KINETICS OF THE REACTION BETWEEN THE SOLID SODIUM CARBONATE AND THE GASEOUS SULPHUR DIOXIDE. VI.*

STATISTICAL MOLECULAR MODEL OF THE EXCESS KINETIC FUNCTION

E. ERDÖS

Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2

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A statistical molecular twodimensional growth model is proposed of the reaction between the solid sodium carbonate and the gaseous sulphur dioxide based on the assumptions that the distance between the molecules and the growth centers and the velocity of the reaction front advancement exhibit a normal distribution. The model proposed reproduces perfectly the course of the excess kinetic function which has been found with this reaction by experiment. The model takes into account even the effect of the gas phase on the reaction rate and interprets the reaction half-time as the mean square time within which the reaction front advancing from the growth center reaches the molecule of the solid. The limitations of the model proposed are discussed.

The results of a rather thorough study of the reaction rate between the solid sodium carbonate and the gaseous sulphur dioxide have been summarized quantitatively into a rate equation[1]

$$r = k(p_{SO_2}, p_{H_2O})\, x^{1/2}(1 - x)^{3/2}\,, \tag{1}$$

where x denotes the conversion degree of the solid phase and the reaction rate r has been referred to one mol of the solid, *i.e.* it has been defined as a time change of the degree of conversion dx/dt. We have succeeded in interpreting the experimentally found dependence of the effective rate constant $k(p_{SO_2}, p_{H_2O})$ on partial pressures of sulphur dioxide, p_{SO_2}, and of water vapour, p_{H_2O}, in terms of the theory of absolute reaction rates[1], nevertheless, the dependence of the reaction rate on the degree of conversion contained in the equation (*1*) remained an empirical description only. In the paper[1] an excess kinetic function, S_E, has been defined

$$S_E = r/k(p_{SO_2}, p_{H_2O})\, [x(1 - x)^{1/2}\,, \tag{2}$$

that had to express the deviations from the reaction course of the simplest twodimensional growth model, and the dependence of which on the degree of conversion has been found empirically in the form

$$S_E = \beta(1 - x)\,, \tag{3}$$

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where β is a proportionality constant. In a subsequent paper[2] we have attempted at interpreting this very simple course of the excess kinetic function by means of a growth model in which we have assumed that all the growth elements are geometrically similar and that they differ in their sizes only. By comparing the above model with the reaction course found experimentally, we have succeeded in deriving a frequency function of growth element sizes, the statistical significance of this function, however, remained unexplained. A probable cause of this difficulty has been seen in the fact that the model mentioned above had not taken into account the possible deformations of growth elements on their mutual contact.

Within the frame of a simple naive model, however, it is very difficult to take quantitatively into account the deformations of elements growing from randomly arranged centers, and therefore, an attempt is made in this paper at interpreting the found kinetic function by means of a statistical model "*ab initio*".

THEORETICAL

Elementary Conceptions

In the same way as previously[2] let us consider a growth model of the given chemical reaction with an instantaneous nucleation. The course of such a reaction is characterized by a growth of a great number of growth elements which grow from growth centers (nuclei) the arrangement of which on the surface of the solid is random. The individual growth elements can grow so long as their growth is not hindered by neighbouring growth element. Owing to the random arrangement of the growth centers on the surface of the solid, all the growth elements cannot attain the same size, and owing to the mentioned deformations of growth elements on their mutual contact, the shape of the growth elements will not be the same.

With respect to the complex nature of the model mentioned above a causal geometric description does not appear feasible, and, therefore, in the following we shall not consider the occurrence probability of different elements[2] but we shall focuss our attention to occurrence probability of molecules of the reactive solid in dependence on their distance from the growth centers of growth elements. Further on, we shall assume that this probability has a random distribution. The term "molecule" is used here and in the following as an abbreviation for a reaction unit of the solid complying with requirements of stoichiometry, *e.g.* a carbonate ion.

In addition to the random arrangement of growth centers in this model, it is necessary to consider that the growth velocity of all the elements will not be the same in a given direction and consequently that the velocity with which the reaction front advances from the growth center towards the considered molecule of the reaction solid will exhibit a random distribution as well. It follows from what has been said that we have to deal with the occurrence frequency of molecules of the reacting solid as well from the point of view of their distance from the growth centers as from the point of view of velocities with which the reaction front approaches them. Lacking

further informations we shall assume that all the primary random quantities exhibit a normal distribution.

Velocity Distribution

In the first approximation, we shall consider the twodimensional growth of elements mentioned above, *i.e.* the advancement of the reaction front as planar. In this case the reaction front can advance in directions of two perpendicular axes of coordinates. Let us denote the velocity component of the advancement in the direction of abscissa as ξ. Then according to the assumption mentioned above the occurrence probability of a molecule which is crossed by the reaction front with a velocity ξ is given by the normal distribution and, therefore, the frequency function $p(\xi)$ of this distribution will be of the following form

$$p(\xi) = [1/\sigma_v \sqrt{(2\pi)}] \exp(-\xi^2/2\sigma_v^2), \tag{4}$$

if the occurrence probabilities in the positive and negative direction are equal. The quantity σ_v in this equation represents a parameter the square of which is equal to the dispersion of this distribution and therefore it may be interpreted as a mean square velocity of advancement in the direction of abscissa. Further on, if the velocity component of the reaction front advancement in the direction of ordinate axis is denoted as η the occurrence probability of a molecule which is crossed by the reaction front with a velocity η is described under the same assumption as above by a frequency function $p(\eta)$ in a similar form

$$p(\eta) = [1/\sigma_v \sqrt{(2\pi)}] \exp(-\eta^2/2\sigma_v^2), \tag{5}$$

where the mean square velocity σ_v is the same as in the equation (*4*) under assumption that the distribution considered is invariant with respect to the exchange of both coordinate axes; in the opposite case the growth in one of both directions would be preferred. Now let us consider the occurrence probability of a molecule which is crossed by the reaction front in an arbitrary direction with an absolute velocity χ. This velocity can be expressed by means of velocities in directions of both coordinate axes through the relation

$$\chi = \sqrt{(\xi^2 + \eta^2)}, \tag{6}$$

sothat the occurrence probability of molecules which are crossed by the reaction front with an absolute value of velocity v or smaller, *i.e.* the distribution function $P(\chi < v)$, will be given by the relation

$$P(\chi \leqq v) = \iint p(\xi, \eta)\, \mathrm{d}\xi\, \mathrm{d}\eta, \tag{7}$$

where the integration is meant over the whole range of variables ξ and η limited by the condition

$$\sqrt{(\xi^2 + \eta^2)} \leqq v\,, \tag{8}$$

and the quantity $p(\xi, \eta)$ represents the density of occurrence probability of a molecule which is crossed by the reaction front with velocities ξ and η in directions of both coordinate axes. If both these velocities are independent the following relation is valid

$$p(\xi, \eta) = p(\xi)\, p(\eta) \tag{9}$$

and on substituting the relations (4), (5), and (9) into the equation (7) we obtain a distribution function

$$P(v) = \mathrm{P}(\chi \leqq v) = \frac{1}{2\pi\sigma_v^2} \iint_{\sqrt{(\xi^2+\eta^2)} \leqq v} \exp\left(-\frac{\xi^2 + \eta^2}{2\sigma_v^2}\right) \mathrm{d}\xi\, \mathrm{d}\eta\,. \tag{10}$$

By transforming the double integral in the equation (10) into polar coordinates we obtain (the functional determinant of this transformation is equal to χ)

$$P(v) = \frac{1}{2\pi\sigma_v^2} \int_0^{2\pi} \int_0^{v} \chi \exp\left(-\frac{\chi^2}{2\sigma_v^2}\right) \mathrm{d}\chi\, \mathrm{d}\Theta \tag{11}$$

and upon integration the distribution function assumes the following form

$$P(v) = 1 - \exp\left(-v^2/2\sigma_v^2\right). \tag{12}$$

From this equation we obtain by differentiation the frequency function $p(v)$ of the distribution of molecules of the solid according to the absolute velocity of advancement of the reaction front in the form

$$p(v) = \left(v/\sigma_v^2\right) \exp\left(-v^2/2\sigma_v^2\right). \tag{13}$$

Distance Distribution

In a similar way as with the velocity distribution, we shall limit our considerations on the distribution of molecules according to the distance from the growth centers to the planar approximation. If the distance component of a molecule from the growth center in the direction of abscissas is denoted as v and the distance component in the direction of ordinate axis as μ, the occurrence probability of a molecule at a distance v from the center will be given by the normal distribution with a frequency function $p(v)$

$$p(v) = \left[1/\sigma_z \sqrt{(2\pi)}\right] \exp\left(-v^2/2\sigma_z^2\right), \tag{14}$$

where the parameter σ_z can be interpreted as a mean square distance of molecules from growth centers in the direction of the abscissa axis. Analogously we obtain the frequency function $p(\mu)$ for the distribution in the direction of ordinate axis

$$p(\mu) = [1/\sigma_z \sqrt{2\pi}] \exp(-\mu^2/2\sigma_z^2), \tag{15}$$

where the parameter σ_z has the same value as in the equation (*14*) under conditions given in the formulation of the equation (*5*).

Further on, let us consider the occurrence probability of a molecule at a distance φ from the growth center in an arbitrary direction. This distance can be expressed in terms of distances in directions of both coordinate axes by the relation

$$\varphi = \sqrt{(\nu^2 + \mu^2)}, \tag{16}$$

so that the occurrence probability of molecules occurring at a distance z or smaller from the growth centers, *i.e.* the distribution function $P(\varphi \leqq z)$, will be given by the relation

$$P(\varphi \leqq z) = \iint_{\sqrt{(\nu^2+\mu^2)} \leqq z} p(\nu, \mu)\, \mathrm{d}\nu\, \mathrm{d}\mu, \tag{17}$$

where the quantity $p(\nu, \mu)$ represents the density of occurrence probability of a molecule at distances ν and μ in directions of both coordinate axes. If these distances are mutually independent, we can arrive from the equation (*17*) in an utterly analogous way which has been used in the velocity distribution to the frequency function $p(z)$ of the distribution of molecules according to their absolute distances from the growth centers in the form

$$p(z) = (z/\sigma_z^2) \exp(-z^2/2\sigma_z^2). \tag{18}$$

Reaction Time

In the preceding paragraphs we have arrived at the probability densities (frequency functions) of molecules which are occurring at a distance z from the growth centers and which are crossed by the reaction front with a velocity v. By means of these two quantities, z and v, we can now define a new quantity τ by the relation

$$\tau = z/v, \tag{19}$$

from which its physical meaning is evident, if the velocity of the reaction front advancement is constant. The quantity τ represents the time in which the reaction front advancing with a velocity v attains the distance z from the growth center.

Therefore, the quantity τ represents the time in which a molecule occurring at a distance z from the growth center and crossed by the reaction front with a velocity v enters the reaction. In agreement with this physical meaning the quantity τ can be denoted as a reaction time of a molecule of the solid.

It follows from the given interpretation of the quantity τ as a reaction time of the molecule that in the moment t from the beginning of the chemical reaction all the molecules have reacted with the reaction time smaller or equal to the value of the current time, *i.e.* all the molecules for which $\tau \leqq t$. The ratio of these reacted molecules to all the molecules which can react is, according to the definition, equal to the conversion degree of the solid x, and in a statistical interpretation this ratio is equal to the probability that in the time t the molecules will react with a reaction time smaller or equal to t, or to the occurrence probability of molecules for which the inequality $\tau \leqq t$ is valid. Therefore, the conversion degree of the solid x is equal to the distribution function $P(\tau \leqq t)$

$$x = P(\tau \leqq t) = P(t)\,. \tag{20}$$

The equation (*20*) gives the degree of conversion x as a function of time t, and to express this dependence explicitly it is necessary to know the distribution of reaction times τ.

Reaction Time Distribution

The law of the distribution of reaction times can be determined from the definition equation (*19*) in combination with the functions (*13*) and (*18*). The density of occurrence probability of molecules occurring at a distance z from the growth center and crossed by the reaction front with a velocity v, *i.e.* the quantity $p(z, v)$, is given according to equations (*13*) and (*18*) by the expression

$$p(z, v) = \frac{zv}{(\sigma_z\sigma_v)^2} \exp\left[-\frac{1}{2}\left(\frac{z^2}{\sigma_z^2} + \frac{v^2}{\sigma_z^2}\right)\right], \tag{21}$$

if both the variables are independent. The occurrence probability of molecules with the reaction time smaller or equal to t, *i.e.* of molecules for which $\tau \leqq t$ or according to (*19*) $z \leqq vt$, is then given by the relation

$$P(z \leqq vt) = \frac{1}{(\sigma_z\sigma_v)^2} \iint_{z \leqq vt} zv \exp\left[-\frac{1}{2}\left(\frac{z^2}{\sigma_z^2} + \frac{v^2}{\sigma_v^2}\right)\right] \mathrm{d}z\,\mathrm{d}v\,, \tag{22}$$

where the integration is meant over the range of variables z and v which fulfil the condition $0 \leqq z \leqq vt$, since all these variables are defined in the range of positive values only. Therefore, the integration of the double integral in the equation (*22*)

may be carried out by a twofold integration, *viz.* first according to z from zero to vt and then according to v from zero to infinity, so that the following relation is obtained

$$P(\tau \leqq t) = P(t) = \frac{1}{(\sigma_z \sigma_v)^2} \int_0^\infty v \exp\left(-\frac{v^2}{2\sigma_v^2}\right) \left[\int_0^{vt} z \exp\left(-\frac{z^2}{2\sigma_z^2}\right) \mathrm{d}z\right] \mathrm{d}v\,. \quad (23)$$

Having carried out both integrations indicated in the equation (*23*), we arrive at an expression for the considered probability in the following form

$$P(t) = \sigma_v^2 t^2 / (\sigma_z^2 + \sigma_v^2 t^2)\,. \quad (24)$$

As mentioned above, the parameter σ_z has the meaning of the mean square distance of molecules from growth centers and the parameter σ_v denotes the mean square velocity of the advancement of the reaction front. In analogy with the equation (*19*) we can now define a new parameter σ_τ by the equation

$$\sigma_\tau = \sigma_z / \sigma_v \quad (25)$$

and in this way the relation (*24*) can be simplified to the form

$$P(t) = t^2 / (\sigma_\tau^2 + t^2)\,. \quad (26)$$

The physical meaning of the parameter σ_τ is evident from its definition (*25*); it can be denoted as a mean square reaction time of molecules of the solid.

Degree of Conversion and Reaction Rate

By combining the equations (*20*) and (*26*) we obtain directly an expression giving the degree of conversion as a function of time

$$x = t^2 / (\sigma_\tau^2 + t^2)\,. \quad (27)$$

By differentiating this expression with respect to time we obtain the reaction rate r as a function of time in the following form

$$r = \mathrm{d}x/\mathrm{d}t = 2\sigma_\tau^2 t / (\sigma_\tau^2 + t^2)^2\,. \quad (28)$$

If the value of t from the equation (*27*) is substituted into the expression (*28*), the final expression for the reaction rate as a function of the degree of conversion follows in the form

$$r = (2/\sigma_\tau)\, x^{1/2} (1 - x)^{3/2}\,. \quad (29)$$

Therefrom, an expression follows according to the definition[1] for the excess kinetic function

$$S_E = \gamma(1 - x)\,, \tag{30}$$

where γ is a proportionality constant the numerical value of which is irrelevant[2].

DISCUSSION

It follows from the comparison of the equation (*1*) with the equation (*29*) that the model described above reproduces the experimentally found dependence of the reaction rate between the sulphur dioxide and the sodium carbonate on the degree of conversion quite exactly in the whole range. The same conclusion is valid of course even for the excess kinetic function as it is evident from a comparison of the equation (*3*) with the equation (*30*). The basic idea of the model described consists in an assumption that the degree of order in the solid sodium carbonate studied is so low that both the advancement of the reaction front and size of growth elements are of random nature. The existing results of the study of crystal structure of sodium carbonate prepared from a melt or by dehydratation of a hydrate indicate[3,4], that a significant gradual decrease of symmetry takes place with decreasing temperature; it may be expected that in samples prepared by the decomposition of the hydrogen-carbonate[1] the degree of order will be even substantially lower, as can be seen from the reactivities of samples prepared from the hydrate and from the hydrogen-carbonate[1] which differ in orders. Therefore, the existing experimental knowledge indicates the palusibility of the basic assumption in the model described.

The quantitative relations obtained from this model permit some interesting interpretations. For instance it is evident from the equation (*27*) that in the moment when the current time assumes the value equal to the mean square reaction time, *i.e.* when $t = \sigma_\tau$, the degree of conversion reaches the value of one half. The statistical parameter σ_τ introduced above with the meaning of the mean square reaction time represents, therefore, a simple macroscopic quantity denoted generally as the reaction half-time.

Further on, the macroscopic effective rate constant k can be interpreted in statistical terms by comparison of equations (*1*), (*25*), and (*29*) from which it follows

$$k = 2\sigma_v/\sigma_z\,. \tag{31}$$

According to the above mentioned assumption of instantaneous nucleation the mean square distance of molecules from the growth centers, *i.e.* the quantity σ_z, will be dependent on the arrangement of growth centers on the surface only; consequently the parameter σ_z will depend on the properties of the solid phase only and not on the properties of the gas phase. On the contrary, it may be expected that the mean

square velocity of the advancement of the reaction front, *i.e.* the quantity, σ_v, will be affected also by the composition of the gas phase. We can assume in the first approximation that the velocity of the reaction front advancement will be proportional to the number of impacts of molecules of the reacting gas component on the surface in the position of the reaction front, *i.e.* that it will be proportional to the partial pressure of the sulphur dioxide. According to what has been said and according to the equation (*31*), the effective rate constant ought to be proportional in the first approximation to the partial pressure of the sulphur dioxide. This prediction following from the statistical model is in full agreement with reality[5] in the range of low partial pressures of sulphur dioxide.

The model described has been originally designed with the purpose to give an interpretation of the excess kinetic function, *i.e.* to interpret the experimentally found dependence of the reaction rate on the degree of conversion of the solid phase only. The results achieved, however, indicate that the capacity of this model is probably greater and that it is principially able to take into account even the effect of the gas phase.

These facts undoubtedly increase the plausibility of the model proposed even though we cannot disregard from some inherent limitations. In the first place, the possibility is lost of forming more sophisticated ideas of the reaction course propre; these limitations are of course inherent in all the theories based on statistics. Further on, however, the possibilities are here rather limited of obtaining characteristic statistical parameters of physical meaning which would open new prospects or would be accessible to an independent verification. It is possible to determine only the mean square reaction time of molecules (its value assumed units or tenthes of minutes according to the reaction conditions) as it has been shown above, however, it is quite impossible to evaluate from the measurements of the reaction rates the mean square velocity of the reaction front or the mean square distance of molecules from the growth centers. On the other hand, it is possible to interpret this fact as a theoretical illustration of a generally known experience that the amount of informations on the reaction course propre which can be obtained from mere kinetic measurements is rather limited.

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