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The Role of Binary and Many-centre Molecular Interactions in Spin Crossover in the Solid State. Part I. Equation for Free Energy

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Summary. A formalism has been developed that describes spin crossover equilibrium in the solid state by taking into account the effects of n nearest neighbours of a given molecule on its partition function. In this way binary and many-body interactions of the order $n+1$ are included into the theoretical model and represented by non-ideality parameters connected with the splitting of free energy levels. Binary interactions are characterised by the main splittings whereas higher order interactions manifest themselves in asymmetries of splittings within multiplets. The contribution of molecular interactions can also be written in terms of formal excess free energies of the second, third, fourth and higher orders. Simple relationships between excess free energies and parameters of multiplets have been found for binary, ternary and quaternary interactions. This formalism is reduced to that of the model of binary interactions when effects of surroundings are additive leading to equidistant free energy multiplets. Higher order interactions may cause an abrupt spin crossover but in a limited range of compositions around the transition point. The regression of experimental transition curves of one-step spin crossover may yield estimates of excess energies up to the fifth order.

Keywords. Solid state; Thermodynamics; Molecular magnets; Spin crossover; Molecular interactions.

Introduction

The phenomenon of spin crossover observed in some complexes of transition metals continues to attract considerable interest (see recent reviews [1–6]). Spin crossover is a unique homogeneous equilibrium between HS and LS complexes of Fe^{2+} and some other ions occurring in the solid state and showing a variety of effects (abrupt spin crossover, two-step spin crossover) originating from molecular

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interactions. Spin crossover occurs at low temperatures making the approximation of ideal crystal a good starting point for a more complicated model. Spin crossover is thus a perfect test-system for general theoretical descriptions of chemical equilibria in the solid state. On the other hand, purely practical problems of the synthesis of promising spin crossover compounds (molecular magnets) require a theory connecting the sharpness of transitions with molecular parameters predictable for model structures.

Dominating theoretical models of spin crossover (see also Ref. [5]) operate either with macroscopic empirical parameters or with microscopic parameters related to sublattices rather than to molecules. They can be divided into two groups: models of effective Hamiltonian and thermodynamic models. Models of the first type are usually based on the *Ising*-like Hamiltonian suggested by *Wajnflasc* and *Pick* [7] and further developed by *Bari* and *Sivardiere* [8], *Zelentsov et al.* [9], and *Varret et al.* [10]. The main variable of this model is the fictitious spin from which the composition of system is derived. The main parameter of this formalism is the interaction constant J (different from the exchange constant). This model gives a correct semi-quantitative description of all known types of spin crossover including the two-step spin crossover.

Thermodynamic models consider spin crossover as a chemical equilibrium between LS (A) and HS (B) isomers (Eq. (1)).

$$A_{(LS)} \rightleftharpoons B_{(HS)} \tag{1}$$

A formal thermodynamic description of gradual and abrupt spin crossover has been given by *Slichter* and *Drickamer* [11] in 1972 employing the model of regular solutions. The sharpness of transition in this model is characterised by the *excess energy of mixing* (ΔE^E) also termed as *cooperativity*. This model predicts the abrupt spin crossover as a result of strong homo-molecular interactions leading to the formation of HS-rich and LS-rich phases manifested by peaks of heat capacity [4] and accompanied by a hysteresis loop. However this model fails to predict the two-step spin crossover.

The domain model, suggested 1974 by *Sorai* and *Seki* [12], assumes 'that a crystal lattice consists of non-interacting domains with uniform size containing n complexes and that the spin state conversion in each domain takes place simultaneously' [4]. The domain model can be advantageously applied to cases of very sharp (abrupt) transitions accompanied by a narrow hysteresis loop, however this model does not directly predict the hysteresis, neither does it predict the two-step spin crossover.

The model of elastic interactions originally suggested by *Ohnishi* and *Sugano* [13] and developed by *Gütlich*, *Spiering et al.* [14–18] explains the cooperativity in terms of 'elastic interaction between HS and LS molecules *via* the image pressure' [14]. In this model a crystal is represented as an elastic isotropic medium in which metal complexes considered as incompressible spheres are embedded. According to Ref. [16] this model quantitatively predicts cooperativity as well as the energy difference between HS and LS states on the basis of experimental data on elastic constants, volumetric and thermal properties obtained in a wide temperature range [15].

Another approach is to employ the potential of elastic interactions in Monte-Carlo simulations of transition curves [18]. A good coincidence of experimental and simulated curves has been achieved employing a combination of the long-range elastic potential with terms reflecting short-range (on molecular scale) interactions [18]. It must however be mentioned that a macroscopically long-range potential itself arises from the short-range molecular forces (see *e.g.* Ref. [19]). Furthermore the range of lattice relaxation is limited to tens of lattice constants therefore elastic forces are not macroscopically long-range.

Quantum chemical calculations provide for the evaluation of electronic energies and vibrational frequencies in model structures representing isolated molecules of spin crossover complexes [20–23]. It has been found [22] that *Hartree-Fock* calculations overestimate the energy gap between HS and LS states leading to the stabilisation of HS species, whereas the DFT calculations show the opposite trend. Apparently the hybrid methods [22] provide for a correct estimation of ΔE^0 and ΔS^0 of spin crossover in model structures. The effect of solvent has been studied in the approximation of polarisable continuum [23].

The development of a molecular theory of spin crossover in the solid state is of importance not only for the general theory of condensed state but also for chemical practice. It is desirable to have a possibility to estimate the sharpness of transition (*i.e.* the sign and magnitude of the excess energy) for a model structure employing simple molecular parameters, such as interatomic distances, bond angles, electric dipole moments, *etc*. It is well known that the representation of thermodynamic functions in terms of molecular parameters is possible within a statistical mechanic formalism. This has been done in the approximation of ideal crystal by considering vibrational contributions towards standard free energy of spin crossover [23, 24]. The approximation of ideal crystal explains several effects in magnetically diluted solid solutions of spin crossover compounds, among them a specific nonlinearity of *van't Hoff* plots [2] in diluted systems. However the abrupt spin crossover cannot be explained within the approximations of ideal crystal.

Some years ago we have suggested a statistical thermodynamic model that provided for the quantitative parameterisation of the two-step spin crossover curves in $[\mathrm{Fe}(2\text{-}pic)_3]\mathrm{Cl}_2\mathrm{C}_2\mathrm{H}_5\mathrm{OH}$ and some other compounds [25–28]. Molecular interactions have been introduced as the effects of two nearest neighbours on the partition function of the central molecule. Neighbouring molecules change the potential energy of a given molecule by distorting the potential cavity in which this molecule resides; distortions of crystal field also quench orbital degeneracy. Both the energy and entropy components of the partition function of a molecule are thus affected. Depending on the actual composition of the environment the state of the molecule A in an equilibrium mixture of A (LS) and B (HS) isomers can be characterised by three free energies: F_{AAA}, F_{BAA}, and F_{BAB}. Similarly the free energy of the molecule B can have the values: F_{BBB}, F_{BBA}, and F_{ABA}. Molecular interaction thus splits the levels of molecules A and B into triplets (Fig. 1). The fundamental simplifying assumption of this model is the pseudo-independence of molecules and motions along spatial coordinates. Molecular interactions are supposed to change parameters of the partition function without causing a correlated behaviour of molecules. This allows one to sum free energy over molecules. Summing free energy over the coordinates is allowed when motions and interactions along the coordinates are

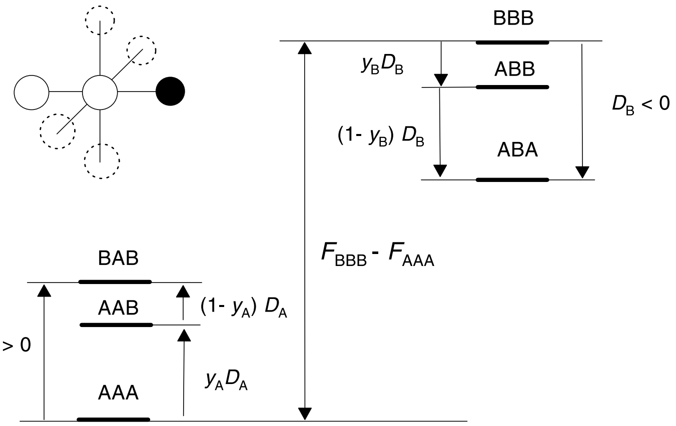

Fig. 1. Free energy level diagram showing the effects of two neighbours on the partition function of central molecule

uncorrelated. To a first approximation these assumptions are valid in systems of weakly interacting molecules[a]. The chain of reasoning when deriving the basic equation of this model is important and will be reiterated below in a concise form.

Under the conditions specified above by summing the free energy for each type of molecules over all surroundings and coordinates one obtains Eqs. (2) and (3).

$$F_A = x_A^2 F_{AAA} + 2x_A x_B F_{AAB} + x_B^2 F_{BAB} \tag{2}$$

$$F_B = x_B^2 F_{BBB} + 2x_A x_B F_{BBA} + x_A^2 F_{ABA} \tag{3}$$

The free energy of a mixture of two kinds of pseudo-independent molecules is pseudo-additive and contains a contribution from the mixing entropy (Eq. (4)).

$$F = x_A F_A + x_B F_B + NkT(x_A \ln x_A + x_B \ln x_B) \tag{4}$$

Combining Eqs. (2), (3), and (4) and substituting $x_B = 1 - x_A$, one obtains [25] the free energy as shown by Eq. (5) in which D_A, D_B, y_A, and y_B are given by Eqs. (5a) and (5b).

$$\begin{aligned} F = {} & x_A^3[(1 - 2y_A)D_A - (1 - 2y_B)D_B] + x_A^2[(1 - 4y_B)D_B - 2(1 - y_A)D_A] \\ & + x_A(D_A + 2y_B D_B - F_{BBB} + F_{AAA}) + F_{BBB} \\ & + NkT[x_A \ln x_A + (1 - x_A)\ln(1 - x_A)] \end{aligned} \tag{5}$$

$$D_A = F_{BAB} - F_{AAA}; \qquad D_B = F_{ABA} - F_{BBB} \tag{5a}$$

$$y_A = \frac{F_{AAB} - F_{AAA}}{D_A}; \qquad y_B = \frac{F_{ABB} - F_{BBB}}{D_B} \tag{5b}$$

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[a] Cases of strong interactions leading to correlations of spin states of complexes in neighbouring lattice centres can be described by a quasi chemical model [27]

The difference $F_{\mathrm{BBB}} - F_{\mathrm{AAA}}$ in the term linear with respect to x_{A}, represents the standard free energy of reaction in the state of pure compounds. The main splittings of free energy levels D_{A} and D_{B} characterise the effects of a complete change of environment from homo-molecular into hetero-molecular. The relative asymmetries of splittings y_{A} and y_{B} characterise the efficiency of the first substitution in the homo-molecular environment. The last four parameters appear as a result of molecular interactions and are therefore the non-ideality parameters of the considered system. The term in Eq. (5) proportional to ${x_{\mathrm{A}}}^3$ apparently arises from triple interactions whereas that proportional to ${x_{\mathrm{A}}}^2$ originates from binary interactions.

When spacings between sublevels in triplets (Fig. 1) are equal, *i.e.* when $y_{\mathrm{A}} = y_{\mathrm{B}} = 1/2$, the formalism is reduced to that of the model of binary interactions with a single non-ideality parameter, the excess free energy $\Delta F^{\mathrm{E}} = D_{\mathrm{A}} + D_{\mathrm{B}}$. In the approximation of zero excess entropy this reduced formalism becomes equivalent to that of the theory of regular solutions.

The phenomenon of ordering plays an important role in spin crossover in the solid state: it brings about the two-step spin crossover. Treating ordering in the *Bragg-Williams* approximation we have derived [25] equations providing for the simulation of two-step transition curves. Correct descriptions can be achieved when two equations are used for two regions of compositions $0 < x_{\mathrm{B}} < 1/2$ and $1/2 < x_{\mathrm{B}} < 1.0$, Eq. (6) for $x_{\mathrm{A}} < 1/2$, in which $u_{1\mathrm{A}} = (1 + \mathrm{s})x_{\mathrm{A}}$, $u_{2\mathrm{A}} = (1 - \mathrm{s})x_{\mathrm{A}}$, and s is the degree of order of the *Bragg-Williams* model, and Eq. (7) for $x_{\mathrm{B}} < 1/2$, in which $u_{1\mathrm{B}} = (1 + \mathrm{s})x_{\mathrm{B}}$, and $u_{2\mathrm{B}} = (1 - \mathrm{s})x_{\mathrm{B}}$.

$$\begin{aligned} F = {} & x_{\mathrm{A}}^3(1 - s^2)[(1 - 2y_{\mathrm{A}})D_{\mathrm{A}} - (1 - 2y_{\mathrm{B}})D_{\mathrm{B}}] \\ & + x_{\mathrm{A}}^2[(1 - 4y_{\mathrm{B}})D_{\mathrm{B}} - 2(1 - y_{\mathrm{A}})D_{\mathrm{A}} + s^2(D_{\mathrm{B}} + 2(1 - y_{\mathrm{A}})D_{\mathrm{A}})] \\ & + x_{\mathrm{A}}(D_{\mathrm{A}} + 2y_{\mathrm{B}}D_{\mathrm{B}}) + x_{\mathrm{A}}F_{\mathrm{AAA}} + (1 - x_{\mathrm{A}})F_{\mathrm{BBB}} + \frac{NkT}{2}[u_{1\mathrm{A}}\ln(u_{1\mathrm{A}}) \\ & + (1 - u_{1\mathrm{A}})\ln(1 - u_{1\mathrm{A}}) + u_{2\mathrm{A}}\ln(u_{2\mathrm{A}}) + (1 - u_{2\mathrm{A}})\ln(1 - u_{2\mathrm{A}})] \end{aligned} \tag{6}$$

$$\begin{aligned} F = {} & x_{\mathrm{B}}^3(1 - s^2)[(1 - 2y_{\mathrm{B}})D_{\mathrm{B}} - (1 - 2y_{\mathrm{A}})D_{\mathrm{A}}] \\ & + x_{B}^2[(1 - 4y_{\mathrm{A}})D_{\mathrm{A}} - 2(1 - y_{\mathrm{B}})D_{\mathrm{B}} + s^2(D_{\mathrm{A}} + 2(1 - y_{\mathrm{B}})D_{\mathrm{B}})] \\ & + x_{\mathrm{B}}(D_{\mathrm{B}} + 2y_{\mathrm{A}}D_{\mathrm{A}}) + (1 - x_{\mathrm{B}})F_{\mathrm{AAA}} + x_{\mathrm{B}}F_{\mathrm{BBB}} + \frac{NkT}{2}[u_{1\mathrm{B}}\ln(u_{1\mathrm{B}}) \\ & + u_{2\mathrm{B}}\ln(u_{2\mathrm{B}}) + (1 - u_{1\mathrm{B}})\ln(1 - u_{1\mathrm{B}}) + (1 - u_{2\mathrm{B}})\ln(1 - u_{2\mathrm{B}})] \end{aligned} \tag{7}$$

Theoretical transition curves are obtained as solutions of conditions of thermodynamic equilibrium with respect to the composition and the degree of order: $\partial F/\partial x = 0$, $\partial F/\partial s = 0$ (see Refs. [25], [26] and Methods). It has been found [25] that the plateau on two-step transition curves is connected with a peak of the degree of order appearing in systems with large negative excess energies $|\Delta E^{\mathrm{E}}| > 2RT_{1/2}$. The approximation of binary interactions ($y_{\mathrm{A}} = y_{\mathrm{B}} = 1/2$) only predicts general features of the two-step spin crossover, whereas adequate descriptions of experimental transition curves could only be obtained in the approximation of triple interactions ($y_{\mathrm{A}} \neq y_{\mathrm{B}} \neq 1/2$).

Although this model provided for a quantitatively adequate description of a wide variety of experimental transition curves [25–27] it suffers form several deficiencies.

- All four non-ideality parameters enter the terms arising from both binary and triple interactions. Although it has been deduced that main splittings characterise binary interactions the coefficients y_A and y_B do not represent directly the contribution of triple interactions.
- Taking into account the effects of only two neighbours of a given molecule makes this model limited to 1D structures or to systems with completely independent motions along coordinates. This might be considered as a too rough simplification.
- Non-ideality parameters in this model are formal adjustable parameters not related to the strength and type of molecular forces. Although their relationship to actual molecular potentials has been established in some special cases [26] the parameterisation of transition curves in terms of molecular potentials has not been explored.

The aim of this paper is to remove these deficiencies. Part I of this paper presents the derivation of equations with parameters directly related to binary and triple interactions. Then the case of a molecule interacting with an arbitrary number of nearest neighbours will be considered yielding a formalism taking into account many-centre interactions of $(n+1)$-th order. Part II is dedicated to the representation of non-ideality parameters *via* binary molecular potentials.

Results and Discussion

Parameters Directly Representing Triple Interactions

The effects of binary and triple interactions can be separated by substituting y_A and y_B in Eq. (5) as shown by Eq. (8).

$$\Delta_1^A = -(1-2y_A)D_A, \qquad \Delta_1^B = -(1-2y_B)D_B \tag{8}$$

Returning to two variables of composition (x_A, x_B) one obtains Eq. (9).

$$\begin{aligned} F = {} & x_A x_B\left[x_A\Delta_1^A + x_B\Delta_1^B + D_A + D_B\right] + x_A F_{AAA} + x_B F_{BBB} \\ & + NkT\left(x_A \ln x_A + x_B \ln x_B\right) \end{aligned} \tag{9}$$

Figure 2 illustrates the physical significance of newly introduced parameters Δ_1^A and Δ_1^B: they are absolute asymmetries of splittings of free energy levels of molecules A and B. The meaning of the index 1 will be clarified in the next section.

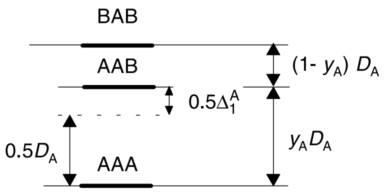

Fig. 2. Physical significance of the parameter Δ_1^A

Equation (9) directly shows that main splittings, D_A and D_B, represent the contribution of binary interactions: $x_A x_B(D_A + D_B)$, whereas the asymmetries Δ_1^A and Δ_1^B characterise triple interactions: $x_A x_B(x_A\Delta_1^A + x_B\Delta_1^B)$. The term $x_A x_B x_A \Delta_1^A$ can be interpreted as reflecting the effect of a B-molecule on the interaction in a neighbouring AA-pair or as the effect of an A-molecule on the AB-interaction. Similarly, the term $x_A x_B x_B \Delta_1^B$ reflects the effect of an A-molecule on the BB-interactions and/or the effect of a B-molecule on the AB-interaction.

If parameters Δ^A and Δ^B are statistically independent then a regression of experimental data according to Eq. (9) cannot yield separate estimates of D_A and D_B; only the excess free energy $\Delta F^E = D_A + D_B$ can be estimated. Initially [25] it was assumed that the asymmetries Δ^A and Δ^B are bound to corresponding main splittings D_A and D_B by Eq. (8). This allows one to estimate D_A and D_B separately (at non-zero Δ^A and Δ^B). The bounds (Eq. (8)) can thus be considered as a kind of regularisation of an essentially overparameterised theoretical model. In the absence of such bounds Eq. (9) virtually contains only two independent non-ideality parameters: $\Delta E^{(2)} = D_A + D_B + \Delta_1^B$ and $\Delta E^{(3)} = \Delta_1^A - \Delta_1^B$ (Eq. (10)).

$$\begin{aligned} F &= x_A(F_{AAA} - F_{BBB}) + F_{BBB} + NkT(x_A \ln x_A + x_B \ln x_B) \\ &\quad + (1 - x_A)x_A[x_A(\Delta_1^A - \Delta_1^B) + \Delta^B + D_A + D_B] \end{aligned} \tag{10}$$

Equations (6) and (7) can be written in terms of the excess free energy $\Delta F^E = D_A + D_B$, and asymmetries Δ_1^A and Δ_1^B as Eqs. (11) and (12).

$$\begin{aligned} F &= x_A x_B(1 - s^2)(x_A\Delta_1^A + x_B\Delta_1^B + \Delta F^E) + s^2 x_A[\Delta F^E + \Delta_1^B(1 - 2x_A)] \\ &\quad + x_A F_{AAA} + x_B F_{BBB} + \frac{NkT}{2}[u_{1A}\ln(u_{1A}) + (1 - u_{1A})\ln(1 - u_{1A}) \\ &\quad + u_{2A}\ln(u_{2A}) + (1 - u_{2A})\ln(1 - u_{2A})] \end{aligned} \tag{11}$$

$$\begin{aligned} F &= x_A x_B(1 - s^2)\left[x_A\Delta_1^A + x_B\Delta_1^B + \Delta F^E\right] + s^2 x_B[\Delta F^E + \Delta_1^A(1 - 2x_B)] \\ &\quad + x_A F_{AAA} + x_B F_{BBB} + \frac{NkT}{2}[u_{1B}\ln(u_{1B}) + (1 - u_{1B})\ln(1 - u_{1B}) \\ &\quad + u_{2B}\ln(u_{2B}) + (1 - u_{2B})\ln(1 - u_{2B})] \end{aligned} \tag{12}$$

At non-zero s Eqs. (11) and (12) contain three parameters $\Delta F^E = D_A + D_B$, Δ_1^A, and Δ_1^B. Ordering thus improves the resolving power of the regression.

The regression employing (i) coefficients $y_{A(B)}$ and (ii) absolute asymmetries $\Delta_1^{A(B)}$ is thus not completely equivalent: the former implicitly uses the regularisation bound (Eq. (8)) which allows one to estimate D_A and D_B separately. However the experimental transition curve of the two-step spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ (data from Ref. [10]) can be approximated by Eqs. (6) and (7) and Eqs. (11) and (12) with equal regression errors (σ_{yx} in the first two rows of Table 1). Theoretical transition curves obtained for these two cases are visibly indistinguishable but the optimisation in terms of ΔE^E, Δ_1^A, and Δ_1^B converges faster than that in terms of D_A, D_B, y_A, and y_B, apparently, due to the smaller number of adjustable parameters.

Equations (11) and (12) admit a special mode of regression, *viz.* that employing $\Delta_1^A = \Delta_1^B$. In this case terms proportional to ${x_A}^3$ and ${x_B}^3$ vanish but parameters arising from triple interactions (asymmetries) remain. It is therefore a special kind

Table 1. Approximation of experimental data [10] on spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ by Eqs. (6) and (7) (first row), and Eqs. (11) and (12) (second row); third row contains estimates of parameters of Eqs. (11) and (12) obtained under the condition $\Delta_1^A = \Delta_1^B$; note that these estimates have been obtained using temperature as the independent variable whereas in Ref. [25] similar data have been analysed using the composition as the independent variable

$\sigma_{yx}\times 10^2$	$\frac{\Delta E^0}{\text{kJ/mol}}$	$\frac{T_{1/2}}{\text{K}}$	$\frac{D_A}{\text{kJ/mol}}$	$\frac{D_B}{\text{kJ/mol}}$	y_A	y_B	$\frac{\Delta E^E}{\text{kJ/mol}}$	$\frac{\Delta_1^A}{\text{kJ/mol}}$	$\frac{\Delta_1^B}{\text{kJ/mol}}$
1.9	7.29 ±0.08	116.4 ±0.2	1.70 ±0.01	−2.15 ±0.01	0.999 ±0.006	0.047 ±0.007	−0.44 ±0.02	1.70 ±0.02	1.945 ±0.031
1.9	6.90 ±0.22	116.1 ±0.2					−0.40 ±0.01	1.69 ±0.02	2.022 ±0.016
2.9	8.99 ±0.48	117.1 ±0.2					−0.54 ±0.02	1.76 ±0.05	1.759 ±0.048

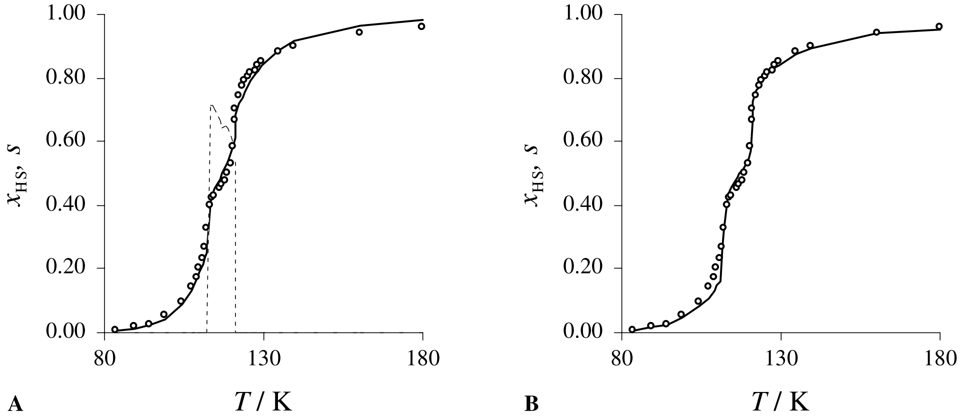

Fig. 3. Two-step spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ parameterised by the model of triple interaction with $\Delta_1^A = \Delta_1^B$ (**A**, third row in Table 1) and by the model of Ref. [10] of the *Ising*-like Hamiltonian (**B**)

of the model of binary interactions. The regression in this mode yields a poorer description (Fig. 3A, third row in Table 1) than the regression with independent Δ_1^A and Δ_1^B, but comparable to that of the model of the *Ising*-like Hamiltonian (Fig. 3B, $\sigma_{yx} = 0.026$ according to the data read from the graph in Ref. [10]). When $\Delta_1^A \neq \Delta_1^B$ triple interactions affect the shape of the transition curve not only within the region of non-zero degrees of order but also beyond it. This apparently is the cause of the better description of experimental data by the model of triple interactions compared to that given by the model of the *Ising*-like Hamiltonian.

Many-body Interactions of an Arbitrary Order

The effects of an arbitrary number n of neighbours of a given molecule can be derived in a similar way. Depending on the composition of the nearest surroundings the state of the central molecule can be characterised by $n + 1$ values of free energy

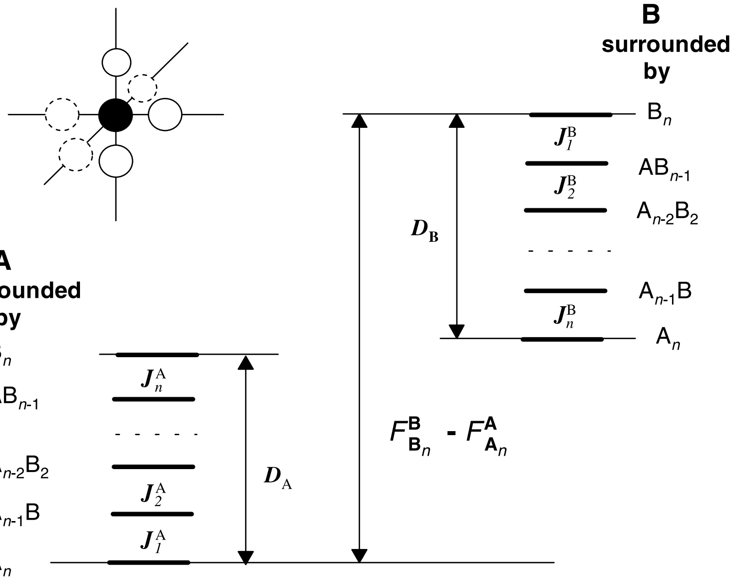

Fig. 4. Free energy level diagram illustrating the effects of n molecules on the partition function of central molecule

$F^{A}_{A_{n-i}B_i}$, with i varying from zero to n. Molecular interactions thus split the level of free energy of a molecule into a multiplet of the order $n+1$ (Fig. 4). This model also implies the pseudo-independence of molecules and is thus applicable to systems with weak interactions. The probability to find a molecule surrounded by $A_{n-i}B_i$ then equals the product of mol fractions to the proper powers multiplied by the binomial coefficient C_i^n reflecting the number of ways in which this surrounding can be realised (Eq. (13)).

$$p_{A_{n-i}B_i} = C_i^n x_A^{n-i} x_B^i; \qquad C_i^n = \frac{n!}{i!(n-i)!} \tag{13}$$

Free energies of molecules A and B can be represented as weighted averages over all surroundings (Eq. (14)) in which $F^{A(B)}_{A_{n-i}B_i}$ are free energies of molecules A(B), surrounded by $(n-i)$ molecules A and i molecules B.

$$F^A = \sum_{i=0}^{n} C_i^n x_A^{n-i} x_B^i F^A_{A_{n-i}B_i}; \qquad F^B = \sum_{i=0}^{n} C_i^n x_A^{n-i} x_B^i F^B_{A_{n-i}B_i} \tag{14}$$

Separating free energies in the states of pure compounds ($F^A_{A_n}$ and $F^B_{B_n}$) one obtains Eqs. (15) and (16) in which $J_k^{A(B)}$ are the spacings between k-th and $(k+1)$-th sublevels in multiplets (Fig. 4).

$$F^A = F^A_{A_n} + \sum_{i=1}^{n} C_i^n x_A^{n-i} x_B^i \left(F^A_{A_{n-i}B_i} - F^A_{A_n}\right) = F^A_{A_n} + \sum_{i=1}^{n} C_i^n x_A^{n-i} x_B^i \sum_{k=1}^{i} J_k^A \tag{15}$$

$$F^B = F^B_{B_n} + \sum_{i=0}^{n-1} C_i^n x_A^{n-i} x_B^i \sum_{k=1}^{n-i} J_k^B = F^B_{B_n} + \sum_{i=1}^{n} C_{i-1}^n x_A^{n-i+1} x_B^{i-1} \sum_{k=1}^{n-i+1} J_k^B \tag{16}$$

The free energy of a mixture of pseudo-independent molecules is pseudo-additive and contains a contribution from the entropy of mixing (Eq. (17)).

$$F = x_{\mathrm{A}} F^{\mathrm{A}} + x_{\mathrm{B}} F^{\mathrm{B}} + NkT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{17}$$

Substituting F^{A} and F^{B} according to Eqs. (15) and (16) one obtains Eq. (18).

$$\begin{aligned} F = {} & x_{\mathrm{A}} F^{\mathrm{A}}_{\mathrm{A}_n} + x_{\mathrm{B}} F^{\mathrm{B}}_{\mathrm{B}_n} + x_{\mathrm{A}} x_{\mathrm{B}} \sum_{i=1}^{n} x_{\mathrm{A}}^{n-i} x_{\mathrm{B}}^{i-1} \left(C_i^n \sum_{k=1}^{i} J_k^{\mathrm{A}} + C_{i-1}^n \sum_{k=1}^{n-i+1} J_k^{\mathrm{B}} \right) \\ & + NkT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \end{aligned} \tag{18}$$

Free energy is thus an additive property with respect to $F^{\mathrm{A}}_{\mathrm{A}_n}$ and $F^{\mathrm{B}}_{\mathrm{B}_n}$ plus an excess term proportional to $x_{\mathrm{A}} x_{\mathrm{B}}$ (Eq. (19)).

$$F = x_{\mathrm{A}} F^{\mathrm{A}}_{\mathrm{A}_n} + x_{\mathrm{B}} F^{\mathrm{B}}_{\mathrm{B}_n} + x_{\mathrm{A}} x_{\mathrm{B}} \Delta F^{\mathrm{E}} + NkT(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}) \tag{19}$$

The coefficient of the excess term (the excess free energy) is a polynomial function of the composition shown by Eq. (19a).

$$\Delta F^{\mathrm{E}} = \sum_{i=1}^{n} x_{\mathrm{A}}^{n-i} x_{\mathrm{B}}^{i-1} \left(C_i^n \sum_{k=1}^{i} J_k^{\mathrm{A}} + C_{i-1}^n \sum_{k=1}^{n-i+1} J_k^{\mathrm{B}} \right) \tag{19a}$$

Separating in Eq. (19a) the term corresponding to $i = 1$ one obtains another polynomial multiplied by $x_{\mathrm{A}} x_{\mathrm{B}}$ (Eq. (19b)).

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}}^{n-1} \left(C_1^n J_1^{\mathrm{A}} + C_0^n \sum_{k=1}^{n} J_k^{\mathrm{B}} \right) + x_{\mathrm{A}} x_{\mathrm{B}} \sum_{i=2}^{n} x_{\mathrm{A}}^{n-i-1} x_{\mathrm{B}}^{i-2} \left(C_i^n \sum_{k=1}^{i} J_k^{\mathrm{A}} + C_{i-1}^n \sum_{k=1}^{n-i+1} J_k^{\mathrm{B}} \right) \tag{19b}$$

This operation can be repeated as long as there are terms with powers of x_{A} and x_{B} higher 1. This allows one to write the equation for free energy in a versatile form. Let us consider it in several examples. An earlier developed model of triple interactions corresponds to $n = 2$ (Eq. (20)).

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}} \left(2J_1^{\mathrm{A}} + \sum_{k=1}^{2} J_k^{\mathrm{B}} \right) + x_{\mathrm{B}} \left(\sum_{k=1}^{2} J_k^{\mathrm{A}} + 2J_1^{\mathrm{B}} \right) \tag{20}$$

Noticing that the sum of all $J_k{}^{\mathrm{A(B)}}$ equals the main splitting $D_{\mathrm{A(B)}}$ (Eq. (21)) we get ΔF^{E} as shown by Eq. (22) or as a function of one variable (Eq. (23)).

$$\sum_{k=1}^{n} J_k^{\mathrm{A}} = D_{\mathrm{A}}; \qquad \sum_{k=1}^{n} J_k^{\mathrm{B}} = D_{\mathrm{B}}, \tag{21}$$

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}} (2J_1^{\mathrm{A}} + D_{\mathrm{B}}) + x_{\mathrm{B}} (D_{\mathrm{A}} + 2J_1^{\mathrm{B}}) \tag{22}$$

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}} \left[\left(2J_1^{\mathrm{A}} - D_{\mathrm{A}} \right) - \left(2J_1^{\mathrm{B}} - D_{\mathrm{B}} \right) \right] + D_{\mathrm{A}} + 2J_1^{\mathrm{B}} \tag{23}$$

From Eq. (23) it directly follows that when $2J_1^{\mathrm{A}} = D_A$ and $2J_1^{\mathrm{B}} = D_B$, (equal spacings between sublevels in a triplet) the coefficient of x_{A} is zero and the excess free energy is independent of the composition. In this case the equation for free energy (Eq. (18)) only contains one excess term ($x_{\mathrm{A}} x_{\mathrm{B}} (D_{\mathrm{A}} + D_{\mathrm{B}})$), reflecting the effect of binary interactions. The contribution of triple interactions can thus be characterised by absolute asymmetries (Eq. (24)).

$$\Delta_1^{\mathrm{A}} = 2J_1^{\mathrm{A}} - D_{\mathrm{A}}; \qquad \Delta_1^{\mathrm{B}} = 2J_1^{\mathrm{B}} - D_{\mathrm{B}} \tag{24}$$

Adding and subtracting D_{B} to the right-hand part of Eq. (23) one obtains Eq. (24a).

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}}\Delta_1^{\mathrm{A}} + x_{\mathrm{B}}\Delta_1^{\mathrm{B}} + D_{\mathrm{A}} + D_{\mathrm{B}} \tag{24a}$$

Free energy of such systems can then be represented as shown by Eq. (24b).

$$\begin{aligned} F = {} & x_{\mathrm{A}}F^{\mathrm{A}}_{\mathrm{A}_n} + x_{\mathrm{B}}F^{\mathrm{B}}_{\mathrm{B}_n} + x_{\mathrm{A}}x_{\mathrm{B}}\left[x_{\mathrm{A}}\left(\Delta_1^{\mathrm{A}} - \Delta_1^{\mathrm{B}}\right) + \Delta_1^{\mathrm{A}} + D_{\mathrm{A}} + D_{\mathrm{B}}\right] \\ & + NkT\left(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}\right) \end{aligned} \tag{24b}$$

The excess free energy is independent of the composition when the effects of triple interactions are either zero ($\Delta_1^{\mathrm{A}} = 0$, $\Delta_1^{\mathrm{B}} = 0$) or compensate each other being equal for molecules A and B ($\Delta_1^{\mathrm{A}} = \Delta_1^{\mathrm{B}}$). In the latter case the system formally follows the model of binary interactions but the excess free energy contains a contribution from triple interactions (Eq. (25)).

$$\Delta F^{(2)} = D_{\mathrm{A}} + D_{\mathrm{B}} + \Delta_1^{\mathrm{A}} \tag{25}$$

The coefficient of x_{A} in square brackets in Eq. (24b), $\Delta_1^{\mathrm{A}} - \Delta_1^{\mathrm{B}}$, can be termed as the excess free energy of the third order $\Delta F^{(3)}$ (Eq. (26)).

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}}\Delta F^{(3)} + \Delta F^{(2)} \tag{26}$$

Let us now consider the case of quaternary interactions ($n = 3$). Derivations similar to those above lead to Eq. (27).

$$\Delta F^{\mathrm{E}} = x_{\mathrm{A}}^2\left(3J_1^{\mathrm{A}} + D_{\mathrm{B}}\right) + x_{\mathrm{A}}x_{\mathrm{B}}\left(3\sum_{k=1}^{2}J_k^{\mathrm{A}} + 3\sum_{k=1}^{2}J_k^{\mathrm{B}}\right) + x_{\mathrm{B}}^2\left(D_{\mathrm{A}} + 3J_1^{\mathrm{B}}\right) \tag{27}$$

Expressing ΔF^{E} as a function of single variable (x_{A}) one obtains (Eq. (28)).

$$\begin{aligned} \Delta F^{\mathrm{E}} = {} & D_{\mathrm{A}} + 3J_1^{\mathrm{B}} + x_{\mathrm{A}}\left[3\sum_{k=1}^{2}J_k^{\mathrm{A}} + 3\sum_{k=1}^{2}J_k^{\mathrm{B}} - 2\left(D_{\mathrm{A}} + 3J_1^{\mathrm{B}}\right)\right] \\ & + x_{\mathrm{A}}^2\left[3J_1^{\mathrm{A}} + D_{\mathrm{B}} - 3\sum_{k=1}^{2}J_k^{\mathrm{A}} - 3\sum_{k=1}^{2}J_k^{\mathrm{B}} + 3J_1^{\mathrm{A}} + D_{\mathrm{B}}\right] \end{aligned} \tag{28}$$

In this case we have two independent spacings between sublevels in a quartet: $J_1^{\mathrm{A(B)}}$ and $J_2^{\mathrm{A(B)}}$ ($J_3^{\mathrm{A(B)}} = D_{\mathrm{A(B)}} - J_1^{\mathrm{A(B)}} - J_2^{\mathrm{A(B)}}$). Therefore many-body interactions are characterised by two asymmetries (Eq. (29)).

$$\Delta_1^{\mathrm{A(B)}} = 3J_1^{\mathrm{A(B)}} - D_{\mathrm{A(B)}}; \qquad \Delta_2^{\mathrm{A(B)}} = 3J_2^{\mathrm{A(B)}} - D_{\mathrm{A(B)}} \tag{29}$$

The equation for free energy (Eq. (18)) can be written for $n = 3$ in terms of these asymmetries as Eq. (30).

$$\begin{aligned} F = {} & x_{\mathrm{A}}F^{\mathrm{A}}_{\mathrm{AAA}} + x_{\mathrm{B}}F^{\mathrm{B}}_{\mathrm{BBB}} + x_{\mathrm{A}}x_{\mathrm{B}}\left[x_{\mathrm{A}}x_{\mathrm{B}}\left(\Delta_2^{\mathrm{A}} + \Delta_2^{\mathrm{B}}\right) + \Delta_1^{\mathrm{A}}x_{\mathrm{A}} + \Delta_1^{\mathrm{B}}x_{\mathrm{B}} + D_{\mathrm{A}} + D_{\mathrm{B}}\right] \\ & + NkT(x_{\mathrm{A}}\ln x_{\mathrm{A}} + x_{\mathrm{B}}\ln x_{\mathrm{B}}) \end{aligned} \tag{30}$$

The term ${x_A}^2{x_B}^2(\Delta_2^A + \Delta_2^B)$ can be considered as arising from quaternary interactions; the term $x_A x_B(x_A\Delta_1^A + x_B\Delta_1^B)$, apparently reflects the effect of triple interactions. Note that Δ_2^A and Δ_2^B appear (similarly to D_A and D_B) as a sum that can be considered as the excess free energy of the fourth order $\Delta F^{(4)} = \Delta_2^A + \Delta_2^A$. When $\Delta_2^A = 0$ and $\Delta_2^B = 0$ or when $\Delta_2^A = -\Delta_2^B$ Eq. (30) becomes formally identical to Eq. (24b) of the model of triple interactions (Eq. (31)).

$$F = x_A F_{A_3}^A + x_B F_{B_3}^B + x_A x_B\left[\Delta_1^A x_A + \Delta_1^B x_B + D_A + D_B\right] + NkT(x_A \ln x_A + x_B \ln x_B) \tag{31}$$

The condition $\Delta_2^A = 0$ and $\Delta_2^B = 0$ means that central splittings of in both quartets exactly equal one third of corresponding main splittings. Physical significances of parameters $\Delta_1^{A(B)}$ in Eqs. (31) and (24b) are different: in the first instance $\Delta_1^{A(B)}$ is the deviation of the lower spacing in a quartet from $1/3D_{A(B)}$, whereas in the second it reflects the deviation of the lower spacing in a triplet from $1/2D_{A(B)}$.

A general rule applies to both Eqs. (24b) and (31): when all spacings are exactly $(1/n)D_{A(B)}$ the excess free energy becomes composition independent and apparently reflects the effect of binary interactions. This case corresponds to additivity of the effects of surroundings. Again the principle of compensation ($\Delta_2^A = -\Delta_2^B$, $\Delta_1^A = \Delta_1^B$) seems to work in both cases.

Much more complicated equations evolve for the case $n = 4$ (interactions of the fifth order leading to the splitting of free energy levels into quintets, Eq. (32)) in which, $\Delta F^{(5)}$, $\Delta F^{(4)}$, $\Delta F^{(3)}$, and $\Delta F^{(2)}$ are given by Eqs. (32a) and (32b).

$$\begin{aligned} F = {} & x_A F_{A_4}^A + x_B F_{B_4}^B + NkT(x_A \ln x_A + x_B \ln x_B) \\ & + x_A x_B\{x_A x_B[x_A \Delta F^{(5)} + \Delta F^{(4)}] + x_A \Delta F^{(3)} + \Delta F^{(2)}\} \end{aligned} \tag{32}$$

$$\begin{aligned} \Delta F^{(5)} &= \Delta_3^B - \Delta_3^A + \frac{\Delta_2^A - \Delta_1^A - \Delta_2^B + \Delta_1^B}{2}; \\ \Delta F^{(4)} &= \Delta_3^A + \frac{(\Delta_2^B - \Delta_1^B)}{2} + \Delta_2^A + \Delta_2^B \end{aligned} \tag{32a}$$

$$\Delta F^{(3)} = \Delta_1^A - \Delta_1^B; \qquad \Delta F^{(2)} = \Delta_1^B + D_A + D_B; \qquad \Delta_k^{A(B)} = 4J_k^{A(B)} - D_{A(B)} \tag{32b}$$

The independence of the term in square brackets of x_A (a formal reduction to the model of quaternary interactions) can be achieved when all differences $\Delta_i^B - \Delta_i^A$ are zero (Eq. (33)).

$$2(\Delta_3^B - \Delta_3^A) + (\Delta_2^A - \Delta_2^B) + (\Delta_1^B - \Delta_1^A) = 0 \tag{33}$$

This condition involves all asymmetries in both quintets, *i.e.* individual asymmetries *cease to reflect the effects of many-body interactions of a given order.* Therefore higher order interactions can be more conveniently characterised by considering excess free energies $\Delta F^{(i)}$ in Eq. (32) as formal coefficients. Apparently the latter are not independent random values. However, they can be used as adjustable parameters in regression of experimental data, *inter alia* in order to establish their relationship.

Effects of Many-body Interactions on the Shape of Transition Curves

Extending the above approach to cases of higher order interactions and assuming excess entropies to be zero, the equation for free energy (Eq. (18)) can be written for $n = 7$ as Eq. (34).

$$F = x_\mathrm{A} F^\mathrm{A}_{\mathrm{A}_6} + x_\mathrm{B} F^\mathrm{B}_{\mathrm{B}_6} + NkT\left(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B}\right) + x_\mathrm{A}x_\mathrm{B}\left\{x_\mathrm{A}x_\mathrm{B}\left[x_\mathrm{A}x_\mathrm{B}\left(x_\mathrm{A}\Delta E^{(7)} + \Delta E^{(6)}\right) + x_\mathrm{A}\Delta E^{(5)} + \Delta E^{(4)}\right] + x_\mathrm{A}\Delta E^{(3)} + \Delta E^{(2)}\right\} \qquad (34)$$

This equation can be conveniently employed in simulations and regression of experimental data.

Let us consider the case of *positive excess energies* (Fig. 5). Large positive excess energies $\Delta E^{(i)}$ bring about abrupt spin crossover but only insignificantly (and those of odd orders alone) shift the transition temperature. Relative sensitivity of the shape of transition curves towards the excess energy rapidly decays with increasing order of interaction: an abrupt spin crossover can be achieved at $\Delta E^{(2)} \approx 3\,\mathrm{kJ/mol}$ but it requires a large $\Delta E^{(4)} \approx 7\,\mathrm{kJ/mol}$. This fact is in agreement with a generally recognized major role of binary interactions. Interactions of higher orders may affect minor features of transitions, for example triple interactions slightly shift the transition temperature and make transition curves asymmetric (Fig. 5b).

The abrupt spin crossover caused by triple interactions (Fig. 5b) is incomplete in its high temperature limit. Higher order interactions ($n \geq 3$) make the abrupt transition incomplete in both high and low temperature limits. The range of compositions corresponding to the 'switch' becomes smaller with increasing order of molecular interactions. These features can be employed in the parameterisation of experimental one-step transition curves.

A complicated nature of a one-step transition curve may proceed from a distribution of domains characterised by different ΔE^0 and/or ΔE^E. However it can also originate from many-body interactions. The latter apparently play different roles in lattices of different dimensionalities: in 1D systems one should expect the combination of binary and triple interactions to be sufficient for an adequate description. Higher dimensionality would require higher number of non-ideality terms.

Transition curves of spin crossover in a series of polymeric one-dimensional complexes $[\mathrm{Fe}(\mathit{fatrz})_3](\mathit{An})_2m\mathrm{H_2O}$, *fatrz* = 4-(formylamino)-1,2,4-triazole [29], can

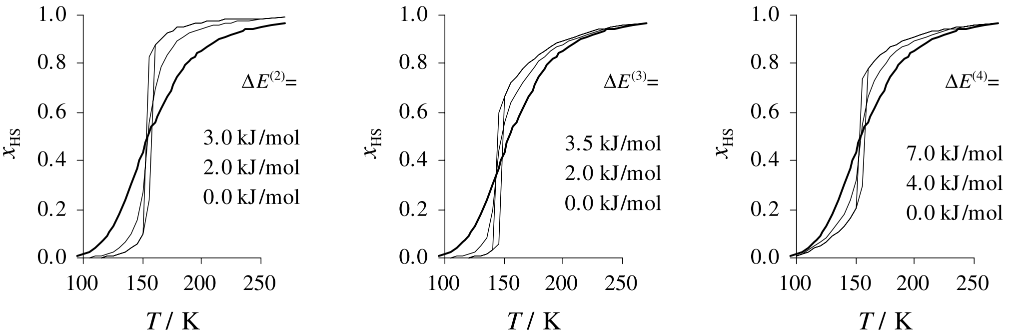

Fig. 5. Changes in the shape of transition curves of spin crossover ($\Delta E^0 = 10\,\mathrm{kJ/mol}$; $\Delta S^0 = 64.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$) caused by the variation of excess energies of different orders

Table 2. Estimates of parameters of Eq. (34) describing experimental data on spin crossover in $[Fe(\mathit{fatrz})_3](\mathit{An})_2m\mathrm{H_2O}$ (data from Ref. [29]); **1**: $An =$ trifluoromethanesulfonate, $m = 3$; **2**: $An = \mathrm{BF_4^-}$, $m = 2$; **3**: $An = p$-tolylsulfonate, $m = 3$; **4**: $An = \mathrm{NO_3^-}$, $m = 1$; standard energy of spin crossover was fixed at the level $\Delta E^0 = 17.2\,\mathrm{kJ/mol}$ according to the calorimetric data [29]; $T_{1/2} = \Delta E^0/\Delta S^0$

	$\sigma_{yx}\times 100$	$\frac{T_{1/2}}{\mathrm{K}}$	$\frac{\Delta E^{(2)}}{\mathrm{kJ/mol}}$	$\frac{\Delta E^{(3)}}{\mathrm{kJ/mol}}$	$\frac{\Delta E^{(4)}}{\mathrm{kJ/mol}}$	$\frac{\Delta E^{(5)}}{\mathrm{kJ/mol}}$
$[Fe(\mathit{fatrz})_3](\mathit{trifl})_2 3\mathrm{H_2O}$ (**1**)	4.5	275.9 ± 0.4	4.71 ± 0.03			
	2.9	274.6 ± 0.3	4.68 ± 0.06	-0.30 ± 0.02		
	2.2	275.0 ± 0.2	5.21 ± 0.07	-0.13 ± 0.03	-1.55 ± 0.23	
	2.2	275.0 ± 0.5	5.13 ± 0.10	-0.11 ± 0.28	-1.33 ± 0.36	-0.10 ± 1.09
$[Fe(\mathit{fatrz})_3](\mathrm{BF_4})_2 2\mathrm{H_2O}$ (**2**)	4.0	283.5 ± 0.7	4.15 ± 0.11			
	1.4	279.3 ± 0.2	5.00 ± 0.05	-1.81 ± 0.07		
	1.5	279.4 ± 0.2	5.03 ± 0.18	-1.78 ± 0.07	-0.05 ± 0.51	
	1.5	279.8 ± 0.3	5.05 ± 0.19	-1.66 ± 0.06	-0.001 ± 0.53	-0.3 ± 1.45
$[Fe(\mathit{fatrz})_3](\mathit{p\text{-}tol})_2 3\mathrm{H_2O}$ (**3**)	2.3	326.7 ± 0.5	4.83 ± 0.07			
	2.0	328.2 ± 0.6	4.60 ± 0.08	0.48 ± 0.10		
	1.2	327.8 ± 0.4	5.54 ± 0.23	0.43 ± 0.09	-2.52 ± 0.66	
	1.1	329.1 ± 0.7	4.96 ± 0.44	1.43 ± 0.46	-0.69 ± 1.57	-3.25 ± 1.8
$[Fe(\mathit{fatrz})_3](\mathrm{NO_3})_2 \mathrm{H_2O}$ (**4**)	2.1	324.4 ± 0.4	4.93 ± 0.05			
	0.8	326.3 ± 0.2	4.62 ± 0.02	0.71 ± 0.02		
	0.8	326.2 ± 0.2	4.70 ± 0.07	0.70 ± 0.03	-0.20 ± 0.21	
	0.9	325.3 ± 0.5	5.13 ± 0.34	0.13 ± 0.44	-1.41 ± 1.27	1.59 ± 1.76

be accordingly separated into two groups involving those of (i) compounds **1** and **3** and (ii) compounds **2** and **4** (see Table 2). In the first instance (**1**, **3**) the regression error gradually decreases with the number of non-ideality terms employed (Fig. 6A) seemingly following a trivial rule: "the more terms the better is the fit". Such a situation is expected for 3D structures in which 4- and higher order interactions play a significant role.

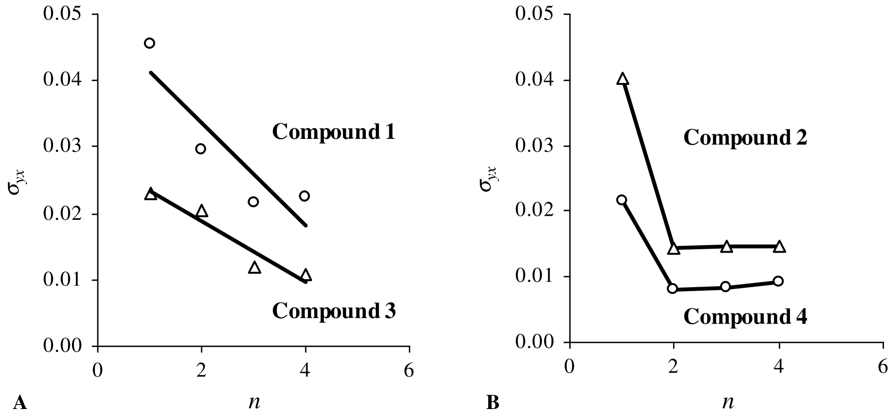

Fig. 6. The regression error of the parameterisation of spin crossover curves in $[Fe(\mathit{fatrz})_3](\mathit{An})_2m\mathrm{H_2O}$ (data from Ref. [29]) as a function of the number of employed non-ideality terms (see Table 3)

In the case of **2** and **4** the regression error sharply falls down at $n = 2$ (triple interaction) and remains constant at larger numbers of non-ideality terms involved (Fig. 6B) in contradiction to the above-mentioned rule. Taking into account only binary and triple interactions is apparently sufficient for the description of the transition curves. Such a situation is expected for 1D structures or systems of non-interacting chains. The fact that spin crossover in similar chain-like molecules (**1**, **3**) requires higher order terms manifests strong inter-chain interactions.

Examples discussed above show the versatility of Eq. (34) in the analysis of one-step transition curves. An alternative representation (Eq. (35)) of non-ideality terms as a formal expansion of free energies over the powers of x_A (or x_B) is not so convenient: it yields a different pattern of the effects of non-ideality parameters (coefficients A_i) on the shape of transition curves.

$$F = F^{B}_{B_6} - x_A(F^{B}_{B_6} - F^{A}_{A_6}) - A_2x_A^2 - A_3x_A^3 - A_4x_A^4 - A_5x_A^5 - A_6x_A^6 - A_7x_A^7 + NkT(x_A \ln x_A + x_B \ln x_B) \qquad (35)$$

Non-ideality parameters in this equation (coefficients A_i) not only change the slope of transition curve but also significantly shift the transition temperature (Fig. 7). The shape of transition curve is strongly dependent on the values of higher order coefficients: an abrupt spin crossover is achieved at either $A_2 = 4.5$ kJ/mol or $A_4 = 1.5$ kJ/mol (compare Fig. 7A and 7C). This does not correspond to the established major role of binary coefficients. Therefore such a representation is merely a regression equation the coefficient of which are only indirectly related to parameters of binary interactions.

Effects of negative excess energies cannot be correctly analysed using Eqs. (18) and (34) because these equations do not take into account the phenomenon of *ordering*. Up to now this phenomenon has been accounted for within the model of binary and triple interactions alone (see Introduction and Refs. [25–28]). Small negative excess energies of the second order merely decrease the slope of transition curves without causing any critical phenomena. When $\Delta E^E = D_A + D_B$ is a large negative ($|\Delta E^E| \geq 2RT_{1/2}$) the ordering can occur leading to a plateau in the transition curve. Detailed explanations of these phenomena in relation to spin crossover

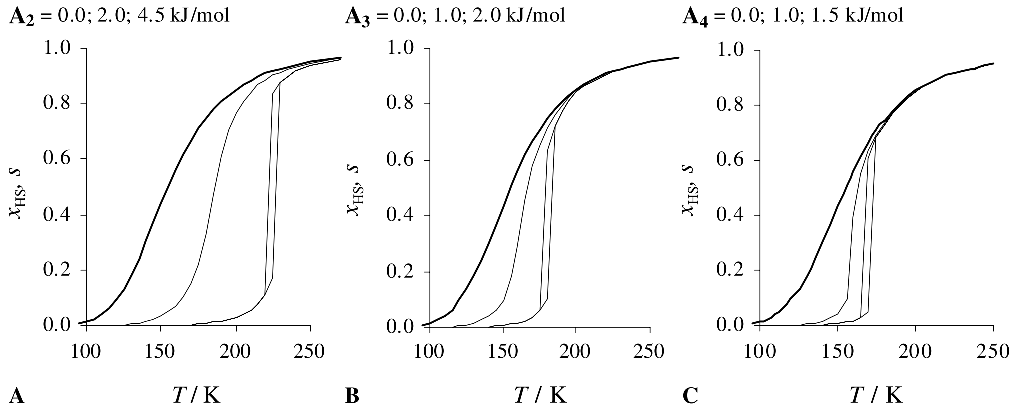

Fig. 7. Changes in the shape of transition curve of spin crossover ($\Delta E^0 = 10$ kJ/mol; $\Delta S^0 = 64.5$ Jmol^{-1} K^{-1}) caused by the variation of coefficients in Ref. (35)

can be found in Refs. [25, 28]. A formalism taking into account higher order interactions and ordering can be developed but this problem is out of scope of the present paper. Below we shall explain some special cases arising within the model of triple interactions.

It has been supposed [25–28] that negative $\Delta E^{\mathrm{E}} = D_{\mathrm{A}} + D_{\mathrm{B}}$, stabilising HS-LS pairs is a necessary requirement for ordering whereas positive asymmetries provide for the sharpness of transitions. It can however be shown that ordering and the two-step spin crossover are controlled by the *difference* $\Delta^{\mathrm{A(B)}} - D_{\mathrm{A}} - D_{\mathrm{B}}$. Let us consider the evolution of ordering at $x_{HS} = 1/2$ in a system with binary and triple interactions. The conditions of thermodynamic equilibrium with respect to the composition and the degree of order s ($\partial F/\partial x_{HS} = 0$, $\partial F/\partial s = 0$) derived in Ref. [25] can be written in terms of $\Delta E^{\mathrm{E}} = D_{\mathrm{A}} + D_{\mathrm{B}}$, Δ_1^{A}, and Δ_1^{B} as shown by Eqs. (36) and (37).

$$T = \frac{\begin{array}{c}\Delta E^0 - 3x_{\mathrm{A}}^2(1-s^2)(\Delta_1^{\mathrm{B}} - \Delta_1^{\mathrm{A}}) + 2x_{\mathrm{A}}[\Delta E^{\mathrm{E}} + 2\Delta_1^{\mathrm{B}} \\ - \Delta_1^{\mathrm{A}} - s^2(\Delta E^{\mathrm{E}} - \Delta_1^{\mathrm{A}})] - \Delta E^{\mathrm{E}} - \Delta_1^{\mathrm{B}}\end{array}}{\Delta S^0 + \frac{R}{2}\left[(s+1)\ln\dfrac{(1+s)x_{\mathrm{A}}}{1-(1+s)x_{\mathrm{A}}} + (1-s)\ln\dfrac{(1-s)x_{\mathrm{A}}}{1-(1-s)x_A}\right]} \tag{36}$$

$$T = \frac{4sx_{\mathrm{A}}[(\Delta_1^{\mathrm{B}} - \Delta_1^{\mathrm{A}})x_{\mathrm{A}} - \Delta E^{\mathrm{E}} + \Delta_1^{\mathrm{A}}]}{R\ln\dfrac{(1+s)x_{\mathrm{A}}(1-(1-s)x_{\mathrm{A}})}{(1-s)x_{\mathrm{A}}(1-(1+s)x_{\mathrm{A}})}} \tag{37}$$

At $x = \frac{1}{2}$ they become as shown by Eq. (38).

$$\begin{aligned} T &= \frac{\Delta E^0 - \frac{3}{4}(1-s^2)(\Delta_1^{\mathrm{B}} - \Delta_1^{\mathrm{A}}) + \Delta_1^{\mathrm{B}} - \Delta_1^{\mathrm{A}} - s^2(\Delta E^{\mathrm{E}} - \Delta_1^{\mathrm{A}})}{\Delta S^0 + R\ln\dfrac{1+s}{1-s}} \\ &= \frac{s\left(\dfrac{\Delta_1^{\mathrm{B}} + \Delta_1^{\mathrm{A}}}{2} - \Delta E^{\mathrm{E}}\right)}{R\ln\dfrac{1+s}{1-s}} \end{aligned} \tag{38}$$

For a special case $\Delta_1^{\mathrm{A}} = \Delta_1^{\mathrm{B}}$ (*i.e.* formal absence of the effects of triple interactions) this equation is significantly simplified (Eq. (39)) leading to Eq. (40).

$$T = \frac{\Delta E^0 - s^2(\Delta E^{\mathrm{E}} - \Delta_1^{\mathrm{A}})}{\Delta S^0 + R\ln\dfrac{1+s}{1-s}} = \frac{s(\Delta_1^{\mathrm{A}} - \Delta E^{\mathrm{E}})}{R\ln\dfrac{1+s}{1-s}} \tag{39}$$

$$\Delta_1^{\mathrm{A}} - \Delta E^{\mathrm{E}} = R\frac{\Delta E^0}{\Delta S^0}\frac{1}{s}\ln\frac{1+s}{1-s} = RT_{1/2}\frac{1}{s}\ln\frac{1+s}{1-s} \tag{40}$$

A direct calculation according to Eq. (40) in the critical point of ordering $s = 0$ yields an indefinite ratio $\Delta_1^{\mathrm{A}} - D_{\mathrm{A}} - D_{\mathrm{B}} = 0/0$, that can be resolved using the *L'Hospital* rule. The derivative of $\ln[(1+s)/(1-s)]$ at $s = 0$ equals 2, therefore we obtain Eq. (41).

$$\Delta_1^{A} - \Delta E^{\mathrm{E}} = 2RT_{1/2} \tag{41}$$

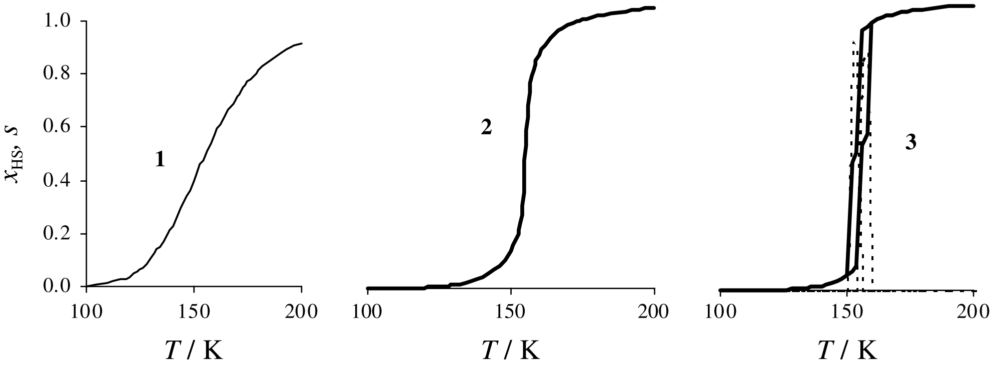

Fig. 8. Effects of increasing asymmetries in a model system with zero excess energy of the second order ($\Delta E^0 = 14\,\text{kJ/mol}$, $T_{1/2} = 155.5\,\text{K}$, $\Delta E^E = D_A + D_B = 0$) and varying $\Delta_1^A = \Delta_1^B = 0(1)$, +2.5 (2) and +3.5 (3) kJ/mol; dashed line represents the degree of order

Ordering thus occurs when $\Delta_1^A - D_A - D_B > 2RT_{1/2}$, *i.e.* at either larger negative ΔE^E or at large positive $\Delta_1^A = \Delta_1^B$. Figure 8 shows simulated transition curves obtained as solutions of Eqs. (36) and (37) for varying $\Delta_1^A = \Delta_1^B$ at $\Delta E^E = 0$. Negative asymmetries merely decrease the slope of transition curves (curve 1, Fig. 8). Positive asymmetries increase the slope, however at large values they yield not an abrupt spin crossover but a specific two-step spin crossover with sharp steps and peaks of the degree of order (curve 5, Fig. 8).

The formalism described above allows one to parameterise the effects of many-body molecular interactions of an arbitrary order on the shape of transition curves of spin crossover in the solid state. This formalism is based on a model considering the effects of n nearest neighbours on the partition function of central molecule. Such interactions split free energy levels of molecules into multiplets of the order $n+1$. Non-ideality is characterised by main splittings of free energy levels (D_A, D_B) and asymmetries (Δ_i^A, Δ_i^B), the latter reflecting deviations from an equidistant pattern. In the approximations of binary, triple, and quaternary interactions individual asymmetries characterise many-body interactions of the corresponding orders. They can therefore be advantageously used in regression of transition curves yielding estimates of parameters having physical significance. However in the models taking into account higher order interactions ($n > 3$) individual asymmetries cease to represent many-body interactions of a given order. In such cases it is more to the purpose to employ formal excess energies $\Delta E^{(i)}$.

Positive excess energies increase the slope of transition curves leading to the abrupt spin crossover and hysteresis. Excess energies of quaternary and higher order interactions cause an abrupt spin crossover in a narrow range of compositions: such sharp transitions are incomplete at both high and low temperatures. The excess energy of triple interactions yields asymmetric transition curves with slightly shifted transition temperatures.

Regression of experimental data allows one to estimate excess energies of up to the fifth order. The behaviour of the regression error with increasing number of non-ideality terms in the equation for free energy yields information on the anisotropy of molecular interactions.

Effects of negative excess energies (requiring the introduction of the degree of order) have been explored for the model of binary and triple interactions alone. A special case of a partial compensation of the effects of triple interactions has been explored and proven to yield a description of the two-step spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ similar to that given by the model of the *Ising*-like Hamiltonian. It has also been shown that ordering can occur not only at negative excess energies but at the combinations of zero ΔE^E and large positive asymmetries.

Although the approximation of triple interactions provided for a rational parameterisation of a wide variety of two-step transition curves [25, 26] it has been found that higher order many-body interactions affect the shape of the one-step transition curve. Therefore a combination of higher order interaction and effects of ordering might be useful in the description of especially "difficult" two-step transition curves.

Methods

Simulation of transition curves and parameterisation of experimental data have been achieved according to the described above equations employing a multipurpose non-linear regression program OPTIMI supplied with the monograph Ref. [30]. Methods of solving equations of the law of mass action with temperature as the independent variable have been described in Ref. [26].

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References

[1] Real JA, Gaspar AB, Niel V, Munoz MC (2003) Coord Chem Revs **236**: 121
[2] Gütlich P, Hauser A, Spiering H (1994) Angew Chem Int Ed **33**: 2024
[3] Haasnoot JG (2000) Coord Chem Rev **200**: 131
[4] Sorai M (2001) Bull Chem Soc Jap **74**: 2223
[5] Boca R, Linert W (2003) Monatsh Chem **134**: 199
[6] Linert W, Grunert M, Koudriavtsev AB (2004) Isoequilibrium and Isokinetic Relationships in Spin Crossover. In: Gütlich P, Goodwin H (eds) Top Curr Chem, vol 235. Springer, Berlin Heidelberg, p 105
[7] Wajnflasz J, Pick R (1970) J Phys Status Solidi **40**: 537
[8] Bari R, Sivardiere J (1972) Phys Rev B **5**: 4466
[9] Zelentsov VV, Lapushkin GL, Sobolev SS, Shipilov VI (1986) Dokl AN SSSR, Ser Khim **289**: 393
[10] Bousseksou A, Nasser J, Linares J, Boukheddaden K, Varret F (1992) J Phys I France **2**: 1381
[11] Slichter CP, Drickamer HG (1972) J Chem Phys **56**: 2142
[12] Sorai M, Seki S (1974) J Phys Chem Solids **35**: 555
[13] Ohnishi S, Sugano S (1981) J Phys C **14**: 39
[14] Spiering H, Meissner E, Köppen H, Müller EW, Gütlich P (1982) Chem Phys **68**: 65

[15] Köppen H, Müller EW, Köhler CP, Spiering H, Meissner E, Gütlich P (1982) Chem Phys Lett **91**: 348

[16] Jakobi R, Spiering H, Gütlich P (1992) J Phys Chem Solids **53**: 267

[17] Romstedt H, Hauser A, Spiering H (1998) J Phys Chem Solids **59**: 265

[18] Spiering H, Kohlhaas T, Romstedt H, Hauser A, Bruns-Yilmaz C, Gütlich P (1999) Coord Chem Rev **190–192**: 629

[19] Alder BJ, Hoover WG (1968) Computational Methods in Statistical Mechanics. In: Temperley HNV, Rowlinson JS, Rushbrooke GS (eds) Physics of Simple Liquids. North Holland, Amsterdam, p 103

[20] Baranovic G (2003) Chem Phys Lett **369**: 668

[21] Baranovic G, Babi D (2004) Spectrochim Acta A **60**: 1013

[22] Scherlis DA, Estrin DA (2002) Int J Quant Chem **87**: 158

[23] Paulsen H, Trautwein AX (2004) J Phys Chem Solids **65**: 793

[24] Bousseksou A, Constan-Machado H, Varret F (1995) J Phys I France **5**: 747; Tuchagues JP, Bousseksou A, Molnár G, McGarvey JJ, Varret F (2004) The Role of Molecular Vibrations in the Spin Crossover Phenomenon. In: Gütlich P, Goodwin H (eds) Top Curr Chem, vol 235. Springer, Berlin Heidelberg, p 84

[25] Koudriavtsev AB (1999) Chem Phys **241**: 109

[26] Koudriavtsev AB, Stassen AF, Haasnoot JG, Grunert M, Weinberger P, Linert W (2003) Phys Chem Chem Phys **5**: 3666

[27] Koudriavtsev AB, Stassen AF, Haasnoot JG, Grunert M, Weinberger P, Linert W (2003) Phys Chem Chem Phys **5**: 3676

[28] Koudriavtsev AB, Jameson RF, Linert W (2001) The Law of Mass Action. Springer, Berlin Heidelberg

[29] Roubeau O, Haasnoot JG, Codjovi E, Varret F, Reedijk J (2002) Chem Mater **14**: 2559

[30] Kudryavtsev A, Linert W (1996) Physico-Chemical Applications of NMR. WSPC, Singapore