Monatshefte für Chemie 132, 235–243 (2001)

Monatshefte für Chemie
Chemical Monthly

Thermally Induced Spin Crossover in the Liquid State: The Effects of Non-Ideality

Andrei B. Koudriavtsev[1] and **Wolfgang Linert**[2,*]

[1] D. Mendeleev University of Chemical Technology of Russia, RU-125047 Moscow, Russia
[2] Institute of Inorganic Chemistry, Vienna University of Technology, A-1060 Vienna, Austria

Summary. A theoretical analysis of the possible effects of non-ideality on the shape of transition curves and parameters of spin crossover equilibria in the liquid phase is given. A statistical mechanical derivation of the law of mass action shows that molar concentrations rather than mole fractions should be used for descriptions of equilibria in the liquid state. The volume changes accompanying spin crossover contribute to the entropy of spin crossover, but this contribution should not exceed $2.1\,\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. The shapes of spin crossover curves are sensitive to the effects of internal pressure. These effects may result in a non-gradual spin crossover in the liquid phase.

Keywords. Spin crossover; Equilibrium; Liquid state.

Introduction

Spin crossover equilibria have attracted considerable interest in recent years [1–4]. The most interesting results so far obtained are for solid state systems, but liquid systems are also being investigated. Spin crossover compounds are usually solid, crystalline substances poorly soluble in any solvent. In the liquid phase, these equilibria can therefore be investigated only in very dilute solution which is believed to be similar to the state of rarefied gaseous mixtures that can be described by the law of mass action pertinent to an ideal gas. Indeed, the interactions between reacting species (HS and LS molecules in equilibrium) are well shielded by solvent molecules, and such a system can be considered as a system of statistically independent particles. There are, however, no fundamental reasons against the existence of a highly soluble, or even a liquid, spin crossover system. In such a system the phenomena connected with strong molecular interactions, *i.e.* steep spin crossover [5] and two-step spin crossover [6], might be observed in the liquid state (*e.g.* in liquid crystals). Also, the effects of interaction with the solvent in dilute solutions are not negligible, and it is of considerable interest to investigate the possible effects of molecular interactions in the liquid phase on the shape of spin crossover transition curves and their parameters.

In the present paper, several forms of the law of mass action applicable to non-ideal liquid spin crossover systems (both pure and in the presence of solvent) will be

---

[*] Corresponding author

derived. Spin crossover transition curves can be found as solutions of the equation of the law of mass action derived from the condition of minimum in the thermodynamic potential. A physically meaningful description can be obtained using a statistical thermodynamic approach.

Results and Discussion

The partition function for an ideal binary mixture (a hypothetical liquid spin crossover compound) at low temperature must be not very different from that for a solid binary mixture ([7], chapter 17):

$$Z = \frac{(N_\mathrm{A}+N_\mathrm{B})!}{N_\mathrm{A}!N_\mathrm{B}!}\left(\frac{2\pi m_\mathrm{A}kT}{h^2}ev\right)^{N_\mathrm{A}} z_{i\mathrm{A}}^{N_\mathrm{A}} e^{-\frac{N_\mathrm{A}\varepsilon_\mathrm{A}^0}{kT}}\left(\frac{2\pi m_\mathrm{B}kT}{h^2}ev\right)^{N_\mathrm{B}} z_{i\mathrm{B}}^{N_\mathrm{B}} e^{-\frac{N_\mathrm{B}\varepsilon_\mathrm{B}^0}{kT}} \tag{1}$$

In Eq. (1), the factor e accounts for the possibility of a molecule migrating within the whole volume of the system, ε_A^0 is the potential energy of the molecule A (comprising the electronic energy and potential energy in the mean field), z_i is the product of the partition functions for internal degrees of freedom including the degeneracy factor, and $v = V/(N_\mathrm{A}+N_\mathrm{B})$ is the volume per molecule.

If we consider the volume per molecule v as invariant, the expressions in parentheses in Eq. (1) are composition independent, and the *Helmholtz* free energy becomes similar to that of an ideal binary crystal:

$$F = -kT\ln Z = \left(N_\mathrm{A}\left(\ln q_\mathrm{A} - \ln\frac{N_\mathrm{A}}{N_\mathrm{A}+N_\mathrm{B}}\right) + N_\mathrm{B}\left(\ln q_\mathrm{B} - \ln\frac{N_\mathrm{B}}{N_\mathrm{A}+N_\mathrm{B}}\right)\right) \tag{2}$$

$$q_\mathrm{A} = \left(\frac{2\pi m_\mathrm{A}kT}{h^2}ev\right)^{N_\mathrm{A}} z_{i\mathrm{A}}^{N_\mathrm{A}} e^{-\frac{N_\mathrm{A}\varepsilon_\mathrm{A}^0}{kT}} \tag{3}$$

In such a case, the free energy is a function of the mole fractions of components. The invariance of the volume per molecule in the liquid phase implies equality of the molar volumes of components. In fact, *Raoult*'s law, formulated with respect to mole fractions, is only applicable to mixtures of molecules of approximately equal volumes.

However, liquid reaction mixtures at constant pressure are generally characterized by invariance of the total volume. The densities of liquids made up of the same atoms are approximately equal. Any reaction mixture at equilibrium consists of the same atoms in the same amounts as the initial mixture of reactants. Therefore, the total volume of a reaction mixture at equilibrium should not significantly differ from that of the initial mixture. For such a case, an equivalent form of the partition function can be obtained from Eq. (1) by replacing v by $V/(N_\mathrm{A}+N_\mathrm{B})$ and applying the *Stirling* formula:

$$Z = \left(\frac{2\pi m_\mathrm{A}kT}{h^2}\frac{eV}{N_\mathrm{A}}\right)^{N_\mathrm{A}} z_{i\mathrm{A}}^{N_\mathrm{A}} e^{-\frac{N_\mathrm{A}\varepsilon_\mathrm{A}^0}{kT}}\left(\frac{2\pi m_\mathrm{B}kT}{h^2}\frac{eV}{N_\mathrm{B}}\right)^{N_\mathrm{B}} z_{i\mathrm{B}}^{N_\mathrm{B}} e^{-\frac{N_\mathrm{B}\varepsilon_\mathrm{B}^0}{kT}} \tag{4}$$

The free energy is then a function of molar concentrations of the components. Therefore, the law of mass action for a reaction in a liquid should, in general, be formulated with respect to molar concentrations rather than mole fractions.

It is also not difficult to show that for liquid systems at not too high (constant) a pressure the *Helmholtz* free energy can be used in the derivation of the law of mass action instead of the *Gibbs* free energy. For a spin crossover in the liquid state without a solvent according to Eq. (5), the *Gibbs* free energy, expressed as a function the current number of molecules of component B (n_{B}), is given by Eq. (6) in which $N = n_{\mathrm{A}} + n_{\mathrm{B}}$ is the total number of molecules.

$$\mathrm{A\ (LS)} \rightleftharpoons \mathrm{B\ (HS)} \tag{5}$$

$$\begin{aligned} -\frac{G}{kT} &= (N - n_{\mathrm{B}})[\ln q_{\mathrm{A}} + \ln eV - \ln (N - n_{\mathrm{B}})] \\ &\quad + n_{\mathrm{B}}[\ln q_{\mathrm{B}} + \ln eV - \ln n_{\mathrm{B}}] - \frac{pV}{kT} \end{aligned} \tag{6}$$

The condition of equilibrium of such a reaction corresponds to $dF/dn_{\mathrm{B}} = 0$. It is well known that the volume of HS species is significantly higher (by *ca.* 30%) than that of LS species [1]. In such a case we must consider the volume V as a function of composition, and the derivative of free energy becomes

$$\begin{aligned} -\frac{1}{kT}\frac{dG}{dn_{\mathrm{B}}} &= -\ln q_{\mathrm{A}} - \ln eV + \ln (N - n_{\mathrm{B}}) + (N - n_{\mathrm{B}})\left(\frac{d\ln V}{dn_{\mathrm{B}}} + \frac{1}{N - n_{\mathrm{B}}}\right) \\ &\quad + \ln q_{\mathrm{B}} + \ln eV - \ln n_{\mathrm{B}} + n_{\mathrm{B}}\left(\frac{d\ln V}{dn_{\mathrm{B}}} - \frac{1}{n_{\mathrm{B}}}\right) - \frac{p}{kT}\frac{dV}{dn_{\mathrm{B}}} = 0 \end{aligned} \tag{7}$$

We see that, although the terms $\ln V$ cancel out (the reaction is isomolar), those containing the derivative of volume by n_{B} do not:

$$\ln \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln \frac{n_{\mathrm{B}}}{n_{\mathrm{A}}} + \frac{N}{V}\left(1 - \frac{pV}{NkT}\right)\frac{dV}{dn_{\mathrm{B}}} = 0 \tag{8}$$

For liquids, the term *pV/NkT* is much smaller than 1 because the volume of a substance in the condensed state is about 1000 times smaller than the volume of the same number of molecules in the ideal gas state (*NkT/p*). This term can therefore be neglected for pressures up to tens of atmospheres. The *Helmholtz* free energy can then be used in the derivation of the law of mass action for reactions under constant pressure in both liquid and solid state, and Eq. (8) can be written as

$$\ln \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln \frac{n_{\mathrm{B}}}{n_{\mathrm{A}}} + \frac{N}{V}\frac{dV}{dn_{\mathrm{B}}} = 0 \tag{9}$$

When the expected volume changes are small, the last term in Eq. (9) can be represented in a logarithmic form: $\pm\delta \cong \ln(1 \pm \delta)$. Taking further into account that $N = n_{\mathrm{A}} + n_{\mathrm{B}}$ and adding and subtracting $\ln V$, the non-ideality term can be transformed into activity coefficients:

$$\ln \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln\left(\frac{n_{\mathrm{B}}}{V}\left(1 - \frac{n_{\mathrm{B}}}{V}\frac{dV}{dn_{\mathrm{B}}}\right)\right) + \ln\left(\frac{n_{\mathrm{A}}}{V}\left(1 + \frac{n_{\mathrm{A}}}{V}\frac{dV}{dn_{\mathrm{B}}}\right)\right) = 0 \tag{10}$$

Taking into account that $dn_{\mathrm{B}}/dn_{\mathrm{A}} = -1$ we can write Eq. (10) as:

$$\ln \frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln\left(\frac{n_{\mathrm{B}}}{V}\left(1 - \frac{n_{\mathrm{B}}}{V}\frac{dV}{dn_{\mathrm{B}}}\right)\right) + \ln\left(\frac{n_{\mathrm{A}}}{V}\left(1 - \frac{n_{\mathrm{A}}}{V}\frac{dV}{dn_{\mathrm{A}}}\right)\right) = 0 \tag{10a}$$

Equations (10) and (10a) clarify the physical significance of activity coefficients, but for a theoretical analysis Eq. (9) is much more useful. In order to obtain the non-ideality term as an explicit function of composition, we can suppose (as a first approximation) that the volume V is additive with respect to the numbers of molecules of components:

$$V = (N - n_{\mathrm{B}})v_{\mathrm{A}} + n_{\mathrm{B}}v_{\mathrm{B}} = N(v_{\mathrm{A}} + x_{\mathrm{B}}\Delta v) \tag{11}$$

v_{A} and v_{B} are the molecular (or molar) volumes of the components, and $\Delta v = v_{\mathrm{B}} - v_{\mathrm{A}}$ is the balance of molecular volumes of products and reactants. The derivative dV/dn_{B} then equals Δv, and the law of mass action (Eq. (9)) becomes

$$\ln\frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln\frac{x_{\mathrm{B}}}{1 - x_{\mathrm{B}}} + \frac{\Delta v}{\nu_{\mathrm{A}} + x_{\mathrm{B}}\Delta v} = 0 \tag{12}$$

or, employing the dimensionless parameter $\alpha_{\mathrm{V}} = \Delta v/v_{\mathrm{A}}$:

$$\ln\frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \ln\frac{x_{\mathrm{B}}}{1 - x_{\mathrm{B}}} + \frac{\alpha_{\mathrm{V}}}{1 + x_{\mathrm{B}}\alpha_{\mathrm{V}}} = 0 \tag{12a}$$

The term $\ln(q_{\mathrm{B}}/q_{\mathrm{A}})$ can be formally represented as:

$$\ln\frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} = -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} \tag{13}$$

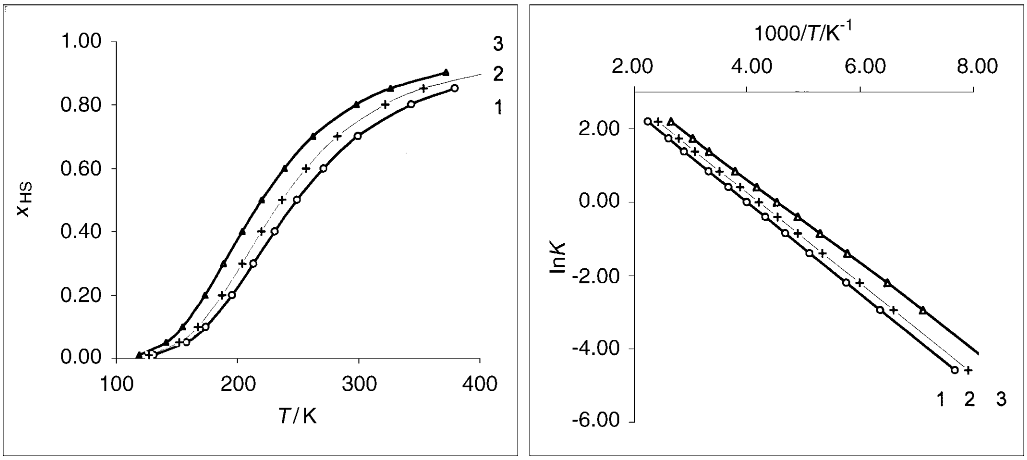
It has to be considered, however, that ΔE^0 and ΔS^0 are not true standard internal energy and standard entropy of reaction, respectively, but their ideal parts corresponding to zero volume changes. Making use of Eq. (14) to calculate temperatures corresponding to given compositions thus enables transition curves to be simulated.

$$T = \frac{\Delta E^0}{\Delta S^0 - \ln\dfrac{x_{\mathrm{B}}}{1 - x_{\mathrm{B}}} + \dfrac{\Delta v}{v_{\mathrm{A}} + x_{\mathrm{B}}\Delta v}} \tag{14}$$

Simulations according to this equation show comparatively small variations of the steepness of the transition curve (Fig. 1). Corresponding *van't Hoff* plots (Fig. 1B) indicate that volume changes affect mainly the entropy of spin crossover: $\Delta S^0 = 42.9\,\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for $\Delta v/v_{\mathrm{A}} = 0.3$ *vs.* $42\,\mathrm{J\cdot mol^{-1}K^{-1}}$ for $\Delta v = 0$. Such a contribution is comparatively small and cannot explain discrepancies between the lowest observed entropies of spin crossover in Fe(II) complexes (about 37.8–$42\,\mathrm{J\cdot mol^{-1}K^{-1}}$ [1]) and the theoretical value of $13.4\,\mathrm{J\cdot mol^{-1}K^{-1}}$ originating from electronic degeneracy. The standard energy of spin crossover is but slightly affected by the volume changes expected for a spin crossover equilibrium: $\Delta E^0 = 11$ $(\Delta v/v_{\mathrm{A}} = 0.3)$ *vs.* $10.5\,\mathrm{kJ\cdot mol^{-1}}$ in an ideal solution. Very large volume changes cause an insignificant decrease in ΔE^0, for example $\Delta E^0 = 9.9\,\mathrm{kJ\cdot mol^{-1}}$ for a doubling of the volume. This type of non-ideality therefore does not predict singularities such as steep spin crossover[1].

---

[1] The tangent at the deflection point of the curve $x_{\mathrm{B}} = f(T)$ can virtually be vertical when either x is negative or $x > 1$, both cases being physically meaningless.



A B

Fig. 1. Transition curves (A) and *van't Hoff* plots (B) simulated for a spin crossover system with $\Delta E^0 = 10.5\,\text{kJ} \cdot \text{mol}^{-1}$ and $\Delta E^0/\Delta S^0 = 250\,\text{K}$; curve 1 corresponds to an ideal solution ($\Delta v = 0$), curve 2 to $\alpha_V = +0.3$, and curve 3 to $\alpha_V = +1.0$

By taking into account volume changes, we have implicitly admitted that molecules have finite volumes, *i.e.* we have accounted for the repulsive interactions between molecules. Non-zero balances Δv also imply that molecular volumes can be non-additive with respect to elemental composition. This is a result of different strengths of interaction and the arrangement of atoms within the molecules of products and reactants. Such a theoretical treatment of an equilibrium in the condensed state corresponds to one of the earliest theories of liquids developed by *Jäger* [8] which considered an ideal liquid as an assembly of hard spheres interacting repulsively but held together by internal pressure. The latter appears explicitly when we take into account the attractive forces between molecules. A useful model of free volume can be advantageously used for the derivation of another form of the law of mass action for the spin crossover equilibrium in the liquid phase. The free volume can be considered as the volume of free motion of the centres of mass of the molecule [9]. This leads to the following relationship between volume and free volume [10] in which κ is a structural constant relating volume to lattice constant ($V = \kappa N a^3$).

$$V_f = V\left[\frac{2\kappa NkT}{p + N(\partial u/\partial V)}\right]^3 \cong V\left[\frac{2\kappa kT}{\partial u/\partial V}\right]^3 \tag{15}$$

The term $N(\partial u/\partial V)$ equals the negative internal pressure. The derivative $\partial u/\partial V$ can be approximated by the molecular vaporisation energy per unit volume (E_V/NV) [10]. Note that the free volume cannot be larger than the volume of a system, and therefore the molecular energy of vaporisation must be higher than $2\kappa kT$.

At a first glance, the substitution of the volume by the free volume in Eq. (9) would not change anything substantially since we can assume the additivity of free volume and obtain the non-ideality term in the form of $\Delta v_f/\langle v_f\rangle$. However, looking more closely, we find that the free volume given by Eq. (15) reflects both the attractive interactions and the repulsive interactions between the hard spheres of *Jäger*'s model. To a first approximation, the energy of attractive interactions (vaporisation energy) can be assumed to be additive.

For the spin crossover equilibrium (Eq. (5)) in the presence of solvent, the additivity of the energy of vaporisation can be written as

$$E_{\mathrm{V}} = N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}(\varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}}) \tag{16}$$

in which ε_{A}, ε_{B}, and ε_{S} are the vaporisation energies of components per molecule (assumed to be independent of the composition), and $N = n_{\mathrm{A}} + n_{\mathrm{B}}$ equals the initial number of molecules of reactants. The free energy can thus be written as

$$\begin{aligned} -\frac{F}{kT} = {} & (N - n_{\mathrm{B}})\left(\ln q_{\mathrm{A}} eV + 3\ln\frac{2\kappa(N+N_{\mathrm{S}})kT}{N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}(\varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}})} - \ln(N - n_{\mathrm{B}})\right) \\ & + n_{\mathrm{B}}\left(\ln q_{\mathrm{B}} eV + 3\ln\frac{2\kappa(N+N_{\mathrm{S}})kT}{N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}(\varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}})} - \ln n_{\mathrm{B}}\right) \\ & + N_{\mathrm{S}}\left(\ln q_{\mathrm{S}} eV + 3\ln\frac{2\kappa(N+N_{\mathrm{S}})kT}{N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}(\varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}})} - \ln N_{\mathrm{S}}\right) \end{aligned} \tag{17}$$

For simplicity sake, we consider the volume as constant and investigate the effects of internal pressure alone. The law of mass action derived from the condition $dF/dn_{\mathrm{B}} = 0$ contains the derivative of vaporisation energy with respect to n_{B}, $dE_{\mathrm{V}}/dn_{\mathrm{B}} = \Delta\varepsilon = \varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}}$:

$$\ln\frac{q_{\mathrm{B}}}{q_{\mathrm{A}}} - \frac{3\Delta\varepsilon(N+N_{\mathrm{S}})}{N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}\Delta\varepsilon} - \ln\frac{n_{\mathrm{B}}}{N - n_{\mathrm{B}}} = 0 \tag{18}$$

Expressing $\ln(q_{\mathrm{B}}/q_{\mathrm{A}})$ as $\Delta E^0/RT - \Delta S^0/R$ we get

$$-\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} - \frac{3\Delta\varepsilon(N+N_{\mathrm{S}})}{N\varepsilon_{\mathrm{A}} + N_{\mathrm{S}}\varepsilon_{\mathrm{S}} + n_{\mathrm{B}}\Delta\varepsilon} - \ln\frac{n_{\mathrm{B}}}{N - n_{\mathrm{B}}} = 0 \tag{18a}$$

Dividing the numerator and denominator in (18a) by N and ε_{A}, we get an expression with respect to the degree of conversion $x = n_{\mathrm{B}}/N$ and the dimensionless parameter $\alpha_{\mathrm{E}} = \Delta\varepsilon/\varepsilon_{\mathrm{A}}$:

$$-\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} - \frac{3\alpha_{\mathrm{E}}(1 + N_{\mathrm{S}}/N)}{1 + (N_{\mathrm{S}}/N)(\varepsilon_{\mathrm{S}}/\varepsilon_{\mathrm{A}}) + x\alpha_{\mathrm{E}}} - \ln\frac{x}{1-x} = 0 \tag{18b}$$

Note that x is not the mole fraction of B $(x_{\mathrm{B}} = n_{\mathrm{B}}/(N + N_{\mathrm{S}}))$.

When the dependence of volume on composition is also taken into account, the resulting law of mass action can be written as

$$\begin{aligned} -\frac{\Delta E^0}{RT} + \frac{\Delta S^0}{R} & + \frac{\alpha_{\mathrm{V}}(1 + N_{\mathrm{S}}/N)}{1 + (N_{\mathrm{S}}/N)(v_{\mathrm{S}}/v_{\mathrm{A}}) + x\alpha_{\mathrm{V}}} \\ & - \frac{3\alpha_{\mathrm{E}}(1 + N_{\mathrm{S}}/N)}{1 + (N_{\mathrm{S}}/N)(\varepsilon_{\mathrm{S}}/\varepsilon_{\mathrm{A}}) + x\alpha_{\mathrm{E}}} - \ln\frac{x}{1-x} = 0 \end{aligned} \tag{19}$$

in which $\alpha_{\mathrm{V}} = \Delta v/v_{\mathrm{A}}$. If α_{V} and α_{E} are not zero and do not compensate each other, the non-ideality terms in Eq. (19) do not vanish at infinite dilution: under the condition $N_S \gg N$, Eq. (19) is transformed into

$$-\frac{\Delta E^0}{RT}+\frac{\Delta S^0}{R}+\frac{\Delta v}{v_S}-\frac{3\Delta\varepsilon}{\varepsilon_S}-\ln\frac{x}{1-x}=0 \tag{20}$$

In such a case, the non-ideality terms are composition independent and contribute to the standard entropy alone. Simulations show that for $\Delta v = 0.3\,v_A$ and $\Delta\varepsilon = 0$ such a state is achieved at $N_S/N > 10$. This contribution depends on the volumetric properties of the solvent, being higher for smaller solvent molecules. In more concentrated solutions non-ideality contributes also to the standard energy.

The effects of internal pressure are more significant than those of volume and may cause a vertical tangent to the transition curve:

$$-\frac{\alpha_V^2(1+N_S/N)}{(1+(N_S/N)(v_S/v_A)+x\alpha_V)^2}+\frac{3\alpha_E^2(1+N_S/N)}{(1+(N_S/N)(\varepsilon_S/\varepsilon_A)+x\alpha_E)^2}-\frac{1}{(1-x)x}=0 \tag{21}$$

For the simple case of $N_S = 0$ and $\alpha_V = 0$, this condition is transformed into

$$3\alpha_E^2(1-x)x-(1+\alpha_E x)^2=0 \tag{22}$$

For $x = 1/2$ we have two values of α_E corresponding to a vertical tangent: $\alpha_E = 1 \pm \sqrt{3}$, *i.e. ca.* 2.7 and $-0{,}7$. Equation (22) has a single solution with respect to α_E at $x = 3/4$ corresponding to the least (in magnitude) balance of vaporisation energy[2] $\Delta\varepsilon = -(2/3)\varepsilon_A$. Both positive and negative $\Delta\varepsilon$ bring about a curvature of *van't Hoff* plots (Fig. 2) which can be interpreted (for small balances $\Delta\varepsilon$) as an increase in the standard energy. Negative balance of vaporisation energy brings about an increase in the standard entropy, whereas positive $\Delta\varepsilon$ decreases it (Table 1). Negative α_E seems to be more probable for spin crossover as arising from lower internal pressure in a system of larger HS molecules unless a strong magnetic interaction between HS species occurs.

Such a behaviour is different from the effects predicted by regular solution theory [6, 11]: theoretical curves corresponding to varying non-ideality should, according to this theory, intersect at a transition point ($x = 0.5$). This difference arises from the fact that the equations for free energy in regular solution theory contain square and linear terms with respect to the degree of conversion, whereas the equation derived above contains cubic and linear terms. The former arises from the inverse cubic dependence of free volume on the internal pressure (which has been assumed to be additive). Further analysis shows that this inverse cubic dependence originates from the model representation of free volume as a volume within which the centres of mass of the molecules can move in a three-dimensional lattice. For a two-dimensional lattice one can easily obtain a quadratic relationship:

$$V_f = V\left(\frac{2\kappa kT}{\partial u/\partial V}\right)^2 \tag{23}$$

---

[2] There are certain limitations with respect to possible values of α_E because, according to the initial assumption, $\varepsilon_{HS}/v \gg p$. Therefore, α_E cannot be equal or less than -1. However, taking into account that the volume per molecule v in liquids is *ca.* 1000 times smaller than in the gaseous phase (*kT/p*), this condition means that $\Delta\varepsilon \gg 10^{-3}\,kT$, which certainly holds at $N_L\varepsilon_A > 8.4\,\mathrm{kJ\cdot mol^{-1}}$ and $\alpha_E > -0.9$.

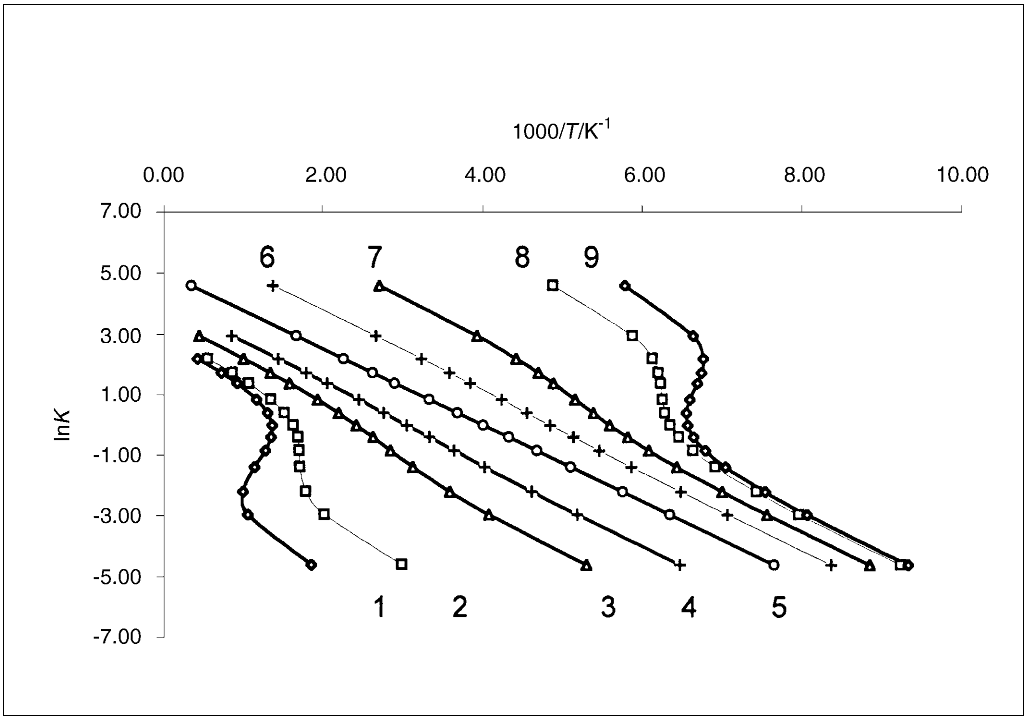


Fig. 2. *van't Hoff* plots calculated for a non-diluted spin crossover system ($N_S = 0$, $\Delta E^0 = 10.5\,\text{kJ} \cdot \text{mol}^{-1}$, $\Delta E^0/\Delta S^0 = 250\,\text{K}$) with a varying balance of molecular vaporisation energies: $\alpha_E = +2.5$ (1), $+2$ (2), $+1$ (3), $+0.5$ (4), 0.0 (5), -0.3 (6), -0.5 (7), -0.66 (7), and -0.7 (8)

Table 1. Approximation of the curves in Fig. 2 by linear *van't Hoff* plots

$\Delta\varepsilon/\varepsilon_A$	$\Delta E^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^0/\text{kJ} \cdot \text{mol}^{-1}\text{K}^{-1}$	T_{SC}/K
2	19.021184	25.007164	760.6
1	13.022646	30.440592	427.9
0.5	11.226852	34.069854	329.5
0	10.460814	41.86	249.9
−0.3	11.042668	53.610102	206.0
−0.5	13.026832	74.00848	176.0
−0.66	18.644444	124.520942	149.7

The cubic term in the expression for the free energy of a binary non-ideal mixture also appears (along with square and linear terms) when the interactions of a molecule with two nearest neighbours (*i.e.* triple interactions) are taken into account [11]. In the present treatment we obtain the cubic dependence as a result of three-dimensional molecular motion. Therefore, these two types of cubic dependence are of a different nature. The cubic term obtained in Ref. [11] originates in a certain model of calculation of potential energy of molecules, whereas that obtained in the present analysis is based on the model of free volume as a space of motion in a three dimensional lattice.

Conclusions

A statistical mechanical derivation of the law of mass action for a chemical equilibrium in the liquid phase shows that, taking into account the approximate invariance of the densities of liquids, molar concentrations should be used rather than mole fractions. The non-ideality of spin crossover equilibria arising from considerable changes in volume brings about a contribution to the standard entropy of *ca.* $2.1\,\mathrm{J \cdot mol^{-1}K^{-1}}$. Considering the possibility of the non-ideality of a binary equilibrium mixture from the point of view of free volume, it was found that singularities (similar to phase transitions in regular solutions) might result from a non-zero balance of molecular vaporisation energy in a reaction.

Acknowledgements

We are grateful to Prof. *R. F. Jameson* (University of Dundee, Scotland, UK) for useful discussions. Thanks are also due to the Austrian Science Foundation (Project 11218-CHE), to the Training and Mobility of Researchers Network (TMR) project 'Thermal and Optical Spin State Switching' (TOSS) supported by the European Community under the Contract number ERB-FMRX-CT98-0199), and to the European Science Foundation (ESF) under the project 'Molecular Magnets'.

References

[1] Gütlich P, Hauser A, Spiering H (1994) Angew Chem Int Ed **33**: 2024
[2] Kahn O (1993) Molecular Magnetism. VCH, New York
[3] Gütlich P, Hauser A (1990) Coord Chem Rev **97**: 1
[4] Linert W, Koudriavtsev AB (1999) Coord Chem Rev **190–192**: 405
[5] Slichter CP, Drickamer HG (1972) J Chem Phys **56**: 2142
[6] Köppen H, Müller EW, Köhler CP, Spiering H, Meissner E, Gütlich P (1982) Chem Phys Lett **91**: 348
[7] Moelwyn-Hughes EA (1961) Physical Chemistry. Pergamon Press, London (quoted according to the Russian edition: Izd Inostr Lit, Moskva, 1962)
[8] Jäger G (1903) Ann Physik **11**: 1077
[9] Eyring H, Hirschfelder JO (1937) J Phys Chem **41**: 249
[10] Glasstone S, Laidler KJ, Eyring H (1941) The Theory of Rate Processes. McGraw-Hill, NY, p 479
[11] Koudriavtsev AB (1999) Chem Phys **241**: 109

Received May 24, 2000. Accepted September 21, 2000