Approach for the Description of Chemical Equilibrium Shifts in the Systems with Free and Connected Chemical Reactions

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Abstract: Approach for the description of chemical equilibrium shifts in the systems with free and connected chemical reactions was elaborated. Driving forces of chemical equilibrium shifts were temperature change (at P = const), pressure change (at T = const), and input or output of reagents or products (at T, P = const). It was demonstrated how the conditions for passing through the extremes of the state parameters (T, P, and components molar numbers) in one of the reactions transmitted to other reactions, connected with the first one by reagents or products.

Keywords: chemical equilibrium shift; dependence of chemical variables on state parameters; isolated and concurrent connected chemical reactions; extreme composition transfer between connected reactions

1. Introduction

The conditions of chemical equilibrium shifts in the systems with single chemical reaction were elaborated in the classical thermodynamic works and are well-known as Le Chatelier-Braun principle or simply Le Chatelier principle. This principle was repeatedly supplemented, justified, and commented on in a number of thermodynamic works, for example, classical monographs [1–7]. Aside from the original author of the principle (Le Chatelier's original article is [8]), it should be noted the fundamental role of J. W. Gibbs in substantiating this principle [4–6]. The authors consider the presentation in the monograph [9] to be the most successful in terms of simplicity, consistency, and generality.

The following paragraph was inserted into Introduction. Let us allow ourselves a digression related to the prehistory of the issue. The principle of Le Chatelier—Brown itself was formulated in 1884 "If a system in stable equilibrium is acted upon from the outside, changing any of the equilibrium conditions (temperature, pressure, concentration, external electromagnetic field etc), then the processes directed to side of resistance to change". Henri Le Chatelier (France) formulated this thermodynamic principle of moving equilibrium, later generalized by Karl Braun. The principle is applicable to equilibrium of any nature: mechanical, thermal, chemical, and electrical. If external conditions change, this leads to

a change in the equilibrium concentrations of substances. In this case, one speaks of a violation or shift in chemical equilibrium. The chemical equilibrium shifts in one direction or another when any of the following parameters change:

- temperature of the system, that is, when it is heated or cooled;
- pressure in the system, that is, when it is compressed or expanded;
- concentration of one of the participants in the reversible reaction.

All these variants of external influences are considered in this article. This principle, in an exceptionally simple and illustrative form, formulates the direction of displacement of the equilibrium state under external action on the system and is truly universal. Despite the fact that the principle itself was formulated a very long time ago and is very well known, the authors dare to assume that they propose some (albeit not too significant) change and expansion of the interpretation of the original principle stated earlier by the authors-Henri Le Chatelier and Karl Braun.

In the opinion of the authors, the scientific novelty of the presented work consists of two main aspects:

(A) Attempts to extend the well-known principle of shifting chemical equilibrium to systems, in the case of the initial substances or reaction products belonging to phases with large (sometimes extremely large) positive deviations from ideality. In these cases, the contribution of the excess partial thermodynamic functions of the components to the equilibrium shift may be comparable and even exceed the contribution of the standard thermodynamic functions of the reaction participants. This aspect, in the opinion of the authors, has not been considered before.

(B) Attempts to extend the well-known principle of shifting chemical equilibrium to systems of several chemical reactions with common reagents, products, or intermediates. In these cases, there is competition between several chemical reactions for both participants in the reaction, and the displacement of the equilibrium in one reaction affects the displacement of the equilibrium in the other reaction. This aspect has not been considered before, as far as the authors know.

Thus, the main goal and results of this work was an attempt to extend the well-known principle of equilibrium displacement to complex interrelated chemical processes occurring in highly nonideal systems. The methodology of consideration, in the opinion of the authors, is quite traditional and corresponds to the general principles of chemical thermodynamics. The poet does not need an additional description.

We also included links to the latest works for 2021 and 2022 in the text (see, for example articles [10,11]). These works (as well as earlier ones) were carried out within the framework of the standard and generally accepted methodology in thermodynamics.

2. Isolated "Free" Reaction Systems

Let us consider isolated equilibrium reactions, where reactions have no common reagents or products. This allows us to consider any reaction separately without taking into account other reactions.

Let us consider equilibrium chemical reaction:

$$\sum_{reagents, i=1}^{n_1} \nu_i A_i = \sum_{products, i=n_1+1}^{n} \nu_i A_i \tag{1}$$
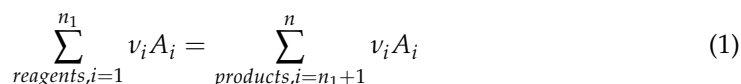
where ν_i is stoichiometric coefficient of molecular A_i in reaction (1), n_1 and n are number of reagents and number of all participants in the reaction (1). Assume, that

$$\nu_i < 0 \text{ for reagents } 1 \leq i \leq n_1; \ \nu_i > 0 \text{ for products } n_1 \leq i \leq n \tag{2}$$

We can simplify Equation (1):

$$\sum_{i=1}^{n} v_i A_i = 0 \tag{3}$$

Differential equation of chemical equilibrium conservation will be the following:

$$\sum_{i=1}^{n} v_i d\mu_i = 0 \tag{4}$$

Differentiating Equation (4) by temperature *(T)*, pressure *(P)*, and molar number of all components (n_i), we get the expression:

$$-\Delta S^{(r)} dT + \Delta V^{(r)} dP - \Delta A f^{(r)} d\xi = 0 \tag{5}$$

where

$$\Delta S^{(r)} = \sum_{i=1}^{n} v_i S_i \tag{6}$$

$$\Delta V^{(r)} = \sum_{i=1}^{n} v_i V_i \tag{7}$$

$$\Delta A f^{(r)} d\xi = \sum_{i=1}^{n} v_i (d\mu_i)_{P,T} = \sum_{i=1}^{n} \sum_{j=1}^{n} v_i v_j G_{ij} d\xi \tag{8}$$

$$\Delta G^{(r)} = \sum_{i=1}^{n} v_i \mu_i = 0 \tag{9}$$

$$\Delta H^{(r)} = \sum_{i=1}^{n} v_i H_i \tag{10}$$

In Equations (6)–(10):

$$S_i = -(d\mu_i/dT)_{P,n_{j\neq i}} \tag{11}$$

$$V_i = (d\mu_i/dP)_{T,n_{j\neq i}}; H_i = \mu_i + TS_i \tag{12}$$

are partial molar entropy, partial molar volume and enthalpy of *i*-th component; $\Delta A f^{(r)}$ is chemical affinity of reaction (3), ξ is its chemical variable, and $G_{ij} = (\partial^2 G/\partial n_i \partial n_j)_{T,P,n_{k\neq j}}$.

According to the physical sense, $\Delta S^{(r)}, \Delta V^{(r)}, \Delta A f^{(r)}, \Delta G^{(r)}$, are change of entropy, volume, chemical affinity, and Gibbs energy in the isotherm-isobaric process of the formation of v_i moles of product $A_i (i = n_1 + 1, n_1 + 2, \ldots n)$ from v_i moles of reagent $A_i (i = 1, 2, \ldots n_1)$ in the mixed phase (or phases) with infinitely large mass, which contains both reagents and products. According to the sense of ξ:

$$dn_j = v_j \xi \tag{13}$$

Bilinear form:

$$\Delta A f^{(r)} = \sum_{i=1}^{n} \sum_{j=1}^{n} v_i v_j G_{ij} > 0 \tag{14}$$

According to Sylvester's criterion, because determinant of the matrix of second derivatives is positive,

$$\Delta^{(n)} = \begin{vmatrix} G_{11} \ldots G_{1n} \\ G_{n1} \ldots G_{nn} \end{vmatrix} > 0 \tag{15}$$

where upper index symbolizes determinant dimension. All minors of main diagonal of $\Delta^{(n)}$ are positive also.

$$\Delta^{(n-1)} > 0, \Delta^{(n-2)} > 0 \ldots \Delta^{(1)} > 0 \tag{16}$$

According to the criterion of phase diffusional stability with respect to infinitesimal state changes. Thus, one can directly determine the signs of the derivatives:

$$(d\xi/dT)_P = \Delta S^{(r)}/\Delta Af^{(r)} = \Delta H^{(r)}/\Delta Af^{(r)}T > (< or =)0, \text{ if } \Delta S^{(r)} \text{ or } \Delta H^{(r)} > (< or =)0 \tag{17}$$

$$(d\xi/dP)_T = -\Delta V^{(r)}/\Delta Af^{(r)} > (< or =)0, \text{ if } \Delta V^{(r)} > (< or =)0 \tag{18}$$

$$(dP/dT)_\xi = \Delta S^{(r)}/\Delta V^{(r)} = \Delta H^{(r)}/\Delta V^{(r)}T > (<)0$$
$$\text{if } \Delta V^{(r)} \text{ and } \Delta S^{(r)} \text{have the same (opposite) sign} \tag{19}$$

Comparison of Equations with the Classical Formulation of the Le Chatelier-Brown Principle for Chemical Equilibrium Shift

Standard well-known equations of the Le Chatelier principle for chemical equilibrium shift are the following [8]:

$$(d\ln K_e/dT)_P = d/dT[\sum_{i=1}^{n} \nu_i \ln a_i]_P = \Delta H^{(0)}/RT^2 \tag{20}$$

$$(d\ln K_e/dP)_T = d/dP[\sum_{i=1}^{n} \nu_i \ln a_i]_T = -\Delta V^{(0)}/RT \tag{21}$$

where K_e is equilibrium constant of reaction (3); a_i is activity of i-th component; $\Delta H^{(0)}$ and $\Delta V^{(0)}$ are the standard change of enthalpy and standard change of volume in the reaction (3), where the formation of ν_i moles of pure products $A_i(i = n_1 + 1, n_1 + 2, \ldots n)$ from ν_i mole of pure reagents $A_i(i = 1, 2, \ldots n_1)$ occurs. Moreover, all reagents and products are separated from each other and belong to different pure phases.

$$(d\ln K_e/dT)_P = [\sum_{i=1}^{n} \nu_i^2(\partial\mu_i/\partial n_i)]_{T,P,n_{j\neq i}} \quad (d\xi/dT)_P = Z(d\xi/dT)_P \tag{22}$$

$$(d\ln K_e/dP)_T = [\sum_{i=1}^{n} \nu_i^2(\partial\mu_i/\partial n_i)]_{T,P,n_{j\neq i}} \quad (d\xi/dP)_T = Z(d\xi/dP)_T \tag{23}$$

where

$$Z = 1/RT\sum_{i=1}^{n} \nu_i^2(\partial\mu_i/\partial n_i)]_{T,P,n_{j\neq i}} > 0 \tag{24}$$

As $(\partial\mu_i/\partial n_i)_{T,P,n_{j\neq i}} > 0$ for all components, according to the criterion of diffusional stability, one can postulate, that, according to the Le Chatelier principle:

$$(d\xi/dT)_P = 1/Z(\Delta H^{(0)}/RT^2) > (< or =)0, \text{ if } \Delta H^{(0)} > (< or =)0 \tag{25}$$

$$(d\xi/dP)_T = -1/Z(\Delta V^{(0)}/RT) > (< or =)0, \text{ if } \Delta V^{(0)} < (> or =)0 \tag{26}$$

This form is very similar to the Equations (17) and (18).
Let us assume a difference.

$$\Delta H^{(r)} = \Delta H^{(0)} + \Delta H^{(mix)}; \Delta S^{(r)} = \Delta S^{(0)} + \Delta S^{(mix)}; \Delta V^{(r)} = \Delta V^{(0)} + \Delta V^{(mix)} \tag{27}$$

where $\Delta F^{(mix)} = \Delta H^{(mix)}; \Delta S^{(mix)}; \Delta V^{(mix)}$ are enthalpy, entropy, and volume of mixing of reagents-components in the reaction (3) phase, respectively. If products or reagents belong to the different phases with constant composition of $\Delta F^{(mix)} = 0$; or, if they form ideal phases-solutions (for example ideal gaseous solutions), then $\Delta H^{(mix)} = 0$, $\Delta V^{(mix)} = 0$, and Equations (25) and (26) become identical to Equations (17) and (18). In the other cases,

when products or reagents belong to the same non-ideal phases, as a rule, the following relations between the functions $\Delta F^{(mix)}$ and $\Delta F^{(0)}$ are observed:

$$\Delta F^{(mix)} << \Delta F^{(0)}(F = H, S, V) \tag{28}$$

Really typical values of $\Delta H^{(mix)}$ and $\Delta H^{(0)}$ by absolute values are:

$$\Delta H^{(mix)} = 0 - 10kJ/mole; \Delta H^{(0)} = 0 - 1000kJ/mole \tag{29}$$

For $\Delta V^{(mix)}$ and $\Delta V^{(0)}$, gaseous solutions at moderate pressures and temperatures are rare and strongly non-ideal:

$$\Delta V^{(mix)} = 0 - 10^{-4}m^3/mole; \Delta H^{(0)} = 0 - 10^{-1}m^3/mole \tag{30}$$

Therefore, approximate identification of Equations (25) and (26) and Equations (17) and (18) is also justified.

Two exceptions are the following:

(A) The extremely unlikely variant of random coincidences: $\Delta H^{(0)} \approx 0; \Delta V^{(0)} \approx 0$, when values of $\Delta H^{(mix)}; \Delta V^{(mix)}$ can become decisive.

(B) Very high and extreme values of positive deviations of excess partial molar functions (activity coefficients -γ_i from the ideality). These cases are realized, particularly in the systems with strong hierarchical association, when standard state of dissolved component (normalized on infinitely diluted solution) is far away from its state in real solutions with finite concentrations. Example of such systems are $UO_2Cl_2 - H_2O$ at 25 °C, where in the solutions close to saturation $\gamma_{UO_2Cl_2} \approx$1500–1700 a.u. [11].Another examples are $C_{60}Sub_n - H_2O$ systems at 25 °C ($C_{60}Sub_n$ is water soluble derivative of fullerene C_{60}, Sub^- is substituent—carboxy, hydroxy, amino-acid, protein etc. residues), where in the comparatively concentrated (but diffusionally stable) solutions: $\ln \gamma_{C_{60}Sub_n} \approx$10–100 a.u. [12].

Naturally, use of classical formulations, such as Equations (25) and (26) is very convenient, because data concerning $\Delta H^{(0)}$ and $\Delta V^{(0)}$ for the reaction are available, and may be simply calculated from tabulated data for all participants of the reaction: standard heats of formation: $\Delta H_{f,i}{}^{(0)}$, or standard heats of combustion: $\Delta H_{c,i}{}^{(0)}$; isobar heat capacity: $C_{p,i}$; standard molar volume: $V_i{}^{(0)}(T, P)$. However, namely the cases (A) and (B) in practice Equations (25) and (26) were not valid for the description of chemical equilibrium shift in an equilibrium mixture of substances in a natural phase state and not formally separated on the pure components, so Equations (17) and (18) look preferable.

3. Once Connected "Un-Free" Reaction Systems

Before consideration of the connection by common reagents or products, equilibrium chemical reaction let us formulate an obvious lemma.

Lemma. If any chemical reactions are carried out in the chemically equilibrium reaction phase (we will call them natural reactions or simply reactions), then any linear combinations of these reactions are carried out there (we will call them quasi-reactions).

Let k be the number of reactions. If for j-th reaction, $\sum_{i=1}^{n} v_i^{(j)} A_i = 0; 1 \leq j \leq k, then$:

$$\sum_{j=1}^{k} \alpha^{(j)} \sum_{i=1}^{n} v_i^{(j)} A_i = 0;$$

$\alpha^{(j)}$ has arbitrary sign or may be equal to zero.

Here is the simplest example of 2 connected reactions:

$$A = B \text{ (reaction-1); } A = C \text{ (reaction-2);}$$

2A = B + C (quasi-reaction-1=sum reaction-1 and reaction-2);

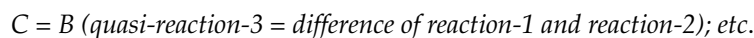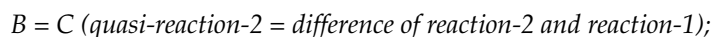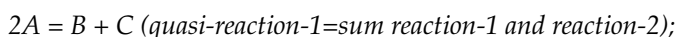*B = C (quasi-reaction-2 = difference of reaction-2 and reaction-1);*

C = B (quasi-reaction-3 = difference of reaction-1 and reaction-2); etc.
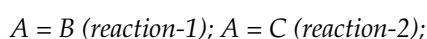
We treat the reaction phase as a "black box" in which we placed a single reagent, *A*, and then discovered two more products, *B* and *C*. If we do not consider the mechanism of the reactions, then we are deprived of the opportunity to figure out how the sum process proceeded:
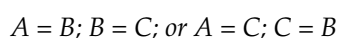
as a combination of two 1 and 2 reactions;
as 1 quasi-reaction;
as a combination of any reaction with 1 quasi-reaction;
as a combination of any reaction with 2 or 3 quasi-reaction.
The last variant may be realized according to schemes:

A = B; B = C; or A = C; C = B

Naturally, all changes of state functions in such quasi-reactions (ΔF) should be linear combinations of changes of state functions in these reactions (ΔF_i) with the same coefficients:

$$\Delta F = \sum_{i=1}^{k} \alpha^{(i)} \Delta F_i \tag{31}$$

4. Un-Free Connected Reactions

Let us consider once connected "un-free" equilibrium reactions, where two or more reactions have common reagents or products, or reagent of one reaction is the product of the other. Consider a pair of connected reactions. This will allow us to consider the competition between two connected reactions for the supplied thermal energy and mechanical energy (relative shift of chemical equilibrium when temperature or pressure changes).

4.1. Case of Common Reagents or Common Products

$$\sum_{i=1}^{n} \nu_i^{(1)} A_i = 0 (reaction-1) \tag{32}$$

$$\sum_{i=1}^{n} \nu_i^{(2)} A_i = 0 (reaction-2) \tag{33}$$

where $\nu_i^{(j)}$ is stoichiometric coefficient of molecular A_i in reaction (*j*), *n* are number of all participants in both reactions (1 and 2). Assume, that:

$\nu_i^{(j)} > 0$ for products;
$\nu_i^{(j)} < 0$ for reagents;
$\nu_i^{(j)} = 0$ for compounds, not involved in the *j*-th reaction.

Assign a number 1 to the common participant of 1 and 2 reaction and divide reaction-1 to $\nu_1^{(1)}$ and reaction-2 to $\nu_1^{(2)}$. Therefore, Equations (32) and (33) may be rewritten as:

$$\sum_{i=1}^{n} \widetilde{\nu}_i^{(1)} A_i = 0 (reaction-1) \tag{34}$$

$$\sum_{i=1}^{n} \widetilde{\nu}_i^{(2)} A_i = 0 (reaction-2) \tag{35}$$

where:

$$\widetilde{\nu}_i^{(1)} = \nu_i^{(1)} / \nu_1^{(1)}; \widetilde{\nu}_i^{(2)} = \nu_i^{(2)} / \nu_1^{(2)} \tag{36}$$

Then, we subtract from the Equations (34) and (35):

$$\sum_{i=2}^{n} \widetilde{v}_i^{(12)} A_i = 0 (quasi - reaction - 12) \tag{37}$$

where:

$$\widetilde{v}_i^{(12)} = \widetilde{v}_i^{(1)} - \widetilde{v}_i^{(2)} \tag{38}$$

According to previous terminology, a quasi-reaction (37) is isolated and can be considered the way as in Section 1.

$$\Delta \widetilde{S}^{(12)} = \sum_{i=2}^{n} \widetilde{v}_i^{(12)} S_i = \Delta S^{(1)} / v_1^{(1)} - \Delta S^{(2)} / v_1^{(2)} \tag{39}$$

$$\Delta \widetilde{V}^{(12)} = \sum_{i=2}^{n} \widetilde{v}_i^{(12)} V_i = \Delta V^{(1)} / v_1^{(1)} - \Delta V^{(2)} / v_1^{(2)} \tag{40}$$

$$\Delta \widetilde{H}^{(12)} = \sum_{i=2}^{n} \widetilde{v}_i^{(12)} H_i = \Delta H^{(1)} / v_1^{(1)} - \Delta H^{(2)} / v_1^{(2)} \tag{41}$$

$$\Delta \widetilde{A}f^{(12)} = \sum_{i=2}^{n} \widetilde{v}_i^{(12)} Af_i = \Delta Af^{(1)} / v_1^{(1)} - \Delta Af^{(2)} / v_1^{(2)} \tag{42}$$

$$d\xi^{(12)} = d\xi^{(1)} / v_1^{(1)} - d\xi^{(2)} / v_1^{(2)} \tag{43}$$

Therefore:

$$-[\Delta S^{(1)} / v_1^{(1)} - \Delta S^{(2)} / v_1^{(2)}]dT + [\Delta V^{(1)} / v_1^{(1)} - \Delta V^{(2)} / v_1^{(2)}]dP + \\ +[\Delta Af^{(1)} / v_1^{(1)} - \Delta Af^{(2)} / v_1^{(2)}](d\xi^{(1)} / v_1^{(1)} - d\xi^{(2)} / v_1^{(2)}) = 0 \tag{44}$$

Again note that:

$$\Delta \widetilde{A}f^{(12)} = \sum_{i=2}^{n} \sum_{j=2}^{n} \widetilde{v}_i^{(12)} \widetilde{v}_j^{(12)} G_{ij} > 0 \tag{45}$$

according to Sylvester's criterion, because the determinant of the matrix of second derivatives and all minors of main diagonals are positive.

Note also, that:

$$d\xi^{(12)}(>;<;=)0, then : d\xi^{(1)} / v_1^{(1)}(>;<;=)d\xi^{(2)} / v_1^{(2)} \tag{46}$$

Thus, to formulate the corollaries of Equation (44):

$$(d\xi^{(12)} / dT)_P = \Delta \widetilde{S}^{(12)} / \Delta \widetilde{A}f^{(12)} = \Delta \widetilde{H}^{(12)} / T\Delta \widetilde{A}f^{(12)}(>;<;=)0, \\ if : \Delta \widetilde{S}^{(12)}(\Delta \widetilde{H}^{(12)})(>;<;=)0 \tag{47}$$

$$(d\xi^{(12)} / dP)_T = -\Delta \widetilde{V}^{(12)} / \Delta \widetilde{A}f^{(12)}(>;<;=)0, if : \Delta \widetilde{V}^{(12)})(<;>;=)0 \tag{48}$$

$$(dP / dT)_{\xi^{(12)}} = \Delta \widetilde{S}^{(12)} / \Delta \widetilde{V}^{(12)}(>;<;=)0 \tag{49}$$

To verbally formulate the Le Chatelier's principle of chemical equilibrium shift (CES-principle):

- With an increase in temperature for a pair of once-connected reactions, the equilibrium shifts towards products more (less) for the reaction, whose specific heat (normalized by 1 mole of the common component) is greater (lower) than the other reaction;
- With an increase in pressure for a pair of once-connected reactions, the equilibrium shifts towards products more (less) for the reaction, whose specific volume

change (normalized by 1 mole of the common component) is lower (greater) than the other reaction;

If there is a system of q once connected equilibrium reactions (it is not necessary that the common products or reagents are the same), we can consider a system of independent pairwise quasi reactions of the type (37) without common participants. One can write the following equation system:

$$-\Delta\widetilde{S}^{(pr)}dT + \Delta\widetilde{V}^{(pr)}dP + \Delta\widetilde{A}f^{(pr)}d\xi^{(pr)} = 0 \tag{50}$$

where $1 \leq p; r \leq q; p \neq r$. All corollaries of the type (47)–(49) will also be valid. All q reactions should be linearly independent, so the rang of matrix of stoichiometric coefficients for the reaction system $\|\nu_i^{(j)}\|$ with the dimension nq should be:

$$rang\|\nu_i^{(j)}\| = q \tag{51}$$

All quasi-reactions naturally are linearly dependent on the reaction system.

4.2. Case of Common Reagent of One Reaction and Product of Other Reaction

Let us consider the system of sequential reactions. Assign again a number 1 to the common participant of the reactions (product for reaction-1, and reagent for reaction-2) and divide reaction-1 to $\nu_1^{(1)}$ and reaction-2 to $\nu_1^{(2)}$. Therefore, Equations (34) and (35) maybe be rewritten, as earlier:

$$\sum_{i=1}^{n}\widetilde{\nu}_i^{(1)}A_i = 0(reaction-1) \tag{52}$$

$$\sum_{i=1}^{n}\widetilde{\nu}_i^{(2)}A_i = 0(reaction-2) \tag{53}$$

where again:

$$\widetilde{\nu}_i^{(1)} = \nu_i^{(1)}/\nu_1^{(1)}; \widetilde{\nu}_i^{(2)} = \nu_i^{(2)}/\nu_1^{(2)} \tag{54}$$

We then add Equations (52) and (53) and exclude 1 component from quasi-reaction:

$$\sum_{i=2}^{n}\widetilde{\nu}_i^{(12)}A_i = 0(quasi-reaction-12) \tag{55}$$

and contrast with Equation (38):

$$\widetilde{\nu}_i^{(12)} = \widetilde{\nu}_i^{(1)} + \widetilde{\nu}_i^{(2)} \tag{56}$$

According to previous terminology, quasi-reactions are isolated and can be considered as previously in Section 3. Thus:

$$-\Delta\widetilde{S}^{(12)}dT + \Delta\widetilde{V}^{(12)}dTdP + \Delta\widetilde{A}f^{(12)}d\xi^{(12)} = 0 \tag{57}$$

where:

$$\Delta\widetilde{S}^{(12)} = \sum_{i=2}^{n}\widetilde{\nu}_i^{(12)}S_i = \Delta S^{(1)}/\nu_1^{(1)} + \Delta S^{(2)}/\nu_1^{(2)} \tag{58}$$

$$\Delta\widetilde{V}^{(12)} = \sum_{i=2}^{n}\widetilde{\nu}_i^{(12)}V_i = \Delta V^{(1)}/\nu_1^{(1)} + \Delta V^{(2)}/\nu_1^{(2)} \tag{59}$$

$$\Delta\widetilde{H}^{(12)} = \sum_{i=2}^{n}\widetilde{\nu}_i^{(12)}H_i = \Delta H^{(1)}/\nu_1^{(1)} + \Delta H^{(2)}/\nu_1^{(2)} \tag{60}$$

$$\Delta \widetilde{A} f^{(12)} = \sum_{i=2}^{n} \widetilde{v}_i^{(12)} A f_i = \Delta A f^{(1)} / v_1^{(1)} + \Delta A f^{(2)} / v_1^{(2)} \tag{61}$$

$$d\xi^{(12)} = d\xi^{(1)} / v_1^{(1)} + d\xi^{(2)} / v_1^{(2)} \tag{62}$$

Naturally, the positive definiteness of the bilinear form (45) is also valid in this case:

$$\Delta \widetilde{A} f^{(12)} = \sum_{i=2}^{n} \sum_{j=2}^{n} \widetilde{v}_i^{(12)} \widetilde{v}_j^{(12)} G_{ij} > 0 \tag{63}$$

Note also, that if:

$$d\xi^{(12)} = d\xi^{(1)} / v_1^{(1)} + d\xi^{(2)} / v_1^{(2)} (>; <; =)0 \tag{64}$$

then:

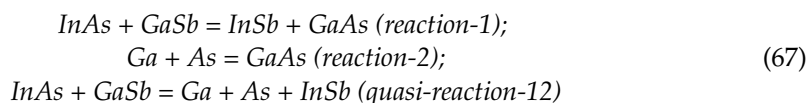$$d\xi^{(1)} / v_1^{(1)} (> \prime <; =) - (d\xi^{(2)} / v_1^{(2)}) \tag{65}$$

In other words, equilibrium molar numbers of common components in the reactions-1,2 increases, decreases, and becomes constant. We then formulated the corollaries of Equation (57), which completely matched with the Equations (47)–(49), excluding the signs in definitions in the Equations (39)–(43) and (58)–(62).

- With an increase in temperature for a pair of once-connected reactions, common component-intermediate was accumulated (consumed) in the reaction phase, if sum heat of the reactions (normalized by 1 mole of the common component) was positive (negative);
- With an increase in pressure for a pair of once-connected reactions, the common component-intermediate was accumulated (consumed) in the reaction phase, if sum volume change of the reactions (normalized by 1 mole of the common component) was negative (positive).
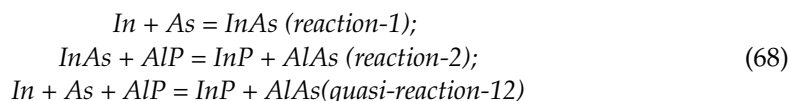
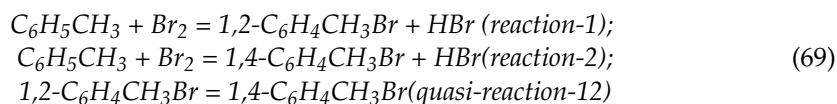Let us give examples of the reactions (for example in A^3-B^5 systems), once-connected by: reagents:

$$\begin{array}{c} \textit{In + As = InAs (reaction-1);} \\ \textit{Ga + As = GaAs (reaction-2);} \\ \textit{In + GaAs = Ga + InAs (quasi-reaction-12)} \end{array} \tag{66}$$

products:

$$\begin{array}{c} \textit{InAs + GaSb = InSb + GaAs (reaction-1);} \\ \textit{Ga + As = GaAs (reaction-2);} \\ \textit{InAs + GaSb = Ga + As + InSb (quasi-reaction-12)} \end{array} \tag{67}$$

sequential reaction:

$$\begin{array}{c} \textit{In + As = InAs (reaction-1);} \\ \textit{InAs + AlP = InP + AlAs (reaction-2);} \\ \textit{In + As + AlP = InP + AlAs(quasi-reaction-12)} \end{array} \tag{68}$$
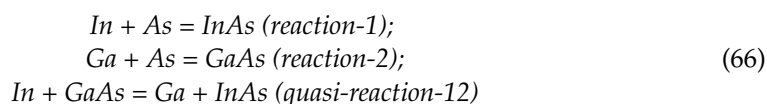
5. Case of Several (More Than One) Common Reagents or Common Products with the Proportional (in Particular, Equal) Stoichiometric Coefficients of Common Participants

Let us give examples of multi-connected (by products or reagents) reactions with equal stoichiometric coefficients for participants. Let us give the example:

$$\begin{array}{c} C_6H_5CH_3 + Br_2 = 1,2\text{-}C_6H_4CH_3Br + HBr \textit{ (reaction-1);} \\ C_6H_5CH_3 + Br_2 = 1,4\text{-}C_6H_4CH_3Br + HBr(\textit{reaction-2);} \\ 1,2\text{-}C_6H_4CH_3Br = 1,4\text{-}C_6H_4CH_3Br(\textit{quasi-reaction-12)} \end{array} \tag{69}$$

In a common case, we will denote all common participants for two reactions as $1, 2 \ldots k$. We can hardly imagine a pair of connected reactions where the number of connected components would be $k > 3$, so reactions are twice or thrice connected.

$$\nu_1^{(1)}/\nu_1^{(2)} = \nu_2^{(1)}/\nu_2^{(2)} = \ldots = \nu_k^{(1)}/\nu_k^{(2)} \tag{70}$$

In this case, similarly to what we did in Section 3, we can exclude common participants from the reactions, form quasi-reactions, and get all the conclusions, which completely match with the Equations (47)–(49) (CES-principle). A quasi-reaction is naturally formed as a sum (not difference) of equilibrium reactions, and the result is a result similar to the one previously obtained in Section 3.

6. About the Possibility of Passing of Composition Variables, Temperature, and Pressure in the System of Components, Connected by Chemical Reaction, through the Extreme

Isotherm-isobar conditions ($dT = dP = 0$).

Let us assign the number 1 to the common component. Imagine that molar number of some non-common 2-d participant of the *1-st* from pair of (1 and 2) once-connected reactions $(n_2^{(1)})$ passes through the extreme at P=const and T=const. Naturally in these cases:

$$dn_2^{(1)} = 0$$

Simultaneously:

$$d\xi^{(1)} = 0 \tag{71}$$

Let us use it now in Equation (57) for such reactions at *P = const and T = const:*

$$\Delta \widetilde{A} f^{(12)} d\xi^{(12)} = 0; (d\xi^{(12)})_{P,T} = d\xi^{(1)}/\nu_1^{(1)} \pm d\xi^{(2)}/\nu_1^{(2)} = 0; (d\xi^{(2)})_{P,T} = 0 \tag{72}$$

$$(dn_i^{(1)})_{P,T} = 0; (dn_i^{(2)})_{P,T} = 0 (i = 1, 2 \ldots n) \tag{73}$$

In other words, molar numbers of all participants of the reactions-1,2 pass through the extreme at *P = const* and *T = const* simultaneously. If quasi-reaction-1,2 (pair of once-connected reactions-1 and -2) is connected with the other *(−1r)* or *(−2t)* quasi-reactions by one common component (it is not necessary that the same as for quasi-reaction)-1,2, then the following is also valid:

$$(d\xi^{(1r)})_{P,T} = 0; (d\xi^{(2t)})_{P,T} = 0; (d\xi^{(r)})_{P,T} = 0;$$
$$(d\xi^{(t)})_{P,T} = 0 (dn_i^{(r)})_{P,T} = 0; (dn_i^{(t)})_{P,T} = 0 (i = 1, 2 \ldots n) \tag{74}$$

Thus, one can postulate that the condition of the extreme of molar numbers of the participants of chemical reactions or the condition of extreme of chemical variable in the system of once-connected equilibrium chemical reactions is transmitted from one reaction to another reaction through a common participant in the reaction. The same conclusion was made for twice or thrice connected to each other reactions, with proportional stoichiometric coefficients of common participants. Unfortunately, in more complex cases of connected reactions, the authors fail to establish the transmission of the extremeness of the composition.

Transfer of the condition of extremeness of the composition from one connected reaction to another can be explained, if we take into account that when the composition changes, there is competition between connected reactions for a common reagent or common product.

One important moment. In our system of connected reactions should be the components not involved in the connected reactions at T, P = const. Otherwise, the number of thermodynamic degrees of freedom will be equal to zero, and system will be non-variant.

We will give the simplest scheme of extreme transfer between connected reactions as an example. Let us consider the reactions scheme at P = const and T = const:

A = B (reaction-1); A = C (reaction-2); C = D (reaction-3); D = E (reaction-4).
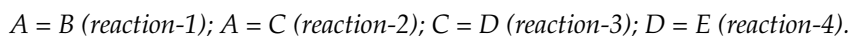
According to chemical equilibrium shift differential equation, one can write that when $(d\mu_A)_{P,T} = 0$:

$$(d\mu_A)_{P,T} = (d\mu_B)_{P,T} = (d\mu_C)_{P,T} = (d\mu_D)_{P,T} = (d\mu_E)_{P,T} = 0 \tag{75}$$

In our conditions, when $(dn_A)_{P,T} = 0$, then:

$$(dn_A)_{P,T} = (dn_B)_{P,T} = (dn_C)_{P,T} = (dn_D)_{P,T} = (dn_E)_{P,T} = 0 \tag{76}$$

or all molar numbers simultaneously pass through the extreme.

At the same time, there should be some other components in the systems, *F, G, H . . .* , for which:

$$(d\mu_F)_{P,T} \neq (d\mu_G)_{P,T} \neq (d\mu_H)_{P,T} = \ldots \neq 0 \tag{77}$$

$$(dn_F)_{P,T} \neq (dn_G)_{P,T} \neq (dn_H)_{P,T} = \ldots \neq 0 \tag{78}$$

Condition of constancy of chemical potentials of components, which also corresponds to the Equation (75), may also be valid. However, for some components, according to the conditions of diffusional stability, derivatives should be:

$$(d\mu_i/dn_k)_{P,T,n_{J\neq k}} \neq 0 \tag{79}$$

Therefore, input (or output) of not those involved in the connected reactions components to the reaction phase cannot make chemical potentials of the last ones constant.

Reaction phase composition may change in different ways: adding or removing component or components (products or reagents) in real experiment, for example, moving along isotherm-isobar curves of multi-phase equilibrium (also in experiment or in correct thermodynamic modeling calculation); moving along curves of open phase processes (when one from several equilibrium phase it is constantly being removed from the sphere of phase equilibrium); and moving along curves of thermodynamic simplification or curves of incomplete extremes etc. (see, for example [9]). In the last cases, it is enough to change in the experiment, the gross composition of heterogeneous system as a whole.

For simplicity and certainty, in the condition of isotherm-isobar composition changes, we shall fix the total number of moles of all components in the reaction phase equal to 1 mole. Then, components molar numbers will convert into molar fractions, $n_i^{(j)} = X_i^{(j)}$, with the conservation all equations and properties of the reaction phase. All extensive properties in the system will transfer into molar properties, in particular, determinant $\Delta^{(n-1)} = \begin{vmatrix} G_{11} \ldots G_{1n-1} \\ G_{n1} \ldots G_{n-1n-1} \end{vmatrix} > 0$, losing dimension by one, remains defined positively with all minors of main diagonal, etc.

In the end of the section, we will give an example of the experiment, where concentrations of participants of the connected reaction simultaneously pass through the extreme (Figure 1). Here, the composition change is caused by artificial displacement of melt composition along liquidus isotherm in quaternary *In-Ga-As-Sb* system and corresponding change of equilibrium solid solution $In_xGa_{1/2-x}As_ySb_{1/2-y}$ composition.
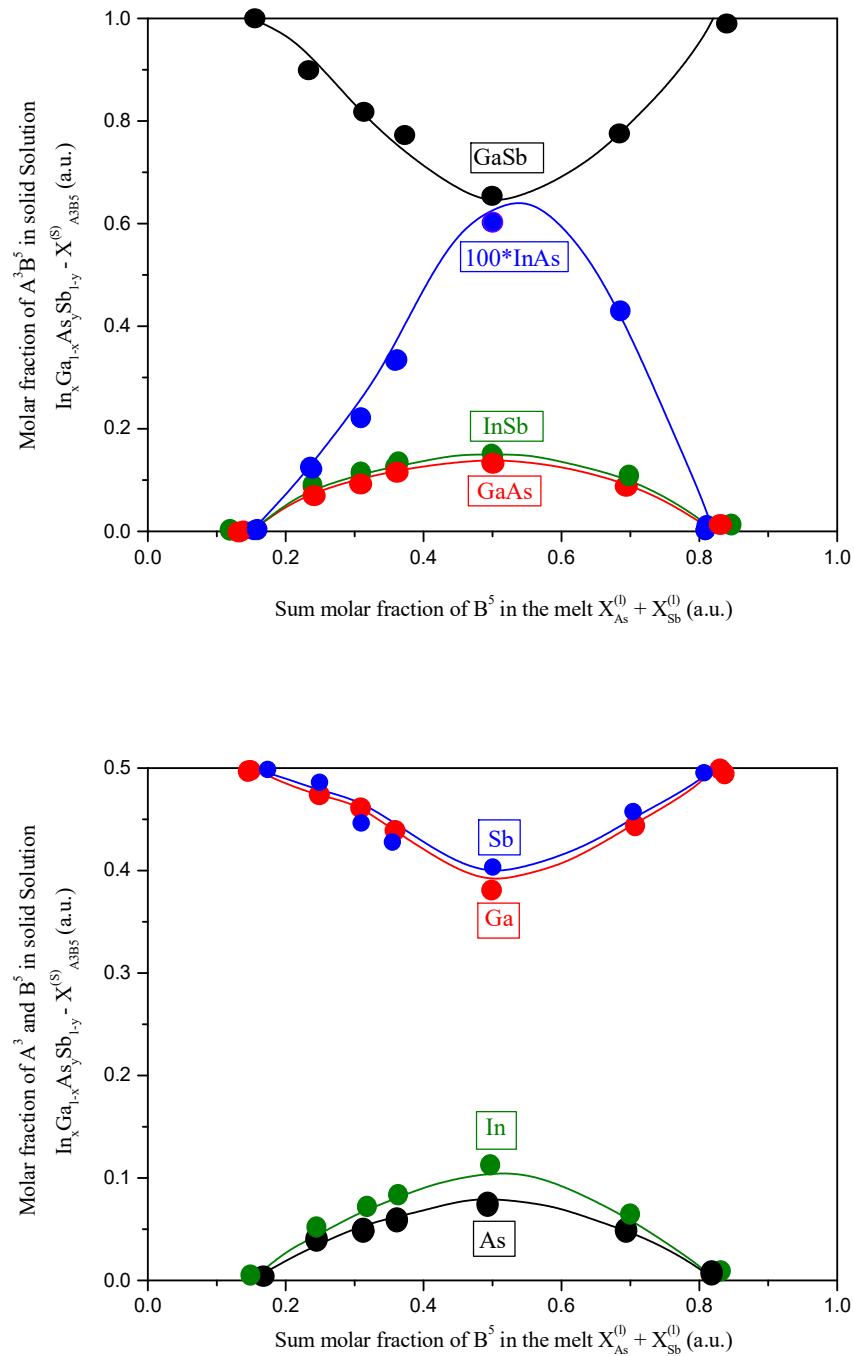
Figure 1. Molar fraction of components A^3(*In*, *Ga*) and B^5(*As*, *Sb*), top fragment, compounds A^3B^5 (*InAs, InSb, GaAs, GaSb*), and bottom fragment in solid solution $In_xGa_{1/2-x}As_ySb_{1/2-y}$ (isoperiodic to the substrate *GaSb*)—$X^{(s)}$, depending on the sum molar fraction of B^5 components in the equilibrium to solid solution melt: $X_{As}^{(l)} + X_{Sb}^{(l)}$ at *T = 873 K* and *P = 1 atm*. (Points are experimental data, lines are calculated by EFLCP model for A^3-B^5 semiconductor systems [13,14].

6.1. Polytherm Isobar Conditions ($dT \neq 0, dP = 0$)

Driving force of chemical equilibrium shift is heat supply or removal in the conditions of mass isolation of the reaction phase. If we consider isolated reactions, then Equation (5) will be:

$$-\Delta S^{(r)}dT + \Delta A f^{(r)}d\xi^{(r)} = 0 \tag{80}$$

and we can postulate, that:

$$(d\xi^{(r)})_P = 0 \text{ or } (\xi^{(r)})_P \text{ is in extreme, when}: \ \Delta S^{(r)}(\Delta H^{(r)}) = 0 \tag{81}$$

Really:

$$T_P \neq const \tag{82}$$

because the thermal diffusional criterion of the reaction phase is valid, i.e.,:
$(dT)_P (>; <)0$, when heat is supplied or removed.

Connected reaction systems. Let us number common components in the *1-st.* Imagine that molar number of some non-common *2-d* participant of the 1-st from pair of (1 and 2) once-connected reactions passes through the extreme at *P = const.* Naturally, in these cases:

$$(dn_2^{(1)})_P = 0, so : (d\xi^{(1)})_P = 0 \tag{83}$$

For the 1-st reaction we can also rewrite Equation (5):

$$- \Delta S^{(1)} dT_P + \Delta Af^{(1)} (d\xi^{(1)})_P = 0 \tag{84}$$

From Equations (83) and (84), we can write that:

$$(dT)_P = 0; T_P \text{ is in extreme} \tag{85}$$

Using Equations (43) and (44) for quasi-reaction-12 at *P = const:*

$$- \Delta \widetilde{S}^{(12)} dT + \Delta \widetilde{A} f^{(12)} d\xi^{(12)} = 0; d\xi^{(12)} = d\xi^{(1)}/\nu_1^{(1)} - d\xi^{(2)}/\nu_1^{(2)} \tag{86}$$

Taking into account Equation (85), one can write that:
$(d\xi^{(12)})_P = 0; (\xi^{(12)})_P$ is in the extreme, and from Equations (83) and (86) it follows that:

$$(d\xi^{(22)})_P = 0; (\xi^{(2)})_P \text{ is in extreme} \tag{87}$$

We can postulate that molar number of all participants of the (12) connected reactions and temperature of the reactions pass through the extreme at *P = const* simultaneously.

$$(dn_i^{(1)})_P = 0; (dn_i^{(2)})_P = 0 (i = 1, 2 \ldots n); dT_P = 0 \tag{88}$$

At the end of the section, we will give an example of an experiment where concentrations of participants of the connected reaction and temperature simultaneously passed through the extreme (Figure 2). Here, the composition change was caused by artificial displacement of melt composition along liquidus polytherm in quaternary system *In-Ga-As-Sb*. In this case, the composition of solid solution was fixed in $In_{0.11}Ga_{0.39}As_{0.08}Sb_{0.42}$. This composition corresponds to the pass of the concentrations in solid solution through the extreme, and this applies both to the simple components A^3(*In, Ga*) and B^5(*As, Sb*), and "complex compounds" A^3B^5 (*InAs, InSb, GaAs, GaSb*), as seen in Figure 1. These data also correspond to the value of the argument, $X_{As}^{(l)} + X_{Sb}^{(l)} \approx 0.5$. Temperature of phase equilibrium in Figure 1 (873 K) should correspond to the extreme of liquidus temperature at the same value $X_{As}^{(l)} + X_{Sb}^{(l)} \approx 0.5$. This is confirmed by Figure 2. Justice of Equation (88) was demonstrated.
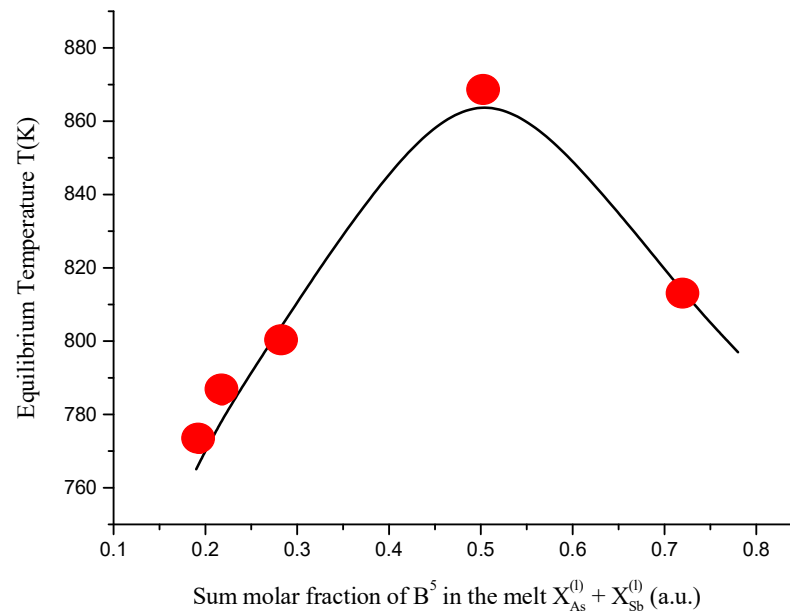
Figure 2. Equilibrium temperature T(K), depending on the sum molar fraction of B^5 components in the equilibrium to solid solution melt: $X_{As}^{(l)} + X_{Sb}^{(l)}$ for solid solutions with constant composition $In_{0.11}Ga_{0.39}As_{0.08}Sb_{0.42}$. Points are experimental data, line is calculated by EFLCP model [13,14].

6.2. Isotherm Polybar Conditions $(dT = 0$ or $dP \neq 0)$

The driving force of chemical equilibrium shift is reaction volume increase or decrease in the conditions of mass isolation of the reaction phase. Imagine that molar number of some non-common *2-d* participant of the 1-st from pair of (1 and 2) once-connected reactions passes through the extreme at *T* = *const.* Naturally, in these cases:

$$(dn_2^{(1)})_T = 0, so : (d\xi^{(1)})_T = 0 \tag{89}$$

If we consider isolated reactions, then Equation (5) will be the following:

$$\Delta V^{(r)}dP_T + \Delta A f^{(r)}(d\xi^{(r)})_T = 0 \tag{90}$$

From Equations (89) and (90), we can write that:

$$(dP)_T = 0; P_T \text{ is in extreme, when}: \Delta V^{(r)} = 0 \tag{91}$$

Really:

$$P_T \neq const \tag{92}$$

because the mechanical diffusional criterion of the reaction phase is valid, i.e.,: $dP_T(>;<)0$.

In reality, condition (91) is incomparably milder than a similar condition (81). For example, the condition is certainly fulfilled for the reaction in ideal gaseous phase (when molar gaseous numbers of reagents and products are equal). This condition is also approximately valid for the reaction in the condensed phases, when pressures are not unnecessarily large.

Connected reaction systems. Using Equations (43) and (44) for quasi-reaction-12 at *T* = *const*:

$$\Delta \widetilde{V}^{(12)}dP + \Delta \widetilde{A}f^{(12)}d\xi^{(12)} = 0; d\xi^{(12)} = d\xi^{(1)}/v_1^{(1)} - d\xi^{(2)}/v_1^{(2)} \tag{93}$$

Taking into account Equation (85), one can write that:

$(d\xi^{(12)})_T = 0$; $(\xi^{(12)})_T$ is in the extreme, and from Equations (89) and (90), it follows that:

$$(d\xi^{(22)})_T = 0; (\xi^{(2)})_T \tag{94}$$

We can postulate that molar number of all participants of the connected 1,2-reactions and pressure of the reaction pass through the extreme at *T = const* simultaneously.

$$(dn_i^{(1)})_T = 0; (dn_i^{(2)})_T = 0 (i = 1, 2 \ldots n); dP_T = 0 \tag{95}$$

The last example of the transmission of the state parameters extreme conditions is represented in Figures 3 and 4.

$1{\rightarrow}2{\rightarrow}3{\rightarrow}4{\rightarrow}R_1{\rightarrow}5{\rightarrow}6{\rightarrow}7{\rightarrow}8$ shows the method of passing the composition of the solution through R_1 point as the result of H_2O-add $+3NaCl \cdot 4CdCl_2 \cdot 14H_2O(1{\rightarrow}2{\rightarrow}3{\rightarrow}4{\rightarrow}R_1)$ and H_2O-evaporation $+ 3NaCl \cdot 4CdCl_2 \cdot 14H_2O$-crystallization $(R_1{\rightarrow}5{\rightarrow}6{\rightarrow}7{\rightarrow}8)$.

In Figure 3, isotherm-isobar (1 atm. of sum pressure) of ternary system $NaCl$-$CdCl_2$-H_2O system at 25 °C consists of four branches: *NaCl*; congruently soluble compounds, $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$, and $2NaCl \cdot CdCl_2 \cdot 3H_2O$. Diagram contains three non-variant points E_i, all eutonics [15]. In the diagram, there are two point types. Van Rijn points in fusibility diagrams, R_i, are realized when all three equilibrium phase points, liquid *(l)* (R_i), solid compound *(s)* $(3NaCl \cdot 4CdCl_2 \cdot 14H_2O$ and $2NaCl \cdot CdCl_2 \cdot 3H_2O)$, and vapor *(v)* H_2O, belong to the same straight lines [15–17]. In the points, R_i isopotentials of H_2O touch the curves of mono-variant equilibrium $(E_i{\rightarrow}R_j{\rightarrow}E_{i+1})$ when moving along these curves, and chemical potential H_2O in the points R_i passes through the extremes (specifically the maximum) [17,18], as in Figures 3 and 4.
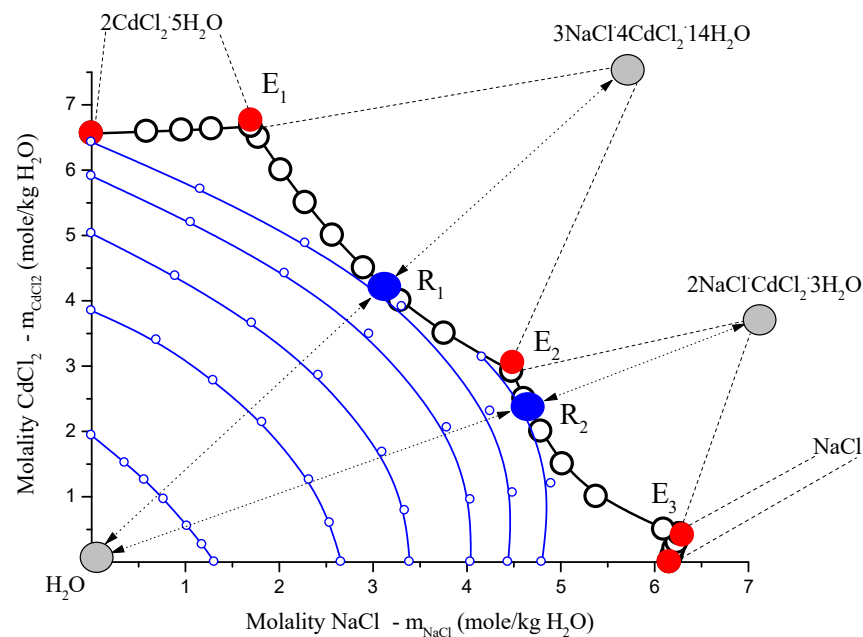
Figure 3. Solubility diagrams in ternary *NaCl–CdCl₂–H₂O* system at 25 °C in rectangular Schreinemakers concentration triangle in the salt molalities: open black circles, calculated by Extended Pitzer's Method [16]; red solid circles, non-variant experimental data [16,17]; blue solid points *(Rᵢ)*, solubility diagram points type Van Rijn points in fusibility diagrams [17]; little open blue points, H_2O isopotentials ($\mu_{H_2O} = const$); gray points, figurative points of coexisting equilibrium vapor *(H₂O)* and solid compounds phases$_c$ and $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$; E_i, eutonics [17,18]; dots with two-directed arrows are nodes: vapor *(v)*, saturated solutions *(Rᵢ)*, and solid compounds *(s)*.
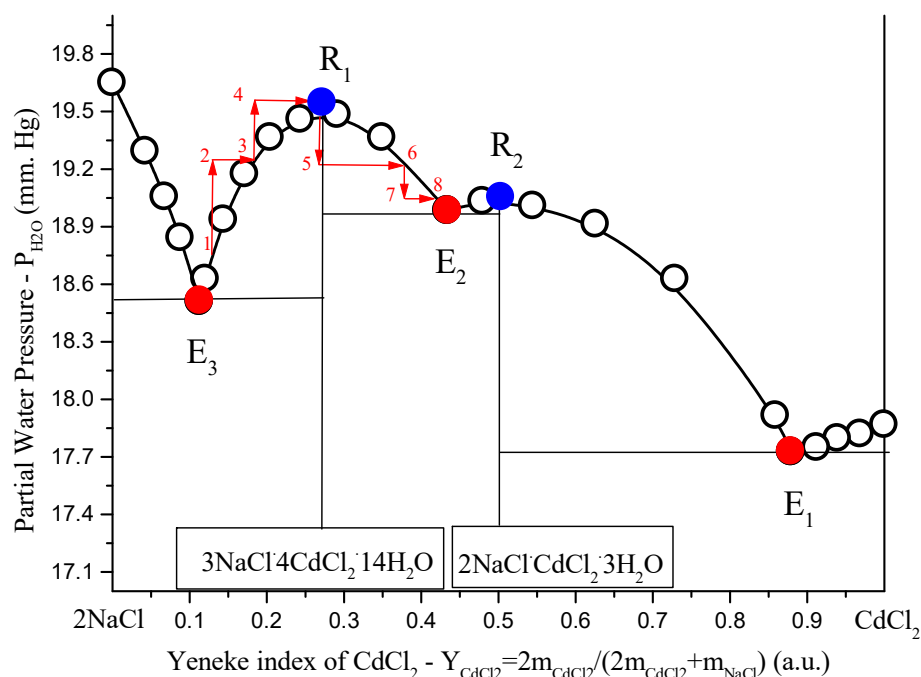
Figure 4. Solubility diagrams in ternary *NaCl–CdCl₂–H₂O* system at 25 °C in the variables: salt Yeneske index H_2O partial pressure: open black circles, calculation by Extended Pitzer's Method [14]; red solid circles, non-variant calculated eutonics data (E_i); blue solid points (R_i), solubility diagram points type Van Rijn points in fusibility diagrams [17,18]; red arrows show the direction.

To describe the behavior of components and molar number during moving liquid composition along curve (for certainty $(E_3 \rightarrow R_1 \rightarrow E_2)$, imagine a thought experiment. It is possible to organize such process only with mass transfer. In a mass transfer in heterogeneous system or conduct such isotherm-isobar open phase process [19]:

- To the heterogeneous system (liquid is point 1 in Figure 4), add some liquid H_2O (liquid pass to point 2);
- Dissolve part of the equilibrium solid compound $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$ in solution until saturation (liquid pass to point 3);
- Repeat this two-stage process until liquid comes to the point R_1 (liquid pass to point 4, to point 5, . . . to point R_1 (Figure 4);
- Evaporate H_2O from liquid R_1 (liquid pass to point 5);
- Crystallize from supersaturated liquid crystals $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$ until liquid become saturated (liquid pass to point 6);
- Repeat this two-stage process until liquid comes to the point E_2 (liquid pass to point 7, to point 8, . . . to point E_2), as in Figure 4.

It is clear, that in the first half of process where $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow R_1$, molar number dissolved in liquid $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$ increased, so simultaneously increased molar numbers of $NaCl$; $CdCl_2$ in liquid. In the second half of process, $R_1 \rightarrow 5 \rightarrow 6 \rightarrow 7 \rightarrow 8$, molar number dissolved in liquid $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$ decreased, so simultaneously decreased molar numbers of $NaCl$; $CdCl_2$ in liquid. In R_1, molar numbers of $NaCl$; $CdCl_2$ pass through the extreme. H_2O molar numbers in R_1 also pass through the maximum, according to criterion of diffusional liquid stability (values of H_2O chemical potential, activity, and partial pressure always (at $P, T = const$) change). It is clear that the compound $3NaCl \cdot 4CdCl_2 \cdot 14H_2O$'s molar number in the solid phase in R_1 also passes through the extreme. Thus, we have confirmed that molar numbers of the substances were connected by a heterogeneous chemical reaction:

$$3NaCl(liquid) + 4CdCl_2(liquid) + 14H_2O(liquid) \rightarrow 3NaCl \cdot 4CdCl_2 \cdot 14H_2O(solid)$$
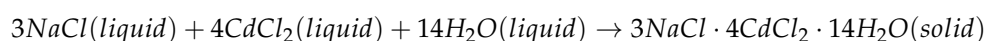
passes through the extreme simultaneously.

To determine the behavior of pressure during moving liquid composition along curve for certainty $(E_3 \rightarrow R_1 \rightarrow E_2)$, we can use the well-known Gibbs rule [9,20]: Temperature (at $P = const$) or pressure (at $T = const$) passes through the extreme when the composition of equilibrium coexisting phases were linearly dependent. In our case, the three-phase equilibrium figurative points of (v)-(l)-(s) are in the points R_i belonging to one curve, as seen in Figures 3 and 4. From Figure 4, one can see that in R_i, partial pressure (P_{H_2O}), but not sum pressure ($P = const = 1\ atm$), passes through the extreme. The contradiction here is apparent, because moderate pressure does not have an impact on the equilibrium between condensed phases. Thus, in experiment, we can remove the main components of the gas phase (air) from the system and leave only the water vapor equilibrium with the solution, and this fact should not affect the solubility diagram. In this case, $P_{H_2O} \approx P$ (at $T = const$) and pressure in points R_i passes through the extreme.

7. About Chemical Equilibrium Shift in the Conditions of Continuous Isothermal-Isobar Input of Reagents or Output of the Products of the Reaction

Input or output of all reagents or all products in stoichiometric ratios.

In the conditions of continuous isothermal-isobar input of reagents or output of the products (the last case corresponds to the removal of the products from the reaction phase), the chemical equilibrium shifts to the products formation. This formulation is at least ambiguous.

At the same time, we believe that:

(A) Assuming that chemical reaction is in the state of chemical equilibrium, equilibrium constant (K_e) as well as chemical variable (ξ), corresponds to equilibrium.

(B) Reagents are continuously introduced into reaction phase in stoichiometric ratios, or products are outputting from reaction phase also in stoichiometric ratios;

(C) Reaction phase are artificially knocked out of equilibrium all and the system strives to return to it all the time.

(D) Thus, one can write that if one artificially changes molar numbers of components (without system drive to equilibrium constant), then the following inequalities are valid:

$$(d\ln K_{une}/dn_{reagents})_{P,T,n_{products}} = \left\{ d/dn_{reagents}\left[\sum_{i=1}^{n_1} \nu_i \ln a_i\right] \right\}_{P,T,n_{products}} < 0 \qquad (96)$$

$$(d\ln K_{une}/dn_{products})_{P,T,n_{reagents}} = \left\{ d/dn_{products}\left[\sum_{i=n_1+1}^{n} \nu_i \ln a_i\right] \right\}_{P,T,n_{reagents}} > 0 \qquad (97)$$

because it is a valid criterion of diffusional stability of the reaction phase:

$$(\partial\mu_i/\partial n_i)_{T,P,n_{products(reagents)}} = RT(\partial \ln_i /\partial n_i)_{T,P,n_{products(reagents)}} > 0 \qquad (98)$$

Value K_{une} in Equation (95) is not equilibrium constant and corresponds to unequilibrium, for example, for one of the reagents:

$$\sum_{i=1}^{n_1} (\partial\mu_k/\partial n_i)_{T,P,n_{products}} = (\partial\mu_k/\partial n_k)_{T,P,n_{i\neq k}} \sum_{i=1}^{n_1} (\partial n_k/\partial n_i)_{T,P}] =$$

$$= (\partial\mu_k/\partial n_k)_{T,P,n_{i\neq k}}[1 + \sum_{i=1}^{n_1} (\partial \nu_i/\partial \nu_k)_{T,P}] > 0 \qquad (99)$$

and for one of the products:

$$\sum_{i=n_1+1}^{n} (\partial \mu_k / \partial n_i)_{T,P,n_{reagents}} = (\partial \mu_k / \partial n_k)_{T,P,n_{i \neq k}} \sum_{i=n_1+1}^{n} (\partial n_k / \partial n_i)_{T,P} =$$
$$= (\partial \mu_k / \partial n_k)_{T,P,n_{i \neq k}} [1 + \sum_{i=n_1+1}^{n} (\partial v_i / \partial v_k)_{T,P}] > 0 \qquad (100)$$

because both multipliers in Equation (96) are positive.

Naturally at the same time:

$$(d\xi / dn_{reagents})_{T,P,n_{products}} < 0; (d\xi / dn_{products})_{T,P,n_{reagents}} > 0 \qquad (101)$$

because:

$$(d \ln K_{une} / dn_{products})_{T,P,n_{reagents}} = Z(d\xi / dn_{products})_{T,P,n_{reagents}} \qquad (102)$$

$$(d \ln K_{une} / dn_{reagents})_{T,P,n_{products}} = Z(d\xi / dn_{reagents})_{T,P,n_{products}} \qquad (103)$$

where $Z > 0$ is determined later (Equation (24)). Chemical variable (ξ) after artificially changing molar numbers of components also becomes un-equilibrium (ξ_{une}).

To return to the state of chemical equilibrium, or to make $K_{une} = K_e; \xi_{une} = \xi_e$, one should transfer some part of reagents into the products (in both cases, of initial input of reagents or output of the products). In both cases, it is valid that:

$$dn_{reagents} < 0; dn_{products} > 0 dn_{reagents} < 0; dn_{products} > 0 \qquad (104)$$

and in the conditions of inequalities (100) one can say, that in both these processes of chemical equilibrium recovery:

$$(d\xi)_{T,P} > 0 \qquad (105)$$

i.e., equilibrium shifts to the products.

We can formulate CES-principle-add: In the conditions of continuous isothermal-isobar input of reagents or output of the products in stoichiometric ratios, the chemical equilibrium is initially collapsing and shifts to the reagents, and in the process of chemical equilibrium recovery, it shifts to the products formation.

Input or output of part of reagents or products.

This case covers, in particular, the very popular option of permanent input of only one reagent to the reaction phase, or output of only one product from the reaction phase (for example, in the form of a precipitate or gaseous from the liquid phase). Unfortunately, one cannot formulate in this case some analog of CES-principle-add. It is so because the principles of the diffusional stability of the reaction phase (Equation (95)) will be valid only for input or output components, but not for the components not involved in mass-change process. We denote the components involved in mass change process as *j*-th and *k*-th, and not involved as *i*-th. Derivatives $(\partial \mu_i / \partial n_j)_{T,P,n_{i,n_{k \neq j}}} = RT (\partial \ln a_i / \partial n_j)_{T,P,n_{i,n_{k \neq j}}}$ or $(\partial \mu_k / \partial n_j)_{T,P,n_{i,n_{k \neq j}}} = RT (\partial \ln a_k / \partial n_j)_{T,P,n_{i,n_{k \neq j}}}$ have an indefinite sign. For example, it is easy to show that for an ideal reaction phase:

$$(\partial \mu_i / \partial n_j)_{T,P,n_{i,n_{k \neq j}}} = (\partial / \partial n_j) [RT(n_i / \sum_{l=1}^{n} n_l)]_{T,P,n_{i,n_{k \neq j}}} = -RT / \sum_{l=1}^{n} n_l < 0 \qquad (106)$$

but one cannot determine the sign of the mixed derivatives for arbitrary non-ideal reaction phase. Thus, inequality (99) cannot be established and CES-principle-add cannot be formulated.

Input or output of all reagents or all products in non-stoichiometric ratios.

In this case, CES-principle-add also cannot be formulated, because the Equations (101) and (102) cease to be fair due to the sign uncertainty of the function Z (see Equation (24)).

8. Conclusions

Description of chemical equilibrium shifts in the systems with free and connected chemical reactions were elaborated in the conditions of temperature change, pressure change, input or output of reagents or products. The principle itself was supplemented by considering the states of chemical equilibrium, in the case when the reactants and reaction products were mixed into a single reaction phase and were not separated in space from each other. In the considered case, this phase can be arbitrarily imperfect. On the other hand, the article considers cases of equilibrium shift in a system of several related reactions at once. This connection can be carried out by any participants in this system of reactions (products, starting materials, or intermediates). The established principle of the joint passage of the concentrations of substances of related reactions through an extreme may, in the opinion of the authors, be of separate interest.

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