



# The origin of extrathermodynamic compensations

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## ARTICLE INFO

### Keywords:

Thermodynamics  
Enthalpy-entropy compensation  
Extrathermodynamic relationships

## ABSTRACT

The way of analysis of thermodynamic systems, which takes into consideration systems' phase volumes, is suggested. A validity of such approach was verified by the example of studying of extrathermodynamic compensations. Several types of exact linear extrathermodynamic compensations as well as their peculiar type, which peculiarity is indefinable compensation temperature, are established. The criteria that specify these types are stated. These results are illustrated by the identified exact extrathermodynamic compensations in formation of pyrene excimers.

## 1. Introduction

Thermodynamics is a rigorous theory, which, however, does not explain some thermodynamic topics. In particular, this remark refers to enthalpy-entropy compensations. The extrathermodynamic effect of enthalpy-entropy compensations, which is known in many fields of physics, chemistry and biology, is inherent in some series of related systems [1, 2, 3, 4, 5]. Its essence is expressed by the linear regression:  $\Delta H_{ab}(j) = T_\alpha \Delta S_{ab}(j) + \alpha$ , where  $\Delta H_{ab}(j)$  and  $\Delta S_{ab}(j)$  are changes in enthalpy and entropy in a certain process between states  $a$  and  $b$  in  $j$ -th system,  $T_\alpha$  is a temperature characteristic of this process (the compensation temperature),  $\alpha$  is a series constant. As regards the circumstances leading to the linearity of compensations  $\Delta H$ - $\Delta S$ , their understanding is the unsolved problem, in relation of which different opinions were advanced [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15].

The inability of thermodynamic theory to solve the problem of extrathermodynamic phenomena seems to be due to ignoring phase volume of systems. The concept of phase volume is completely absent in thermodynamics. The reason is that thermodynamics usually considers a system, whose phase volume is a predetermined and invariable magnitude. Nevertheless, one can show that extrathermodynamic phenomena include several types of linear extrathermodynamic compensations, which origin is connected precisely with phase volumes of systems [16, 17, 18]. In addition, this study is the first to pay attention to the new type of extrathermodynamic compensation that is very peculiar. Its origin is also related to the behavior of phase volume in a series of systems. The peculiarity of this type of compensation is the plot of enthalpy changes vs. entropy changes represents the only point, and hence, the compensation temperature is undefinable. Up to now such type of

extrathermodynamic compensations has been out of eyeshot of anyone.

This work purpose is to develop such approach to the analysis of totalities of thermodynamic systems, which could provide a unified view of compensation for all its types. In the next section the main points of this extrathermodynamic approach are set out.

## 2. Method

The basic equation of thermodynamics for heat quantity  $\delta Q$  is

$$\delta Q = dE + \sum A_i da_i \quad (1)$$

Here  $E$  stands for energy of a system,  $A_i$  stands for  $i$ -th generalized force, which is developed by a system in a direction of the generalized coordinate  $a_i$ . In terms of mathematics, Eq. (1) represents the Pfaff form. At one time, Carathéodory noticed this fact and formulated the theorem on integrating denominator of this form [19]. He showed that the Pfaff form is able to possess this denominator only if near to each equilibrium state of a system there are such its states, which are unachievable in any equilibrium adiabatic way. This condition is essentially an expression of the second law of thermodynamics. Surely, if integrating denominator of the Pfaff form exists and this denominator is absolute temperature  $T$ , a division of heat quantity by temperature yields the exact differential of entropy,  $\delta Q/T = dS$ , and Eq. (1) will be holonomic:

$$\delta Q = dE + \sum A_i da_i = TdS \quad (2)$$

It is apparent that the second law of thermodynamics evidences a noncoincidence of the isotherm and adiabat for equilibrium processes.

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This thesis can be illustrated with Fig. 1. The plot of  $P$  (pressure that is the generalized force) vs.  $V$  (spatial volume that is the generalized coordinate), which represents the isotherm of ideal gas, is there depicted. The transition of ideal gas from state 1 to state 2 is possible in the reversible way along the isothermal curve (trajectory 1→2) and in the adiabatic way, by irreversible gas expansion in emptiness (trajectory 1→1'→2'→2). State 2 is precisely a state unattainable from state 1 by any reversible adiabatic process.

In the general case, generalized forces and coordinates can be very various. Therefore, it is impracticable to establish any analytical dependence between  $S$  and  $E$  (or  $H (=E + PV)$ ) based on Eq. (2). For this reason, the enthalpy–entropy compensation is a controversial topic of thermodynamics.

The connection between  $S$  and  $H$  can be established based on the premise related to phase volume of thermodynamic systems. To discover here this premise, let us return to Fig. 1, which illustrates isothermal and adiabatic transitions between gas states 1 and 2. The adiabatic transition is uncompensated and hence irreversible; therefore, for this process it is true:

$$TdS > dE + PdV. \tag{3}$$

Both of these transitions take place under constant phase volume. However, when phase volume is variable, one more adiabatic way of transition between gas states 1 and 2 becomes possible. This way can be seen after correction of Eq. (3):  $TdS = dE + PdV + TdS_0$  or

$$dE + PdV = dH = Td(S - S_0). \tag{4}$$

Here  $S_0 = Nk \ln \Omega$ ,  $N$  is a number of particles,  $k$  is the Boltzmann constant, and  $\Omega$  is phase volume. Eq. (4) shows that a change of phase volume can compensate for a change in entropy.

Eqs. (2) and (3) on the one hand and Eq. (4) on the other differ fundamentally in kind. The fundamental difference is that Eqs. (2) and (3) describe a thermodynamic system with stationary  $\Omega$ , whereas Eq. (4) deals with variable phase volume of a system. Just as diverse thermodynamic reversible transitions are characterized by Eq. (2), diverse extrathermodynamic reversible transitions are characterized by a few equations like Eq. (4). Here the term “thermodynamic” is applied to processes occurring under constant phase volume and the term “extrathermodynamic” is associated with changes in phase volume. Generally, the term “extrathermodynamic” is perceived as synonymous with the concept “empirical” [1, 3], but we consider this term is the appropriate term for defining the reversible transitions featured by equations like Eq. (4). Below are all types of such equations.

There are two extrathermodynamic ways of heat expenditure and, accordingly, two extrathermodynamic basic equations:

$$\delta Q = dH = T_\Omega d\sigma_\Omega, \tag{5}$$

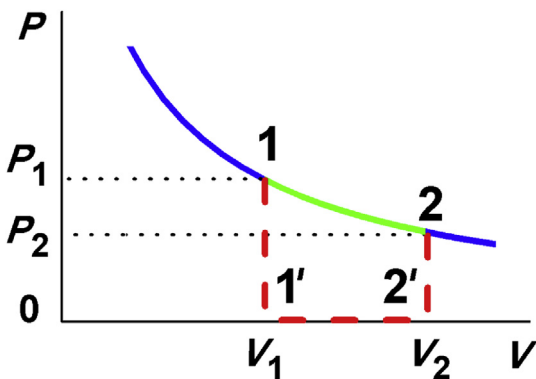


Fig. 1. Transitions between ideal gas states 1 (pressure is  $P_1$ , volume is  $V_1$ ) and 2 (pressure is  $P_2$ , volume is  $V_2$ ): reversible (along the isotherm, trajectory 1→2) and irreversible (by adiabatic expansion, trajectory 1→1'→2'→2).

$$\delta Q = dH = T_M d\sigma_M. \tag{6}$$

Here enthalpies and statistical quantities  $\sigma_\Omega$  and  $\sigma_M$  make unequal sense. The sense of the quantity  $\sigma_\Omega$  appearing in Eq. (5) can be easily seen. So, let us imagine that a system that exist initially in the original state with  $E, V, \omega, \Omega = 0$  obtains the increments  $\delta Q = E + PV = T_\Omega Nk \ln(\omega/\Omega)$ . Here  $\omega$  is a statistical weight that defines entropy  $S = Nk \ln \omega$ . It is obvious that one and the same value  $\delta Q$  and the same increments  $V$  and  $\ln \Omega$  will give a spectrum of correlated values  $E$  and  $S$ . This spectrum of the  $E$ – $S$  pairs defines a series of systems of the  $\Omega$ -type. A series displays exact  $E$ – $S$  compensation:  $E(j) + PV = T_\Omega Nk \ln(\omega(j)/\Omega)$ , where  $V$  and  $\Omega$  are constants of a series. It is apparent that the quantity  $\sigma_\Omega = Nk \ln(\omega/\Omega)$  represents the normalized entropy, and enthalpy in Eq. (5) is the quantity with the same value  $V$ .

For others  $\Omega$  and  $V$ , which values depend on temperature  $T_\Omega$ , other series of systems of the  $\Omega$ -type can be obtained from the same initial system.

In that case, where  $\delta Q$  is expended on increments of both  $\omega$  and  $E$ , and  $\Omega$  and  $V$ , a series of systems is characterized by the quantity  $\sigma_M$  (Eq. (6)). This quantity, which can be termed the normalized extraentropy, will be  $\sigma_M = Nk \ln(\omega\Omega/M)$ . Such definition of  $\sigma_M$  was argued in the work [17]. However, the sense of quantity  $M$  remained obscured. The sense of normalizing divider  $M$  can be shown in such way.

In the field of statistical mechanics the Gibbs thermodynamic potential,  $\Psi_G = E + PV - TS$ , can be defined as  $dW(X, V) = e^{\frac{\Psi_G - E(X) - PV}{kT}} dXdV$ . Here  $X$  is the set of canonical variables of a system, and  $dW(X, V)$  is probability of that a system is in the state with values of variables between  $X$  and  $X + dX$  as well as  $V$  and  $V + dV$ . After integrating this equation over the layer  $\Omega(\mathcal{E})V(\mathcal{E})d\mathcal{E}$ , which lies between the surfaces of constant energy  $\mathcal{H}(X, V) = \mathcal{E}$  and  $\mathcal{H}(X, V) = \mathcal{E} + d\mathcal{E}$ , it is possible to obtain the energy distribution of states in an isothermal–isobaric ensemble:

$$e^{-\frac{\Psi_G}{kT}} = \int e^{-\frac{\mathcal{E}}{kT}} \Omega(\mathcal{E})V(\mathcal{E})d\mathcal{E}. \tag{7}$$

In a system with variable  $\Omega$ , along with  $V$ , quantity  $1/\Omega$  acts as a coordinate, and the Hamiltonian function becomes

$$\mathcal{H}\left(X, V, \frac{1}{\Omega}\right) = E(X) + PV + TNk \ln \Omega \text{ [17]}. \text{ Then Eq. (7) can be modified:}$$

$$e^{-\frac{\Psi_G}{kT}} = \iint e^{-\frac{\mathcal{E}}{kT}} \frac{\Omega(\mathcal{E})}{\Omega} V(\mathcal{E}) d\mathcal{E} d\left(\frac{1}{\Omega}\right). \text{ Because } \int \Omega(\mathcal{E}) d\mathcal{E} = \int dX = \Omega,$$

quantity  $\frac{\Omega(\mathcal{E})}{\Omega}$  does not depend on  $\Omega$ , but  $V(\mathcal{E})$  is related with  $\Omega$ . We consider only equilibrium states of a system; this means that spatial volume of a system does not exceed some its maximal value  $M = \int_0^{V_{\text{Max}}} dV$ . Normalizing  $V(\mathcal{E})$  to this volume  $M$ , one can determine

$$e^{-\frac{\Psi_M}{kT}} = \frac{\Omega}{M} e^{-\frac{\Psi_G}{kT}} = \int e^{-\frac{\mathcal{E}}{kT}} \frac{\Omega(\mathcal{E})}{\Omega} \frac{V(\mathcal{E})}{M} d\mathcal{E}. \tag{8}$$

Eq. (8) describes the energy distribution of states in an extrathermodynamic ensemble of the  $M$ -type with the potential  $\Psi_M = H - TS - TNk \ln \Omega + TNk \ln M$ . At a selected compensation temperature  $T_M$ , Eq. (8) features a series of systems that exhibit an exact  $H$ – $(S + Nk \ln \Omega)$  compensation:  $E(j) + PV(j) = T_M Nk \ln(\omega(j)\Omega(j)/M)$ , where  $M$  is a series constant. At other temperatures  $T_M$ , Eq. (8) describes other series that are united by the same value of  $M$ .

Provided that  $V$  is a constant, from Eq. (8) the following can be obtained,  $e^{-\frac{\Psi_\Omega}{kT}} = \int e^{-\frac{\mathcal{E}}{kT}} \frac{\Omega(\mathcal{E})}{\Omega} d\mathcal{E}$ , that defines the extrathermodynamic potential  $\Psi_\Omega$  as  $\Psi_\Omega = H - TS + TNk \ln \Omega$ .

Thus, in thermodynamics all reversible transitions are featured by the one equation (Eq. (2)), which defines the one type of integrating denominator – temperature  $T$  – and the one type of statistical quantity – entropy. In the extrathermodynamic case, reversible transitions are featured by two equations,

$$\delta Q = dH = T_{\Omega} d\sigma_{\Omega} = T_{\Omega} Nk d \ln \frac{\omega}{\Omega}, \quad (9)$$

$$\delta Q = dH = T_M d\sigma_M = T_M Nk d \ln \frac{\omega \Omega}{M}, \quad (10)$$

that gives two types of integrating denominator – temperatures  $T_{\Omega}$  and  $T_M$  – and two types of statistical quantities – the normalized entropy  $\sigma_{\Omega} = Nk \ln(\omega/\Omega)$  and normalized extraentropy  $\sigma_M = Nk \ln(\omega\Omega/M)$ .

In the case, where  $\delta Q = 0$ , there is one more extrathermodynamic equation that features the peculiar process:

$$\delta Q = dH = T d\sigma_0 = TNk d \ln \frac{\omega}{\Omega}. \quad (11)$$

Eq. (11) characterizes transitions between the systems, for which  $\omega = \Omega$ , but, unlike Eq. (9), both  $\omega$  and  $\Omega$  are variables. Hence,  $\sigma_0$  represents the third type of extrathermodynamic statistical quantity. As  $\sigma_0$  is always zero, the concept of integrating denominator becomes here meaningless. Eq. (11) defines series of systems, which can be named series of the zero-type.

Eqs. (2), (9), (10), and (11) feature real or imaginary processes. A reversible chemical reaction is the real process featured by Eq. (2). Creating phase volume is a trick; therefore, Eqs. (9), (10), and (11) feature imaginary reversible transitions. Eq. (2) can feature imaginary reversible transitions, too. For instance, it is the isothermal process of gas expansion (trajectory 1→2, see Fig. 1). In principle, it is a realizable process, but this implementation (infinitely slowly and infinitely long) is possible only theoretically. Despite it, this theoretical possibility gives grounds to compare gas states, which are parted by a reversible thermodynamic transition. On the contrary, there are no grounds to compare gas states, which are separated by the irreversible thermodynamic transition along the adiabatic trajectory 1→1'→2'→2 (see Fig. 1). However, in the latter case there is a theoretical possibility for reversible extrathermodynamic transitions, which are featured by Eq. (11).

The conditions of reversibility for a thermodynamic process are continuous changes of generalized forces and coordinates. Thermodynamic irreversibility of the free expansion of gas is associated with discontinuity of values of the generalized force; in the present case, this is pressure. The example with ideal gas shows that extrathermodynamics allows analyzing irreversible thermodynamic transitions of this type.

The situation with real systems is similar to that with ideal gas. Consider that a system, say system  $j = 1$ , can be transformed in a reversible thermodynamic way into a state that corresponds to system  $j = 2$ . Such transition is theoretically possible, but in actual practice it is impossible to provide compensations to all generalized forces. The thermodynamic transition between these states should be considered as an irreversible transition. At the same time, prepared series of experimental samples can be considered as the systems formed from scratch by the reversible extrathermodynamic transitions, which are described by Eqs. (9), (10), and (11).

The following can complete the above reasoning. The canonical variables  $X$  represent pairs of  $q$  and  $p$ , where  $q$  is coordinates and  $p$  is pulses in directions of these coordinates. In the statistical mechanics there is the theorem on equipartition of energy on degrees of freedom [20]. As for coordinates, this theorem reads  $\overline{q \frac{\partial \mathcal{Z}}{\partial q}} = kT$ , where the overhead line denotes ensemble average. Note that here a nonzero value of  $kT$  can be considered as the condition determining the possibility of motion in a direction of the coordinate  $q$ . Extrathermodynamic ensembles are described by two conjugate extracoordinates:  $V$  and  $1/\Omega$ . As was mentioned earlier [18],  $\frac{1}{\Omega} \frac{\partial \mathcal{Z}}{\partial (1/\Omega)} = -kT$ , so that  $V \frac{\partial \mathcal{Z}}{\partial V} + \frac{1}{\Omega} \frac{\partial \mathcal{Z}}{\partial (1/\Omega)} = 0$ . This shows that in the extrathermodynamic case any transitions in directions of the coordinates  $V$  and  $1/\Omega$  is not supposed. Therefore, it is not correct to speak about the extrathermodynamic potentials  $\Psi_{\Omega}$  or  $\Psi_M$ . Hence the logical conclusion: extrathermodynamic states create a coordinate space for diverse thermodynamic transitions.

Really, Eq. (2) contains coordinates along which there can be thermodynamic transitions between equilibrium states of a system. Each such state is uniquely determined by values of the coordinates  $a_i$ . To feature these states of a system, it is necessary to take into account an indeterminate number of generalized coordinates. At the same time, series of extrathermodynamic states can create a two-dimensional coordinate space for reversible thermodynamic transitions. The scales of this space are preset by the temperatures  $T_{\Omega}$  and  $T_M$ , which can be determined from experiments. A pair of values  $T_{\Omega}$  and  $T_M$  uniquely indicates each of physically permissible equilibrium states of a system. Values  $\Delta H$  and  $\Delta S$  of any reaction  $a \rightleftharpoons b$ , which proceeds in a system, are functions of the variables  $T_{\Omega}$  and  $T_M$ . Values  $\Delta H$  and  $\Delta S$  develop into surfaces in some ranges of values  $T_{\Omega}$  and  $T_M$ , which are specific for each reaction.

A straight line can better or worse approximate any array of  $\Delta H$ – $\Delta S$  data that feature a reaction. However, an exact linear compensation will be only for those data, which will be mapped in space  $(T_{\Omega}; T_M)$  on lines  $T_{\Omega} = \text{const}$  (compensations of the  $\Omega$ -type),

$$\Delta H_{ab}(j) = T_{\Omega} \Delta S_{ab}(j) - T_{\Omega} Nk \Delta \ln \Omega_{ab}, \quad (12)$$

or on lines  $T_M = \text{const}$  (compensations of the  $M$ -type),

$$\Delta H_{ab}(j) = T_M (\Delta S_{ab}(j) + Nk \Delta \ln \Omega_{ab}(j)) - T_M Nk \Delta \ln M_{ab}. \quad (13)$$

As can be seen, in the literal sense of the word, the exact linear  $\Delta H$ – $\Delta S$  compensation does not exist at all, but there are two other exact linear compensations:  $\Delta E$ – $\Delta S$  and  $\Delta H$ – $(\Delta S + Nk \Delta \ln \Omega)$ .

Extrathermodynamic transitions are not limited to Eqs. (9), (10), and (11). A system can form more than one state. In particular, if the system, which is characterized by a certain value of  $M$ , gets a chance to form  $n$  states, Eqs. (9) and (10) take the form

$$\delta Q = \sum dH_n = T_{\Omega} \sum d\sigma_{\Omega_n} = T_{\Omega} Nk \sum d \ln \frac{\omega_n}{\Omega_n}, \quad (14)$$

$$\delta Q = \sum dH_n = T_M \sum d\sigma_{M_n} = T_M Nk \sum d \ln \frac{\omega_n \Omega_n}{M}. \quad (15)$$

Then, if the states reveal themselves individually, one can observe  $n$  series of systems of the  $\Omega$ -type:

$$\begin{aligned} \Delta H_{ab1} &= T_{\Omega} Nk \Delta \ln \frac{\omega_{ab1}}{\Omega_{ab1}}; \dots \\ \Delta H_{abn} &= T_{\Omega} Nk \Delta \ln \frac{\omega_{abn}}{\Omega_{abn}}, \end{aligned} \quad (16)$$

and  $n$  series of systems of the  $M$ -type:

$$\begin{aligned} \Delta H_{ab1} &= T_M Nk (\Delta \ln \omega_{ab1} \Omega_{ab1} - \Delta \ln M^n); \dots \\ \Delta H_{abn} &= T_M Nk (\Delta \ln \omega_{abn} \Omega_{abn} - \Delta \ln M^n). \end{aligned} \quad (17)$$

Strictly speaking, Eq. (16) define only one series of system of the  $\Omega$ -type and Eq. (17) define only one series of system of the  $M$ -type. Simply in this case enthalpy and entropy of systems undergo  $n$ -fold degeneration.

The following are examples of all of the referred types of extrathermodynamic compensation.

### 3. Discussion

#### 3.1. Compensations of the $\Omega$ - and $M$ -types

Two systems can be assigned to the same type of  $\Omega$ , if values of their magnitude  $\Delta \ln \Omega$  are the same. Phase volume of a system whose equilibrium transitions are defined by Eq. (2) is a quantity that considers all degrees of freedom of a system, which connect with its coordinates  $a_i$ . Eqs. (12), (13), (16), and (17) do not contain any special coordinates  $a_i$ ; therefore, phase volume of the system states that are obtained by the extrathermodynamic transitions takes into account only the canonical

variables featuring these states. Because series of systems of the  $\Omega$ - and  $M$ -types are defined with constant temperatures  $T_\Omega$  and  $T_M$ , here only the configurational part of phase volume is significant.

Thus, it may be found that values of phase volume of any reaction  $a \rightleftharpoons b$  have some connection with the size of its reactionary area. As a chemical modification can change the size of reactionary area, it should be expected that series of systems of the  $M$ -type are associated with chemical modifications, whereas series of systems of the  $\Omega$ -type are associated with a change in physical influence on a system. Evidently, in many cases such statement is correct. However, there may be exceptions, when chemical modifications of reagents lead to a result like a change in properties of medium, but do not noticeably affect the size of reactionary area; though, perhaps, there may be an opposite situation, where a specific solvent influences reactionary area. Therefore, it is essential to find out a concrete situation for each case at hand. Anyway, the fact of a change in phase volume can be definitely established by measuring changes in  $\Delta V$ .

The  $\Omega$ - and  $M$ -compensations can be illustrated by the example of data from the work [21], which concern a formation of intramolecular pyrene excimers in bichromophores. Excimers are physical dimers of chromophores that are stable only in an excited state [22]. The interest of these data lies in their variety, in such variety, which is not in data from other publications. As we have already reviewed these data in the works [16, 17, 18], here we briefly dwell on them, but present the analysis in new, better visual perspectives.

The  $\Delta H$ - $\Delta S$  data relating to the formation of excimers are presented in Fig. 2. These data are presented in the form, in which they were presented in the work [21]. These data apply to *meso*-2,4-di (2-pyrenyl) pentane; *rac*-2,4-di (2-pyrenyl) pentane; 1,3-di (2-pyrenyl) propane; 1,16-di (1-pyrenyl) hexadecane, and 1,3-di (1-pyrenyl) propane, which are dissolved in various organic solvents. 1,3-Di (1-pyrenyl) propane forms two excimer states  $d_1$  and  $d_2$ :  $d_1 \rightleftharpoons Py + Py^* \rightleftharpoons d_2$ , whereas the other bichromophores form only one excimer state  $d$ :  $Py + Py^* \rightleftharpoons d$  [21]. The state of  $Py + Py^*$  is a monomeric ( $m$ ) state, where  $Py$  and  $Py^*$  denote unexcited and excited pyrene, accordingly. It should be noted that the scheme  $d_1 \rightleftharpoons Py + Py^* \rightleftharpoons d_2$  presents a special case of formation of several states in a system. This scheme corresponds to value  $n = 2$  in Eqs. (14) and (15).

As can be seen, all data in Fig. 2 excellently fall on the lines L1 and L2.

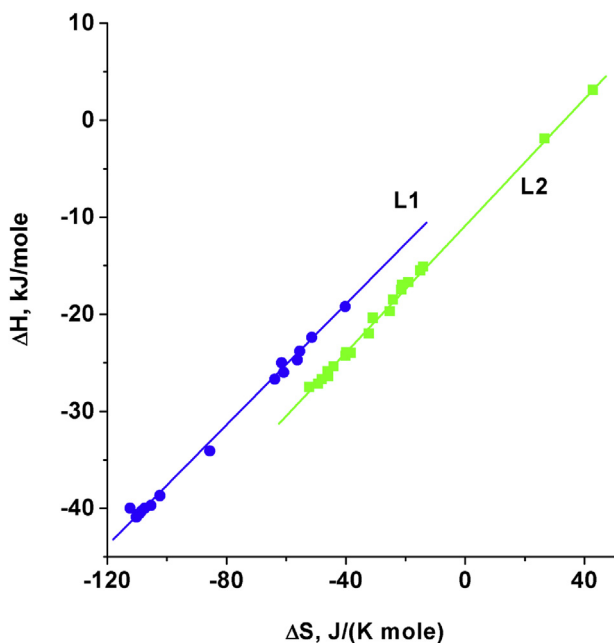


Fig. 2. Plot of  $\Delta H$  vs.  $\Delta S$  for intramolecular excimers formation with a number of dipyrenylalkanes in various solvents. Data from Ref. 21.

However, these lines do not make sense. It is rather an illustration of that that statistics can be very deceptive. At the same time, six lines shown in Fig. 3 are not without meaning. These are the same data as in Fig. 2, but they are organized in four series of systems of the  $\Omega$ -type (Eq. (12)) and in one series of systems of the double  $\Omega$ -type (the case of Eq. (16), where  $n = 2$ ). It was guessed here that a solvent does not influence an area of interchromophoric interaction in bichromophores. It was also accepted that a change of intramolecular area of interaction between pyrene moieties, that is, a change in excimer's phase volume, is attributed only to changes in a structure of interchromophoric chains. Compensation temperatures and other parameters concerning the  $\Omega$ - and  $M$ -series that were calculated within the frame of such assumptions are listed in the work [18].

For series of the  $\Omega$ -type, the values  $\Delta \ln \Omega$  can be founded at intersections of the dependences  $\Delta H/T_\Omega$  with the line  $\Delta S = 0$  (see Fig. 3). According to Eq. (12), these values are rigidly related to the compensation temperatures  $T_\Omega$ . The dependence in Fig. 4 shows that a higher compensation temperature  $T_\Omega$  corresponds to a smaller volume of reactionary area.

The compensations of the  $M$ -type that characterize the formation of pyrene excimers in series of systems with variable  $\Omega$  are presented in Fig. 5. All of them were calculated using values  $\Delta \ln \Omega$ , which were determined from the dependences shown in Fig. 3. As was expected, the set of linear relations breaks up into two clusters. These data fall on two lines (the lines L1 and L2) with different values of intercept: ( $R\Delta \ln M$  and  $2R\Delta \ln M$ ). Notice that the lines L1 and L2 in Fig. 5, and the lines L1 and L2 in Fig. 2 fit different pluralities of systems.

Four series of systems that are considerably divergent with the general body of data (see Fig. 5) are undoubtedly a result of experimental errors. All these series consist only of two systems, and even inappreciable errors in determining their parameters can lead to significant errors in determining temperatures  $T_M$ , and so, of magnitudes  $\Delta \ln M$ .

Thus, although all data in Fig. 5 feature the same nominal reaction – the formation of pyrene excimers, here are two different thermodynamic systems. It is impossible to perform transitions between states of these two thermodynamic systems in a reversible way. The reason for this is the discrete nature of a change in values in the line of quantities  $M, M^2 \dots M^n$  (see Eq. (17)).

Fig. 6 presents surface  $\Delta H(T_\Omega, T_M)$  for pyrene excimers forming as

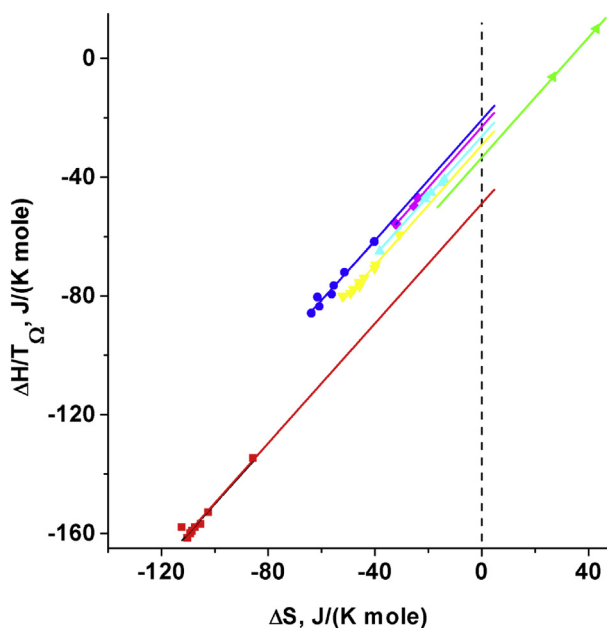


Fig. 3. Plot of  $\Delta H/T_\Omega$  vs.  $\Delta S$  for intramolecular excimers formation with a number of dipyrenylalkanes in various solvents.



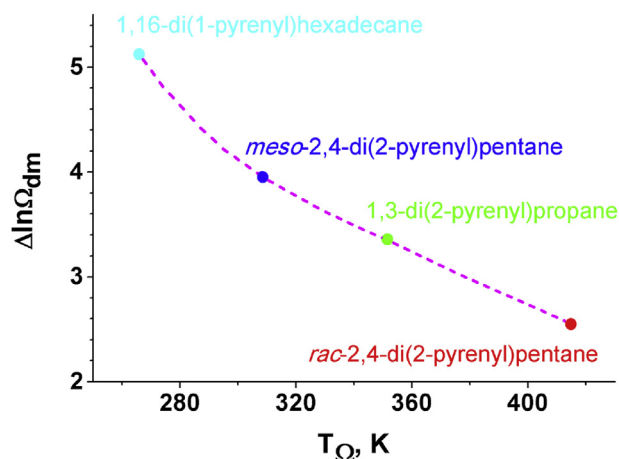


Fig. 4. Connection between compensation temperatures of  $T_{\Omega}$  and values of phase volume of pyrene excimers in various bichromophores.

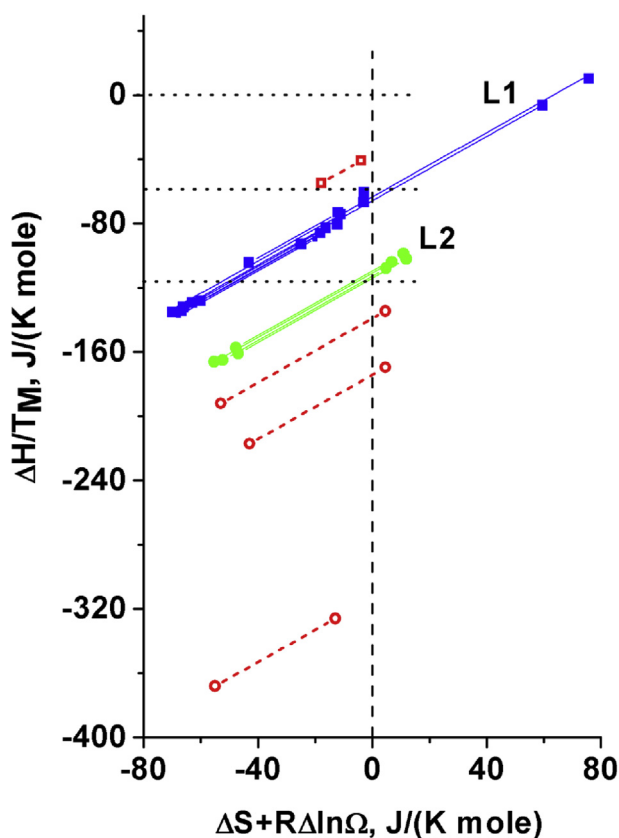


Fig. 5. Plot of  $\Delta H/T_M$  vs.  $\Delta S + R\Delta \ln \Omega$  for intramolecular excimers formation with a number of dipyrenylalkanes in various solvents.  $R$  is the universal gas constant.

$Py + Py^* \rightleftharpoons d$ . Analogous surface for pyrene excimers forming  $Py + d_1 \rightleftharpoons Py + Py^* \rightleftharpoons d_2$  is shown in Fig. 7. Inasmuch as in the latter case there are two excimers, this surface is two-layer. It is evident that there is not enough data to plot a full-fledged two-layer surface. Actually, whereas Fig. 6 presents four series of systems of the  $\Omega$ -type and eight series of systems of the  $M$ -type, Fig. 7 presents only one series of the doubly  $\Omega$ -type, which consists of seven doubly degenerated systems. Each of seven "series" of the doubly  $M$ -type contains only one doubly degenerated system. Despite this, Eq. (17) allow us to estimate temperatures  $T_M$  for these single-system "series".

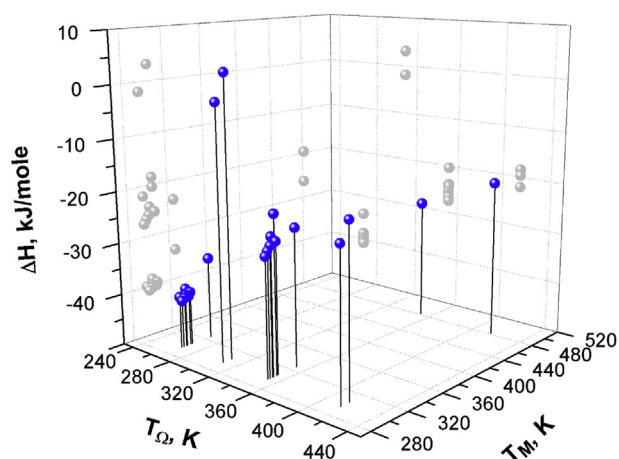


Fig. 6.  $\Delta H$  as function of temperatures  $T_{\Omega}$  and  $T_M$  for the systems, data of which are laid on the line L1 in Fig. 5. The grey points mark the orthogonal projections on corresponding planes.

### 3.2. A compensation of the zero-type

Eq. (11) combines systems differing only in the scale of phase space, which therefore do not create any coordinate axis for thermodynamic transitions. A series of systems of such zero-type is a series of gas equilibrium states parted by an irreversible adiabatic thermodynamic transition. However, it is a model. As for experiments, extrathermodynamic compensations of this type were not known before. Meanwhile, there is the regularity, which origin can be explained only as the manifestation of the enthalpy-entropy compensation of the zero-type.

The way, in which extrathermodynamic compensation of the zero-type reveals itself, can be seen in Fig. 8, where the fluorescence spectra of some pyrene-containing systems are presented. Here the structured fluorescence is emission of monomer chromophore and the broad structureless band pertains to excimers. The dependences of  $d \ln I(\nu) / d\nu$  that characterize the excimer components of these spectra, are inserted in the upper part of Fig. 8. It is visible that all these dependences are intercrossed at the one point close to wavenumber  $\nu = 19600 \text{ cm}^{-1}$ . Such characteristic point in spectra of pyrene excimers was previously reported [23]; however, no possible explanation was suggested to this observation. This point is precisely a manifestation of the extrathermodynamic compensation of the zero-type.

Indeed, each excimer state that is characterized by some emission wavenumber  $\nu$  arises due to the exciton-resonance interaction between chromophores [22], which causes a splitting of the  $^1L_a$  (in the Platte notation [24]) molecular level of energy. Different values of  $\nu$  correspond to different degrees of overlapping of molecular electron shells. In doing so, attracting exciton-resonance forces compete with repulsive forces between electrons that forms a certain potential surface for an excited chromophore in the action field of its unexcited partner (or viceversa). This surface in coordinates  $q$  can be featured by the thermodynamic potential  $\Psi_G(\nu) = E(\nu) + PV(\nu) - Tk \ln \omega(\nu)$ . Energy  $E(\nu)$  is a result of superposition of attractive and repulsive forces in those excimer structures, which provide an overlapping of molecular electron shells that corresponds to the given value  $\nu$ . The magnitude  $V(\nu)$  can be presented as the difference of  $\nu(\nu)$  and  $\nu(\nu + d\nu)$ . Magnitudes  $\nu(\nu)$  and  $\nu(\nu + d\nu)$  are spatial volumes of an overlapping of molecular electron shells in the configurations that correspond to emitting states  $\nu$  and  $\nu + d\nu$ . Hence, values  $V(\nu)$  are one and the same throughout the entire spectrum  $\nu$ , but the same cannot be said of entropies  $S(\nu) = k \ln \omega(\nu)$ . The excimer state that corresponds to energy  $E(\nu)$  can be realized in many configurations, which number  $\omega$  is a function of  $\nu$ , and, moreover,  $\omega(\nu) = \Omega(\nu)$ .

Accordingly, fluorescence intensity in an excimer band is  $I(\nu) \sim e^{-\frac{\Psi_G(\nu)}{kT}}$ , whence follows  $\frac{d \ln I(\nu)}{d\nu} = -\frac{1}{kT} \frac{d\Psi_G(\nu)}{d\nu}$ . That is, the de-

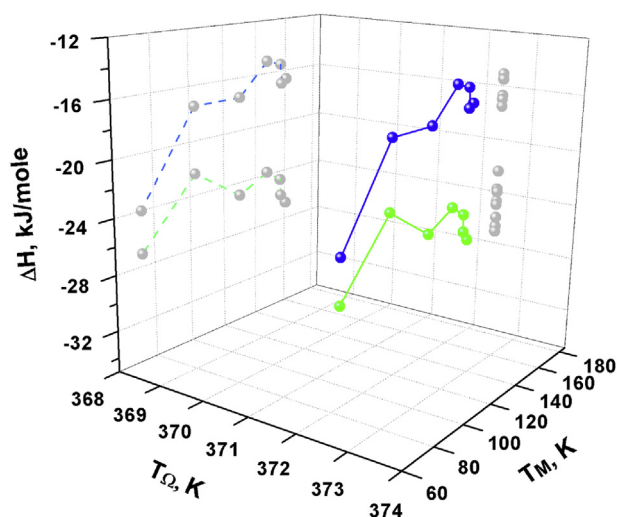


Fig. 7.  $\Delta H$  as function of temperatures  $T_{\Omega}$  and  $T_M$  for the systems, data of which are laid on the line L2 in Fig. 5.

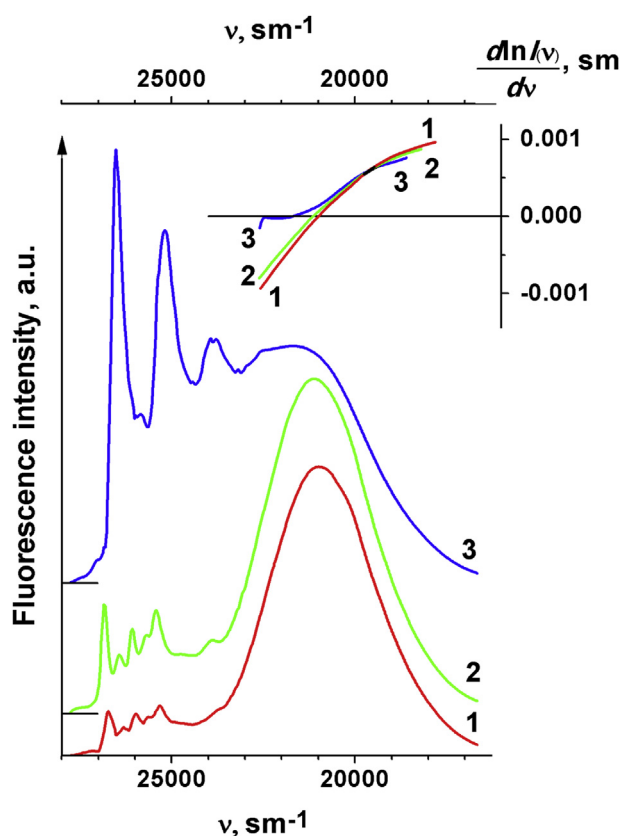


Fig. 8. Bottom: steady-state fluorescence spectra (excitation wavelength is 337 nm) of pyrene liquid solutions in metaxilol ( $1.2 \cdot 10^{-4}$  mole/l, 1) and ethanol ( $1.3 \cdot 10^{-2}$  mole/l, 2), and solid solution of 1-pyrene sulfonic acid in poly(vinyl alcohol) ( $5 \cdot 10^{-3}$  mole/l, 3). The spectra were recorded with LOMO SDL-2 spectrometer at a room temperature. Top: 1–3 are the dependences of  $d \ln I(\nu)/d\nu$  for spectra 1–3, respectively.  $I(\nu)$  is intensity in spectra of fluorescence.

pendences shown in the upper part of Fig. 8 characterize interchromophoric potentials in excimer. The scheme of kinetic processes in excimer can be defined as  $\dots \rightleftharpoons D(\nu) \rightleftharpoons D(\nu + d\nu) \rightleftharpoons \dots$ , where  $D(\nu)$  denotes an excimer state emitting the light with wavenumber  $\nu$ . It is visible that the

equilibrium thermodynamic transition between excimer states, that is, the reaction, where  $\frac{1}{d\nu}(dE(\nu) + PdV(\nu) - Tkd \ln \omega(\nu)) = 0$ , is possible only at the one point. This is the point at a minimum in the potential  $\Psi_G(\nu)$  (a maximum of the excimer band), which, depending on an environment of excimer, can shift on  $\nu$ . However, for reversible extrathermodynamic transitions, the equilibrium reaction is only such reaction, where  $\frac{1}{d\nu}(dE(\nu) + PdV(\nu) - Tkd \ln \frac{\omega(\nu)}{\Omega(\nu)}) = 0$ . As  $dV(\nu) = 0$  and  $\omega(\nu) = \Omega(\nu)$ , this reaction proceeds at the point of a minimum in potential  $E(\nu)$ . For pyrene, this is  $\nu_0 \cong 19600 \text{ sm}^{-1}$ , as it is indicated by the position of the characteristic point in the fluorescence spectra shown in Fig. 8. Magnitude  $\frac{d \ln I(\nu)}{d\nu}|_{\nu=\nu_0}$  at this point is nothing else than  $\frac{d \ln I(\nu)}{d\nu}|_{\nu=\nu_0} = \frac{d \ln \omega(\nu)}{d\nu}|_{\nu=\nu_0}$ . Its value does not depend on temperature, because here the compensation temperature does not exist. Therefore, it can be predicted that this characteristic point will be observed under thermochromic transformations of excimer spectra, too.

The presented example of the zero-type compensation can be formalized as

$$\frac{1}{d\nu} dH(j)|_{\nu=\nu_0} = \frac{Tk}{d\nu} d \ln \frac{\omega(j)}{\Omega(j)}|_{\nu=\nu_0} = 0. \quad (18)$$

The distinction between the above formula and expressions for linear extrathermodynamic compensations is that Eqs. (12), (13), (16), and (17) contain the finite differences  $\Delta$ , whereas in excimer it is the reaction between the infinitesimally close states  $\nu_0$  and  $\nu_0 + d\nu$ .

### 3.3. Closing remarks

The results stated in Section 2 are derived from the first principles and are not specific. Therefore, they can be valid for any systems. One can specify some of the work, the results of which are consistent with the above ideas about the origin of extrathermodynamic compensation. So, the authors [25], analyzing the enthalpy-entropy compensation in complexation of different cations with organic ligands like crown ethers, described this process in such way,  $\Delta H = T\Delta S - T\Delta S_0$ , that is similar to Eq. (12). Values of slopes in the  $\Delta H - T\Delta S$  plots (that is, the compensation temperatures) and the intercepts  $T\Delta S_0$  depended on the nature of the ligand. Interpretation of the intercept is interesting here: “ $T\Delta S_0$  value is the intrinsic entropic gain upon complexation for each ligand, which is mostly attributable to the desolvation of the complexed cation. This intrinsic entropic gain indicates to what extent the cation solvation is replaced by the ligand donors”.

In the work [26], for the isotropization processes occurring in europium complexes with organic ligands, it was found that the  $\Omega$  values differ in the cases of monodisperse and polydisperse ligands. Calculated values of the magnitude  $M$  that figures in Eq. (13) turned out to be the same in both cases. This result of analysis is similar to the construction of the line L1 shown in Fig. 5.

In this work, various types of extrathermodynamic compensations were presented precisely on the example of a formation of pyrene excimers that allowed us to show a more full range of extrathermodynamic relationships. It is obvious that the advantage of excimers as a model system for studying of extrathermodynamic compensations is a possibility of determining of their energy parameters by spectral methods. In particular, this circumstance made it possible to detect the compensation of the zero-type and to distinguish excimers  $d_1$  and  $d_2$  that are formed in bichromophores. Calorimetric measurements, for example, if there would be such possibility, would hardly be able to determine the contribution of each of excimers  $d_1$  and  $d_2$  to the total heat efficiency of their formation.

#### 4. Conclusions

The main result of this work is the basic extrathermodynamic relations represented by Eqs. (11), (14), and (15). Eqs. (9) and (10) are a particular case of the last two equations (if  $n = 1$ ). The approach used here to achieve this result makes it possible to draw very concrete conclusions with regard to extrathermodynamic compensations, one of the types of which is the well-known enthalpy-entropy compensation. It is shown that extrathermodynamic compensations are exact regularities, the specific type of which is determined by the nature of the behavior of systems' phase volume in their series. At present time, the samples of extrathermodynamic compensations, which are described by Eqs. (12), (13), and (18) as well as by Eqs. (16) and (17) (for the case  $n = 2$ ), are found. In this paper, all these types of compensation are shown on the example of data relating to a formation of pyrene excimers.

#### Declarations

##### Author contribution statement

Oleg A. Khakhel', Tamila P. Romashko: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

##### Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

##### Competing interest statement

The authors declare no conflict of interest.

##### Additional information

No additional information is available for this paper.

#### References

- [1] J.E. Leffler, E. Grunwald, *Rates and Equilibria of Organic Reactions as Treated by Statistical, Thermodynamic, and Extrathermodynamic Methods*, Wiley, New York, 1963.
- [2] E. Tomlinson, Enthalpy-entropy compensation analysis of pharmaceutical, biochemical and biological systems, *Int. J. Pharm.* 13 (1983) 115-144.
- [3] L. Liu, Q.-X. Guo, Isokinetic relationship, isoequilibrium relationship, and enthalpy-entropy compensation, *Chem. Rev.* 101 (2001) 673-696.
- [4] A. Yelon, B. Movaghar, R.S. Crandall, Multi-excitation entropy: its role in thermodynamics and kinetics, *Rep. Prog. Phys.* 69 (2006) 1145-1194.
- [5] J.D. Chodera, D.L. Mobley, Entropy-enthalpy compensation: role and ramifications in biomolecular ligand recognition and design, *Annu. Rev. Biophys.* 42 (2013) 121-142.
- [6] L. Liu, Q.-X. Guo, A General theoretical model of enthalpy-entropy compensation, *Chin. J. Chem.* 19 (2001) 670-674.
- [7] K. Sharp, Entropy-enthalpy compensation: fact or artifact? *Protein Sci.* 10 (2001) 661-667.
- [8] W.R. Kirk, Entropy-enthalpy compensation behavior revisited, *J. Theor. Comput. Chem.* 03 (2004) 511-520.
- [9] D.M. Ford, Enthalpy-entropy compensation is not a general feature of weak association, *J. Am. Chem. Soc.* 127 (2005) 16167-16170.
- [10] E.B. Starikov, B. Norden, Enthalpy-entropy compensation: a phantom or something useful? *J. Phys. Chem. B* 111 (2007) 14431-14435.
- [11] C. Piguet, Enthalpy-entropy correlations as chemical guides to unravel self-assembly processes, *Dalton Trans.* 40 (2011) 8059-8071.
- [12] K.F. Freed, Entropy-enthalpy compensation in chemical reactions and adsorption: an exactly solvable model, *J. Phys. Chem. B* 115 (2011) 1689-1692.
- [13] U. Ryde, A fundamental view of enthalpy-entropy compensation, *Med. Chem. Commun.* 5 (2014) 1324-1336.
- [14] A. Pan, T. Kar, A.K. Rakshit, S.P. Moulik, Enthalpy-entropy compensation (EEC) effect: decisive role of free energy, *J. Phys. Chem. B* 120 (2016) 10531-10539.
- [15] S. Khrapunov, The enthalpy-entropy compensation phenomenon. Limitations for the use of some basic thermodynamic equations, *Curr. Protein Pept. Sci.* 19 (2018) 1088-1091.
- [16] O.A. Khakhel', Linear free energy relationship, *Chem. Phys. Lett.* 421 (2006) 464-468.
- [17] O.A. Khakhel', T.P. Romashko, Y.E. Sakhno, One more type of extrathermodynamic relationship, *J. Phys. Chem. B* 111 (2007) 7331-7335.
- [18] O.A. Khakhel', T.P. Romashko, Extrathermodynamics: varieties of compensation effect, *J. Phys. Chem. A* 120 (2016) 2035-2040.
- [19] C. Carathéodory, Untersuchungen über die Grundlagen der thermodynamik, *Math. Ann.* 67 (1909) 355-386.
- [20] M.A. Leontovich, *Vvedenie v termodinamiku. Statisticheskaya fizika* [Introduction in thermodynamics. Statistical Physics, in Russian], Nauka, Moscow, 1983.
- [21] K.A. Zachariasse, G. Duvencek, Linear free energy relationships for excimers, *J. Am. Chem. Soc.* 109 (1987) 3790-3792.
- [22] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970.
- [23] O.A. Khakhel', A characteristic point in fluorescence spectra of molecular excimers, *Russ. J. Phys. Chem.* 76 (2002) 1161-1167.
- [24] J.R. Platt, Classification of spectra of cata-condensed hydrocarbons, *J. Chem. Phys.* 17 (1949) 484-495.
- [25] Yo. Inoue, T. Hakushi, Enthalpy-entropy compensation in complexation of cations with crown ethers and related ligands, *J. Chem. Soc. Perkin Trans. II* (1985) 935-946.
- [26] S. Guerra, Th. Dutronc, E. Terazzia, K.-L. Buchwalder, L. Guénée, R. Deschenaux, S.V. Eliseeva, S. Petoud, C. Piguet, Taking a last look at lanthanidomesogens? The use of basic thermodynamics for programming the temperature domains of existence of luminescent liquid crystals, *Coord. Chem. Rev.* 340 (2017) 79-97.