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ON THE POSSIBILITIES OF THEORETICAL ANALYSIS OF KINETICS OF THE THERMAL DECOMPOSITION OF SOLIDS

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Abstract

The main reasons for changes in the environment surrounding us are discussed on the basis of thermodynamics of irreversible processes. Subsequently, relations between thermodynamics of irreversible processes and chemical kinetics are shown, then the possibilities of theoretical determination of rate constants on the framework of the modified RRKM theory are presented. These latter considerations are supplemented by a discussion concerning the possibilities of determining the activation barriers and structural changes (necessary to account for entropy changes upon reaction) in molecules kept on the surface of crystalline phases by combination of quantum chemistry methods for isolated molecules with those reflecting the influence of the environment (i.e. interaction within the lattice). Finally, the future of theoretical methods in examining the reactivity of solid state systems is briefly discussed.

Keywords: kinetics, solid-state systems, theory

General problems

Objects of studies

The objects of our common interest are artificial or natural products of applicative or scientific importance. From the chemical point of view each object is a collection of atoms formed as the result of their natural affinity to interact. On the basis of thermodynamics, this tendency to interaction is expressed by changes in energy (*E*) (enthalpy, *H*) or free energy (*F*) (enthalpy, *G*) accompanying the formation of objects from atoms, considering the latter as a reference state. As the above-mentioned thermochemical quantities (functions of state) depend on coordinates of all atoms, changes of these can be represented, in general, in multidimensional space. Schematically, however, changes in values of functions of state (e.g. energy) can be presented as demonstrated in Fig. 1. The region outside the closed area represents free atoms to which certain values of energy are imparted. If atoms are brought closer, attractive interactions occur

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which become the driving force for the formation of various molecular systems (objects in the afore-mentioned meaning). Such systems correspond to certain states characterized by the minima on an energy surface. However, too close

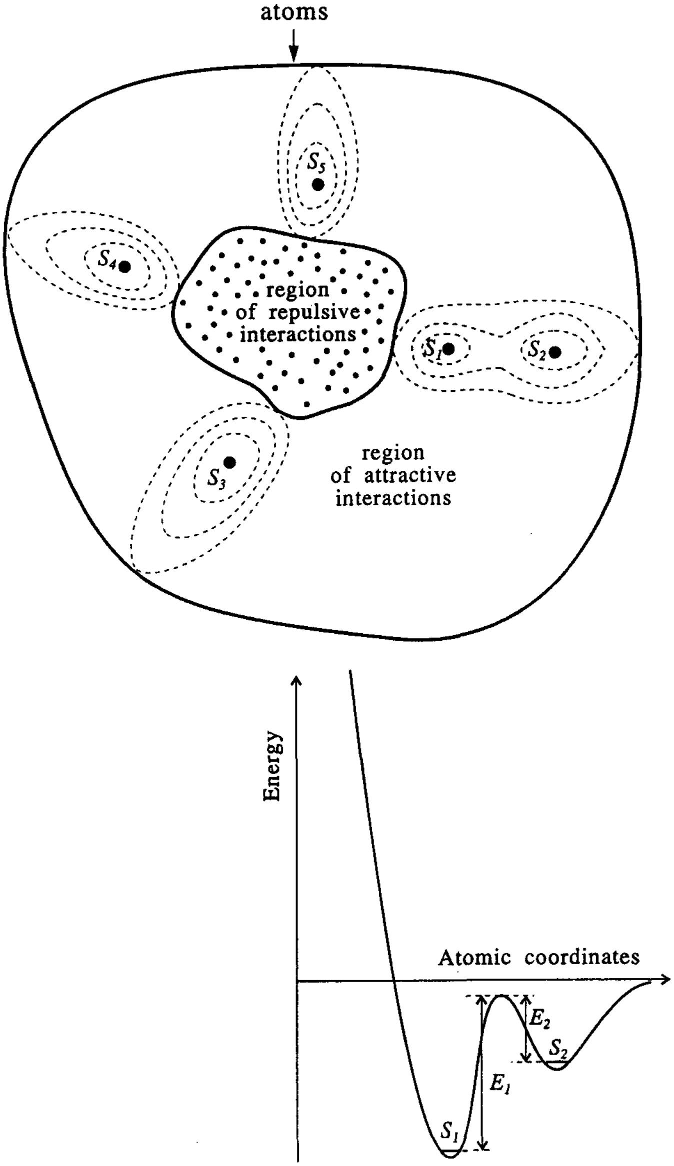

Fig. 1 Schematic representation of energy of molecular system *vs.* atomic coordinates: downward projection - upper graph and S_1–S_2 cross-section-lower graph. $S_1 \cdots S_5$ represent stationary states (energy minima) of a given collection of atoms, E_1 -energy barrier for passage $S_1 \rightarrow S_2$ and E_2 –energy barrier for passage $S_2 \rightarrow S_1$

proximity of atoms causes strong repulsive interactions (reflected by the inner area in Fig. 1) which arise from the deformation of their outer electron shells. A similar picture to that exhibited in Fig. 1 would be obtained if entropy changes were included, i.e. when considering free energy changes versus atomic coordinates. The aim of our activity is to describe possible states of the system and to reveal direction of changes upon its transformation from one state to another, which can be achieved on the basis of thermodynamics of reversible processes, as well as to determine how fast systems pass from one state to another, which is the domain of thermodynamics of irreversible processes.

Place of chemical kinetics in the thermodynamics of irreversible processes

The world surrounding us undergoes continuous changes which can be described on the basis of thermodynamics. In thermodynamics two categories of processes are considered: reversible and irreversible. Reversible processes, mainly of theoretical importance, are such upon which surroundings and the system continuously adjust each other. In consequence, exchange of energy and entropy only, take place. The attribute of such processes is the infinite time of their realization. Upon irreversible processes, occurring in finite times, energy is exchanged between the system and surroundings according to the energy conservation rule, while entropy exchange is not balanced, i. e. the sum of entropy of the system and surroundings increases. Therefore, entropy is created during the course of irreversible processes and this forms a foundation on which thermodynamics of irreversible processes is based. These describe passages of the system between various states occurring in finite time. Only such processes really take place in the world surrounding us and only insight into their nature enables understanding of everything happening around us.

The thermodynamics of irreversible processes is based on the assumption that thermodynamic fluxes (e. g. chemical reaction, heat or mass fluxes) occur as the consequence of the existence of relevant thermodynamic driving forces (e. g. chemical potential, temperature or concentration gradients). In the simplest development of this method each thermodynamic flux is a linear function of all gradients appearing in the system. If the gradient of the chemical potential is the only one which occurs, or fluxes caused by gradients other than chemical potential are much faster than the flux of chemical reaction, then the problem reduces to consideration of the latter flux. Such cases are the subject of interest of chemical kinetics. In the latter method changes in the system are related to the volume (or initial amount of reactants), at constant temperature, and the flux of chemical reaction, named rate of reaction, determines changes in concentration (c) (or extent of reaction (α)) in time (t), i. e. $\mathrm{d}c/\mathrm{d}t$ ($\mathrm{d}\alpha/\mathrm{d}t$). Thermo-

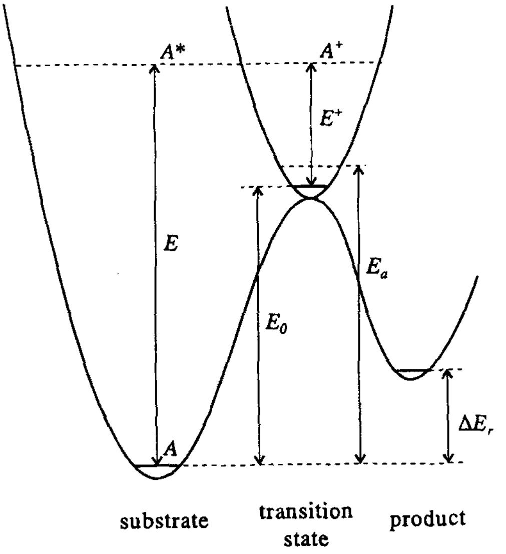

Fig. 2 Diagram illustrating energies considered in the unimolecular reaction rate theory (E, E_0 and E^+), Arrhenius activation energy (E_a) and energy change for reaction (ΔE_r)

dynamic driving force causing this flux is defined by the equation: $1 - K/K_a$, where K and K_a are products of activities of reactants raised to powers equal to stoichiometric coefficients (positive for products and negative for substrates) at a certain stage of reaction (K) or in an equilibrium (K_a). In the simplest description of time dependencies of chemical changes, the flux (rate of reaction) and driving force are assumed to be linearly dependent, which is revealed in the general kinetic equation [1]

$$dc/dt\ (d\alpha/dt) = kf(c)\ (f(\alpha))\ (1-K/K_a) \tag{1}$$

where $f(c)$ ($f(\alpha)$) is a function reflecting the mechanism (kinetic model) of the reaction and k the rate constant. The equation admits a simpler form if the process proceeds far from the equilibrium state. Then the term ($1-K/K_a$) equals 1 and the problem boils down to the determination of rate constant for the most probable reaction mechanism [1, 2].

Rate constant determination

In the phenomenological description of reaction kinetics the models reflecting reaction mechanisms are represented by relatively simple functions of c (or α) [3–9]. To reveal these models experimental $c(\alpha)$ *vs.* t dependencies are approximated by various possible mathematical functions and the one fitting best is believed to reflect the mechanism for the process. To each mathematical function a certain value of a rate constant is imparted at constant temperature (T). Temperature, therefore, influences rate constant $k(T)$, which in the simplest way expresses the Arrhenius equation [10]

$$k(T) = B\ \exp(-E_a/RT) \tag{2}$$

in which B is the constant (named sometimes the frequency factor) and E_a–kinetic energy barrier for the process (named activation energy) (Fig. 2). B and E_a can be obtained knowing rate constants in several temperatures.

The above presented phenomenological approach enables to reveal rate constants, when changes in the system are determined experimentally. From the beginning of development of chemical kinetics, efforts directed towards the discovery of methods affording theoretical evaluation of rate constants were undertaken however. The most advanced of these is the RRKM theory [11] which, unfortunately, applies only to unimolecular processes in the gaseous systems. Here we show how the RRKM method can be modified so as to apply to reactions proceeding on the surface of the crystalline phase. The basic concept of this theory is expressed by Eqs (3)–(5)

$$A + M \underset{k_d}{\overset{k_a}{\rightleftarrows}} A^* + M \tag{3}$$

$$A^* \rightleftarrows A^+ \tag{4}$$

$$A^+ \xrightarrow{k(E)} \text{products} \tag{5}$$

A represents a molecule on the surface of the crystal which upon collision with any molecule from the gaseous phase (M) may become energized (A^*) (an energized molecule is one, the energy of which exceeds the activation barrier for the process). This theory, therefore, assumes that energy necessary to commence chemical changes is provided to the system upon collisions. This remains in accord with the commonly recognized mechanism of the heat transfer. In Eqs (3) and (4) k_a and k_d denote energization and deenergization rate constants, respectively. An energized molecule, which retains the structure of a parent molecule, undergoes internal transformation towards activated molecule (A^+), of structure relevant to the transition state, until equilibrium between both species is reached. Finally, the activated molecule decomposes with a rate, reflected by $k(E)$, dependent on the excess of energy above the activation barrier. Assuming that the existence of processes (3) and (5) creates a stationary state in the kinetic sense

$$k_a\ [n(A)]\ [n(M)] = k_d\ [n(A^*)]\ [n(M)] + k(E)\ [n(A^+)] \tag{6}$$

(where n is the number of molecules of species indicated in parentheses and square brackets denote concentrations) and that equilibrium between A^* and A^+ is achieved

$$K^+ = [n(A^+)]/[n(A^*)] \tag{7}$$

one obtains expression for the rate constant ($k(T, P, S)$–T, P, S indicate that rate constant depends on temperature, pressure of M and surface area of the solid phase, respectively)

$$k(T,\ P,\ S) = \frac{K^+k(E)(k_a/k_d)}{1 + K^+k(E)/k_d\ [n(M)]} \tag{8}$$

remembering that the basic equation for the unimolecular decomposition is as follows

$$-\frac{\mathrm{d}[n(A)]}{\mathrm{d}t} = k(E)\ [n(A^+)] = k(T,\ P,\ S)\ [n(A)] \tag{9}$$

From the statistical thermodynamics it results that the equilibrium constant can be expressed as

$$K = \frac{Q_{A^+}\ q_{A^+}}{Q_{A^*}} \cdot \mathrm{e}^{-\Delta \mathrm{E}_0/\mathrm{RT}} \tag{10}$$

where $Q_{A^+}\ q_{A^+}$ is the partition function of activated molecule (q_{A^+}-partition function for critical vibration) and Q_{A^+}-partition function of energized (original) molecule, while ΔE_0 denotes energy difference between molecules remaining in equilibrium. As we are dealing with the same molecule existing in different structures, thus $\Delta E_0 = 0$. Furthermore, partition functions can be replaced by numbers (sums) of energy states ($N(A^+)$ and $N(A^*)$ for activated and energized molecules, respectively, and $p(A^+)$ for critical vibration) in the narrow energy range (ΔE^+)

$$K = \frac{N(A^+)p(A^+)}{N(A^*)} \tag{11}$$

$k(E)$ can be estimated from the Heisenberg uncertainty principle, which says that the lifetime of the molecule (given by $1/k(E)\times$ uncertainty of energy $(\Delta E^+/p(A^+)) \geq h$ (Planck constant). In the boundary case therefore

$$k(E) = \frac{\Delta E^{+}}{hp(A^{+})}\frac{L^{+}}{N_0} \tag{12}$$

where N_0 is the Avogadro number (introduced in order to refer $k(E)$ to 1 mol of substance) and L^{+} -reaction path degeneracy (i. e. statistical factor representing the number of routes of reactions leading to the same products). The ratio k_a/k_d reflects the energy distribution function, namely

$$\frac{k_a}{k_d} = \frac{N(A^{*})\cdot e^{-E/RT}}{Q_A} = \frac{\text{numberof molecules of energy } E}{\text{total numberof molecules}} \tag{13}$$

The rate constant for the energization can be expressed as

$$k_a = \frac{C_{AM}}{[n\,(M)]}\cdot e^{-E_0/RT} \tag{14}$$

where E_0 is the critical energy barrier for the decomposition process (Fig. 2) and C_{AM} the frequency of collisions with surface

$$C_{AM} = \frac{SP(M)N_0}{(2\pi M_s\, RT)^{1/2}} \tag{15}$$

(where S denotes surface are, $P(M)$–pressure of M and M_S –molar mass of M). Finally, the combination of Eqs (13) and (14) gives

$$\frac{1}{k_d\,[n(M)]} = \frac{N(A^{*})\cdot e^{-E^{*}/RT}}{Q_A}\cdot\frac{1}{C_{AM}} \tag{16}$$

where E^{+} is the excess of energy over the critical energy of molecule ($E=E_0+E^{+}$; Fig. 2).

Substituting expressions for K, $k(E)$, k_a/k_d and $1/k_d\,[n(M)]$ to the equation for $k(T, P, S)$ one obtains

$$k(T,P,S) = \frac{L^{+}}{N_0hQ_A}\cdot e^{-E_0/RT}\;\frac{\int_{E_0}^{\infty} N(A^{+})\cdot e^{-E^{+}/RT}\,dE^{+}}{1 + \frac{L^{+}}{N_0hQ_A}\cdot\frac{1}{C_{AM}}\int_{E_0}^{\infty} N(A^{+})\cdot e^{-E^{+}/RT}\,dE^{+}} \tag{17}$$

Expression (17) accounts for both energy and entropy changes upon reaction. Energy changes are included in exponential terms, while entropy changes can be identified with Q_A, $N(A^{+})$ and L^{+}. The term C_{AM} reflects the way of providing energy to the system.

According to Eq.(17) the rate constant for decomposition of molecules on the surface of the crystal should depend not only on temperature, as Arrhenius equation predicts [10], but also on pressure of the surrounding gaseous phase and surface of the solid phase. The rate constant will decrease drastically when P or S become small. On the other hand, if P or $S \rightarrow \infty$, denominator in Eq. (17) → 1, and the rate constant reaches high pressure or surface limit [11]. Such a rate constant becomes dependent only on temperature and can be identified, in certain conditions, with the phenomenological rate constant.

Methods of disclosure the mechanism of reaction

In the phenomenological description of reaction kinetics the function $f(c)$ (Eq. (1)) reflects the so-called mechanism of reaction. In simple cases $f(c)$ equals c or c^2 and this is identified with unimolecular or bimolecular elementary processes [7]. Often, however, functions which fit experimental $c = f(t, T)$ (or $\alpha = f(t,T)$ dependencies are more complex, which makes it impossible to reveal the mechanism. Moreover, what we measure may be the result of a superposition of numerous elementary processes proceeding in consecutive or parallel sequence. This creates the need for the use of theoretical methods in search of a reaction mechanism. There are many examples of successful application of quantum chemistry methods to examine the mechanism of unimolecular decomposition or transformation of isolated molecules [12–14]. Such an approach permits determination of structure and energies of molecules in equilibrium and transition states (saddle points), thus enabling evaluation of the critical energy for the process (E_0 in Eq. (17)). Furthermore, vibrational frequencies and rotational constants can be predicted, which are subsequently used for determination of values of other quantities necessary for theoretical determination of rate constants [11, 15].

The situation with which we are dealing in condensed phases is quite different from that in a gaseous phase since intermolecular interactions come to light. The magnitude of these interactions is relatively easily to evaluate in the case of crystalline substances which attain perfect constitution [15]. Such systems seem, therefore, to be convenient models for commencing theoretical studies on the mechanism and kinetics of decomposition of solids. Between crystalline phases a large group are ionic substances to which numerous inorganic solids belong. Ionic systems are the most convenient for studies since intermolecular interactions in these (reflected in the lattice energy) are determined by the electrostatic interactions of charged centres (ions) which are well approximated by the Coulomb interactions of point charges (Madelung energy) [15]. Information regarding the mechanism of chemical processes occurring on the surface of an ionic crystal can be obtained extending the transition–state–theory–type approach, commonly applied to reactions in the gaseous phase, in such a way as to include the influence of surroundings. This can be done supplementing total energy (Hamilton) operator (H) in the Schrödinger equation [7]

$$\hat{H}\Psi = \varepsilon\Psi \tag{18}$$

(where Ψ is the wavefunction of the molecule A and ε-total energy relevant to Ψ) with extra term ($E_{\mathrm{p(solid\ phase)}}$), associated with the electron or nucleus-neighbouring ions interactions

$$\hat{H} = -(h/(2\pi))^2(\Sigma_\mathrm{i}(1/(2m))\nabla_\mathrm{i}^2 + \Sigma_\mathrm{j}(1/2M_\mathrm{N}))\nabla_\mathrm{j}^2\ ) + E_\mathrm{p} + E_{\mathrm{p(solid\ phase)}} \tag{19}$$

(where m and M_N are the masses of electron and nucleus, respectively, while ∇^2 denotes Laplace operator expressed by $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$), E_p is the potential energy term resulting from electrostatic interactions of charged particles insight the molecule and $E_{\mathrm{p(solid\ phase)}}$–the potential energy arising from electrostatic interactions of all particles forming molecule with neighbouring ions, represented by point charges on atoms. In general, $E_{\mathrm{p(solid\ phase)}}$ can be expressed as

$$E_{\mathrm{p(solid\ phase)}} = \frac{1}{4\pi\varepsilon_0}\left(-\frac{1}{2}\Sigma_\mathrm{i}\ \Sigma_\mathrm{k}\ \frac{Z_\mathrm{k}e^2}{r_\mathrm{ik}} + \frac{1}{2}\ \Sigma_\mathrm{j}\ \Sigma_\mathrm{k}\ \frac{Z_\mathrm{j}\,Z_\mathrm{k}\ e^2}{r_\mathrm{jk}}\right) \tag{20}$$

where ε_0 is the permittivity of free space, Z denotes relative charge, r-distance and i, j, k indicate electron in the molecule A, nucleus in the molecule A and charge in the surroundings, respectively. Since the charged centres in the lattice are located periodically, the summations in Eq. (2) present series which always converge poorly [15]. This may necessitate some simplifications. One such possibility creates the Evjen method [16, 17]. In this approach only point charges, from the nearest neighbourhood of the reacting molecule are considered. These charges are however chosen such as to reflect the interactions of the reactive unit with the whole lattice. The advantage of the use of the Evjen method is that the calculations remain, in practice, on the quantum chemistry level. Such an approach permits the use of standard quantum mechanical methodologies (like SCF or MCSCF) to determine stationary points (minima and saddle points) on the potential energy surface of the reacting species [12–14]. Such an approach would therefore enable critical energy for the reaction to be revealed and the extraction of other data necessary to determine rate constant according to Eq.(17). The subsequent use of Eq. (9) would create a direct possibility of determining macroscopic changes in the system.

Importance of theoretical methods in examination of reactivity of solids

Numerous attempts have been undertaken in the past to develop methods which would enable description of kinetics of thermal processes involving solids [1, 3, 4, 6, 8, 9]. Commonly applied phenomenological approach based on Eq. (1) and Arrhenius type dependency (Eq. (2), being actually the extension of one developed for reactions in the gaseous phase, is not able to provide any information on changes in the system on the molecular level, although it is very valuable if one intends to approximate experimental data with simple mathematical functions. Widely used functions for the description of so-called reaction mechanisms in the solid phase, actually reflect only physical processes (e. g. nucleation, crystallization, diffusion or changes in surface area) [3–6, 8, 9] and do not take into account the chemical nature of these. The approach presented here emphasizes the importance of chemical changes in solid state processes and affords an insight into transformations of the system on the molecular level. Actually, only these latter changes truly account for what we observe in a bulk phase.

The new approach presented here is now verified for examining thermal decomposition of calcium oxalate monohydrate and chloride salts of mononitrogen organic bases. The aim of these efforts is to predict theoretically thermoanalytical curves and to compare them with experimental ones. Preliminary results seem to indicate that conformity is satisfactory. This would mean that completely new possibilities would appear for studying the properties, behaviour and reactivity of ordered solid phase systems.

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Zusammenfassung — Auf der Basis der Thermodynamik irreversibler Prozesse werden die Gründe für die Veränderung der uns umgebenden Umwelt besprochen. Anschließend werden Beziehungen zwischen der Thermodynamik und der Kinetik sowie die Möglichkeiten zur theoretischen Bestimmung von Geschwindigkeitskonstanten an der grundlegenden Struktur der modifizierten RRKM-Theorie gezeigt. Letztere Betrachtungen werden durch eine Diskussion bezüglich der Möglichkeiten zur Bestimmung der Aktivierungshürden und der Strukturveränderungen (erforderlich zur Deutung der Entropieänderungen während der Reaktion) in Molekülen ergänzt, die an der Oberfläche kristalliner Phasen festgehalten werden, wobei eine Kombination von quantenchemischen Methoden für isolierte Moleküle mit solchen angewendet wird, die den Einfluß der Umwelt widerspiegeln (z.B. Wechselwirkungen mit dem Gitter). Abschließend wird kurz die Zukunft von theoretischen Methoden bei der Untersuchung der Reaktivität von Feststoffsystemen diskutiert.