R_j = 0. \tag{33}$$

We will describe this case on the base of the results obtained by Zharov [27–29], who was one of the first to set and solve the problem of a correct thermodynamic approach to the phase equilibria in reactive mixtures. For the sake of simplicity we will confine ourselves to considering a single reaction in a system consisting of four substances where the total number of moles is unchanged:

$$\sum_{j=1}^{4} v_j R_i = 0, \tag{34}$$

or

$$R_1 + R_2 = R_3 + R_4, \tag{35}$$

where v_i are stoichiometric coefficients, and $v_1, v_2 = -1$, $v_3, v_4 = +1$. Combining the condition expressed in Eq. (34) with the fundamental equation for the Gibbs energy

$$dg = -s\,dT + v\,dP + \sum_{j=1}^{4} \mu_j\,dx_j, \tag{36}$$

we obtain the equation

$$dg = -s\,dT + v\,dP + \sum_{j=1}^{3} \mu_j\,d\left(x_j - \frac{v_j}{v_4}x_4\right), \tag{37}$$

which, as against Eq. (36), includes only three values of the chemical potentials, namely for the components 1–3. The form of Eq. (37) makes it possible to introduce, in a rational manner, new composition parameters—the values in brackets after the summing symbol in the right-hand side of Eq. (37). On the surface of chemical equilibrium the composition of the solution is characterised by three parameters α_j (accounting for the v_j values)

$$\alpha_1 = x_1 + x_4, \qquad \alpha_2 = x_2 + x_4, \qquad \alpha_3 = x_3 - x_4. \tag{38}$$

The quantities α_j are interrelated through an equation following from Eq. (37)

$$\alpha_1 + \alpha_2 + \alpha_3 = 1. \tag{39}$$

And from Eq. (38)

$$0 < \alpha_1 < +1, \qquad 0 < \alpha_2 < +1, \qquad -1 < \alpha_3 < +1. \tag{40}$$

Therefore, on the surface of chemical equilibrium (the surface of a zero chemical affinity, $A = 0$) the composition of a given reactive mixture can be presented in the concentration square of the variables α.

It should be noted that the surface of chemical equilibrium itself presents a surface inside the concentration tetrahedron. The complete set of points that belong to the tetrahedron includes all the compositions, both chemically equilibrium and non-equilibrium. All four planes of the tetrahedron correspond to chemically non-equilibrium ternary systems, two of the six edges correspond to the non-equilibrium binary systems (R_1–R_2, R_3–R_4), and the remaining four edges correspond to chemically inert binary systems (R_1–R_3, R_1–R_4, R_2–R_3, R_2–R_4) that can be formally treated as being in chemical non-equilibrium.

Fig. 6 shows the surface of chemical equilibrium of the system involving an esterification–hydrolysis reaction

$$CH_3COOH + CH_3CH_2OH \Leftrightarrow CH_3COOCH_3CH_2 + H_2O \tag{41}$$
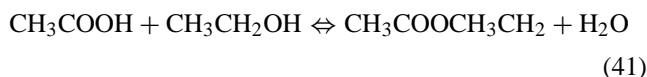
in the concentration space using a rectangular co-ordinate system (the surface is built using the data from [30]). Obviously, such presentation of the data makes it difficult or insufficiently illustrative to draw isotherms–isobars for the phase equilibrium. The use of the concentration square of
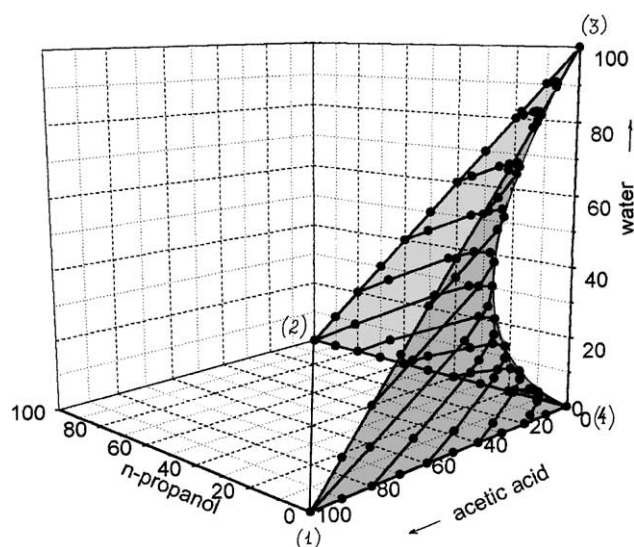

Fig. 6. The surface of chemical equilibrium in the system: acetic acid(l)–propanol(2)–water(3)–propyl acetate(4) at 318.5 K. Points on the surface are experimental results from [30].
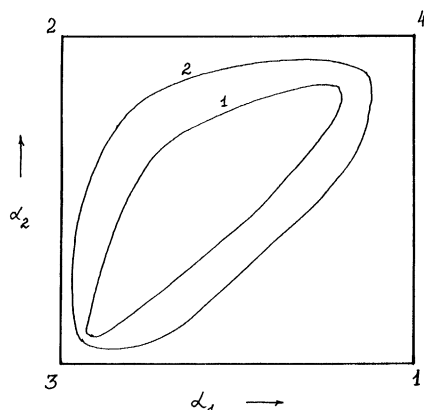
Fig. 7. Isotherms–isobars for the liquid phase for vapour–liquid equilibrium on the chemical equilibrium surface for acetic acid(1)–propanol(2)–water(3)–propyl acetate(4) at 318.5 K: (1) 100, (2) 90 mm Hg.

the α-parameters makes possible a more convenient representation. In this case, the isotherms–isobars can be presented in the plane rather than in a 3D diagram. Figs. 7 and 8 display the isotherms–isobars of the surface of pressure for the liquid and the equilibrium vapour in the state of chemical equilibrium of the reaction (41) [30,31]. The shape of the curves in Figs. 7 and 8 shows that there is a point on the surface of chemical equilibrium that corresponds to the extreme (maximum) of vapour pressure over the solution. Meanwhile, this point is not a common azeotrope since here the composition of vapour and liquid are not equal. In accordance with the Gibbs–Konovalov theorem the condition of equality of phase compositions is valid only in the point of absolute extreme of P or T rather than in that of the conditional extreme. As for the extreme in the chemical equilibrium states, it corresponds only to the conditional extreme on the surface $A = 0$.
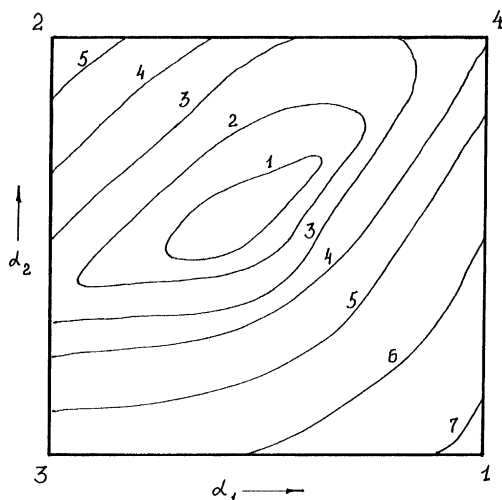

Fig. 8. Isotherms–isobars for the vapour phase for vapour–liquid equilibrium on the chemical equilibrium surface for acetic acid(1)–propanol(2)–water(3)–propyl acetate(4) at 318.5 K: (1) 100, (2) 90, (3) 80, (4) 70, (5) 60, (6) 50, (7) 40 mm Hg.

Among other works dealing with the vapour–liquid equilibria in reactive systems we will note the paper [24] introducing the concept of azeotropy in reactive systems (reactive azeotrope), papers [22,23,25] presenting reviews of the problem, and some other works [32–34]. For example, in the paper [34] a somewhat different approach to presenting the composition of a reactive system is presented.

6. Thermodynamic verification and calculation of vapour–liquid equilibria

In the numerous publications in the literature on the thermodynamics of vapour–liquid equilibria the key attention seems to be paid to problems of thermodynamic verification of the data. This is for two reasons. The first one is the practical importance of data verification methods for any physico-chemical experiment. The second one is the relative simplicity and the possibility of almost direct use of even the fundamental equations of thermodynamics for the data verification. The very evident illustration of the usefulness of thermodynamics for solving practical problems is in the thermodynamic methods of data verification. Obviously, the importance of the problem gave birth to a very wide range of thermodynamic research works aimed at the development of thermodynamic data verification methods. In this section, we will give a brief review of the main approaches and directions in qualitative and quantitative thermodynamic verification of data on equilibrium between one or several liquid phases with the vapour in multicomponent systems. A possible classification of the methods can be presented as follows:

- methods based on the direct use of conditions of equilibrium and the respective consequences in differential form;
- methods based on integrating the differential equations describing the equilibrium;
- methods based on the use of thermodynamic inequalities—stability criteria and their consequences;
- methods using thermodynamic–topological analysis of phase diagrams.

The direct use of thermodynamic relationships (conditions of equilibrium or stability criteria) seems to be the most reliable approach to data verification. For example, violation of the first rule of Konovalov in the case of binary systems points to the incorrectness of the data obtained, certainly if all the requirements are met with regard to the rule's origin. Therefore, the differential methods of data verification enable one not only to form conclusions about the correctness of the data at a given point (points) of the phase diagram, but to evaluate the phase diagram as a whole and to differ between thermodynamically consistent structures and unfeasible structures.

The differential thermodynamic relationships that follow from the conditions of equilibrium are presented by, e.g.,

Maxwell's equations:

$$\frac{\partial X_i}{\partial Y_k} = \frac{\partial X_k}{\partial Y_i}, \qquad \frac{\partial Y_k}{\partial X_i} = \frac{\partial Y_i}{\partial X_k}, \qquad \frac{\partial X_i}{\partial X_k} = -\frac{\partial Y_k}{\partial Y_i}, \quad (42)$$

where X_j is an intensive parameter (T, $(-P)$, μ_1, $\mu_2, \ldots, \mu_n$), and Y_j the conjugate extensive parameter (S, V, $m_1, m_2, \ldots, m_n$). Another example is the triple product for the derivative of a thermodynamic function, Z:

$$\left(\frac{\partial Y_3}{\partial Y_2}\right)_{Z_1, Y_1} \left(\frac{\partial Y_1}{\partial Y_2}\right)_{Z_2, Y_2} \left(\frac{\partial Y_2}{\partial Y_1}\right)_{Z_3, Y_3} = -1, \quad (43)$$

where $Z_i = \partial Z / \partial Y_i$ [2,35]. Eq. (43) can be expanded to the case of an arbitrary number of parameters Y_i [36].

Eqs. (42) and (43) and the analogous relationships can be applied to verify (and calculate) the mutual position of constant value lines (isolines) for thermodynamic properties. For example, for the case of isolines of relative volatility α_{ik}

$$\alpha_{ik} = \frac{x_i^{(2)}/x_i^{(1)}}{x_k^{(2)}/x_k^{(1)}},$$

which is an important parameter in the theory of vapour–liquid equilibria, the following equation is valid determining the position of the $\alpha_{ik} = $ const isolines in a ternary system [36]:

$$\left(\frac{dx_3}{dx_1}\right)_{\alpha_{31}} \left(\frac{dx_2}{dx_3}\right)_{\alpha_{23}} \left(\frac{dx_1}{dx_2}\right)_{\alpha_{12}} = 1, \quad (44)$$

where the subscript α_{ik} means that the derivative is taken under the condition $\alpha_{ik} = $ const, i.e., along the respective isolines. Eq. (44) and similar equations (e.g., the rule of Schumann for the isolines of chemical potentials [37]) can be easily visualised geometrically. Fig. 9 presents isolines of relative fugacity together with the respective tangents (at their cusp point). From Eq. (44), the following method
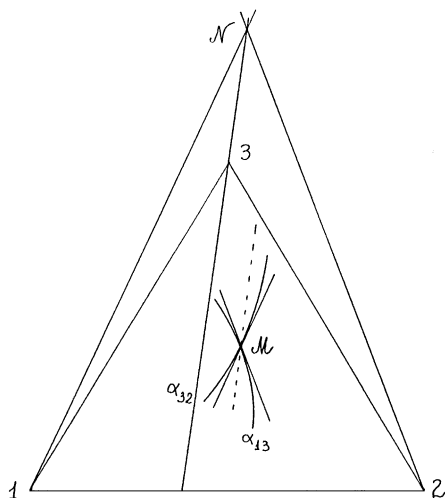

Fig. 9. Isolines of relative volatility and tangents to them. The calculation of the direction of the isoline $\alpha_{12} = $ const at point M from the location of curves $\alpha_{32} = $ const and $\alpha_{31} = $ const (for a description see text).

follows which enables one to determine the direction of the isoline α_{12} on the basis of the direction of the other ones (α_{13} and α_{23}) at the given point M. If one draws straight lines through the apexes 1 and 2 of the concentration triangle parallel to the tangents of the curves α_{32} and α_{13}, respectively, then the straight line passing through their cusp point M and apex 3 should be parallel to the tangent of the isoline $\alpha_{12} = $ const at the point M.

A significantly large number of similar specific rules is worked out in the theory of vapour–liquid equilibrium. These rules are mostly published in original papers and in only a few monographs (e.g., [7,12]). Among the other examples of the direct use of thermodynamic differential relationships we will note the method of qualitative verification of the direction of isotherms–isobars of vapour in ternary systems, which is based on the use of the equation of the isotherm–isobar for an ideal vapour. The paper [38] gives the following modified equation for the isotherm–isobar of an ideal vapour

$$\left(\frac{dx_2^{(2)}}{dx_1^{(2)}}\right)_{T,P} = -\frac{\alpha_{31} - 1}{\alpha_{32} - 1}. \quad (45)$$

When presenting experimental data for ternary systems with the use of the isotherms–isobars of the vapour there appear several problems due to the direct (i.e., without using models) approximation of the curves. The reason for this follows from the fact that usually experiments on studying vapour–liquid equilibria are carried out under an ordered pre-setting of the solution compositions, the equilibrium vapour compositions are determined in the course of the experiment and thus the corresponding figurative points in the concentration triangle are positioned in an unordered way. As a result, the presentation of the isotherms–isobars of the vapour or the surface of pressure in the ternary system occurs with more pronounced errors than the presentation of the respective curves and surfaces for the solution. This fact determines, to a large degree, the value of the method proposed in [38].

The directions of the isotherms–isobars calculated with Eq. (45) for the composition points studied in the experiments must accord with the approximate direction of the isotherms–isobars. Fig. 10, taken from [38], illustrates well this method for the methyl acetate–chloroform–methanol system. The figure presents experimental points for the vapour, tangents to isotherms–isobars of the vapour in these points, and the isotherms–isobars themselves, their direction being calculated from the experimental data. Fig. 11 presents the results of the analogous verification for the homogeneous range of the dibutyl ether–water–n-butyl alcohol system [39] in which phase separation occurs. It should be noted that several rules follow from Eq. (45), which determine the mutual position of the isotherms–isobars and tie-lines in ternary systems.

The second group of data verification methods for the vapour–liquid equilibria is of methods based on integrating
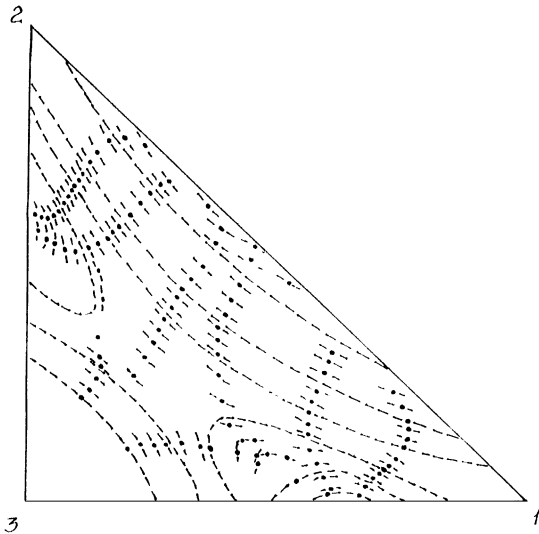
Fig. 10. The test of the location of isotherms–isobars for the vapour in the system methyl acetate(1)–chloroform(2)–methanol(3) by the method of Eq. (45): experimental points of vapour composition, tangents to isotherms–isobars at these points and isotherms–isobars (dotted lines) [38].

thermodynamic differential equations. The classical example is the often-used method due to Herington [40] and Redlich and Kister [41]. The attractiveness of the integral methods is that they test the thermodynamic consistency of a complete set of experimental data, e.g., data on the equilibrium for the whole concentration range of a binary system. Most versions of the methods in question use equations for the excess

thermodynamic properties. For example, if the activity coefficients γ_i of a binary system components are normalised symmetrically ($\gamma_i \to 1$ when $x_i^{(1)} \to 1$) the following equation becomes valid:

$$\int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1^{(1)} = 0, \tag{46}$$

and can be used for the direct verification of the isothermal data for the equilibrium. It should be remembered that the integrated function in Eq. (46) can be expressed using the average molar excess Gibbs energy, g^E, as

$$\frac{g^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2, \tag{47}$$

$$d\left(\frac{g^E}{RT}\right)_{T,P} = \ln \gamma_1 \, dx_1 + \ln \gamma_2 \, dx_2 = \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1. \tag{48}$$

At first glance, the integral relationship of Eq. (46) does not include parameters characterising the vapour phase. In fact, it is supposed that the quantities γ_i or g^E are calculated from the data on the equilibrium vapour, either ideal or not. For a non-ideal vapour, to calculate activity coefficients one has to use the data for the parameters taking into account the deviation of the vapour from the ideal behaviour (association constants, virial coefficients, etc.).

The existing methods exhibit some difference between the verification of isobaric and isothermal data. As a rule, one may neglect the influence of pressure on chemical potentials and accordingly on activity coefficients in the liquid
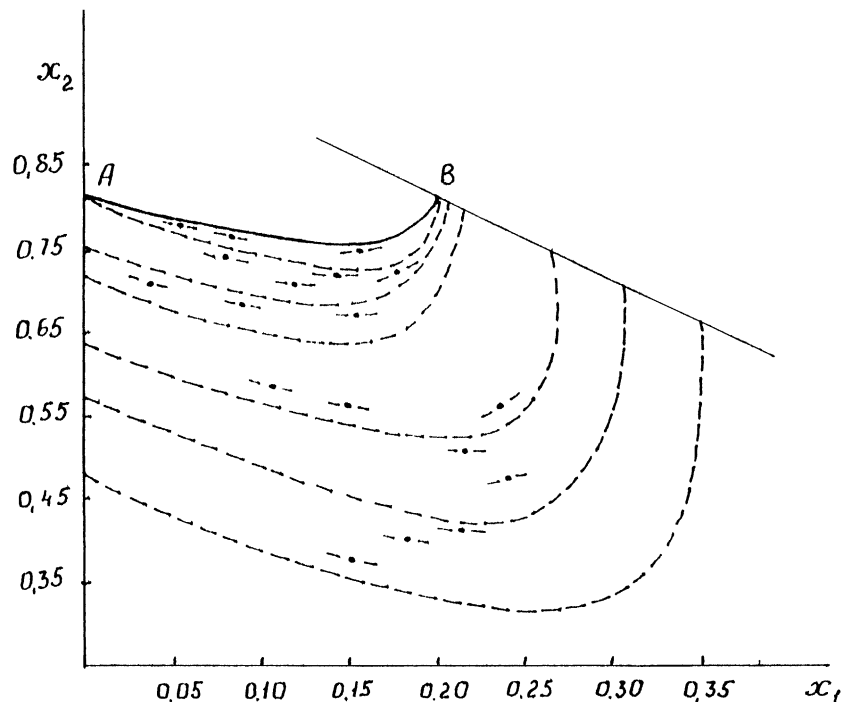

Fig. 11. The test of the location of isotherms–isobars for the vapour in the homogeneous region of a system with limited miscibility (dibutyl ether(1)–water(2)–butyl alcohol(3) at 323.15 K) by the method based on Eq. (45): experimental points of vapour composition, tangents to isotherms–isobars at these points and isotherms–isobars (dotted lines) [39].

phase. This embeds the same insignificant error into the calculations as neglecting the compressibility of liquids or the volume of the liquid phase compared to the volume of the vapour. But the enthalpy term in the fundamental equations, which directly reflects the dependence of thermodynamic properties on temperature, cannot be so neglected.

In using the integral methods of data verification one has to keep in mind that in this case a positive result is a necessary, but not sufficient, condition of the thermodynamic consistency of the data. Several original papers, e.g. [42–44], analyse what is "good" and what is "bad" with regard to the results of integral thermodynamic data verification. Together with the increase in the number of experimental works on studying vapour–liquid equilibria, the sophistication of the phase structure of the systems, the increase in the number of components, and the study of reactive systems, came the development of data verification methods based on integrating fundamental thermodynamic equations. Nowadays one of the most popular methods is the one proposed by Van Ness (see, e.g., [45–47]).

It should be noted that in the case of multicomponent systems when integrating fundamental equations one has to pre-set a definite direction of the composition change. For example, in ternary vapour–liquid–liquid systems data verification can be performed on shifting the composition along the curves of three-phase equilibrium. We can note Refs. [48–51] among the pioneer works on data verification methods in ternary vapour–liquid–liquid systems. Several aspects of data verification with regard to the vapour–liquid equilibrium at the surface of chemical equilibrium are discussed in [52].

Thermodynamic equations used for data verification can equally well be used for calculations. In fact, when we have an equation linking k thermodynamic parameters, then we can calculate the property k from the other $k - 1$ ones. However, thermodynamic data verification using the same equation obviously becomes senseless except for a few special cases. For example, the Duhem–Margules equation for a binary system

$$x_1^{(1)} \frac{\partial \ln p_1}{\partial x_1^{(1)}} - x_2^{(1)} \frac{\partial \ln p_2}{\partial x_1^{(1)}} = 0 \tag{49}$$

enables one to calculate the partial pressures and composition of an ideal vapour from data on total pressure [4]. But one cannot then perform verification of the set of experimental and calculated thermodynamic data using Eq. (49). But in this case, as in some other cases, the use of the thermodynamic equation for the calculation can be quite reasonable even though it prevents the use of this equation for subsequent data verification. This can be explained by the increased simplicity and accuracy of experimental measurement of the total pressure of the equilibrium vapour compared to the experimental determination of its composition.

It should be noted that the development of calculation methods based on the models of solutions accounts for the significant decrease of interest among the practical researchers and engineers in the rigorous thermodynamic methods of calculation and data verification. In fact, when a model or an empirical equation is used to express the average excess molar Gibbs energy through the parameters of state, it follows that the activity coefficients calculated from the empirical equation for g^E using rigorous thermodynamic equations become thermodynamically consistent (in particular, they are consistent with the Gibbs–Duhem equation). Subsequent thermodynamic verification becomes evidently useless. Meanwhile, notwithstanding the degree of flexibility of the model of solution, the capabilities of the model are restricted to a wide but definite class of physico-chemical systems. The practical value of phase equilibria calculations on the base of the model approach is certainly very significant. Though, as Frenkel said, "a good theory of complex systems must be nothing but a good caricature of these systems" [53]. A physical model has the right to be the same. As for thermodynamics, we can follow Van Ness in saying: "The thermodynamic mill grinds slowly, but it grinds exceeding fine" [43].

We will restrict ourselves to making these notes, since a review of the models of solutions used to calculate vapour–liquid equilibria was not the aim of this work. The works on the models of solutions are numerous and they are widely known. We will note [54,55] among the recent works. Two other directions of developing data verification methods with regard to vapour–liquid equilibria, mentioned above, are directly linked to the content of the following sections, which describe thermodynamic–topological methods and methods based on the theory of stability.

7. Thermodynamic–topological methods

Topology is relatively abstract compared to other fields of higher mathematics. The subject of topology is to determine the most general relationships between mathematical objects. Together with algebra, topology is the basis of modern mathematics. The aim of topology is the mathematical investigation of the idea of continuity that has a fundamental meaning in the natural sciences. If, e.g., the conformity between the objects in classical geometry is established in terms of equality, similarity, etc., then topology introduces the notion of homeomorphism as the key idea in the theory. When it becomes possible to establish a reciprocation (a continuous mapping) of two topological spaces, the spaces are referred to as homeomorphous. For example, a circle is homeomorphous to any square, a cube is to a sphere, but a leg is not homeomorphous to a circle.

The term "topology" is often treated in a narrow sense in the natural sciences. For example, in the theory of phase equilibria, the topology of phase diagrams is used by many researchers to mean a geometrical structure of a diagram in a common sense. The geometry of phase diagrams was studied in the works of Van der Waals [8], Korteweg [56] and

Schreinemakers [57,58] about 100 years ago. In Russia (i.e., the former Soviet Union) a significant contribution to the development of geometric concepts in the theory of phase equilibria was made by the school of Kurnakov [59–62], which established the foundations of *physico-chemical analysis*.

Meanwhile, the capabilities of topology are not limited to the studies of the common geometry among phase diagrams. In the theory of phase equilibria both purely geometrical and topological methods must be used together with the thermodynamic approach. We will describe here some results of the thermodynamic–topological analysis of vapour–liquid equilibrium phase diagrams.

In 1958, the Journal of Physical Chemistry (USSR) published a paper by Gurikov [63] "On the structure of vapour–liquid equilibrium diagrams of ternary homogeneous solutions" describing the results of the author's diploma thesis in the Department of the Theory of Solutions (now the Department of Chemical Thermodynamics and Kinetics) under the leadership of Prof. A.V. Storonkin. The thermodynamic–topological analysis of ternary vapour–liquid systems was performed in this work on the basis of a correct combination of thermodynamic rules (conditions of equilibrium and stability criteria) and the qualitative theory of differential equations. The main results of the work included:

- local regularities in the vicinity of singularities of the simple distillation diagrams in ternary systems (pure components, binary and ternary azeotropes);
- non-local regularity rules for correlations between the number and type of singularities in ternary vapour–liquid systems (azeotropy rules);
- thermodynamic–topological classification of ternary vapour–liquid systems.

General problems of the thermodynamic–topological analysis of multicomponent heterogeneous systems of different physico-chemical types were solved in the works of Serafimov and Zharov (see, e.g., [64–72]). Besides having a large scientific and theoretical significance, these works are also of practical importance for chemical engineering, being the basis of working out sequences of separation processes (distillation, rectification, etc.) [73,74].

We now discuss several results of the thermodynamic–topological analysis of ternary systems. Analysis of the peculiarities of behaviour of simple distillation curves (distillation lines) described by the differential equations of Eq. (31) together with the conditions of equilibrium made it possible to determine possible types of singularities in the simple distillation diagrams for ternary systems. Pure components, binary and ternary azeotropes, are characterised by two types of singularities: nodes and saddles (but not centres or focuses) (Fig. 12). The formula expressing the non-local rules for the concentration triangle was obtained as a result of the use of Poincaret's formula for the sphere [7],
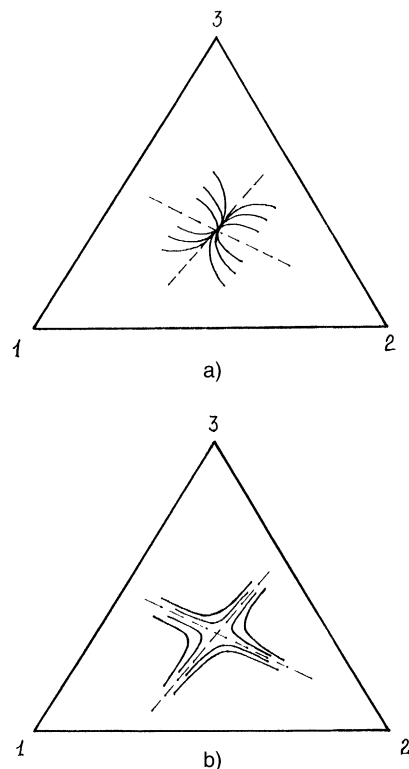
$$N + N' + F = C + C' + 1, \tag{50}$$

Fig. 12. Simple distillation lines in the vicinity of singular points for ternary azeotropes: (a) node, (b) saddle.

where N, C and F are the number of nodes, saddles and focuses at a hemisphere, and $2N'$ and $2C'$ the number of nodes and saddles at the equator of the sphere.

A triangle is not a figure homeomorphous to a sphere. The use of the topological formula of Eq. (50) for a sphere in this case can be justified if one considers a triangle or a set of triangles as a surface obtained by cutting an enclosed surface homeomorphous to a sphere. The thermodynamic–topological formula for a ternary system then looks as follows [7,63,70]:

$$2C_3 + C_2 + 2 = 2N_3 + N_2 + N_1, \tag{51}$$

where C_3 and C_2 are the numbers of ternary and binary saddle points, and N_3, N_2, and N_1 the numbers of ternary, binary and unary (pure components) nodes on the residue curve map for a ternary system. Eq. (51) expresses the azeotropy rule for ternary systems. It should be noted that the diagram of isotherms–isobars can be easily built on the basis of the diagram of distillation lines. In fact, according to the stability criteria, the simple distillation lines and isotherms–isobars cannot both touch (tangentially contact) and coincide with each other [7]. Therefore, there is a conformity between the two types of diagrams: simple distillation lines and isotherms–isobars. An example is given in Fig. 13 where simple distillation lines are represented together with isotherms–isobars.

As an example of a structure that does not correspond to Eq. (51) one can take the diagram included in the
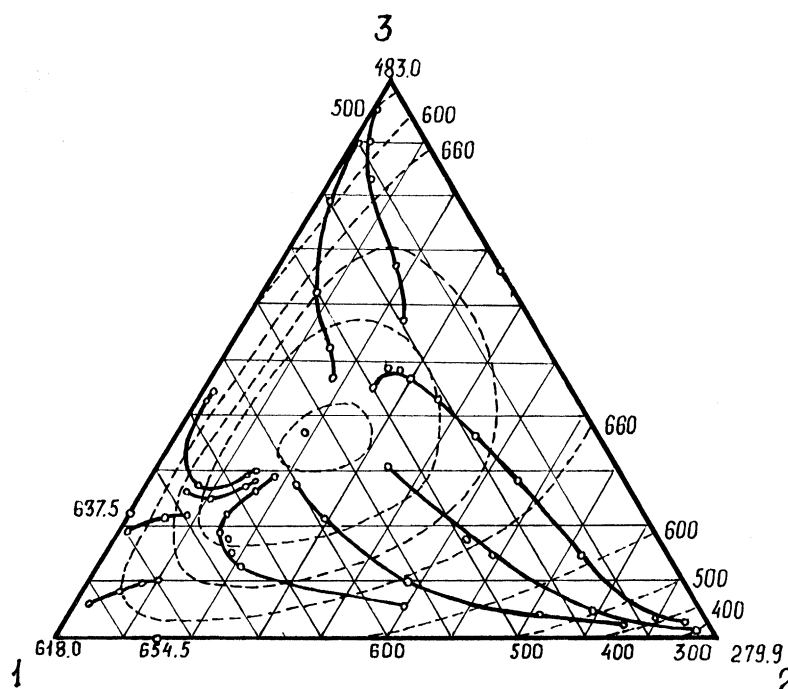
Fig. 13. Simple distillation lines and isotherms–isobars (dotted lines) for one variant of the possible structure of diagrams with three binary and ternary azeotropes: the system chloroform(1)–ethanol(2)–hexane(3) at 328.15 K [76,105].

classification of vapour–liquid ternary systems by Reinders and de Minjer [74] (Fig. 14). In fact, in the case shown in Fig. 14, $C_3 = 0$, $C_2 = 0$, $N_3 = 0$, $N_2 = 1$, $N_1 = 2$, i.e., Eq. (51), is not obeyed. Note that, rigorously speaking, Fig. 14 is not impossible from the thermodynamic viewpoint, but refers to a thin unstable structure appearing as a result of a bifurcation. In this case, the apex 3 of the concentration triangle is a point of a tangential azeotrope. Small changes in parameters lead to changes in the topological structure, transformation of tangential azeotropes into common diagrams that obey the condition expressed in Eq. (51) (see, e.g., [70,73,75]).
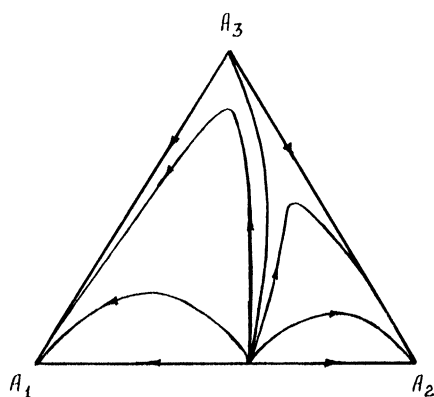

Fig. 14. Diagram from [74] that is contrary to the azeotropic rule (Eq. (51)).

Non-local regularity rules are the basis of the classification of multicomponent vapour–liquid systems. The classification of ternary systems by Gurikov [63] was later complemented by Serafimov who also proposed his own classification [63], taking into account the position of thermodynamic isolines of constant volatility K_i,

$$K_i = \frac{x_i^{(2)}}{x_i^{(1)}}. \tag{52}$$

The rules for these isolines as well as for the isolines of relative volatility α_{ik} [21,76,77] refer not only to singularities but to non-singular points of diagrams of simple distillation lines. The condition $K_i = 1$ corresponds to the touching of a simple distillation line to the line of compositions $x_i^{(1)} = $ const, while the condition $\alpha_{ik} = 1$ corresponds to the touching of a simple distillation line to the line $(x_i^{(1)}/x_k^{(1)}) = $ const. These rules follow directly from the differential equation, Eq. (31). Assuming that there can be no more than one binary azeotrope in a binary system and no more than one ternary azeotrope in a ternary system the classification of Serafimov gives 38 types of diagrams in ternary vapour–liquid systems. Unfortunately, it is impossible to show these diagrams and discuss them in this brief review.

With the above-mentioned limitations on the number of binary and ternary azeotropes, Eq. (51), expressing the azeotropy rule, can be transformed to the form

$$2C_3 + M + 2 = 2N_3 + 2N_2 + N_1, \tag{53}$$

where M is the total number of binary azeotropes. When using the rule of azeotropy one should take into account that the number of nodes cannot be less than two. These nodes correspond to the compositions of the solutions having the lowest and highest boiling temperatures (vapour pressures).

An interesting consequence of the azeotropy rule is the possibility of predicting in some cases the thermodynamic–topological structure of a phase diagram of a ternary system using data on only the binary subsystems. For example, for a ternary system with a single binary azeotrope which displays the following relationships between the boiling temperatures of pure components and the azeotrope

$$T_{12} < T_3 < T_1 \text{ and } T_2 \quad \text{or} \quad T_{12} > T_3 > T_1 \text{ and } T_2$$

(T_{12}, T_1, T_2, T_3 are the boiling temperatures of the binary azeotrope and the corresponding pure components), a ternary saddle point (azeotrope) should exist in the system. The diagram of the isotherms–isobars corresponding to these cases is given in Fig. 15. This is an experimental example, the system toluene–dioxane–isobutyl alcohol [78].

Investigation of the possible structures containing ternary (and multicomponent) heteroazeotropes can be found in [79,80]. Ref. [17] discusses problems of the thermodynamics of an n-component azeotrope in the metrics of the Gibbs energy.

To terminate this section we will finally note that the significant development of the azeotropy rule and, in particular, its expansion to the cases of tangential azeotropy and polyazeotropy was carried out in the works of Serafimov et al., who continue their research work in this direction (among recent works see, e.g., [73,80,81] and other papers).
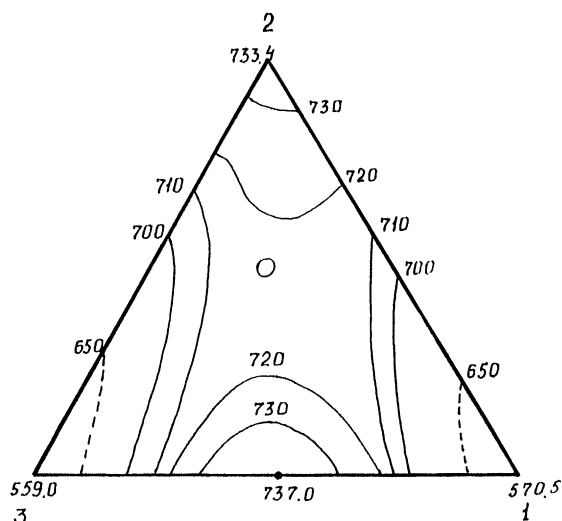

Fig. 15. Diagram with one binary and ternary azeotropes. Isotherms–isobars for the liquid phase in toluene(1)–dioxane(2)–isobutyl alcohol(3) at 253.15 K (pressure shown in mm Hg). (●) and (○) binary and ternary azeotropic points.

8. Analysis of vapour–liquid equilibrium on the base of stability criteria

In the final section of this review we will discuss several aspects of the use of stability criteria to calculate and verify vapour–liquid equilibrium data. Obviously, stability criteria have to be considered together with and inseparably from the conditions of equilibrium since together they represent the foundation of the thermodynamics of heterogeneous systems. Meanwhile, it has to be noted that, according to Gibbs, these conditions are formulated as two separate statements, i.e., principles of equilibrium and stability criteria; this is due to the axiomatic foundations of the Gibbs theory as analogues of the extremum principles in mechanics. Therefore, it is possible to develop the theory on the basis of the conditions of equilibrium only, an approach often used in equilibrium thermodynamics (including the thermodynamics of vapour–liquid equilibria, in particular) when solving practical problems. In this approach, the stability criteria are given a minor role. In particular, the fundamental equations reflect only the conditions of equilibrium since they set out the heat effect, δQ, as

$$\delta Q = T \, dS \tag{54}$$

arising from the Carnot–Clausius relationship

$$dS \geq \frac{\delta Q}{T}. \tag{55}$$

This is an equality only for an equilibrium process. In practice, therefore, the inequality set out in Eq. (55) is ignored that reflects the law of entropy increase in an adiabatic system, or, in the general case, the law of the positive internal entropy change. In this case, the main sense of the second law of thermodynamics, i.e., thermodynamic demands for the direction of processes occurring in nature, remains unexploited. It should be admitted, though, that the advantages of using the conditions of equilibrium when studying heterogeneous systems seem evident in some aspects. In fact, if one considers a continuous set of equilibrium states of a vapour–liquid system, transition between these states is described as the equilibrium process by the Gibbs fundamental equation

$$dU = T \, dS - p \, dV + \sum_{i=1}^{n} \mu_i \, dm_i, \tag{56}$$

or by the fundamental equations for other thermodynamic potentials. To integrate the fundamental equation (56) one needs to know the functional dependence of internal energy on S, V, $m_1, m_2, \ldots, m_n$

$$U = U(S, V, m_1, m_2, \ldots, m_n). \tag{57}$$

In this case, one can solve the problem of the correlation between the parameters of different states of the system. Here the dependence of Eq. (57) for the internal energy or analogous dependencies for other thermodynamic potentials

is found with the use of models and empirical relationships. Though, as was said above, notwithstanding the practical value of such an approach, the use of empirical equations significantly narrows the generality of the results obtained. Using thermodynamic inequalities, i.e., relationships that are the consequences of stability criteria, one can find a more rigorous solution of the problem of correlations between the parameters of different states of the system. These relationships may also be derived directly from the inequalities that express the second law (the law of increase of entropy). On integrating the main inequality of thermodynamics

$$\mathrm{d}U < T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_{i=1}^{n} \mu_i\,\mathrm{d}m_i \tag{58}$$

the parameters T, P and μ_i can be fixed and keep the values corresponding to the final state of the system. Therefore, knowing the functional dependence of U on the parameters of state is not needed in this case and the problem can be solved without using empirical dependencies. Meanwhile, the very form of the dependence of Eq. (58) is an inequality rather than an equation and determines the qualitative rather than quantitative character of the calculation results, which, obviously, decreases the interest of this relationship in solving problems in engineering. But one should not underestimate the practical value of thermodynamic inequalities like both Eq. (58) and the stability criteria. Some practical results will be described in this section.

Following Gibbs, we will consider not the inequality of Eq. (58) that characterises an actual irreversible process, but the relationships describing the virtual shifts—the disturbances of the equilibrium state, i.e., stability criteria. Main attention will be paid to practically useful results and their illustration. Therefore, many important aspects of stability theory will be discussed only briefly. In particular, as in the case of the conditions of equilibrium, the principal item of the theory is the problem of the difference between the differential and integral relationships and the limitations with regard to the use of integral thermodynamic inequalities [82,83]. Integrating the inequalities is directly related to the problem of stability with regard to finite disturbances of the equilibrium, which was discussed in Section 2. This problem is noted by such researchers as Gibbs [1], Munster [2] and Glensdorf and Prigogine [84]. We will limit ourselves to saying that the inequalities in the integral form will be fair if we consider only stable homogeneous and heterogeneous systems, but not the metastable states [82,83,85].

One of the examples of the use of differential thermodynamic inequalities is the study of the regularities of isothermal–isobaric changes of chemical potentials of components in ternary systems [86,87]. Since, according to the stability criteria

$$\left(\frac{\partial \mu_i}{\partial m_i}\right)_{T,P,m_1,m_2,\dots,m_{i-1},m_{i+1},m_{i+2},\dots,m_n} > 0, \tag{59}$$

then on shifting the composition along the straight line passing through the ith apex of the concentration triangle the chemical potential of the component i must increase with the increase of its concentration. Let $i = 1$, then

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P,x_2/x_3} > 0. \tag{60}$$

The conditions of stability, Eqs. (59) and (60), must be obeyed for both a homogeneous phase and a heterogeneous system. In the latter case, the quantities m_j and x_j can refer to both the separate phases and the heterogeneous complex of the phases (gross concentration and gross molar fractions of the component i) including the number of moles and mole fraction of the component i in the system as a whole.

Let x_1 be the gross molar fraction of the component 1 in the vapour–liquid system. Fig. 16 shows isotherms–isobars of coexisting phases r_1 and r_2 as well as the tie-lines A–C. According to the stability condition (60), on shifting the composition along the dotted lines a–c towards the top 1 of
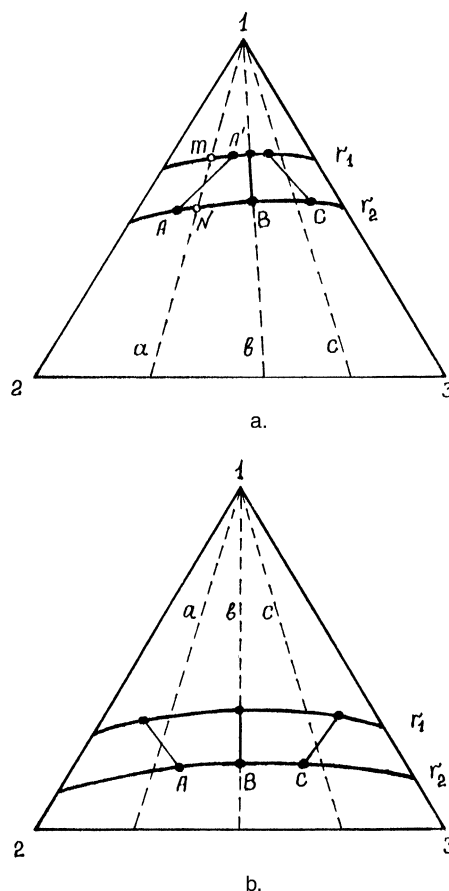

Fig. 16. Illustration of the rule for the location of tie-lines and the isothermal–isobaric change of chemical potentials: r_1 and r_2 isotherms–isobars for coexistence phases, A–C vapour–liquid tie-lines (for a description see text).

the concentration triangle (i.e., on adding the substance 1 to the system) the chemical potential μ_i increases. This is valid for the heterogeneous range also (in Fig. 16 this is the range between the curves r_1 and r_2). Meanwhile, along the tie-lines A–C the chemical potentials of the components do not vary. Therefore, the following inequality holds, e.g., for the tie-line A and the dotted line a

$$\mu_1^m > \mu_1^{A'} = \mu_1^A > \mu_1^N, \tag{61}$$

where the upper indices indicate that the quantity μ_1 refers to the points m, A′, A and N, respectively. Considering other tie-lines in Fig. 16a in a similar way it is easy to show that on shifting the composition along the isotherms–isobars r_1 and r_2 from the side 1–2 towards the tie-line B and from the side 1–3 towards the tie-line B, μ_i decreases while for the tie-line B itself it takes the extreme (minimal) value. When the tie-lines are positioned as in Fig. 16b the tie-line B corresponds to the maximal value of the chemical potential μ_1 and on shifting the composition along the isotherms–isobars r_1 and r_2 towards this tie-line μ_1 increases. Obviously, for the vapour–liquid systems, analogous rules should be valid for the partial pressure of a component. These rules relating the changes of chemical potentials and the position of the tie-lines, according to the way they were derived, have a general thermodynamic sense and are valid for not only vapour–liquid systems, but for systems of other physico-chemical types. The analysis of such regularities for multicomponent systems was carried out in [86–89].

Another example of the use of thermodynamic differential inequalities is the analysis of the values of second derivatives of thermodynamic potentials according to the way the parameters are fixed. Interpreting the stability criteria in this case is analogous to interpreting the known thermodynamic condition

$$C_P > C_V > 0, \tag{62}$$

where C_P and C_V are heat capacities at constant pressure and volume, respectively, as a consequence of the thermodynamic inequality

$$\left(\frac{\partial S}{\partial T}\right)_P > \left(\frac{\partial S}{\partial T}\right)_V > 0. \tag{63}$$

Thermodynamic relationships of this type are referred to as the Le Chatelier–Brown principle by many authors (see, e.g., [2,7,15,90–99]).

In this section, we will set out some conclusions for vapour–liquid systems. We will use the fact that it is possible to write the fundamental equations in a generalised form denoting extensive parameters $(S, V, m_1, m_2, \ldots, m_n)$ as Y_i and the conjugate intensive parameters $(T, (-P), \mu_1, \mu_2, \ldots, \mu_n,$ respectively) as X_i. It was shown in [96,98] that for a two-phase system the following chain of inequalities

is valid

$$\left(\frac{\partial X_1}{\partial Y_1}\right)_{Y_2^{(1)},Y_3^{(1)},\ldots,Y_{n+2}^{(1)}}$$
$$> \left(\frac{\partial X_1}{\partial Y_1}\right)_{(X_2^{(1)}-X_2^{(2)}),Y_3^{(1)},\ldots,Y_{n+2}^{(1)}} > \cdots$$
$$> \left(\frac{\partial X_1}{\partial Y_1}\right)_{(X_2^{(1)}-X_2^{(2)}),(X_3^{(1)}-X_3^{(2)}),\ldots,(X_{n+1}^{(1)}-X_{n+1}^{(2)}),Y_{n+2}^{(1)}} > 0,$$
$$Y_2, Y_3, \ldots, Y_{n+2} = \text{const.} \tag{64}$$

where the symbols without upper indices refer to the heterogeneous system as a whole. The condition $Y_i^{(1)} = \text{const}$ (when $Y_i = \text{const}$) indicates the absence of a phase transition for the parameter i: entropies of phases, volume of phases or the amount of a given substance in phases are constant. The condition $X_i^{(1)} - X_i^{(2)} = \text{const}$ means the corresponding phase transition and, in particular, when $X_i^{(1)} - X_i^{(2)} = 0$, the equilibrium of the phases with regard to the parameter i (partial equilibrium). According to Eq. (64) from the comparison of the derivatives

$$\left(\frac{\partial X_1}{\partial Y_1}\right)_{Y_2^{(1)},Y_3^{(1)},\ldots,Y_{n+2}^{(1)}} > \left(\frac{\partial X_1}{\partial Y_1}\right)_{(X_i^{(1)}-X_i^{(2)})=0,Y_{n+2}^{(1)}} > 0,$$
$$i = 2, 3, \ldots, n-1, \tag{65}$$

it follows that the derivative $\partial X_1/\partial Y_1$ when the compositions of the phases are constant (lack of equilibrium) is always larger than when the equilibrium between the phases is maintained. The inequality, Eq. (65), can be interpreted in a wider way: if the process of establishing the equilibrium between the phases relative to the parameters i is slower than the process of changing X_1 and Y_1 then the derivative $\partial X_1/\partial Y_1$ has a larger value than at the moment equilibrium is established. For example, for the partial pressure of component 1 with regard to the relationship

$$\mu_1 = \mu_1^0(T) + RT \ln p_1,$$

we obtain for $T, P = \text{const}$

$$\left(\frac{\partial \ln p_1}{\partial m_1}\right)_{m_2^{(1)},m_3^{(1)},\ldots} > \left(\frac{\partial \ln p_1}{\partial m_1}\right)^{\text{equilibrium}} > 0, \tag{66}$$

i.e., on introducing a component into the system its partial pressure increases, but then somewhat decreases in the process of establishing the equilibrium with regard to all the components. This result illustrates the possibility of using the criteria of stability of *equilibrium* to characterise the *non-equilibrium* process. Analogous relationships can be obtained for other parameters that are second derivatives of thermodynamic potentials. For example, at $P = \text{const}$ for a two-phase multicomponent system

$$\left(\frac{\partial S}{\partial T}\right)_{P,\mu_i^{(1)}=\mu_i^{(2)}} > \left(\frac{\partial S}{\partial T}\right)_{P,m_i^{(1)}} > 0,$$
$$m_i = m_1, m_2, \ldots = \text{const.} \tag{67}$$

Since the heat capacity at constant pressure, C_P, can be expressed by the derivatives in Eq. (67)

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P,$$

then the statement follows from Eq. (67), in particular: if under the change of temperature of the system stable phase equilibrium is not established (or has no time to establish) then the heat capacity becomes lower than the equilibrium heat capacity.

Of practical interest is the next limiting case when the initial state of the system is a single-phase state, i.e.,

$$Y_1^{(1)} = Y_1, \qquad Y_2^{(1)} = Y_2, \dots, Y_{n+2}^{(1)} = Y_{n+2},$$

but the second phase can appear when the state changes. Then it follows from Eq. (65) that, e.g., the parameter $\partial X_1 / \partial Y_1$ in a metastable homogeneous state has a larger value than in the corresponding stable two-phase state. The difference between the derivatives in Eq. (65) has a finite value [96]. It follows then that the transition from a homogeneous range to the inhomogeneous one is accompanied by the jump in the value of $\partial X_1 / \partial Y_1$. The latter conclusion can be compared to some known results for configuration effects and heat capacities [4,18,88].

The analogous differential thermodynamic inequalities for the systems with chemical reactions also follow from the stability criteria [99].

We will consider now several results of the application of integral thermodynamic inequalities to vapour–liquid systems. We will pay attention to the one important aspect, namely the evaluation (verification, calculation) of parameters of multicomponent systems from data on constituent systems with less number of components. Condition (6) is a result of combining two conditions of stability for the adjacent phases [1,7].

$$(T'' - T')S'' - (P'' - P')V'' + \sum_{i=1}^{n} (\mu_i'' - \mu_i')m_i'' > 0, \quad (68)$$

$$(T'' - T')S' - (P'' - P')V' + \sum_{i=1}^{n} (\mu_i'' - \mu_i')m_i' > 0, \quad (69)$$

where the quantities with the indices (') and ('') are the parameters of two infinitely close (adjacent) states. It can be shown that for stable states Eqs. (6), (68) and (69) are valid also for finite differences (states differing in any way). Some consequences from this inequality can be used to verify and correlate equilibrium data.

Let us change the sign in Eq. (6) (> for =). This equation will correspond to the border of the stability. We consider now the connection between multicomponent (n-components) systems and subsystems (k-components, $k < n$). For calculations we must find the solution of Eq. (68) or (69) with the equality sign. It gives the boundary of possible values for a given thermodynamic variable

in $T–P–m_i$ co-ordinates. The sign of the inequality gives the position of the region of possible values with respect to this boundary. The calculated values are called the limiting values of the equilibrium thermodynamic variables.

For ternary systems containing vapour and a few liquid phases, the following inequalities may be deduced from Eq. (68) [100,101]:

$$y_2 \leq \exp \left[(x_1 \ln p_1 + x_2 \ln p_2)^{12} - x_1^{12} \ln \left(\frac{y_1}{y_2} \right) - \ln P \right],$$
$$T = \text{const.} \quad (70)$$

$$y_2 \leq \exp \left[\frac{T - T^{12}}{RTT^{12}} (x_1^{12} L_1^0 + x_2^{12} L_2^0) \right.$$
$$\left. + (x_1 \ln y_1 + x_2 \ln y_2)^{12} - x_1^{12} \ln \left(\frac{y_1}{y_2} \right) \right],$$
$$P = \text{const.} \quad (71)$$

where we use symbol y_i for the mole fraction of component i in the ideal vapour phase, x_i the same in homogeneous or heterogeneous solution. The values with superscript 12 refer to the binary subsystem 1–2; those without to the ternary system. The same relationships hold for y_1 and y_3 (after change of indices). We assume that any non-ideality of the vapour may be neglected; otherwise appropriate corrections must be made through the use of the second virial coefficients or association constants [102].

Eqs. (70) and (71) are evaluated using the data for the binary systems involved, and give the curves on a triangular plot of the equilibrium compositions. These curves describe the feasibility limits for the area of possible vapour compositions for a given pressure P or temperature T.

For multicomponent systems, the relationships for vapour composition have the following form [101,103]:

$$\sum_{i=1}^{n-1} x_i' \ln y_i \leq \left(\sum_{i=1}^{n-1} x_i' \ln p_i' \right) - \ln P, \quad T = \text{const.} \quad (72)$$

$$\sum_{i=1}^{n-1} x_i' RT \ln y_i \leq \sum_{i=1}^{n-1} x_i' \left[\frac{L_i'}{T'} (T - T') + C_{P_i}' \right.$$
$$\left. \times \left(T \ln \left(\frac{T}{T'} \right) + T' - T \right) + RT \ln y' \right],$$
$$P = \text{const.} \quad (73)$$

where C_{P_i} is the average value of the partial molar heat capacity of component i in the vapour within the temperature interval $[T, T']$; values with the symbol $'$ refer to subsystems of the multicomponent system, those without the symbol $'$ to the multicomponent system itself. These relationships hold for all the k-component subsystems ($k = n - 1, n - 2, n - 3, \dots$).

For practical purposes Eq. (73) may be simplified. Terms in Eq. (73) that include C_{P_i} may be neglected; L_i can be
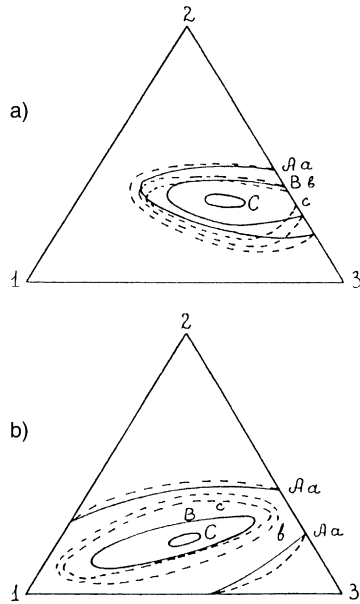
Fig. 17. Isotherms–isobars for vapour (curves A–C) and borders of the possible compositions (lines of limiting compositions dotted lines a–c) in chloroform(1)–ethanol(2)–hexane(3) ($T = 228.15$ K; A, a 600; B, b 680; C, c 700 mm Hg; (a)) [105] and methanol(1)–cyclohexane(2)–acetone(3) ($T = 208.15$ K; A, a 360; B, b 380; C, c 400 mm Hg; (b)) [104].

approximated by L_i^0, the molar heat of vaporisation of the pure component i. Eq. (73) then takes the form:

$$\sum_{i=1}^{n-1} x'_i RT \ln y_i \leq \sum_{i=1}^{n-1} x'_i \left[\frac{L_i^0}{T'}(T - T') + RT \ln y'_i \right]. \quad (74)$$

For the case where $n = 3$ Eq. (71) follows from Eq. (74).

In Fig. 17, the results of calculations for the systems chloroform–ethanol–hexane and methanol–cyclohexane–acetone are compared to experimental data [104,105]. The compositions for this and all the remaining figures are expressed in mole fractions.

For quaternary systems the following form of Eq. (74) may be used for practical calculations:

$$\sum_{i=1}^{3} x'_i RT \ln y_i \leq \sum_{i=1}^{3} x'_i \left[\frac{L_i^0}{T'}(T - T') + RT \ln y'_i \right],$$
$$P = \text{const}, \quad (75)$$

or Eq. (72) for $n = 4$ ($T = \text{const}$):

$$\sum_{i=1}^{3} x'_i \ln y_i \leq \left(\sum_{i=1}^{3} x'_i \ln p'_i \right) - \ln P. \quad (76)$$

The solution of *equalities* set out in Eqs. (75) and (76) can be expressed in the forms: $y_i = y_i (T, y_i/y_k, y_j)$ and $y_i = y_i(P, y_i/y_k, y_j)$, or equivalent forms. The values y_i ($i \neq k \neq j$; $i, k, j = 1, 2, 3$ or 4) also depend on binary and pure component data. As a results of calculations using the *equalities* of Eqs. (75) or (76) one can
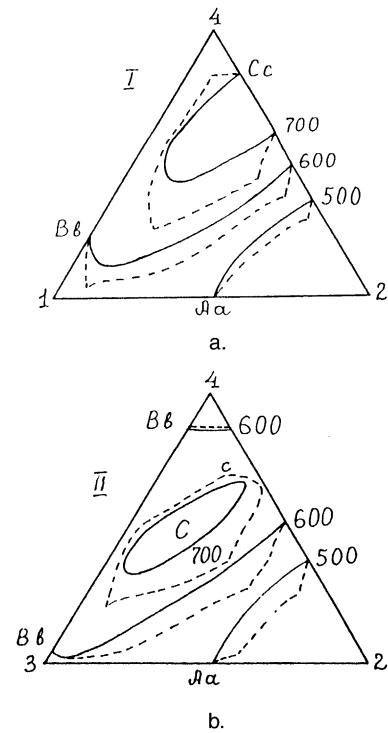

Fig. 18. Isotherms–isobars of vapour (curves A–C) and borders of the possible compositions (lines of limiting compositions dotted lines a–c) in the system chloroform(1)–ethanol(2)–acetone(3)–hexane(4) at 228.15 K for the plates of the concentration tetrahedron $y_i = \text{const}$; (I) $y_3 = 0.25$, (II) $y_1 = 0.25$. Numbers in the apexes of the triangles correspond to the components k with concentration $y_k = 0.75$. Pressures are in mm Hg.

obtain the hyper-surfaces of limiting values for the concentration tetrahedron. The results of calculations for the quaternary system chloroform–ethanol–acetone–hexane in comparison with experimental data [106] at 228.15 K are shown in Fig. 18 for the planes $y_i = \text{constant}$ in the concentration tetrahedron. Curves A–C in Fig. 18 correspond to projections of isotherm–isobars of ideal equilibrium vapour on these planes (in order of rising pressure). The course of lines a–c (lines of limiting values for vapour composition at these pressures) corresponds to *inequality* (76).

Another kind of results holds for *temperature and vapour pressure limiting values*. For constant pressure the following relationship must hold [103]:

$$\frac{1}{T} \leq \frac{1}{T'} - R \frac{\sum_{i=1}^{k} x'_i \ln(y_i/y'_i)}{\sum_{i=1}^{k} x'_i L_i^0}, \quad k < n, \quad (77)$$

where the primed values are related to the k-component subsystems of an n-component multicomponent system. This inequality determines the minimum possible boiling temperature of a multicomponent solution. Eq. (77) is set out for practical purposes and is approximate. The strict equation includes partial molar heats of vaporisation and partial molar heat capacities of the subsystems' components. Vapour-phase non-ideality, if necessary, can be accounted

for using the second virial coefficients or association constants as appropriate.

For the equilibrium pressure in a multicomponent system [103]:

$$P \le P' \exp\left(\sum_{i=1}^{k} x'_i \ln\left(\frac{y'_i}{y_i}\right)\right), \quad T = \text{const.} \quad (78)$$

Limiting values of temperature, pressure and other thermodynamic variables can be calculated both for a particular composition, and for overall n-component systems. Limiting values of temperature, T^*, can be determined by the substitution of data for all the subsystems into the right-hand side of the equality, Eq. (77). The minimum of these values of T for a given composition for the n-component system gives the limiting value of T^* of T for this composition. A set of T^* values for differing compositions of the n-component system allows the limiting (i.e., minimum) value of the boiling temperature for the overall system to be obtained.

Eq. (77) was used for a priori estimation of the limiting boiling temperature values in 23 ternary systems [107]. For these calculations were used binary vapour–liquid equilibrium data [108] and surfaces of the limiting values on the concentration triangles were obtained. These surfaces exhibit minima in temperature, which, while not corresponding to azeotropic points, may be close to them. Some of these points and experimental azeotropic points [109] are shown in Fig. 19.

In the same way some predictions for azeotropic compositions also can be obtained. The limiting values of compositions for ternary homo- and heteroazeotropes were calculated from Eqs. (70) and (71) from pressure or boiling temperature data. These calculations permit the estimation a priori of real azeotrope compositions. But there is another possible use of thermodynamic inequalities in these cases, especially for heteroazeotropes. The results of calculations for some heteroazeotropes are shown in Fig. 20, together with experimental composition data [109] at the same conditions. Here the bounded areas around the azeotropic points
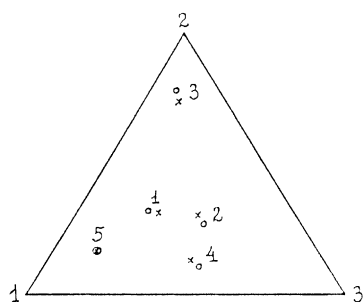

Fig. 19. Azeotropic points (○) and minimum points on the surface of limiting boiling temperatures in some ternary systems at atmospheric pressure. (1) Ethanol(1)–hexane(2)–chloroform(3) (homoazeotrope); (2) acetone(1)–methanol(2)–*cyclo*hexane(3) (homoazeotrope); (3) ethanol(1)–chloroform(2)–water(3) (heteroazeotropc); (4) heptane(1)–1-butanol(2)–water(3) (heteroazeotrope); (5) nonane(1)–1-butanol(2)–water(3) (heteroazeotrope).
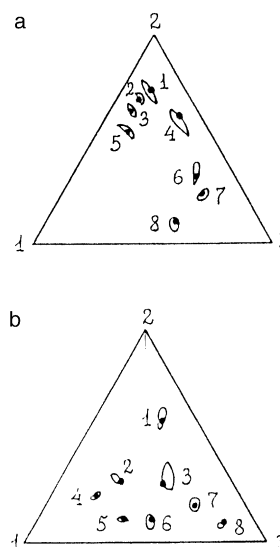

Fig. 20. Azeotropic points (●) and results of calculation of limiting azeotropic concentration values (curves) for systems water, A_1 (1)–component (2)–component (3). (a) 1: A_1–chloroform–ethanol; 2: A_1–*tetra*chloromethane–1-propanol; 3: A_1–*tetra*chloromethane–allyl alcohol; 4: A_1–chloroform–methanol; 5: A_1–chloroform–allyl alcohol; 6: A_1–ethanol–cyclohexane; 7: A_1–ethanol–n-hexane; 8: A_1–1-propanol–benzene. (b) 1: A_1–ethanol–heptane; 2: A_1–1-propanol–toluene; 3: A_1–ethanol–benzene; 4: A_1–1-butanol–octane; 5: A_1–1-butanol–chlorobenzene; 6: A_1–1-butanol–n-heptane; 7: A_1–2-propanol–cyclohexane; 8: A_1–1-propanol–n-hexane.

are the regions of possible compositions, their boundaries being the lines giving the limiting values of composition.

Good agreement between the limiting values and the experimental data is evident. For heteroazeotropes the results of the computations of the limiting values are for practical purposes the calculation of actual azeotropic compositions, since the size of the area of possible compositions corresponds approximately to the usual experimental errors.

For systems with chemical reactions, limitations on the isotherms–isobars (as well as the isotherms–isobars themselves) can be set out in a respective concentration space (see Section 4). Fig. 21 presents the illustration of the results of such an evaluation for the system water–propyl acetate–acetic acid–propyl alcohol at 318.5 K [31].

Computations on the basis of thermodynamic inequalities (stability conditions) show good agreement between limiting values and the experimental data. For ternary heteroazeotropes results that give directly heteroazeotrope compositions and boiling temperatures (and so vapour pressures) were obtained. Similar equations for other equilibrium thermodynamic variables (i.e., Gibbs energy) have also been deduced [110]. Such calculations may well be of practical significance for process synthesis.

It may well be possible to use such methods for the direct thermodynamic calculation of vapour–liquid equilibria. For instant, the good agreement shown in Fig. 17 suggests that it may be possible to construct real isotherm–isobars for the
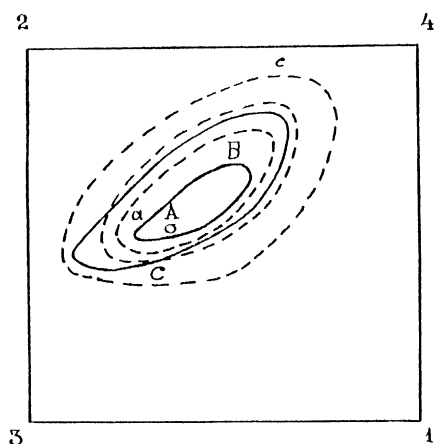
Fig. 21. Thermodynamic limitation (dotted lines a–c) for the location of the point of the maximum pressure and for the location of isotherms–isobars for the vapour on the chemical equilibrium surface (the point A and curves B, C, respectively) in acetic acid(l)–propanol(2)–water(3)–propyl acetate(4) (318.5 K) calculated from the data on binary subsystems without chemical reactions [31]. (A) 104, (B) 100, (C) 90 mm Hg.

vapour phase from the lines of limiting values with the use of some additional factors.

9. Conclusions

This review includes thermodynamic results related to the studies of vapour–liquid equilibria that seem to the authors to be important and significant. The review does not pretend to be complete; such a review would go beyond the limits of a journal paper. In particular, we have not reviewed works dealing with the calculation of thermodynamic properties on the basis of models and empirical equations.

The most important aspect of the thermodynamic methods is their universality and applicability to systems of different physico-chemical types. Limitations of thermodynamic methods in their application to studies of vapour–liquid equilibrium are due to the shortcomings of the existing models that describe this equilibrium. We think that modelling and calculations on the basis of this approach must develop together with the development of the thermodynamic methods. First, within the framework of the thermodynamic theory the optimal approach to the calculations can be selected. Second, thermodynamics enables one to control the correctness of a model or an empirical relationship. Third, the combination of the model and thermodynamic approaches can stimulate the development of thermodynamic theory on the basis of empirical rules that generalise the experimental data.

In this review we have considered both classical thermodynamic results, together with methods of analysing vapour–liquid equilibria, and the relatively new methods based on the use of criteria of stability of the equilibrium. One of the possible prospective developments of the theory is in the use of the results of irreversible thermodynamics.

In particular, on the basis of the linear and non-linear relationships of irreversible thermodynamics one can perform calculations for the changes of parameters under disturbances in the equilibrium, which would enable one to move from the qualitative relationships of the theory of stability to the quantitative ones.

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