Enthalpy–entropy compensation on a finite-size hierarchical tree

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Abstract. A Cayley tree model for activation entropy–enthalpy compensation in charge transport kinetic processes is extended to cover the anticompensation mode. The present model incorporates a negative confinement entropy contribution due to the finite spatial extension of the activation complex.

1. Introduction

Certain groups of thermally activated processes can be characterized by a linear relationship between the logarithm of the pre-exponential factor in the Arrhenius-type expression for the rate constant and the corresponding energy of activation [1–4]. In charge transfer in solids, this dependence is known as the Meyer–Neldel rule [2–4]. In such cases, the temperature dependence of the rate constant can be expressed by

$$r \propto \exp(-(E_a/k)(1/T - 1/T_0)) \tag{1}$$

where r is the rate constant, E_a is the activation energy and T_0 is a constant characteristic of a particular group of thermally activated processes. According to the activation complex theory, the relationship given in (1) is equivalent to a linear dependence between the enthalpies and the entropies of activation in a particular group of thermally activated processes. This dependence is known as the kinetic compensation effect, where T_0 indicates the temperature for which all the kinetic processes in the group have the same rate constant independent of the particular activation energy [1].

A simple model for an activation complex characterized by (1) was suggested in a previous publication [5]. This model consists of a spatially distributed hierarchy of self-similar activation steps represented by the branching points on a Cayley tree. The charge is transferred from the top of the tree to its base. Every additional branching point crossed adds one unit of energy to the overall activation energy and multiplies the number of the available pathways by the factor α. For a binary Cayley tree, $\alpha = 2$. The total energy of activation is then linearly proportional to n, the number of activation steps or tree levels. The number of the available pathways is 2^n, so the entropy of activation, $k \ln(2^n)$, is also linearly proportional to n. The total energy of activation is then linearly dependent on the entropy of activation. Note that in this early model, the only contribution to the entropy of activation is the exponential increase in the number
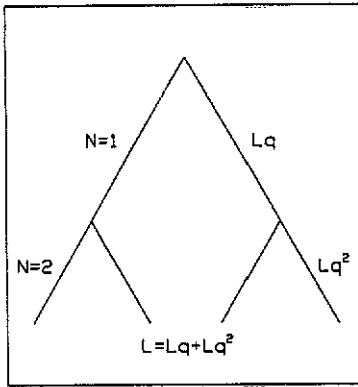
Figure 1. A schematic representation of a two-level binary tree. The pathways connecting the top of the tree to its base are of a fixed linear length, L. In the specific case illustrated, the ratio, q, between the lengths of the successive branches is, $(\sqrt{5} - 1)/2$. The overall length of two successive branches, $Lq + Lq^2$, is then exactly L. In the case of $q \rightarrow \frac{1}{2}$, the successive branches form an infinite geometrical series with the total length converging to L. N denotes the level number of the tree.

of the available pathways with the number of the tree levels, n. An additional contribution to the entropy of activation in finite-length trees comes from the spatial constraint to the activation barrier crossing as it occurs at a definite spatial position determined by the location of the maximum of the energy barrier. This contribution and its dependence on the geometry of the Cayley tree will be discussed below

2. The model

The maximum of the energy barrier in the Cayley tree model for the activation complex is the base of the tree [5]. In a realistic model for the activation complex, the linear extension of the pathways connecting the top of the tree and its base should be finite. This length will have a finite value, provided the lengths of the successive branches form a converging geometrical series. Given a finite total length L, and a constant ratio between the lengths of the successive levels, the number of the levels in the tree can be obtained from

$$L = Lq + Lq^2 + Lq^3 + \ldots + Lq^{n-1} = L(1 - q^n)/(1 - q) - L \qquad (2)$$

where the right-hand side of the equation contains the well known expression for the sum of the geometrical series, $L + Lq + Lq^2 + \ldots + Lq^{n-1}$. Note that the number of levels is the integer, n, minus one, as the first level of the tree corresponds to the second member of the geometrical series, $L + Lq + Lq^2 + \ldots$, (see figure 1). An explicit expression for n can be obtained from (2) in the form

$$2(1 - q) = (1 - q^n)$$

or

$$n = \ln(2q - 1)/\ln q. \qquad (3)$$

For $q \rightarrow \frac{1}{2}$, the number of tree levels approaches infinity, while for $q \rightarrow 1$, the variable n approaches 2 which is equivalent to a single level as discussed above. In the first case, lengths of branches of the base level approach zero, while in the second case the entire tree is a single level consisting of α branches of length L. For many-level trees, i.e. for $q \rightarrow \frac{1}{2}$, the number of levels, N, can be expressed as $N = n - 1 \simeq n$.

The entropic contribution due to the confinement of particles to a fraction, x, of a total available space is [6] $k \ln x$ per particle. In the present case, particles at level n

occupy a fraction $Lq^n/L = q^n$ of the total linear extent, L. Therefore the entropic contribution due to spatial confinement is $k \ln q^n$. In the case of $q \to \frac{1}{2}$, the particles reaching the base are confined to infinitesimally small branches leading to a large negative entropy contribution. While this has the effect of increasing the free energy of activation and decreasing the rate constant, the probability of charge transfer from the base levels approaches unity as the charges are localized exactly at the base edge of the tree. For finite-extent base levels, the probability of charge transfer is one minus the value of the probability of finding the particle inside the entire tree.

From (3), the probability of charge transfer from the base level, $1 - q^n$, is equal to $2(1 - q)$. For $q = 0.501$ and $q = 0.500\,01$, the transfer probabilities are 0.998 and 0.999\,98, respectively. Thus, in the vicinity of $q = \frac{1}{2}$, the transfer probability depends marginally on q and its value is $\simeq 1$. In other words, any charge reaching the base level has a unit probability of crossing the barrier. In this case, the temperature-independent pre-exponential factor in the Arrhenius expression for the rate constant is a function of the confinement and branching entropies only. Using (3), the confinement entropies, $nk(\ln q)$, for $q = 0.501$ and $q = 0.500\,01$ are $-6.21k$ and $-10.82k$ respectively. This significant dependence of the confinement entropy on q results from the fact that the expression, $nk(\ln q)$, is dominated by the diverging factor n, for $q \to \frac{1}{2}$. Both the confinement entropy, $nk(\ln q)$, and the branching entropy, $nk(\ln \alpha)$, are linearly dependent on the diverging factor n, for $q \to \frac{1}{2}$. The total entropic contribution at $q \to \frac{1}{2}$ is therefore

$$\Delta S^{\ddagger} = nk(\ln q) + nk(\ln \alpha) = nk(\ln q\alpha). \tag{4}$$

Using the explicit expression for n as a function of q in (3),

$$\Delta S^{\ddagger} = \frac{k \ln(2q - 1)}{\ln q} \ln(q\alpha). \tag{5}$$

The total enthalpy of activation is the single-step enthalpy, E, times the number of the levels:

$$\Delta H^{\ddagger} = \frac{E \ln(2q - 1)}{\ln q}. \tag{6}$$

Comparison of (5) and (6) shows an asymptotically linear dependence between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for $q \to \frac{1}{2}$, as both expressions diverge with the same factor, $\ln(2q - 1)/\ln q$, while the factor $\ln(q\alpha)$ approaches a constant. The asymptotically linear relationship between $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in the vicinity of $q = \frac{1}{2}$ can be verified by substitution of $0.501 > q > \frac{1}{2}$ into (5) and (6). The compensation temperature, $T_0 = \Delta H^{\ddagger}/\Delta S^{\ddagger}$, is given by

$$T_0 = E/k \ln(q\alpha). \tag{7}$$

For a binary tree ($\alpha = 2$), and the asymptotic condition given by $q \to \frac{1}{2}$, the compensation temperature approaches infinity. An infinite compensation temperature is equivalent to a normal Arrhenius behaviour or to isoentropic kinetics with the pre-exponential factor independent of the activation enthalpy (see (1)). In this case, the confinement factor is the inverse of the branching factor at all levels of the tree. Therefore the overall entropy change is zero, irrespective of the number of the tree levels and of the overall enthalpy of activation. This is in contrast with the earlier model [5], where an infinite compensation temperature occurs at $\alpha = 1$. In the present case, the non-branching activation complex ($\alpha = 1$) is characterized by a negative compensation temperature,

$T_0 = -E_0(\ln 2)/k$. Negative compensation temperatures are not experimental temperatures as they are derived from an extrapolation of the Arrhenius-type plots and indicate the position of the intersection point of the plots relative to the $1/T$ axis. Negative compensation temperatures were derived from the experimental data for several systems [1]. The physical significance of the negative compensation temperatures is the anticompensation behaviour, i.e. the logarithm of the pre-exponential factor decreases linearly with an increase of the activation energy [1, 7]. According to the present model, anticompensation is the result of an increasingly negative contribution from the confinement entropy as the number of the tree levels and the activation enthalpy increase, whereas the positive entropic contribution from branching is absent ($\alpha = 1$). Positive compensation occurs in trees with $\alpha \geq 3$, where the positive branching entropy contribution is larger than the negative confinement entropy contribution.

The fractal dimension of a non-compensating tree is

$$D_f = -\frac{\ln \alpha}{\ln q} = 1 \qquad \text{for } q \to \tfrac{1}{2} \text{ and } \alpha = 2. \tag{8}$$

It should be noted that this fractal dimension is larger by unity than that of the non-compensating tree of the earlier model, which is characterized by $\alpha = 1$ and $D_f = 0$. The extra dimension provides the additional degree of freedom for the compensation of the negative entropy contribution introduced in the present model. The negative entropy contribution uncompensated for by the positive branching contribution in the case of $\alpha = 1$, and $D_f = 0$, results in there being an anticompensation kinetic effect.

The lowest-dimension ($D_f = 0$) tree of the earlier model is not anticompensating, as it does not include the negative confinement entropy contribution as noted above.

3. Conclusion

The constraint of finite-length conduction pathways in an activation complex adds a negative confinement entropy contribution to the positive branching entropy contribution inherent to the Cayley tree model. The interdependence between the number of levels in the tree and the ratio between the lengths of successive levels, imposed by the finite-length constraint, results in an asymptotically linear relationship between the entropies and enthalpies of activation in many-level trees. The negative confinement entropy contribution extends the former model [5] to cover the anticompensation mode.

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