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COMPENSATION EFFECT AS A CONSEQUENCE OF VIBRATIONAL ENERGY TRANSFER IN HOMOGENEOUS AND ISOTROPIC HEAT FIELD

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By kinetics of decomposition of solids in both isothermal and non-isothermal conditions, the compensation effect (CE) is rather a rule.

The topic of this work is to suggest an activation mechanism which leads to the dependences similar with CE.

The solid is assimilated to a system of the harmonic oscillator with a Bose–Einstein energy distribution.

Considering an activation process due to a vibrational energy transfer from a homogeneous and isotropic field of thermic oscillators to the solid-state oscillator, the thermodynamic functions are in the relationship

$$\Delta S^{*}=\Delta H^{*}/T_{is}$$

where ΔH^* and ΔS^* are the activation functions and T_{is} is the isokinetic temperature.

Taking into account the definitions of H and S by means of the partition function, the isokinetic temperature is assimilated with the characteristic temperature

$$T=\hbar\theta/k_B$$

An important consequence, a correlation between the isokinetic temperature and the spectroscopic wavenumber of the activated bond, is illustrated by a number of decomposition reactions under non-isothermal conditions.

Keywords: *activation mechanism, compensation effect, isokinetic temperature, vibrational energy*

Introduction

The compensation effect (CE) first observed by heterogeneous catalyzed reactions [1] describes a linear relationship between the activation energy (E) and the logarithm of the pre-exponential factor ($\ln A$) for a set of homologous reactants on the same catalyst or for one reaction occurring on homologous catalysts.

Also in non-isothermal kinetics or reactions in solid-state CE is rather a rule [2–3].

Unfortunately, in both case CE is a source of continuous debates [4–6], the reality of this effect being sometimes questioned. In order to explain the CE, different hypotheses were suggested: a non-uniform energy distribution in solid-state [7], a linear relation between the entropy and enthalpy of activation [8–10], changes in the energy levels of the transition state [11–14] or changes in the concentration of active state *vs.* temperature [15]. All these hypotheses are correct, but in our opinion these cover only peculiar facts of a more complex phenomenon.

The topic of the present paper is to suggest and to discuss an activation mechanism able to justify the CE as a real phenomenon by thermal induced reactions in solids.

Theory

Which expression of CE is appropriate?

A set of $\ln A$ and E pairs shows a CE if

$$\ln A=aE+b \tag{1}$$

with the isokinetic temperature

$$T_{is}=\frac{1}{aR} \tag{2}$$

The same pair $\ln A$ and E allows to calculate the rate constant k_i by means of the Arrhenius equation and from the transition state theory [16] the enthalpy ΔH^* and entropy ΔS^* of the transition state (TS) will be determined by

$$k_i=\frac{k_B T_i}{h}e^{\Delta S^*/R}e^{-\Delta H^*/RT} \tag{3}$$

where k_B and h denote the Boltzmann and Planck constants, respectively.

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With the corresponding pair ΔS^* and ΔH^* the CE is expressed by

$$\Delta S^* = a'\Delta H^* + b' \qquad (4)$$

in which the isokinetic temperature is given by

$$T_{\mathrm{is}} = \frac{1}{a'} \qquad (5)$$

Now a supplementary question appears in the debate on CE: which pair of activation parameters, ln*A* *vs.* *E*, respectively ΔS^* *vs.* ΔH^*, are suitable to lead to a deeper knowledge of the reaction mechanism. Although a relationship according to Eq. (4) was suggested and used as a starting point in some papers [6, 17–19], this one was not justified as a reliable rule by thermodegradative reactions in solid-state.

The differential form of Eq. (4) is equivalent to:

$$\mathrm{d}H = T\mathrm{d}S \qquad (6)$$

which is well-known in thermodynamic.

This relation between entropy and enthalpy can be justified theoretically, in comparison with the more empirical Eq. (1). This means that Eq. (4) showed be favored to the detriment of Eq. (1).

Activation mechanism

- In order to describe reactions in solid-state, only the vibrational levels are significant.
- The decomposition starts by breaking of a certain bond of the molecular structure. This breaking is due to a selective vibrational energy accumulation from a homogeny and isotropic heat field to the molecular structure in solid-state.

The solid is assimilated to a system of harmonic oscillators with a Bose–Einstein energy distribution. In almost all practical situations the particle density is enough low and the temperature is so high that

$$\frac{N}{V} << (2\pi m k_{\mathrm{B}} T/h^2)^{3/2} \qquad (7)$$

in which case the Bose–Einstein statistics leads to the classical Boltzmann statistics [20]. In addition, if the number of particles, *N*, is fixed (a reasonable hypothesis by activation of solid-state), the canonical distribution has to be used [21] with the free energy *F* as potential. More exactly

$$F = -k_{\mathrm{B}} T \ln Z_{\mathrm{v}} \qquad (8)$$

where the vibrational partition function is

$$Z_{\mathrm{v}} = (1 - \mathrm{e}^{-\hbar\omega/k_{\mathrm{B}}T})^{-1} \qquad (9)$$

where ω denots its frequency and $\hbar = h/2\pi$.

At constant volume and pressure (also a reasonable hypothesis), the free energy can be expressed by

$$F = H - TS \qquad (10)$$

where *H* and *S* are the enthalpy and entropy, respectively.

Signification of isokinetic temperature

According to the above discussions, the thermodynamic functions provided by the vibrational partition function, i.e. the enthalpy, is given by [22].

$$H = k_{\mathrm{B}} T^2 \frac{\partial \ln Z_{\mathrm{v}}}{\partial T} \qquad (11)$$

so that the entropy becomes

$$S = k_{\mathrm{B}} \left[\ln Z_{\mathrm{v}} + T \frac{\partial \ln Z_{\mathrm{v}}}{\partial T} \right] \qquad (12)$$

in accord with Eqs (8), (10) and (11).

One realizes that, Eq. (9) become

$$Z_{\mathrm{v}} = \frac{k_{\mathrm{B}} T}{\hbar\omega} \qquad (13)$$

for large *T*-values. Accordingly, these is

$$\frac{\partial \ln Z_{\mathrm{v}}}{\partial T} = \frac{1}{T} \qquad (14)$$

Introducing Eqs (13) and (14) in Eqs (11) and (12), one sees that Eq. (6) leads to

$$T = \frac{\hbar\omega}{k_{\mathrm{B}}} = \frac{hc}{k_{\mathrm{B}}} \bar{\nu} \qquad (15)$$

where *c* is the light velocity and $\bar{\nu}$ is the wave number.

Remembering that the isokinetic temperature is the temperature at which all the (decomposition) reaction of similar solids would have the same rate constant and that, according to the second hypothesis, the same bond would be activated/broken, it means that the isokinetic temperature can be assimilated with the characteristic temperature of the activated vibration.

Peculiarities of thermal decompositions under non-isothermal conditions

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

$$T = T(t) \qquad (16)$$

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

$$\varepsilon_{\mathrm{B}} = k_{\mathrm{B}} T \qquad (17)$$

This energy would be transferred to a certain bond of the solid-state if this will be assimilated to an anharmonic oscillator:

$$U_{\mathrm{M}} = 1/2k(r - r_0)^2 + 1/2f(r - r_0)^3 \qquad (18)$$

where r_0 is the equilibrium distance in the fundamental state.

One would than obtain

$$(r_0' - r) = f\frac{U_\mathrm{M}}{k^2} \tag{19}$$

where f is the anharmonicity constant and k is the quasielastic force constant.

Equation (19) justify the condition of Eq. (6). Indeed, breaking means that $(r_0 - r)$ is a maximum, i.e. $\mathrm{d}U_\mathrm{M}=0$ at constant volume and pressure. This is equivalent to $\mathrm{d}F=0$ and so Eq. (10) leads to Eq. (6).

On the other hand, the internal energy say $\tilde{U}_\mathrm{M}$ is quantified by the vibration number v. Expressing Eq. (19) in spectral terms via $G=\tilde{U}_\mathrm{M}\hbar c$ [23], one obtains

$$G_\mathrm{M}(v) = \bar{\nu}\nu - xv^2 \tag{20}$$

Equation (20) is another expression for the correlation between the vibrational characteristics of the activated bond and the thermally induced energetics of that bond. Indeed, with Eqs (15)–(19) the dependences

$$T \to \varepsilon_\mathrm{B} \to U_\mathrm{B} = \varepsilon_\mathrm{B} N \to \bar{\nu} \tag{21}$$

where N is the Avogadro's number, is evidenced.

Therefore a correspondence between a kinetic parameter like the isokinetic temperature, T_is, and a calculated vibrational parameter is possible. With $\bar{\nu}$ in cm^{-1} and T in K, the calculated wavenumber from kinetic data is

$$\bar{\nu}_\mathrm{calc} = \frac{k_\mathrm{B}}{hc}T_\mathrm{is} = 0.695T_\mathrm{is} \tag{22}$$

Because the breaking bond has an anharmonic behavior, the specific activation is possible due to more than one quantum (or by a higher harmonic), i.e.

$$\bar{\nu}_\mathrm{sp} = n\bar{\nu}_\mathrm{calc},\ n\in \mathrm{N} \tag{23}$$

where $\bar{\nu}_\mathrm{sp}$ is the assigned spectroscopic wavenumber for the activated/broken bond.

Under non-isothermal conditions, with the increasing of temperature, two simultaneous processes take place:

- increases of the number n_i of the excited bonds corresponding to T_i equivalent with $\bar{\nu}_\mathrm{i}$:

$$n_\mathrm{i} = 1.44T/T_\mathrm{i},\ T>T_\mathrm{i} \tag{24}$$

This accounts for the temperature dependence of reaction rate.

- the activation of another bond with ν_f, corresponding to $T_\mathrm{f}>T_\mathrm{i}$.

If the values of the two specific wavenumber, ν_i and ν_f respectively, are too near and/or the heating rate is too high, those two activation processes should be superposed and the correspondence $T_\mathrm{is} \to \bar{\nu}_\mathrm{calc} \to \bar{\nu}_\mathrm{sp}$ should be distorted.

Results and discussion

Some examples of the data processing according to Eqs (21) and (22) are systematized in Table 1.

Example no. 1 is related to dehydration of metal-carboxyl crystal-hydrates $\mathrm{M(RCOO)_n{\cdot}}x\mathrm{H_2O}$, where M is one of Mn, Co, Ni, Cu, Zn, Cd, La, Eu, Sm and R is $\mathrm{H^-}$, $\mathrm{CH_3^-}$ or $\mathrm{C_2H_5^-}$. In the TG/DTG diagrams, the first mass loss step is assigned to the loss of crystallization water [18]. By plotting ΔS^* *vs.* ΔH^* for each series of carboxylates, the isokinetic temperature (Eq. (5)) was determined.

The series of formats and acetates exhibit rather the same value of T, which is significantly different from that for propionates. But taking into account the activation mechanism presented above and according to Eq. (23), there are good agreements with the IR range active by OH or water.

Example no. 2 is related to the second step in decomposition of the mentioned salts, i.e. the decomposition of the anhydrous carboxylates. According to the above presented mechanism, it is reasonable to assume that the destruction of the molecular architecture is due to the selective energy absorption by the carboxylate group. Again very close values for the isokinetic temperatures corresponding to formates and acetates. Noticeable are also the low values of n (Eq. (23)). This means a rather high efficiency of the vibrational energy accumulation.

In examples no. 3–7 also a very good agreement between the wavenumber calculated from the isokinetic temperature and the corresponding wavenumber accepted in IR spectroscopy was observed for the bonds suggested to be broken. So it is possible to analyze the thermal 'sensitive' part of a molecule.

By examples no. 4–6, the sensitive part is the carboxylic group.

Conclusions

- By the thermal decomposition of solid compounds, the activated state is attained by exciting only the vibration level.
- The use of the thermodynamic function ΔH^* and ΔS^* of the activated complex allows a reasonable understanding of the decomposition mechanism and the identification of the group responsible for the molecule destruction.
- This kind of data processing allows a less speculative interpretation of the kinetic data. Obviously, the difference between the exactness of the spectro-

Table 1 Correspondence between T_{is} and $\bar{\nu}_{sp}$ for some reactions under non-isothermal conditions

Ex. no.	Reaction	Compounds	T_{is}/K	ω_{calc}/cm^{-1}	Ascrib. value *n*	Concl. $n\omega_{calc}$/cm^{-1}	Assignment [24, 25] for ω_{sp}/cm^{-1}
1 [18]	Dehydration	formates acetates propionates (of d and f metals)	308 315 528	214 219 367	16 16 9	3424 3504 3303	water loss 3400–3500
2 [19]	Decomp. of anhydrous salts	formates acetates propionates butyrates (of d and f metals)	479 463 511 716	333 322 355 498	4, 5 4,5 4 3	1332, 1665 1288, 1610 1420 1494	absorption by carboxylate group 1330–1440(ν_s) 1550–1650(ν_{as})
3 [26]	Decomp.	$Na_2S_2O_5$ $K_2S_2O_5$	286 415	200 288	5 3	1000 866	absorption by bi-sulphite anion 900–1000
4 [26]		$Na(CH_3COO)$ $K(CH_3COO)$	286 625	200 434	7 3	1400 1303	ν_s(C=O) by carboxyl anions 1330–1440
5 [26]		glutamic acid	372	258	10	2580	O–H in carboxyl group
6 [26]		citric acid	379	263	6 7 12	1580 1844 3424	ν(C=O) by sat. carbox. ac. 1700 OH in carboxylic group 3500–3550
7 [26]		nifedipine	491	341	4 5	1364 1705	Ester of arom. acids 1250–1300 C=C and C–H stretch 1580–1650 ν_s(C–CH_3) 1370–1385 ν_{as}(C–CH_3)) 1435–1470

scopic, respectively kinetic data, must be taken into account.

- It is possible to analyze the thermal 'sensitive' part of a molecule, by means of an adequate processing of the thermogravimetric data in connection with the IR spectra.

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