Special Review

# KINETIC PARAMETERS*

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The wide variations of calculated activation energies for solid decomposition suggests that there is no discrete activated state. Further, the statistical distribution on which the calculations are based is not a realistic concept. The lowest energy possible — and most frequently occurring — is the energy of the bulk crystal. Within the crystalline solid, vibrational interactions transfer energy so rapidly that a substantial difference from the average energy is not achievable within the crystal. The lack of a statistical distribution rules out the use of the Arrhenius equation unless it is independently verified for the particular system.

In calculating chemical kinetic parameters we are faced with a number of problems. Some are philosophical; some depend upon definition of terms; some depend upon the validity of assumptions adopted for mathematical convenience; and some are related to our ability to make suitable measurements.

First taking up the philosophical, let us remember that the goal is to describe the process. That is, reactions do not follow or obey equations. The equation must describe the reaction. This means that we must not expect every reaction to fit any of our formal models. Because the material itself does not know any of our mathematics it reacts in response only to its immediate environment. If we make measurements, then try to fit them to equations which describe our set of model reactions, we must not expect in all cases an exact fit with any model. We must also avoid the trap of concluding that the closest fitting model actually describes the reaction.

This leads to the second major philosophical point: we advance our knowledge by finding the weaknesses of current theory, not by assuming that we have, in our literature, a set of truths. That is, experiment does not have to agree with theory. When our experimental data deviate from accepted theory or theoretical models, the proper course is to seek ways to extend the theory – or, if necessary, reject it.

As to questions of definition, we can first look at the activation energy, illustrated in Fig. 1. This quantity is defined – in homogeneous kinetics – as the energy needed to raise the initial reactant or reactants to some activated state, from which it can either drop back to the reactant state or react to become the final product,

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either process happening so rapidly that it is not a rate limiting step. If the relative probability of forming product remains unchanged, the rate is determined by the fraction of reactant reaching the activated state.

In homogeneous systems, the distribution of energy states can be defined with reasonable certainty by statistics, and plotted as in Fig. 2a. As the average energy increases, the fraction having some particular extra energy increases. Under both these influences, the fraction having total energy enough to reach the activated state ($E^*$ or $T_R$) increases with temperature. In effect, we are measuring the temperature dependence of this rate.

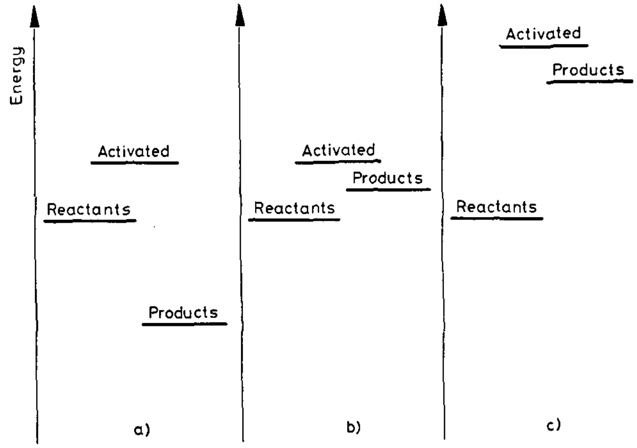


Fig. 1. Energy levels for the average energies of the reactant and product states and for the activated state in homogeneous kinetic theory. Curve *a* describes a typical homogeneous exothermic process; *b* a typical homogeneous endothermic process: and *c* typical heterogeneous process

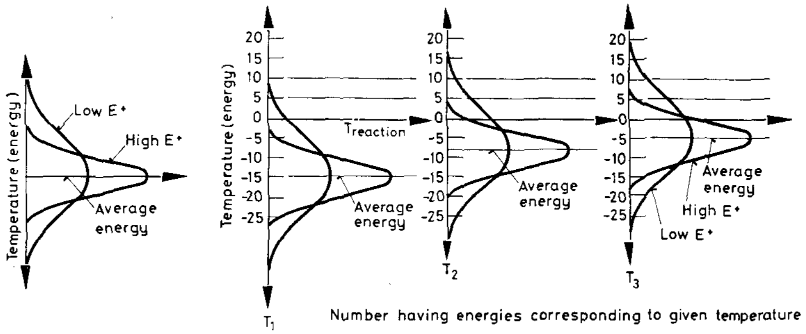
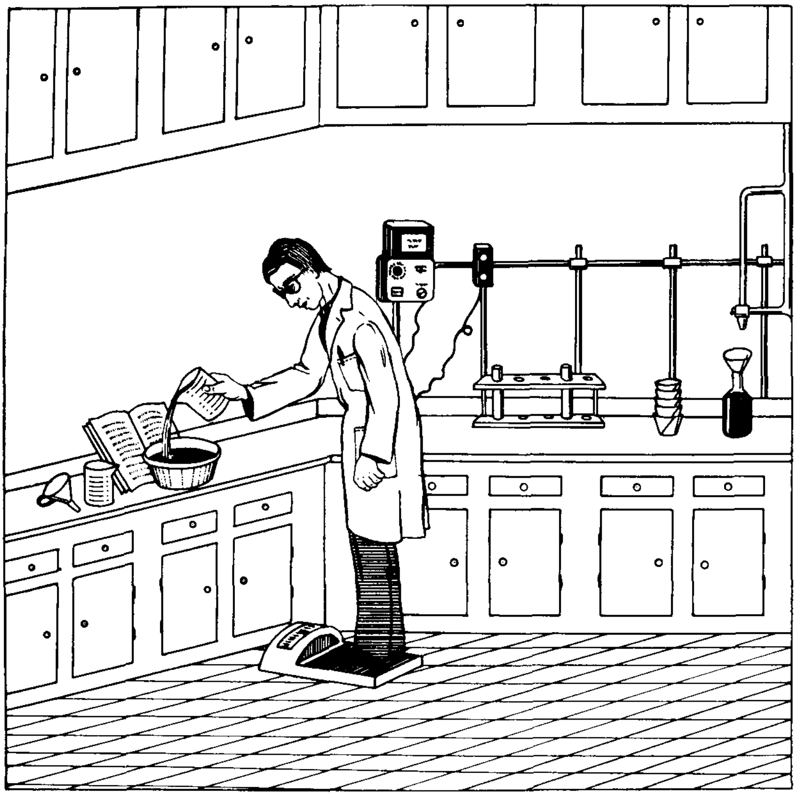


Fig. 2. The statistical energy distribution for a high and a low activation energy process at several temperatures (average energies), $T_1$, $T_2$, $T_3$. Assuming a fixed energy (apparent temperature). $E^*$, for the activated state, the fraction reaching the equivalent temperature, $T_r$, and higher temperatures can be computed for each average temperature

Having reached that energy, some will release a portion of its energy to the system but consume that portion known as the enthalpy change ($\Delta H$ in fig. 1). The distribution of energies in the reactant species readjusts to the loss in total energy by either lowering its temperature in an adiabatic system or by accepting compensating energy in an isothermal or dynamic temperature system.



"...add 120 gram potassium iodide..."

Fig. 3. Measurement by difference

To illustrate the method of determination of the classical activation energy with the simplifying assumption of a specific temperature of reaction, we can look at the behavior of two materials with energy distributions as shown.

As the samples reach average energies $T_1, T_2$, or $T_3$ in Fig. 2b, such that a fraction is at or above $T_R$, reaction can begin. Our measures of the homogeneous activation energies come from the relative rates at a few temperatures over a small range. The same kinds of measurements are made with solid samples, and assuming the same kind of distribution. So a quotation used in one of the chemistry text books can be paraphrased as a precaution. [1] *Everybody believes in the exponential law of energy distribution; the experimenters because they think it can be proved by mathematics; and the mathematicians because they believe it has been established by observation.* The error curve is purely statistical, and statisticians tell us that we should rely on statistics only when we lack other information.

This concept of activation energies presents no great problem in homogeneous reactions, where the calculated activation energies are ordinarily smaller than the enthalpy changes. Furthermore, the enthalpy changes are usually known from calorimetry. In solid reactions we have calorimetric data in many cases, but not all – nor is it always taken into account. More important, the calculated activation energy for decompositions is much higher than for typical homogeneous processes – 20 to 50 or more kilocalories per mole as compared to 1 to 10 kilocalories per mole; now we encounter a problem because of our measurement methods. The literature contains many sets of values for the decompositions of calcium carbonate and for kaolinite. Both of these require enthalpy increments of about 40 kilocalories per mole, and many of the activation energy data fall within the 40 – 50 kilocalorie range. That is, the energy required for reaction is by far the major portion of the calculated activation energy (Fig. 1c), so that if there is a real extra energy barrier it is effectively concealed (Fig. 3) because we are measuring a large quantity when we are trying to determine a smaller quantity. It has been suggested that the activation energy has – for a lower limit – the enthalpy change, but some reports show values less than the enthalpy change. Ingraham [2] has separated the enthalpy and estimates seven kilocalories per mole as the true activation energy for calcium carbonate, but this is still based upon subtraction of the known enthalpy change from the calculated activation energy.

Let us next face the question – what are the true fixed values for a reacting system, the intensive properties which are characteristic and accurately reproducible?

Of the energy states considered, it is clear that (if we neglect minor differences from imperfections) the molar enthalpy of the reactants and of the products are fixed quantities at a particular temperature (Fig. 4) and hence their difference is

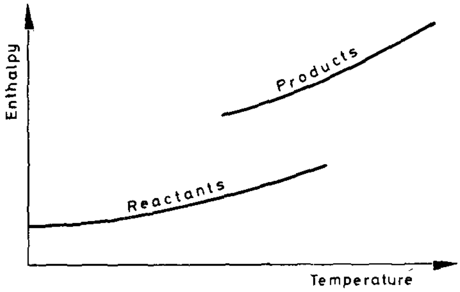


Fig. 4. Molar enthalpies of reactants and products of an endothermic process as a function of temperature

fixed – with, of course, a small temperature variation. This is true for either homogeneous or heterogeneous systems.

If the energy of the reactants is a function only of the temperature and the activated state is a definable or describable energy state, the calculated activation energy ought to be nearly constant. Some data assembled by Gallagher and Johnson [3] for calcium carbonate are given in Table 1. In their survey of the literature, they found a wide range of values, most of the authors treating the reaction by some order-of-reaction equation and still finding differing results. We can conclude that the activated state has not yet been uniquely described in terms of energy. Further, we can see immediately that not only have differing activation energies been calculated but also different rate limiting processes have been found. The basis for each of these conclusions has been the mathematical treatment, not a direct test.

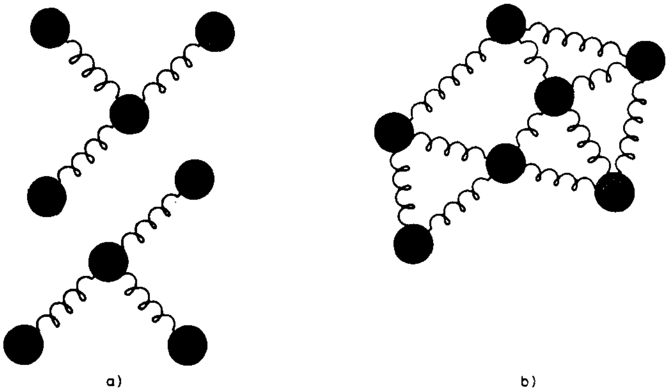


Fig. 5. Ball and spring models showing *a*, the intramolecular interactions in a fluid, and *b*, the interatomic vibrations in a crystalline solid. The mobility of the fluid can permit coexistence of molecules of differing energies, whereas the forced interaction in a solid limits the range of energies

Now let us examine the characteristics of energy content and of energy distribution. The enthalpy is, of course, the summation of all the heat capacity from absolute zero. Taking as an example a material with an average heat capacity of half a calorie per gram and a formula weight of one hundred and reaching one thousand degrees kelvin, the total enthalpy is about fifty kilocalories per mole, we can examine the possibility that a material needing only forty kilocalories (equivalent to 800°) more in order to react would have a measurable fraction of its component molecules or ion pairs in a sufficiently high energy state to react. The statistical probability based upon homogeneous systems is already small, but even that is misleading for two principal reasons. One of these is the rapidity of redistribution of energy and another is physical constraint.

The distribution of energies in a liquid or gas is not quite homogeneous in any small system. The mobility enables more or less elastic collisions so that even in a liquid a distribution of energies can be maintained (Fig. 5). If extra energy is added, for example from a wall, convection currents are set up because the hotter fluid can move about more easily than it can dissipate its extra energy by collision. Solids have no such option.

Whether an atom in a solid is connected to its neighbor by covalent or ionic bonds or by electron pair sharing or Van der Waal's forces, the constant interactions through vibrations provide a means of distributing any extra energy to its neighbors. The energy in any small region will have a narrow distribution. Under a driving force – such as a heat source – the energy is passed on from atom, molecule, or ion to its neighbor. Is this mere speculation? No, there are several kinds of evidence. I'll just cite two.

First, the thermal conductivities of solids are typically much greater than those of their melts; and second, a nuclear magnetic resonance spectrum which is clearly resolved in the liquid phase degrades into a broad band in the solid phase because the extra energy of the activated nucleus is dissipated by other interactions with its neighbors. We are using NMR in our laboratory to establish the *solidus* in impure systems. [17]

These considerations tell us that the probability of a fraction of the solid material having a much higher energy than the average energy is very low indeed. So if we depended upon a discrete activated state for a solid, we would have to wait a long time at temperatures at which we already know the reaction proceeds.

Continuing on to constraints on energy, the same interactions which enable the rapid distribution of energy prevent the accumulation of very nuch excess energy in any molecule or ion. The energy accretion is neither translational nor, in most cases, rotational; it is necessarily vibrational. But within a crystal lattice, any particular vibrational mode causes interaction with neighbors, for example, a high amplitude of the stretching vibration of a carbon oxygen bond in a carbonate necessarily causes the oxygen to encroach more deeply into the fields of its neighboring atoms; synchronized movement being impossible, energy is transferred from one vibrating system to the other.

It is clear that we cannot describe an activated state which is homogeneously distributed. Impurities, defects, or anisotropy may permit higher that average vibrational states within the molecule, but a statistical energy distribution accounting for both surface and solid is not to be expected.

As an example, the dehydroxylation of brucite, mineral magnesium hydroxide, has been shown to be a surface reaction, [18–20] the dehydroxylation of a few surface layers leading to cracking and exposure of new surface. We are looking at brucite in its relation to other layered minerals; Figure 6 shows an example of the behavior.

Heating a small single crystal to three hundred degrees leads to rapid evolution of water, detected by a mass spectrometer, a decrease until new surface is exposed, one or more repetitions, then a general increase as the cracking becomes more nearly random, followed by a nearly steady state loss until near completion of the process. I decline to derive or even try to write an equation describing the process.

Looking next at the method of determining the activation energy, it is customary to assume not only that a discrete state exists but also that it is related to the rate constant through the Arrhenius equation which was developed for the homogeneous model in which a describable statistical distribution of energies exists. Using the usual procedure of defining the rate constant as a function only of the temperature and the fraction remaining, we can take logarithms and declare that the negative logarithm of the rate constant is related to reciprocal temperature by the activation energy divided by $R$, then if a function of the fraction reacted can be found which yields a straight enough line to satisfy the observer, this function is concluded to be descriptive of the process and the model from which the function was obtained is taken to *identify the mechanism of the process.*

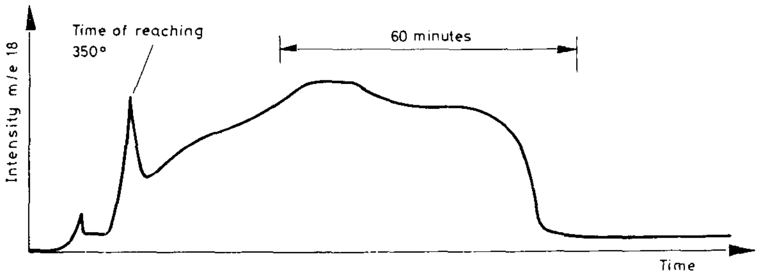


Fig. 6. Dehydration of brucite. The variations of rate with time show that a simple mathematical description is unobtainable.

In practice, we measure the rates at two or more temperatures as illustrated in Fig. 2 – assume the Arrhenius equation – and learn that if there is a large difference in rates, there is a high activation energy. But now we need to remember an important aspect of solids – the perfect crystal represents the lowest possible energy state (Fig. 7), so in all our calculations, the closest we can come to the statistical distribution is something approaching the upper half of the curve. That is, a solution or description based upon a statistical distribution is not in agreement with known properties of solids.

Another consequence of the acceptance and use of the Arrhenius equation is the variation in the pre-exponential factor. Taking the logarithmic expression, $\ln k = \ln Z - \frac{E}{RT}$, because we measure over a small range of rates, we must adjust $Z$ whenever we find a change in the calculated activation energy. From analytical geometry, $\ln Z$ is simply the intercept of our plot with $\ln k = 0$, but because of the limited temperature range of data, $\ln k$ changes so little compared to the other parameters that it can be treated as a virtual constant. Therefore, if we assume the Arrhenius equation, the appearance of a "kinetic compensation effect" is inevitable whenever the process depends primarily upon the achievement of a particular temperature. [21–23] The pre-exponential term cannot be shown to have a physical meaning when substantial variations are found. The only cause for the linear variation of $\ln Z$ with $E$ is the need to reach a temperature necessary for a particular reaction to occur, this temperature being defined reasonably well by $T = \frac{1}{R} \cdot \frac{\Delta E}{\Delta \ln Z}$.

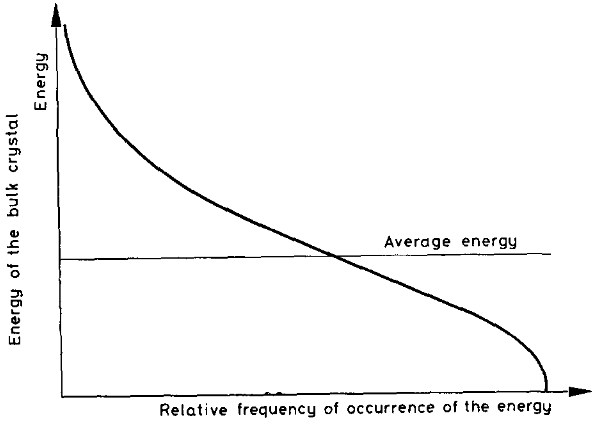


Fig. 7. Hypothetical energy distribution curve for a crystalline solid. The non-existence of energy states lower than that of the perfect array in the bulk precludes the use of a statistical treatment and the forced interaction, precludes the existence of a substantial energy difference except at the surface or imperfections. The actual distribution of energies would give a greater weight to energies near that of the bulk crystal

Nearly all Arrhenius plots show curvature at the lower or both temperature extremes, suggesting that if lower temperatures are used, the equation does not apply. Experimentation is not so convenient because longer times are required, but – as dedicated seekers of truth – we should not be deterred.

We have performed some limited testing of the Arrhenius equation using as the test reaction the formation of nylon 6.6 in the solid state from nylon salt. [24] Extension to lower temperatures was not successful, because the rate-limiting process changed quite sharply with temperature. Mr. Dasgupta is just completing the writing of the dissertation. At this stage, the mechanism appears to change with degree of reaction because of destruction of the crystal lattice. Whether or not we even see the early stages depend upon the temperature.

Going back to our model material let us examine the energy requirements. In order to carry out the reaction we must supply four hundred calories per gram, an amount which would otherwise raise the temperature about eight hundred degrees. That is, if we have heated the sample at a steady rate to one thousand degrees when we start the reaction, we must supply heat at much greater rate or the sample will cease to heat at the same rate. This does not depend upon the reversibility or irreversibility of the process. Now we are in position to examine the reason and form of the appearance of a temperature dependence of the reaction.

The most straightforward test is to examine a process which is not chemically rate limited. Taking the case of an interface reaction such that the material reacts when it reaches a fixed temperature, it can be shown that processes to which no activation energy can be ascribed will still show a dependence of rate upon heating rate or temperature and hence will permit a *calculated* activation energy. [25] This possibility arises from the need to transport heat. Thermal diffusion itself is an activated process. The important result from this work is that our present methods of calculation will provide an activation energy for processes which do not involve an activated state such as a melting, so we may conclude that any calculated activation energy is suspect until an actual rate equation is verified. That is, for many reactions we simply re-discover the enthalpy change. Even so, there are many cases of variation of calculated activation energy for a single reaction by a single group of workers. The source of the variation arises in most cases from deliberate, known changes in the experimental conditions. For example, in our own laboratory we have changed the pressure in a kaolinite sample held in a self-generated atmosphere [26]. Anthony found rates which would yield calculated activation energies ranging from sixty to two hundred forty kilocalories per mole if we used the orthodox model which fit the data best, the nucleation and growth model, with an exponent which varied from 1.10 to 2.16 over an eight-fold change in pressure [27].

Later, in an attempt to sort out heat transfer effects, using the same sample holder but with smaller samples and high conductivity plugs to fill the cavity and distribute the heat better, Selvaratnam [28] found a "best fit" for two-dimensional diffusion over a large fraction of the reaction, using as an aid plots of ($d\alpha/dT$ *vs* $T/T_{1/2}$. [29] This is a one step improvement over the method of Sharp and others, [30] who plotted $\alpha$ *vs* $T/T_{1/2}$.

Other experimental conditions have yielded several other "best fits" for other models. Achar et al. [31] pointed out the difficulty of finding the correct model for kaolinite, their experimental data fitting one model well in the early steps but another model better in the later steps.

Gallagher and Johnson [3] tested the sample size effect for calcium carbonate, finding quite drastic changes in the calculated activation energies over the size range of 1 – 16 milligrams or with heating rates from 2 – 20°/min. Later, Caldwell et al. [32] pointed out the variation in apparent activation energy with different inert atmospheres.

For the same reaction, Zsakó and Arz [33] calculated activation energies from less than 40 to 377.5 kilocalories per mole, depending upon the partial pressure of carbon dioxide. Berlin and Robinson [4] had found a calculated activation energy in carbon dioxide of 210 kcal/mole as compared to 40 kcal in nitrogen. But if the activation energy varies with experimental conditions it is necessarily true that:

1. There is no uniquely describable activated state and consequently the Arrhenius equation has no application to solid reactions; or

2. the assumption that the rate is a function only of temperature and the fraction remaining is incorrect; or
3. both.

I might add that Gál et al. [34] measured the enthalpy changes using the Van't Hoff equation, finding 39 – 45 kcal for thin layer and powdered calcium carbonate.

I shall treat the concept of an order of reaction very briefly. In any reaction which takes place at an interface as in Fig. 8, patterned after a drawing by the Pauliks, [35] no matter what the process, the material at the interface reacts in response to its

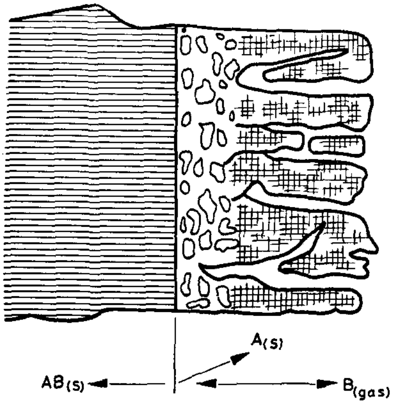


Fig. 8. Decompositions at an interface. The rate of reaction is in no way dependent upon the amount of unreacted material beyond the immediate reaction zone

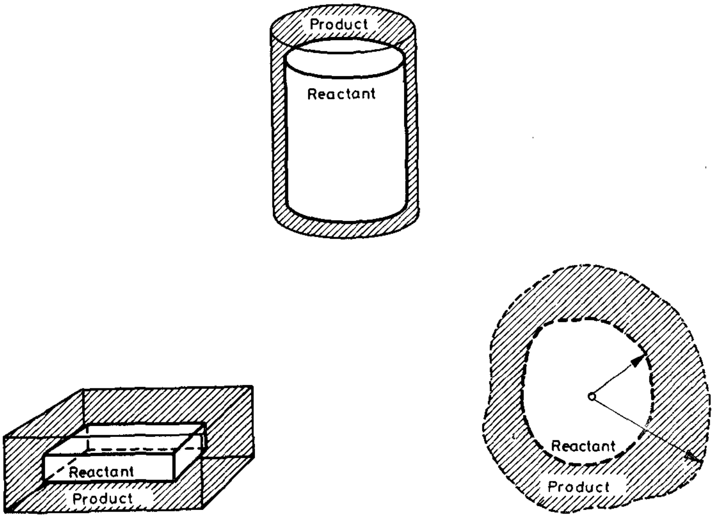


Fig. 9. Uniform advance of the interface in different geometries. Purely from differences in geometry, different equations may describe zero-order processes [36]

immediate surroundings; the rate is not dependent upon the amount of material not yet reacted. The several reports of orders of reaction based upon geometry have one common theme – uniform advance of a reaction front into a sphere, cylinder or other chosen form. [36] The views in Fig. 9 are taken from Ingraham [2] and Rouquerol. [37] That is, a reaction whose progress is dependent only upon time, and is therefore zero order may, if the sample is all of one shape and size, appear to follow an order of reaction equation. This is a rare case, indeed.

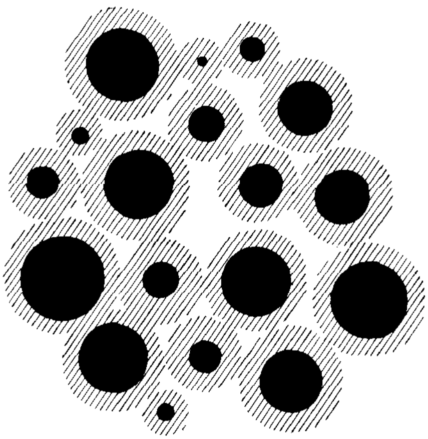


Fig. 10. Interface reactions on different sizes of particles of zone shape. Small particles completely disappear early, leading to a tailing-off the apparent rate

In the typical case, there is a distribution of sizes, as in Fig. 10 [36] so that some particles are completely reacted before the equation demands completion. An order of reaction for crystalline solids has no real meaning.

So far, I have spoken only of the possible error and not how to determine whether or not it applies to our own studies. There are several tests which can be made easily:

1. Changing the geometry of the sample from a thin layer to a thick layer will not change the rate constant if the rate equation is complete. The same size of sample on a pan or in a covered crucible should react identically.
2. Large samples or small should react identically if the rate equation is complete.
3. The atmosphere is important in some cases for heat transfer, in some cases as a diffusion inhibitor, and in some cases as a participant in the process. In any of these cases, the actual effect can be determined to learn whether or not error is being introduced.
4. The test of a theory or an equation is its ability to predict as compared to explain. Extrapolation of data from a four hour experiment to a temperature at

which it is complete in forty or one hundred hours enables overnight or week-end isothermal runs which will provide excellent tests of the calculated values.

5. For DTA, test of calculation methods with a melting will give a measure of the influence of heat transfer.

6. Finally, examination on a microscope hot stage during reaction or ofsectioned samples from interrupted experiments may enable verification of the reaction mechanism.

If substantial variations of the calculated data result from any of these changes, the experiment has very probably tested the apparatus rather than measured the kinetics of the chemical process.

To conclude, there are a number of effects which complicate our studies of kinetics of thermal processes in solids. Some lead to very serious errors in determining mechanisms.

On the other hand, there are rather simple ways of testing whether or not the effects actually influence our own experiments so that appropriate changes can be made.

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Résumé — Les variations notables des énergies d'activation calculées pour la décomposition des corps solides laissent supposer qu'il n'y a pas d'état activé discret. En outre, la distribution statistique qui sert de base pour le calcul ne représente pas un concept réel. L'énergie la plus faible possible — rencontrée très fréquemment — est l'énergie du cristal entier. Dans le corps solide cristallin, les interactions des vibrations transmettent l'énergie d'une façon si rapide qu'à l'intérieur du cristal une déviation substantielle de l'énergie moyenne n'est pas possible. A moins que sa validité ne soit prouvée indépendamment pour le système particulier, l'équation d'Arrhenius ne peut pas être employée en l'absence d'une distribution statistique.

Zusammenfassung — Die umfangsreichen Variationen der für die Festkörperzersetzung berechneten Aktivierungsenergien gestatten die Annahme, daß es keinen diskreten aktivierten Zustand gibt. Ferner stellt die den Berechnungen zu Grunde liegende statistische Verteilung kein reelles Konzept dar. Die niedrigstmögliche — und sehr häufig vorkommende — Energie ist die des Gesamtkristalls. Im kristallinen Festkörper übertragen die Vibrationswechselwirkungen die Energie so schnell, dass eine bedeutende Abweichung von der Durchschnittsenergie im Kristall nicht möglich ist. Da eine statistische Verteilung nicht vorhanden ist, kann die Arrhenius-Gleichung nicht angewandt werden, nur wenn sie für das spezielle System unabhängig bestätigt worden ist.

Резюме — Широкий разброс вычисленных энергий активации в случае разложения твердых тел приводит к предположению, что там нет дискретного активированного состояния. Кроме того, статистическое распределение, на котором основаны все вычисления, является неприемлемой концепцией. Наинизшая возможная энергия, которая наиболее часто и встречается, является энергия массы кристалла. Внутри кристаллического твердого тела колебательные взаимодействия так быстро передают энергию, что существенное различие от средней энергии недостижимо в объеме кристалла. Потеря статистического распределения исключает использование уравнения Аррениуса, если только это не подтверждено для данной конкретной системы.