Special Review

TOPOCHEMICAL REACTIONS.
PARTICULARITIES OF THEIR MECHANISM AND OUTLOOK
ON THEIR RESEARCH, PART I.*

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A survey of topochemical reactions is given and the theory of their kinetics is discussed.

Kinetic analysis of solid-state reactions utilizing non-isothermal data obtained by DTA, TG, DSC and other methods is receiving increasing attention [1]. This interest is based above all on the widespread view that non-isothermal methods lead to the acquisition of information on the main kinetic parameters much more rapidly than by using isothermal methods.

In many cases this view may have a sound foundation. Nevertheless, the basic assumption used to derive the equations of non-isothermal kinetics for solid-state reactions, namely the approximation of the solid-state reaction kinetics by the simple mathematical function $(1 - \alpha)^n$ or α^n is far from being always justifiable. It therefore appears that the application of the great number of rapid non-isothermal methods must be considered in many cases as an oversimplification in this research field.

This is particularly the case with topochemical reactions that proceed by means of nucleus formation and growth [2−5]. An exact kinetic description of such processes is a most intricate problem, even under isothermal conditions [9]. Their approximation by means of simple empirical functions may lead to serious errors in the calculated kinetic parameters. It is therefore of great importance and very timely to investigate such processes by taking into account their topochemical nature.

The objective of the present paper is to give a short introduction to the theory of topochemical processes. It is well known that many solid-state reactions do not take place over the total volume (or total surface) of the solid, but are localized at distinct sites in the crystal. In accordance with this characteristic feature, such reactions are designated "topochemical" reaction [6].

The localization of topochemical reactions is manifested by their starting from distinct sites where the reactivity is highest. These sites are termed the "potential centres" of the reaction. After the reaction has started at a definite site, it con-

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tinues to extend from this site to neighbouring parts of the crystal. This phenom-
enon is termed the autolocalization of the process.

Owing to this particular feature of topochemical reactions, in their kinetic
analysis it appears indispensable to consider not only the time relationship, as is
normally done in chemical kinetics, but also the spatial relationship. This, of
course, makes the problem much more difficult.

In the case of reactions taking place in liquids and gases, the rate of reaction is
a function of the reactant concentrations:

$$\frac{dn}{dt} = k(n_a, n_b, \ldots)$$

For heterogeneous reactions proceeding on the surface (e.g. catalytic reactions),
the rate of reaction is proportional to the concentrations of the reactants and to
the surface area S_R on which the reaction takes place, this area remaining con-
stant throughout the reaction:

$$\frac{dn}{dt} = k(n_a, n_b, \ldots) S_R$$

In contrast, in topochemical reactions the rate of reaction is proportional,
in addition to the concentrations of the reactants, to the surface (or layer) area in
which the reaction is localized (usually termed the reaction zone), this area chang-
ing in the course of the process [7−9]:

$$\frac{dn}{dt} = k(n_a, n_b, \ldots) q(s)$$

In the general case, the value of the reaction zone $q(s)$ at a given moment t
may be estimated by means of the number of potential centres of the reaction
where the reaction had started at $t = y$, and the growth of the nuclei thus formed
during the interval $(y - t)$.

In the general form:

$$q(s) = M \int_0^t v(t, y) \left[\left(\frac{dN}{dt} \right)_{t=y} \right] dy$$

where M is the shape factor allowing transformation from the volume of the prod-
uct nuclei to the value of the reaction zone, $v(t, y)$ is a function describing the
growth of the nuclei, and $\left(\frac{dN}{dt} \right)_{t=y}$ is the rate of nucleus formation in the potential
centres.

Two different approaches exist to the study of the kinetics of topochemical
reactions. One can derive equations describing the development of the reaction
zone with time and leading to the values of the specific rates of reaction, this being
indispensable to bring experimental data on topochemical reactions into confor-

mity with the notions of common chemical kinetics. This branch of kinetics has even received a special name "topokinetics".

Another aim in the study of the kinetics of topochemical reactions is to throw light on the physical-chemical causes that lead to the localization and autolocalization of the process. In other words, attempts are made to explain why and where the topochemical reaction starts in the crystal, why in some processes nucleus formation dominates, while in other processes nucleus growth plays the decisive role, what physical-chemical causes will lead to the autolocalization of the process etc.
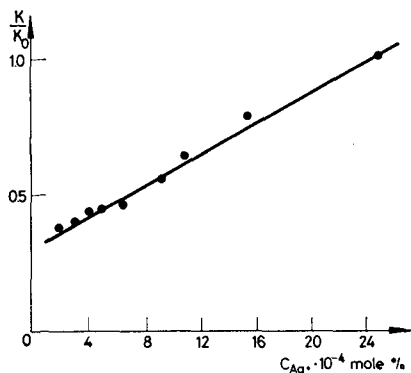

Fig. 1. Rate of reaction vs. concentration of interstitial silver ions under the decomposition of silver oxalate

As a first approach, the factors affecting the degree and character of localization in topochemical reactions can be arranged into two groups. The first group includes those factors that create potential conditions for the preferential localization of the chemical reaction at a given site in the crystal. These preferential conditions for the start of a topochemical reaction, i.e. increased reactivity, exist in the solid before the actual reaction. The factors belonging to this group will be termed "potential" factors.

The second group consists of those factors that control the change in the degree of localization in the course of the process, i.e. the probability that the process starting at some point of the crystal will continue to develop at this same site or close to it. Let us by agreement term this group of factors "dynamic" factors.

Potential factors determining the unequal reactivities of the different regions in the solid include the presence of defects in the crystals, comprising differences between the surface and bulk properties of the crystal. Other factors belonging in this group are: non-equivalent reactivities at different points of the surface, and effects of crystal defects and lattice defects on the breaking of bonds and on transfer processes in the crystal.

Thus, the problem is reduced to the study of the effect of defects in the crystal on reactivity. Such studies have been made in our laboratory for several years.

Since their results have been published in detail in many papers specifically dealing with this topic [10 – 15], we shall limit their discussion here to the main conclusions drawn from these studies.

We have found that the nature of the effect of defects on the rate of topochemical reactions depends upon the particular features of the reaction mechanism, and have proposed a classification of thermal decomposition reactions into two groups. In reactions belonging to the first group, the breaking of bonds during thermolysis proceeds locally. In reactions belonging to the second group, for the thermolysis to proceed it is necessary that charge be transferred over distances much longer than interatomic distances. We have demonstrated that when the thermal decomposition reaction belongs to the first group, its rate is mainly affected by defects that change the ratio between the surface and the volume of the crystal (changes in crystal habit, presence of various types of surface defects, dislocations and their aggregations). Some examples of this type of dependence: experimental data on the thermal decomposition of pyrite, indicating that the initial rate of reaction is proportional to the external surface of the crystals [16]; results on the acceleration of the dehydration of magnesium sulphate heptahydrate, connected with a change in the habit of the crystals [17]; and experimental results on the effect of dislocations in crystals on the rate of their thermal decomposition [11, 18]. When the thermal decomposition reaction belongs to the second group, i.e. the elementary act of the bond includes charge transfer over a distance much longer than the interatomic distance, lattice defects (foreign ions, ion vacancies, interstitial ions, etc.) begin to exercise the principal effect on the rate of reaction.

This takes place, for example, in the thermal decomposition of silver oxalate, where one of the most important elementary stages is the transfer of intersitial silver ions in the oxalate lattice to the sites where silver nuclei come into existence and grow [19 – 21]. As a result, initialy the rate constant is linearly dependent on the concentration of the interstitial ions (Fig. 1).

Similarly, the initial rate of thermal decomposition of ammonium perchlorate depends on the concentration of point-like defects that may serve as proton donors or acceptors [23 – 26].

The relationships deduced between the nature of the effects produced by defects and the mechanism of the thermal decomposition reactions led to the solution of several important questions in the field of solid-state chemistry.

They gave rise, for instance, to the development of methods for the governed control of the rates of solid-state chemical reactions by using different methods to create exactly those crystal defects to which the reaction in question is most sensitive.

The thermal decomposition of magnesite, for example, proceeds (as for all alkali metal carbonates) by local breaking of the oxygen-carbon bond [27].

According to our classification, therefore, this reaction, belongs to the first group. Hence, if the task is to intensify the thermal decomposition of magnesite, attention should be focused on creating defects in the magnesite crystals during the manufacturing operations, disintegration, etc. In this case it would not serve

the purpose to create lattice defects by doping. On the other hand, in the task of stabilizing silver acetylide, i.e. of reducing the rate of its thermal decomposition, it is indispensable that electrons and interstitial silver ions be transferred over distances much longer than interatomic distances. The main strategy for governed control of thermal stability in this case will therefore consist in changing the concentration of lattice defects in the silver acetylide, e.g. by doping that would change the concentration of interstitial silver ions, or by hetero-phase additives that are electron acceptors or donors [28].
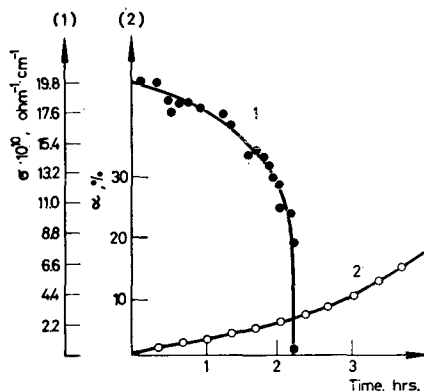

Fig. 2. Change in conductivity of silver oxalate crystals in the course of decomposition.
1 Change in conductivity 2. Change in oxalate conversion

The relationships also allow solution of the reverse problem in order to find out how different defects affect the rate of thermal decomposition and to draw conclusions on the mechanism of some topochemical reaction. This was how we came to the conclusions that the most important stage in the thermal decomposition of silver oxalate is transfer of interstitial silver ions and their incorporation in the growing silver nucleus [20], that the mechanism of the thermal decomposition of alkali metal permanganates includes the transfer of an electron from one permanganate ion to another [22], that the most important stage in the thermal analysis of ammonium salts is proton migration over distances much greater than interatomic distances [23], etc.

Our results, as well as our mode of approach to the study of solid-state chemical processes and to their governed control, have been successfully applied not only in our laboratory, but also in the work of other researchers [9, 29 − 32]. Nevertheless, however fruitful this approach has proved in studies on topochemical reactions and in solving problems of their governed control, more detailed investigations, carried out first in our laboratory and subsequently in other laboratories, have demonstrated the obvious deficiencies of the method. In particular, it was found that by limiting the estimation of reactivity in the crystal solely to the potential conditions of the localization of the process, reliable information is obtained only as regards the initial stage of the reaction.

If we attempt to follow the effect exerted by these factors on later stages of the process, however, substantial errors may arise. The fact is that, in many cases, a reaction starting at a certain site of the crystal may essentially change those properties of the crystal on which the reactivity depends.

Among the many examples that might be cited, let us again turn to the thermal decomposition of silver oxalate. As stated above, the rate of this process is initially proportional to the concentration of interstitial silver ions (Fig. 1).

This relationship, however, does not hold good in the later stages. Fig. 2 shows two curves taken in the course of thermal decomposition [33]. One of the curves corresponds to the change in oxalate conversion (α vs. t), the other to the change in conductivity (σ vs. t). It is a known fact that conductivity in silver oxalate is due to interstitial silver ions. The second curve may therefore be accepted as characterizing the changes in the concentration of interstitial silver ions in the course of the decomposition process.

A comparison of the two curves demonstrates that the conductivity (and consequently the concentration of interstitial silver ions) decreases sharply during the decomposition, but the rate of thermal decomposition continues to increase, owing to the catalytic action of the solid product formed in the initial stage.

In an analogous manner, the external surface of potassium permanganate crystals changes, owing to self-disintegration, during its thermal decomposition, and the correlation between the rate of decomposition and the previous size of the crystals is again limited to the initial stage only [34].

Hence, the reactivity of solids cannot be estimated merely from the potential conditions leading to localization; dynamic factors responsible for the autolocalization of the process must necessarily be taken into consideration too.

How can factors that may be responsible for autolocalization be characterized? The usual means applied in such cases [8, 35] is to use the fundamental concepts of phase transformations for a description of topochemical reactions [36−41].

According to this theory, the appearance of nuclei of the new phase may be regarded as the result of heterophase configurational fluctuations [36−41].

The change in the free energy of formation of the new phase is a result, on the one hand, of the chemical reaction and may be characterized by the product of the number of moles and the difference between the chemical potentials of the starting material and the reaction product. On the other hand, it is a result of the energy of formation of the new interface.

If the system has reached supersaturation (and such systems are considered mainly in the theory of phase transformations), these two terms have opposite signs. Hence, the change in free energy in the course of nucleus growth will pass through an extreme value, after which the nucleus will become stable. If the values of the energy of formation of the critical nucleus and of the energy of activation of the molecular interchange process between the nucleus and the medium are known, the rate equation for nucleus formation can be written in the following form:

$$v = k_1 \, e^{-E/RT} \cdot e^{-A/RT}$$

The dependence of the rate on the values characterizing supersaturated systems can have different forms. For crystallization from the melt, supersaturation may be characterized by the degree of supercooling of the system. Since supercooling is involved in the numerator of the exponent in the second power term, the changes in the first and second factors of the above multiplication product on decrease of will proceed in opposite directions. Hence, an extreme value will appear in the rate of reaction vs. supercooling curve.

After their having reached the critical value, the growth of nuclei is considered in the theory of phase transformations as a process leading to the formation of two-dimensional nuclei on the surface of the growing crystal. The same train of thought described above may be applied for two-dimensional nuclei, with the only differences that (since in this case the growth of nuclei proceeds in two dimensions) the form of the rate equation will be different and the extreme value on the rate vs. supercooling curve will also be situated at a different place. Depending on the degree of supersaturation in the system, therefore, different cases will be met: (i) only nucleus formation occurs in the system, (ii) only nucleus growth proceeds in the system, (iii) both nucleus formation and growth proceed in the system.

For other types of phase transformations, the changes in the two factors of multiplication in the equations describing the formation and growth of nuclei do not necessarily proceed in opposite directions as was found in the case of crystallization from the melt. They may change in the same direction: in this case, no extreme value will appear on the rate vs. supersaturation curve. However, the temperature-dependence of the rate of reaction will be rather complicated in this case too, and will differ from the Arrhenius-type dependence [42].

Hence, if the fundamental assumptions of the theory of phase transformations, developed mainly for kinetics of simple processes like melting, condensation, solidification and crystallization, are compared to the situation arising in topochemical processes, it will be found that the analogy between simple phase transformations and topochemical reactions, if any, is far from always being complete.

In the theory of phase transformations, the central feature has been shown to be the formation of a new phase from an already existing material present in the medium (gas, liquid or solid) surrounding the nucleus, and the process is considered as controlled by this stage.

In the case of topochemical reactions, the rate of reaction is not necessarily controlled by the process of formation of the new phase, but may also be controlled by the decay of the starting solid [42]. In many cases both processes occur simultaneously and are interrelated, thereby making it difficult, or even impossible, to consider topochemical reactions on analogy with condensation, separation or crystallization from the melt.

In addition, another specific feature of solid-state reactions distinguishes them from other phase transformations (e.g. crystallization from a solution or from a melt), namely that the chemical stage (connected with a change in composition) and the phase transformation stage (connected with a change in structure) may be separated both in time and in space. This may be due to purely thermodynamic

factors connected with minimization of free energy. Depending on the temperature and the heat of mixing of the two solid phases in contact [43], this may occur at definite values of the thickness and composition of the layer in which the reaction takes place.

On the other hand, purely kinetic factors may be responsible for the appearance of a transition layer separating the starting material phase from the reaction prod-uct phase. These factors can, for example, be related to the rate of the chemical reaction being higher than the rate of the phase transformation. This is the case, for instance, in processes of dehydration of crystalline hydrates [44 – 46].

Finally, in the course of the solid-state chemical reaction, atoms or ions from the product phase may migrate into the starting material phase [49] or vice versa. This migration can also contribute to the formation of a reaction layer of finite thickness [48, 49] instead of a two-dimensional reaction zone. This three-dimen-sional reaction layer, appearing instead of the two-dimensional boundary surface between the initial phase and the product phase normally postulated in the theory of phase transformations, must necessarily manifest itself both in the localization [48, 49] and autolocalization of solid-state processes and in the quantitative expression describing the rate of solid-state chemical reactions.

The causes leading to autolocalization in topochemical processes therefore require separate discussion.

References

1. V. V. BOLDYREV, Trudy 2-go Vsesoyuznoe soveshchaniya po termografii AN SSSR, Kazansky filial (Proceedings of the 2nd All-Union Conference on thermography, Kazan Department of the Academy of Science of the U.S.S.R.), Kazan, 1961. p. 373.
2. J. R. McCALLUM and J. TANNER, Nature, 225 (1970) 1127.
3. J. M. THOMAS and T. A. CLARKE, J. Chem. Soc. Sect. A. (1968) 457.
4. T. A. CLARKE and J. M. THOMAS, Nature, 219 (1968) 1149.
5. J. SESTAK, Silikaty, 11 (1967) 153.
6. V. KOHLSCHÜTTER, Z. anorg. Chem., 105 (1918) 7.
7. D. YOUNG, Kinetika razlozheniya tverdykh veshchestv (Kinetics of the decomposition of solids, Russian translation), Izd. Mir. Moscow, 1969.
8. P. JACOBS and F. TOMPKINS, Khimiya tverdogo sostoyaniya, pod redaktsiey V. Garnera (Chemistry of the solid state, ed. W. Garner, Russian translation), Izd. Inostrannaya Lit., 1961.
9. B. DELMON, Kinetika geterogennykh reaktsy (Cinétique des réactions hétérogènes, Rus-sian translation), Izd. Mir, Moscow, 1972.
10. V. V. BOLDYREV, Kinetika i kataliz, 1 (1960) 203.
11. V. V. BOLDYREV, Vlianie defektov v kristallakh na skorost termicheskogo razlozheniya tverdykh veshchestv (Effect of crsytal defects on the rate of thermal decomposition of solids), Izd. Tomskogo gosudarstvennogo universitata, Tomsk, 1963.
12. V. V. BOLDYREV, Kinetika i kataliz, 6 (1965) 924.
13. V. V. BOLDYREV, Z. für Chem., 12 (1968) 453.
14. V. V. BOLDYREV, Bull. Soc. chim. France (1969) 1054.
15. V. V. BOLDYREV, Fizika shchelochnogaloidnykh kristallov, Trudy 2-go Vsesoyuznogo soveshchaniya, Latvysky gosuniversitet, Riga (Physics of alkali halogenides, Proceedings of the 2nd All-Union Conference, Latvian State Universitat, Riga). 1962. p. 520.

16. E. G. AVVAKUMOV, V. V. BOLDYREV and I. D. KOSOBUDSKY, Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. khim. No. 9, Issue 4 (1972) 45.
17. V. V. BOLDYREV, A. V. BOLDYREVA, A. V. SAFIULINA and B. I. TRECKOVA, Zh. fiz. Khim., 34 (1960) 2184.
18. V. V. BOLDYREV, V. P. DOLGOVA and .A A. SHINT, Nauchn. dokl. Vysshey Shkoly, ser. khim. i. khim. tekhnologiya, 1 (1959) 24.
19. V. V. BOLDYREV, YU. A. ZAKHAROV, V. M. LYKHIN and L. A. VOTINOVA, Kinetika i kataliz, 4 (1963) 672.
20. V. V. BOLDYREV, V. I. EROSHKIN, V. T. PISMENKO, I. A. RYZHAK, A. A. MEDVINSKY, I. V. SHMIDT and L. M. KEFELI, Kinetika i kataliz, 9 (1968) 260.
21. V. V. BOLDYREV, V. I. EROSHKIN, I. A. RYZHAK, and L. M. KEFELI, Dokl. AN SSSR, 173 (1967) 117.
22. V. V. BOLDYREV, J. Phys. Chem. Solids, 30 (1969) 1215.
23. V. V. BOLDYREV, Dokl. AN SSSR, 181 (1968) 1406.
24. V. V. BOLDYREV, YU. P. SAVINTSEV, T. V. MULINA and G. V. SHCHETININA, Kinetika i kataliz, 11 (1970) 1131.
25. V. V. BOLDYREV, YU. P. SAVINTSEV and T. V. MULINA, Reactivity of Solids, Proc. 7th Internat. Symposium on the Reactivity of Solids, Bristol 17—21 July 1972, Chapman and Hall, London, 1972.
26. V. V. BOLDYREV, V. V. ALEKSANDROV, A. V. BOLDYREVA, V. I. GRITSAN, YU. YA. KARPENKO, O. P. KOROBEYNICHEV, V. N. PANFILOV and E. F. KHAIRETDINOV, Combustion and Flame, 15 (1970) 71.
27. R. D. SHANNON, Trans. Faraday Soc., 60 (1964) 1902.
28. V. V. BOLDYREV and V. P. PRONKIN, Zh. Vsesoyuzn. khim. obshch. im Mendeleeva, 6 (1961) 466.
29. V. P. KORNIENKO and M. N. DUBROVSKAYA, Ukrainsk. khim. zh., 29 (1963) 262.
30. O. KADLEC and V. DANES, Collection Czech. Chem. Commun., 32 (1967) 1781.
31. E. V MARGULIS and YU. S. REMEZOV, Sborn. Trud. Vsesoyuzn. NII tsvetnoy metallurg. 6 (1960) 149.
32. W. KOMATSU, B. H. KIM and H. ISHIKAWA, J. Chem. Soc. Japan, Ind. Chem. Sect., 74 (1971) 1987.
33. V. K. ZHURAVLEV and JU. I. MICHAILOV, Festkörperchemie, Beiträge aus Forschung und Praxis, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1973.
34. E. PROUT and F. TOMPKINS, Trans. Faraday Soc., 40 (1944) 488.
35. O. A. ESIN and P. V. GELD, Fizicheskaya khimiya pirometallurgicheskikh protsessov (Physical chemistry of pyrometallurgical processes), Metallurgizdat, 1962. vol. 1, part IV, p. 375.
36. W. GIBBS, Termodinamicheskie raboty (Works on Thermodynamics, Russian translation), I. T. T. L., Moscow, 1950.
37. M. VOLMER, H. MARK and M. POLÁNYI, Kinetik der Phasenbildung (vol. 4, Die chemischen Reaktionen), Dresden, 1939.
38. M. I. FRENKEL, Kineticheskaya teoriya zhidkostey (The kinetic theory of liquids), Izd. AN SSSR, 1945.
39. R. BECKER, Kinetika obrazovyniya zarodyshchey i statisticheskaya teoriya kristallizatsii. Sbornik Novye issledovaniya po kristallografii i kristallokhimii (Kinetics of nucleus formation and the statistical theory of crystallization, Russian translation in the collection Recent research on crystallography and crystal chemistry), Izd. Inostr. Lit, 1950.
40. W. DANNING, Teoriya obrazovaniya kristallicheskikh zarodyshchey v parakh, zhidkostyakh i tverdykh sistemakh. V sbornik Khimiya tverdogo tela (Theory of crystalline nucleus formation in vapours, liquids and solid systems, Russian translation in the collection Chemistry of solid state), 1961.
41. V. I. DANILOV, Stroenie i kristallizatsiya zhidkostey (Structure and crystallization of liquids), Izd. AN SSSR, 1956.
42. S. Z. ROGINSKY, Zh. fiz. Khim., 12 (1938) 427.

43. J. W. CAHN and J. E. HILLARD, J. Chem. Phys., 28 (1958) 258.
44. W. E. GARNER and T. E. JENKINS, Proc. Roy. Soc., A 224 (1954) 460.
45. G. R. FORD and G. B. PROST, Can. J. Chem., 34 (1956) 591.
46. S. Z. ROGINSKY, A. B. SHEKHTER, A. I. ECHEISTOVA, N. N. KVATARADZE and M. YA. KUSHNEROV, Dokl. Acad. Nauk SSSR, 68 (1949) 879.
47. R. A. W. HILL, Reactivity of Solids, Proc. 4th Internat. Symp., Elsevier Publ. Comp., 1961, p. 294.
48. J. H. DE BOER, The Dynamic Character of Desorption, Oxford, Clarendon Press 1953, p. 138.
49. J. H. DE BOER, Discussions Faraday Soc., 23 (1957) 171.

RÉSUMÉ — On présente une étude d'ensemble sur les réactions topochimiques en discutant la théorie de la cinétique.

ZUSAMMENFASSUNG — Eine Übersicht über die topochemische Reaktion wird gegeben und die Theorie ihrer Kinetik erörtert.

Резюме—Представлено обозрение топохимических реакций и обсуждены их кинетические теории.