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STUDY ON THE MECHANISM OF THE SELECTIVE ACTIVATION OF SOLIDS IN A HOMOGENEOUS AND ISOTROPIC THERMAL FIELD

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The topic of this work is to suggest an activation mechanism of condensed phase in a homogeneous and isotropic heat field. More specifically, we will approach the problem of how the molecule can become activated in a condensed phase.

The bonds in the solid state are assimilated to a system of Morse oscillators. The thermal decomposition starts by breaking of a certain bond of the Morse oscillators. This breaking is due to a selective vibrational energy accumulation from a homogeneous and isotropic heat field. Between the Morse oscillators and oscillators in the heat field it is a non-linear kinetic coupling. A correlation between the isokinetic temperature and the spectroscopic observable wave number of the activated bond is suggested.

The main advantage of using the vibrational model is the possibility of identification of that part of a molecule responsible for beginning of the thermal degradation. Our model does not imply any specific path to be followed after the activated state is attained.

Keywords: *activation mechanism, Morse oscillators, vibrational energy transfer*

Introduction

The development of the non-isothermal kinetics in the last decades has proved as a rule the existence of compensation effect (CE) by the non-isothermal decomposition of various solids [1–5]. The CE is related to a simple linear relationship (Eq. 1) between the observed experimental Arrhenius parameters A and activation energy E:

$$\ln A = bE + c \tag{1}$$

where b and c are constants. This CE effect presumes the existence of a 'is kinetic' temperature:

$$T_{\text{is}} = \frac{1}{bR} \tag{2}$$

In some recent papers [6–8] the CE was discussed at molecular level by decomposition reactions under non-isothermal conditions.

The topic of the present paper is to analyze the possibility of a specific activation of the molecules in a homogeny and isotropic heat field, taking into account a simple oscillator model treated in a supersymmetry concept. This is an extension of our ideas presented in a recent paper [9], and is focused on a less speculative significance of the 'isokinetic' temperature.

More specifically, we will approach the problem of how the molecule can become specifically activated in a condensed phase, so that a destroying of the molecular architecture would be possible.

It is well known that the process of dissipation proceed rapidly in condensed phases [10]. One may then ask: how is it possible for a molecule to stay excited in order to react? In this letter we should like to answer this question.

In the Appendix of our work we propose two methods of satisfactory approximating the partition function of the Morse systems on large domains of temperatures using only elementary functions, not in the terms of analytical functions which were already used in many general books of statistical thermodynamics [11, 12].

Mechanism of selective activation in a homogeneous and isotropic heat field

We suggest a specific activation mechanism based on the following hypotheses: i) The bonds in the solid are assimilated to a system of Morse oscillators. ii) The thermal decomposition starts by breaking of a certain bond of the Morse oscillators. This breaking is due to a selective vibrational energy accumulation from a homogeneous and isotropic heat field. iii) Between the Morse oscillators and the oscillators in the heat field it is a non-linear kinetic coupling.

Now, the energy levels of the Morse oscillator, growing up due to vibrational energy, can be described as an energy spectrum.

We use the concept of supersymmetry (SUSY) shape invariance [13, 14] to determine the eigenvalue

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spectrum and energy eigenfunction for the Hamiltonian associated to Morse potential.

In comparison with the well-known Schrödinger way, this method provides a very elegant and synthetic way of presenting the operational method [14] to handle several problems in quantum mechanics:

Given a SUSY Hamiltonian, we can generate from it a chain of SUSY Hamiltonians in such a way that two consecutive ones have the same spectrum except for the lowest ground state. This chain allows us to build a sequence of Ricatti equations equivalent to the original Schrödinger equation.

Using partner potentials $V_{\pm}$ defined by:

$$V_{\pm}=W^2\pm\frac{h}{2\pi m}W' \tag{3}$$

where W denote the SUSY 'superpotential' and it has the form:

$$W=-\frac{\hbar}{(2m)^{1/2}}\frac{\psi'_0}{\psi_0} \tag{4}$$

with ψ_0 the ground state wave function and ψ'_0 their first derivate function.

Let us start, for Morse potential with [14]:

$$W(x)=A-B\mathrm{e}^{-\alpha x} \tag{5}$$

Then it is easily shown that the two supersymmetric partner potentials $V_{\pm}$ are

$$\begin{gathered}V_-(x,A)=A^2+B^2\mathrm{e}^{-2\alpha x}-\\ -2B\left[A+\frac{\alpha\hbar}{2(2m)^{1/2}}\right]\mathrm{e}^{-\alpha x}\end{gathered} \tag{6}$$

and

$$\begin{gathered}V_+\left(x,A-\frac{\alpha\hbar}{(2m)^{1/2}}\right)=\\ =\left[A-\frac{\alpha\hbar}{(2m)^{1/2}}\right]^2+B^2\mathrm{e}^{-2\alpha x}-2BA\mathrm{e}^{-\alpha x}\end{gathered} \tag{7}$$

The complete bound state spectrum of $V_-(x, A)$ is given by (n=0, 1, 2,...)

$$\begin{gathered}E_\mathrm{n}^{(-)}(A)=A^2-\left(A-\frac{n\alpha\hbar}{\sqrt{2m}}\right)^2,\\ E_0^{(-)}(A)=0\end{gathered} \tag{8}$$

where α is a positive characteristic parameter of this potential and A has the form:

$$A=\frac{1}{\alpha}\sqrt{\frac{m}{2}}\left(\omega-\frac{\hbar\alpha^2}{2m}\right) \tag{9}$$

with, ω is the angular frequency.

The harmonic limit of the Morse oscillator requires the simultaneous accomplishment of the limiting operations, and E_n as it results from Eq. (8), in first approximation for n, is expressed in the form:

$$E_\mathrm{n}\approx\hbar\omega n \tag{10}$$

Under non-isothermal conditions, the surrounding temperature depends on the time t

$$T=T(t) \tag{11}$$

so that the main energy of the oscillators (Boltzmann statistics) given by

$$\varepsilon_\mathrm{B}=k_\mathrm{B}T \tag{12}$$

increases continuous in respect of time.

This energy would be transferred to a certain bond of the solidstate if this will be assimilated to an anharmonic oscillator (see hypothesis ii).

According to the hypothesis iii) the energy is specifically transferred by vibrational quanta, not only at the fundamental, but also at the nearest harmonics. At the same time the activation will be possible by absorption of more than one quantum. This both facts will be expressed by the relation:

$$E_\mathrm{n}=n_1\varepsilon_\mathrm{B} \tag{13}$$

with n_1=number of thermal quanta.

Equation (13) expresses the resonance condition necessary for the energy transfer according to hypothesis ii). These resonance conditions for some representative chemical bonds are exemplified in Table 1. In fact, Eq. (13) is the expression of hypothesis (iii), and the data in Table 1 seems to support this hypothesis. Of course the probability of a selective activation increases if n_1 is as low as possible.

With increasing temperature the necessary thermal quanta decreases. But noticeable is that this n_1 value differs significantly from a bond to other, at the same temperature. For example, at 700 K, for activation of C–C bond n_1=2, while for C–H, n_1=6. Consequently the activation of C–C bond at 700 K is more rapid in comparison with the C–H bond and in this way the selectivity is attained.

A second important observation is that under non-isothermal conditions, at each moment another oscillator will be activated (Eq. (11)). Supposing at temperature T_i a bond corresponding to $(E_\mathrm{n})_\mathrm{i}$ is in resonance (Eq. (13)) and would be broken. After a time period Δt, the temperature T_j will be attained and the breaking of the bond corresponding to $(E_\mathrm{n})_\mathrm{j}$ becomes possible. If the values of the two specific wave numbers ω are too near and/or the heating rate is too high, those two activation processes should be superposed, a frequent situation by thermal analysis under non-isothermal conditions.

Table 1 Temperature dependence of the resonance condition by different chemical bonds

Bonds	Spectroscopic wave number for the activated/broken bond ϖ/cm^{-1}	T/K	n_1
C≡C	1650	300	8
		400	6
		480	5
		600	4
		800	3
C–H (stretch)	2905	300	14
		420	10
		600	7
		700	6
		840	5
C–H (deformation)	1400	290	7
		400	5
		500	4
		680	3
C–C	1000	290	5
		360	4
		480	3
		700	2
H–H	3496	640	10
		800	8
I_2	214	300	1

With increasing of the temperature a parallel phenomenon takes place: the increasing of the number of oscillators/bonds activated. Indeed, the number of oscillators with the eigenvalue $(E_n)_i$, corresponding to T_i, increase at a temperature T according to [15]:

$$\bar{n}_i = 1.44T/T_i, \qquad T>T_i \tag{14}$$

This is a direct relationship with the increase of reaction rate.

These two parallel phenomenon taken places by increasing of temperature are the source of the major difficulty by the kinetic analysis, i.e. the discrimination between two or more simultaneous processes developed under non-isothermal conditions.

Conclusions

The main argument of the presented activation model is this that a decomposition reaction in a homogeny and isotropic heat field is facilitated by a proper vibrational energy transfer directed towards that vibration mode of the reactant molecule where it is best needed.

The main advantage of using the suggested vibrational resonance model is the possibility of identification of that part of a molecule responsible for beginning of the thermal degradation. It must be stressed here that our resonance model does not imply any specific path to be followed after the activated state is attained.

In the next section of this work, we will present two methods of approximating the partition function of the Morse oscillators which are complementary to each other, covering the whole domain of temperatures that may be of chemical and physical interest.

Appendix 1

Approximations the partition function for Morse oscillators

The Morse potential is one of the most simple and realistic anharmonic potential models, which has proven to be very useful for solving various problems from diverse fields of physics and chemistry (e.g., vibrational motion of diatomic and polyatomic molecules, spectroscopy, photodissociation, intra- and intermolecular energy transfer).

Vibrational contribution to various thermodynamic functions is expressed in terms of a partition function and of its first two derivatives (internal energy and respectively, heat capacity).

The statistics of an ideal gas of identical diatomic molecules, modeled by Morse oscillators, in thermodynamic equilibrium with a reservoir of temperature T is described by the quantum canonical distribution [10]. This gives the partition function of the discrete spectrum:

$$Z=\sum_{n=0}^{n=N}e^{-\beta E_n},\ \beta=\frac{1}{k_BT} \tag{A1}$$

where E_n are the discrete spectrum of Morse oscillator from Eq. (8) and N is the maximal number of vibrational bound state, n=0, 1, 2,...N,
which can be put in the form:

$$Z(x,N)=\sum_{n=0}^{N}x^{\frac{(N-n)^2}{2N+1}}=x^{\frac{N^2}{2N+1}}F(x,N),x=e^{\beta\omega} \tag{A2}$$

where was introduced the function:

$$F(x,N)=\sum_{n=0}^{N}x^{\frac{-n(2N-n)}{2N+1}} \tag{A3}$$

defined on the domain $x\in[1,\infty)$ for any integer N. This function is maximal for $x=1$ where $F(1,N)=N+1$ and decreases rapidly to 1 for $x\to\infty$ such that $\lim_{x\to\infty}[x\partial_xF(x,N)]=0$. In these circumstances the internal energy is given by the formula:

$$\begin{aligned}U(x,N)&=-\frac{1}{Z(x,N)}\frac{\partial Z(x,N)}{\partial\beta}=\\&=-\frac{\hbar\omega}{2}\frac{N^2}{N+1}-\frac{\hbar\omega x}{F(x,N)}\frac{\partial F(x,N)}{\partial X}\end{aligned} \tag{A4}$$

whose first term is just the energy value at $T=0$ K.

The problem now is to find a satisfactory closed formula which should approximate the function $F(x,N)$ by elementary functions in the case of $\varepsilon=0$.

There are many possibilities that may be selected according to the desired accuracy for the temperatures of physical interest. In what follows we propose two methods of satisfactory approximating the partition function on large domains of temperatures.

Approximations for low temperatures

The first solution we propose here is to consider functions:

$$\tilde{F}(x,N)=\exp\{\exp[\nu f(x,N)]-1\} \tag{A5}$$

where, $\nu=\ln[\ln(N+1)+1]$ and $f:[1,\infty)\to[0,1]$ must be an elementary function, f is a polynomial of the rank $k+1$ in $1/x$:

$$f(x,N)=\sum_{i=1}^{i=k}\frac{C_i(N)}{x^i} \tag{A6}$$

whose coefficients represent fit parameters:

$$\sum_{i=1}^{i=k}C_i(N)=1 \tag{A7}$$

The next step is to fixe up the integer k and determines the linear independent coefficients, C_1, C_2, C_k, using a convenient fit method.

The functions F and $\tilde{F}$ behave similarly when x goes to one or infinity. $x=1$, $f(1,n)=1$ and respectively, when $x\to\infty$, $\lim x\to\infty f(x,n)=0$.

The partition function (A2) may be approximated by the function:

$$\tilde{Z}(x,N)=\sum_{n=0}^{N}x^{\frac{(N-n)^2}{2N+1}}=x^{N^2/2N+1}\tilde{F}(x,N) \tag{A8}$$

which gives internal energies:

$$\begin{aligned}\tilde{U}(x,N)=&-\frac{\hbar\omega}{2}\frac{N^2}{N+1}-\\&-\hbar\omega x\frac{\partial f(x,N)}{\partial x}e^{\nu f(x,N)}\end{aligned} \tag{A9}$$

with simple algebraic structures, suitable for calculations.

The conclusion is that the above method is suitable for approximating the function F only in the domain of low temperatures, $x>2$. In this domain, relative differences $\delta F=\tilde{F}/F\ 1$ remains smaller than 10^{-2} for $k=2$ or smaller than $1.5\cdot10^{-3}$ if $k=5$.

Approximations for high temperatures

In the domain of high temperatures it is convenient to consider the variable:

$$y=\frac{1}{\ln x}=\frac{k_BT}{\hbar\omega} \tag{A10}$$

and the function $G(y,N)=F(e^y,N)$. This function can be approximated by the new function:

$$\tilde{G}(y,N)=(N+1)\frac{g(y)}{N+g(y)} \tag{A11}$$

where $g(y)$ is a polynomial of the rank K of the form:

$$g(y)=\sum_{i=1}^{i=K}C_iy^i \tag{A12}$$

depending on the fit constants C_1, C_2,.... Then the approximate partition function:

$$\tilde{Z}(y,N)=e^{\frac{1}{y}\frac{N^2}{2N+1}}\tilde{G}(y,N) \tag{A13}$$

produces internal energies that read

$$\tilde{U}(y,N)=-\frac{\hbar\omega}{2}\frac{N^2}{(N+1)}+\frac{\hbar\omega Ny^2}{g(y)[N+g(y)]}\frac{dg(y)}{dy} \tag{A14}$$

As in previous case, the coefficients C_i have to be determined using the method of least-squares for approaching the functions g and $NG/(N+1-G)$.

The concrete examples point out that this method of approximation lead to partition functions very close to the real ones. The errors can be showed considering the function $dG=\tilde{G}/(G-1)$ which has to measure the degree of accuracy.

Thus we can conclude that is enough to consider the case of $K=3$ for obtaining satisfactory approximations of the partition function at high temperatures, $y>2$.

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