ON THE RÔLE OF SUPERSATURATION AND ON THE LIMITING STAGE IN TOPOCHEMICAL REACTIONS.

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When chemical reactions are accompanied by the disappearance or the birth of solid bodies, these latter processes are usually located at interphase surfaces. This led to the introduction of the conception of spatially connected or topochemical reactions [1]

A topochemical reaction consists of a certain series of chemical and crystallisation stages, the mutual relations of which have as yet been little investigated. The nature of the limitating stage, although very essential for correct orientation is, in particular, unknown. In the present work this question is discussed and the decisive rôle of the distance from the equilibrium (supersaturation of the reaction) in topochemical kinetics is shown.

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[1] Kohlschütter, *Z. anorg. allg. chem.*, 1918, **105**, 7 ; 1920, **111**, 193.

To simplify the theoretical analysis we shall examine only the cases of monocrystals, and of powders consisting of crystals of the same type and the same size. We shall not consider the case (more akin to the usual experimental conditions) of a polydispersed powder with separated crystals, differing not only in their size, but also in their crystallisation form and their degree of purity.

1.

The simplest case is represented by the chemical change of a solid body into wholly gaseous reaction products. The only crystallisation stage in reactions of this first type is the destruction of the crystal lattice of the initial solid body; the most difficult process (formation of new space nuclei) is absent; there remain only effects connected with the supplementary marginal energy which is spent at the beginning of the plane lattice destruction. This quantity, analogous to the energy of the plane nucleation, can create a considerable delay only near the equilibrium. Therefore the activation energy of the total process depends as a rule upon the chemical stage and cannot differ essentially for different faces of a crystal and for crystals of different size. In the simplest cases the pre-exponent must be of the order of $P_s . \nu$, where P_s is the total number of atoms on the planes, limiting the crystal, and ν is the frequency of heat oscillations.

The dependence of velocity upon temperature must follow the Arrhenius equation, its dependence upon the concentration of gaseous products is entirely defined by the inverse reaction.

In a monocrystal or in a powder consisting of crystals of equal size we should expect the reaction velocity to be proportional to $m_t^{2/3}$, where m_t is the mass of the compound kept unchanged * until the time t:

$$V = km_t^{2/3} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Deviations from such a simple picture may occur very near to the equilibrium because of the incipient evaporation of a plane film along the edges and tops.†

At very high supersaturations the deviations are of another character. Quite generally, in topochemical reactions the probability of processes leading to the formation of forms with lesser stability increases with the increase of supersaturation; this increase is the quicker the larger the free energy of the corresponding form.[2]

Therefore, when supersaturation is large enough, there is a definite probability of processes leading to a change inside a solid phase. Since the pre-exponent in the simplest case is $P_v . \nu$ (where P_v is the total number of atoms in a crystal minus the surface atoms) the reaction may lose its surface character, which is strictly obligatory at and near equilibrium. Under these extreme conditions the topochemical restriction has no

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* For a polydispersed powder there must occur (depending upon the distribution law of the crystal size) deviations from the formula $V = km_t^{2/3}$ in the direction of a sharper, as well as in the direction of a slower, decrease of velocity with the decrease of the mass.

† In fact a molecule evaporating from an angle of the plane lattice creates two marginal atoms, while a similar molecule, ejected from the edge of a plane furnishes three marginal atoms, and from the face four marginal atoms. The removal of the further molecules is evidently also easier near the place of evaporation of the first atom from an edge or from a top than from a face.

[2] Roginsky, *Acta phys.-chim. U.S.S.R.*, 1936, **4**, 729; 1938, **8**, 376.

longer any meaning, and the kinetics must approach that of homogeneous classical or chain reaction. All the transitions between these extreme cases are possible.

As an example of a simple topochemical reaction of the type under consideration we may cite the pyrolysis of mercury oxide.[3, 4] When heated in high vacuum decomposition of HgO occurs before any perceptible evaporation sets in,[5] and therefore under the usual conditions this process really is of the type I.

The relation $V = km_t^{2/3}$ is very well fulfilled during the decomposition in the presence of catalysts. During thermal decomposition considerable deviations from this law are observed; this is quite natural for a polydispersal powder. The limiting rôle of the chemical stage is clearly determined by the choice of catalysts,[5] which catalysts also serve for analogous homogeneous reactions. No analogy has been found between the crystal types of the catalyst and of the mercury oxide respectively.

In the case of a catalytic reaction the localisation of the reaction on the crystal surface can be deduced from the increase of velocity with the quantity of catalyst:—

$$\frac{1}{v^0_{m_k}} = \frac{1}{v^0_{\sim}} + \frac{m}{m_k}\alpha. \quad . \quad . \quad . \quad . \quad (2)$$

This equation is based on the conception that the reaction located on the contact surface of the catalyst particles with the particles of the reacting substance $v^0_{m_k}$ is the initial decomposition velocity of the amount of the oxide of mass m mixed homogeneously with a quantity of the catalyst m_k; $v^0_{\sim}$ is the limit towards which the velocity tends with increase of the amount of the catalyst; α is a coefficient, including the relation of the densities, the sizes of the crystals, etc.

Group I comprises possibly also some cases of decomposition of unstable endothermic compounds of the type of nitrogen iodide, recently investigated,[6] but here we are dealing with very high supersaturations and high decomposition energies, with all their kinetic consequences.

2.

As another simple extreme case of topochemical reactions consider the formation of crystals by chemical reaction in the gaseous or liquid phase. For reactions of this very common second type all variations are possible from an entire limitation of the crystallisation stage up to the limitation of the homogeneous chemical reaction antecedent to the formation of the crystalline substance.

The first of these extreme cases is typical of reactions involving formation of ionic lattices by exchange reactions in solutions; such reactions do not need any considerable chemical activation energies for any of their stages.

The kinetics of such reactions do not differ essentially from those of crystallisation out of melts or solutions; whence, there arises quasi-stable supersaturated systems, exhibiting spatial nucleation with the work

$$W_{\text{3-dimens.}} = \frac{\beta}{T^2 ln^2 c/c_{\sim}} \quad . \quad . \quad . \quad . \quad (3)$$

and the plane nucleation with the work

$$W_{\text{2-dimens.}} = \frac{\gamma}{T ln c/c_{\sim}} \quad . \quad . \quad . \quad . \quad (4)$$

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[3] Taylor and Hullett, *J. physic. Chem.*, 1913, 565.

[4] Kandall and Fuchs, *J. Am. Chem. Soc.*, 1921, **43,** 2017.

[5] Roginsky, Sapognikoff and Kutsherenko, *Ukr. Chem. J.*, 1929, **4,** 99 (Russian).

[6] Garner and Latchem, *Trans. Faraday Soc.*, 1936, **32,** 567.

where β and γ are specific constants, independent of temperature, degree of dispersion and the supersaturation.

The relation $c/c_{\sim} > 1$ containing the concentration fractions respectively in equilibrium ($c_{\sim}$) and during the reaction (c) serve as a measure of the supersaturation.

For decomposition there is $c/c_{\sim} < 1$ and we must take $c_{\sim}/c$ as the measure of supersaturation.[7]

If we neglect the new formation of space nuclei during the reaction, these processes at constant supersaturation are, kinetically, autocatalytic, the velocity increase for a separated crystal or for the sum of equal monocrystals is proportional to $\chi_t{}^i$, where χ_t is the mass of the solid reaction product, formed in time t and i equals 2/3, 1 or 4/3, according to the sequence of the stages in the dominating type of crystal growth.

The equation

$$v = k\chi_t{}^i \quad . \quad . \quad . \quad . \quad . \quad (5)$$

with i=2/3; 1; 4/3; corresponds to the substitution of a discrete growth, with halts for mean time τ (required under given experimental conditions for the completion of the critical plane nuclei of each new film) instead of to the continuous propagation of the reaction zone, usually adopted in topochemical investigations.

Designate the value of τ at the tops of the crystal through (τ_t), at the edges (τ_e), at the faces (τ_f). When such a nuclei has arisen, it will, during a time $\tau' \ll \tau$, grow into a plane lattice covering the face with a continuous film.

Since the number of particles in the plane of a single face is proportional to $\chi_t{}^{2/3}$, while the number of top atoms does not depend upon χ_t, and the number of edge atoms increases proportionally to $\chi_t{}^{1/3}$, we obtain the relations mentioned above.

Equation (1) shows that with the increase of the supersaturation the nucleation work will decrease on all the surface elements; at the same time the relations between the nucleation work on faces, or edges, or tops will decrease,[2] as (for a cube):

$$P_f = \tfrac{1}{6}P_{\text{surf.}} \gg P_e \gg P_t.$$

When the values of the nucleation work approach one another, either the edge or the face case must predominate.

In fact, when the supersaturation is sufficiently large, in addition to the nuclei already existing (dust, wall), spontaneous new space nuclei formations will grow, and owing to the appearance of anomalous faces and complex growth figures, the growth itself will lose the simple character expressed by the equations.

Clearly the appearance of a newly-formed space nuclei corresponds to an addition to the velocity expression of factors containing a power of χ_t exceeding i. Consider only the simplest case of constant supersaturation, supposing that the growth of a new crystallisation centre is equally probable at every moment of the time lag $\theta + \Delta\theta$ (θ being the time of appearance of a certain group of nuclei). Then we get for the reaction velocity:

$$v = At^j + \int_0^t A_1(t - \theta)^j \mathrm{d}\theta \quad . \quad . \quad . \quad (6)$$

After integration we get:

$$v = At^j + Bt^{j+1} \quad . \quad . \quad . \quad . \quad (7)$$

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[7] Vollmer and Weber, *Z. physik. Chem.*, 1926, **119**, 277; Brandes, *ibid.*, 1927, **126**, 196; Vollmer and Marder, *ibid.*, 1931, **154**, 97.

Analogous equations were obtained by Ismailov[8] and Erofeev,[9] for particular cases, as approximations for a topochemical type with an interface of the type: solid 1/solid 2.

Neglecting the more complicated cases we emphasise two characteristic peculiarities of reactions of the second type, proceeding under conditions of a limiting crystallisation stage. It must be pointed out that power terms of type (6) are exact solutions only for $v = k\chi_t^{2/3}$. Already $v = k\chi$ corresponds to $j = \sim$ and to exponential growth of the velocity, which usually is considered a criterion of the chain character of the reaction. For separated parts of the exponential curve $v = k\chi_0 e^{+kt}$ a sum of the type (6) may be a fairly good approximation. Analogous remarks are also valid for $v = k\chi^{4/3}$.

(i) An anomalous (not Vant-Hoff) influence of the concentration of reaction partners, which does not obey the law of mass action, but is related to $\ln c/c_\sim$, this expression being included in the denominator of the expression for the nucleation work of the given type of nuclei. This work being included in the apparent activation energy E^1,

$$E^1 = W$$

we may expect a thoroughly specific velocity dependence upon concentration differing entirely from the usual one.

Since the expression for the plane nucleation work contains the first power of $\ln c/c_\sim$, and that for the space nucleation work contains the square of $\ln c/c_\sim$, the rôle of the second member of (7) will increase continuously with consequent increase of the supersaturation.[2]

The value of j also will increase within the allowed limits.

Finally, if several forms with different free energies of formation can possibly be formed, the fraction of crystals, belonging to a less stable form, the fraction of anomalous faces and the fraction of disturbed places in a crystal will increase with the increase of concentration and consequently of the supersaturation.

These results obtained for systems which obey the laws of ideal gases, were recently generalised by L. E. Gurevitsh for systems with any state equation, including the liquid phase also.[10]

(ii) The temperature dependence. Actually E^1, equalling W_{pl}, W_{sp} or a linear function of these quantities, contains in the denominator, not only T due to the Boltzman distribution law, but also the first power of T for the plane nuclei and the square of T for space nuclei. Further, in the general case, $c_\sim$ is an exponential function of T, with a negative or positive exponent, depending on the sign of the thermal effect. Therefore, in the rare case, when $c_\sim$ is not much affected by T, *i.e.*, for $Q \approx 0$ we may expect the velocity constant to increase proportionally to

$$K = K_0\, e^{-n/RT^2} \quad \text{or} \quad K = K_0\, e^{-n/RT^3} \qquad . \quad . \quad (8)$$

according to the supplementary type of nucleating.

Experimentally, this type can be distinguished from the usual Arrhenius' growth within a large temperature range only as, when

$$\frac{T_1 - T_2}{T_1} = \frac{\Delta T}{T_1} \leqslant 1$$

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[8] Ismailoff, *Phys. Zs. Sovietun.*, 1933, **4**, 835.

[9] Erofeeff, *Z. Physic. Chem.* (Russian), 1937, **9**, 828.

[10] Gurewitsh, *Bulletin of the Inst. of Chem. physics*, 1938.

the expressions :

$$\frac{1}{T_1 + \Delta T}; \quad \frac{1}{(T_1 + \Delta T)^2}; \quad \frac{1}{(T_1 + \Delta T)^3};$$

can be substituted (as a first approximation) respectively by :

$$\frac{1}{T}\left(1 - \frac{\Delta T}{T_1}\right); \quad \frac{1}{T^2}\left(1 - \frac{2\Delta T}{T_1}\right); \quad \frac{1}{T^3}\left(1 - \frac{3\Delta T}{T_1}\right). \quad . \quad . \quad (9)$$

For $Q \neq 0$ the predominating rôle will belong to the exponential change of $c_{\sim}$ with T; at considerable Q values this must give sharp diversions from the Arrhenius' velocity dependence upon temperature.

The above concerns only the simplest case of constant concentration and constant T.

Under actual experimental conditions we have to deal very often with a supersaturation which decreases continuously with the precipitation of the crystals (m = const.). In this case the velocity must pass through a maximum, and the picture is much more complicated.

The other extreme case of processes of the second type appears when the velocity of the chemical process is small (due to a large E-value or a small steric factor), while the crystallisation proceeds relatively easily, owing to a small nucleation work or to the presence of a large crystallising surface. The limiting stage of the sequence :

$$\Sigma A_{\text{homog.}} \overset{\xrightarrow{v_1}}{=} \Sigma B_{\text{homog.}} + C_{\text{homog.}} \overset{\xrightarrow{v_2}}{=} \Sigma B_{\text{homog.}} + C_{\text{cryst.}} \quad . \quad (10)$$

may, in this case, be the first homogeneous stage which obeys the usual kinetic laws. The concentration c will, on the contrary, all the time be kept at a level ensuring that $v_1 = v_2$.

An intermediate and, apparently, more frequent case takes place when the whole formation process of the solid phase consists of a typical chemical reaction with large E, located at the contact surface of the product $C_{\text{cryst.}}$ with the initial gas (solution).

This can occur if the activation energy is considerably larger in the homogeneous phase than at the surface $C_{\text{cryst.}}$, or if the energy of the separated proceeding of the first stage of the scheme (10) is strongly negative.

Then the activation energy E of the total process, consisting of one basic stage, equals

$$E = E_{\text{chem.}} + E^1 \quad . \quad . \quad . \quad . \quad (11)$$

where E is the W of one of the crystallisation stages or a simple linear function of $W_{3\text{-dim.}}$ and $W_{2\text{-dimens}}$.

In this case all we have said as to E^1 still holds, but the kinetic effect of the variation of E^1 will be the less, the smaller the fraction E^1/E. Since $E_{\text{chem.}}$ may be supposed constant, the above-mentioned effects should be detected at low T and small supersaturations, *i.e.*, under conditions unsuited for kinetic measurements ; therefore specially favourable conditions are needed to corroborate the correctness of equation 11.

3.

The third type of topochemical reactions is characterised by the simultaneous presence of solid bodies in the initial substances, as well as in reaction products. During recent years the greatest part of kinetic investigations have dealt with reactions of this group.

All the basic elements of this third type of reactions were contained in the two types already analysed. The only new feature is the simultaneous presence of crystalline bodies in the initial and final substances.

Under definite extreme conditions the presence of this new factor may have no considerable influence on the kinetics of the process ; we can approach as near as we like to a stage of reaction, where the limiting process is of the first or of the second type. In the general case, however, the simultaneous existence of the two solid phases must be taken into consideration.

As in the cases considered above the basic parameters are the supersaturation and the energetic characteristics of the process.

Let us begin with small values of $c/c_{\sim}$.

When c approaches $c_{\sim}$, kinetic and thermostatic considerations lead us necessarily to localise the process at the contact boundary of two solid phases. The reaction products must, further, under these conditions be brought down in form of large crystals, free from distortion ; every diversion from these conditions involves an increase of the free energy of the system.[2]

If the growth scheme with plane nucleation may also be applied to the interface of two solid bodies, it follows that, for monocrystals or homeo-disperse powders, the topochemical equation deduced above must be true as a first approximation.

Reactions of type III are very different in kind in respect to their chemical character. They range from the allotropic transitions, decomposition and formation of molecular compounds of the crystallohydrate and ammoniate type (for which we have no reason to expect any chemical activation energy, and where only the thermal effect of the reaction and the nucleation work are present) up to reactions, accompanied by deep chemical change (as, *e.g.*, the reduction of oxides and sulphides, or the decomposition of complicated groups, with a change of the bound valence) involving a real and considerable activation energy.

In the simplest case, where $E_{\text{chem.}} = 0$ and Q (being positive or very little negative) is small relative to the space nucleation work under given conditions, the process located on the interphase boundary will have a typical crystallisation character with all its consequences (temperature dependence not following Arrhenius' law, anomalous dependence upon $c/c_{\sim}$ etc.). Time dependence gives S-form curves, always observed in reactions of this type, as can be readily explained in this case. If $E_{\text{chem.}} \gg 0$ and all the peculiarities connected with the localisation of the process on the two phases interface are preserved, the character of the limiting stage will be essentially changed and will be of a definite chemical character. This will tell on weakly displayed kinetical anomalies which are typical for crystallisation processes (a normal dependence upon T, a weak dependence upon $c/c_{\sim}$, except at the very start of the reaction).

Simultaneously there may arise real catalytic accelerations, connected with the decrease of the activation energy of the chemical stage, and not with the facilitating influence of the crystallisation. In these cases foreign additions may (within the limits defined by the topochemical character of the reaction) be stronger accelerators than the decomposition products. The latter may, moreover, provoke purely crystallisation as well as purely catalytic acceleration.

Further, in a crystallisation type, there may occur, in contrast with the chemical type, a noticeable increase of the linear velocity of propagation with increase of the supersaturation ; this is connected with the facilitation of the plane nucleation which is of no importance in the chemical type.

Thus, the typical cases of crystalline or chemical topochemistry must, in spite of the analogy of their time dependence, differ sharply in several other respects.

With the increase of $c/c_{\sim}$ the restrictions due to thermostatics get looser ; in addition to simple displacement, an increase of the interface becomes possible on account of the formation of new crystal nuclei, in contact with those existing already ; finally, the formation of tridimensional nuclei of the new phase on those parts of the initial crystal which are not touched by the reaction, can obtain a measurable value at great supersaturations.

At very large supersaturations there may occur a breakdown of the reaction along the surface and a transition of the reaction inside the initial solid body.

A nucleation arising at sufficiently high supersaturation contributes to the removal of obstacles created by the difference of the geometrical forms of the lattices of either the initial or the final crystal ; in practice, considerable velocities can only be so attained. The larger the relation of the nucleation velocity to the growth velocity, the higher is the degree dispersion of the reaction products. When there is no recrystallisation, a dispersion not resolvable by an X-ray photograph can be reached in this way. This is apparently the cause of the formation of amorphous powders in many topochemical reactions.

On the contrary, we see no reason for the assumption [11] of a necessary intermediate formation of an amorphous phase in topochemical reactions. Such a scheme is not only kinetically less probable, but is thermodynamically impossible at small supersaturations.

The addition of a surface nucleation provokes, equation (7), an increase of the order in the kinetic equations. This is analysed by Ismailov,[8] who has given a perfect formal analysis, without considering the physical peculiarities of the process.

If the reaction is to proceed in space the free energy of the system (including the decomposition products in the lattice of the initial body) must be equal to or smaller than the free energy of the initial system. This can be reached by a suitable choice of sharply exothermic processes. When the specific volumes either of the initial or of the final systems (gases) differ sharply one from the other, a storing of the decomposition products inside the lattice can provoke a segregation of crystals ; the possible influence of such a process was pointed out by Hinshelwood and Bowen.[12] The existence of such effects was recently shown in the decomposition of lead azide by Chariton and Belayev.[13] Very large supersaturation seems the essential. Under these conditions crystallisation effects must play a small rôle for sharply endothermic compounds, and the reaction must approach, kinetically, to reactions of the first type. A system possessing a large decomposition energy and a high supersaturation must have a considerable activation energy if it is to be relatively stable, *i.e.*, if it can exist at all. But a large value of $E + Q$ is just one of the basic assumptions of chain. Data, available in the literature on the kinetics of topochemical reactions,

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[11] Slonym, *Z. Elektrochem.*, 1930, **36**, 444.

[12] Hinshelwood and Bowen, *Phil. Mag.* (6), 1920, **40**, 569.

[13] Chariton and Belayeff, *Acta phys. chim. U.S.S.R.*, 1936, **5**, 757, 767, 777.

confirm generally the correctness of the above scheme, in which the basic rôle in the kinetics of reactions of this type is ascribed to the value of the supersaturation and to the reaction heat.

Pease and Taylor[14] have described the different influence of moisture on the kinetics of copper oxide reduction by hydrogen at the beginning and at the subsequent stages of reaction. We find that nickel and iron oxides behave in a quite analogous way.

This confirms the different influence of supersaturation whether on the nucleation or on the growth in typical topochemical reactions. The practically complete absence of any reaction of untouched crystals near the equilibrium, often observed, comes in the same category.

As an illustration of the influence of supersaturation on the character of the kinetical equation, consider the simple topochemical kinetics of the dehydration of crystal hydrates and of the decomposition of carbonates, as well as the complicated exponential autocatalytic character of the kinetics of the decomposition of unstable and energy rich forms.[15, 16] Also the phenomenon of aggregation for systems of this type and of the amorphous decomposition products mentioned by Slonym and many other authors. In particular there must be mentioned the interesting series of articles of Zawadzki and Bretsnajder. These authors having expressed opinions very near those mentioned above upon reactions involving two solid phases and have corroborated them with interesting experiments on the kinetics of decomposition and formation of carbonates.[17]

4.

By way of additional illustration we mention some of our recent experimental data.

The criteria, whether of chemical or of crystallisation autocatalysis, which serve to establish the type of the limitating stage, have been pointed out above. We have provoked them in the decomposition of permanganates of mono- and bi-valent metals :—

$$2\ \mathrm{Me^{I}\,MnO_4} = \mathrm{Me_2^{I}O}\ ;\ 2\ \mathrm{MnO_2} + 1\tfrac{1}{2}\ \mathrm{O_2}$$

$$\mathrm{Me^{II}(MnO_4)_2} = \mathrm{Me^{I}\ O}\ ;\ 2\ \mathrm{MnO_2} + 1\tfrac{1}{2}\ \mathrm{O_2}.$$

In chemical respect all the reactions of this group ** involve splitting off of the excess oxygen from the amion $(\mathrm{MnO_4})^-$ of the heptavalent manganese with the transition of this latter into a tetravalent form; the cation remains unchanged. We shall expect the limitating stage to be of a predominantly chemical character with possible chemical catalytic effects. Such an influence should be particularly exerted by the cation in the lattice. If so, there should be a regular decrease of the chemical stability of permanganates with increasing deforming influence on the ion.

Comparing the decomposition velocity of permanganates of a series of metals, we find quite definitely, although only qualitatively, that the

[14] Pease and Taylor, *J. Am. Chem. Soc.*, 1921, **43**, 2179 ; 1922, **44**, 1635 ; Lorson and Smith, *ibid.*, 1925, **47**, 364.

[15] McDonald and Hinshelwood, *J. Ch. Soc.*, 1926, **127**, 2761 ; Garner and Hailes, *Proc. Roy. Soc.*, 1933, **139**, 576 ; Garner and Hamm, *J. Chem. Soc.*, 1931, 2123 ; Hailes, *Trans. Faraday Soc.*, 1933, **29**, 342.

[16] Sieverts, *Z. physik. Chem.*, 1922, **100**, 463.

[17] Zawadzki and Bretsnajder, *C.R.*, 1932, 1160 ; *Z. physik. Chem., B*, 1933, **22**, 79 ; *Z. Elektroch.*, 1935, **41**, 215.

** Except $\mathrm{AgMnO_4}$, see ref. [17].

decomposition of all the compounds investigated has a sharply expressed autocatalytic character (see Fig. 1). For all except lithium permanganate, the velocity increase conforms rather well to $X_t^{2/3}$, and the velocity decrease to $m_t^{2/3}$. The velocity constants, however, are very different. For brevity we compare only the temperatures at which the maximum, $t_{\text{max. vel.}}$, was reached roughly during the same time ($\sim$ 120 minutes) for all the salts examined (Table I).

Clearly, the permanganates according to their increasing stability can be arranged, for univalent ions,* as follows: Ag^+; Li^+; Na^+; K^+; Rb^+; $(Cs)^+$. For bivalent ions we have the sequence: Mg^{++}, Ba^{++}, which is exactly in accord with the series of deforming ions of Fajans, Grimm and others. The same is true for stability differences of the salts of neighbouring metals of the I and II group. For the permanganate with the smallest stability (Li), the simple topochemistry is not maintained. Lithium permanganate gives a velocity increase approximating the exponential one. On X-ray investigation of the products of decomposition of $AgMO_4$,[18] no separate lines are observed, but only a general very strong absorption.

TABLE I

Substance.	Temperature.	Substance.	Temperature.
$LiMnO_4$	$\sim$ 100° C.	$Mg(MnO_4)_2$	110° C.
$NaMnO_4$	$\sim$ 150° C.	—	
$KMnO_4$	$\sim$ 200° C.	—	
$RbMnO_4$	$\sim$ 250° C.	$Ba(MnO_4)_2$	170° C.
$CsMnO_4$	? (280° C.)	—	
$AgMnO_4$	$\sim$ 90° C.	—	

These experiments confirm the chemical character of the limitating stage and are quite in accord with analogous observations of Roginsky and Schulz on the catalytic influence of foreign solid substances on the reaction.[19]

Because of the difficulty of approaching the equilibrium, the decomposition of permanganates may be of little use for investigating the influence of supersaturation on kinetics.

Therefore we have studied the decomposition of (1) nickel carbonate (at different constant CO_2 pressures within the limits of every experiment), and (2) the reduction of nickel oxide. All results obtained are in accord with our supposition.

Interesting experiments on the change of the kinetic character of the decomposition of nickel formate, avoiding initiation centres, were carried out by T. Zelinskaja and D. Dobytshin.[20] Nickel formate decomposes mainly according to the equation $Ni(HCOO)_2 = Ni + H_2 + 2CO_2$. This process has a clearly expressed topochemical character. On decomposition in vacuo or in a gas the velocity increases in accord with the law $V = Kt^2$. This corresponds to the development of preliminary given reaction centres without any space nucleing.

The reaction will also proceed under a layer of mineral or vegetable oil (paraffin oil, hydrogenated vegetable oil, etc.). In this case, however, the reaction proceeds much more slowly, and the temperature corresponding to equal velocity is nearly 100° higher. It is natural to explain this fact by a blockage of the normally existing nuclei by organic molecules.

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* The data for Cs are only preliminary.

[18] Hein, *Z. anorg. allg. Chem.*, 1937, **255**, 25.

[19] Roginsky and Schulz, *Z. physik. Chem.*, 1928, **138**, 21; see also Moles and Crespi, *Ann. Soc. esp. Fis. Quim.*, **23**, 198.

[20] Dobytshin and Zelinskaja, *Bull. of the Inst. of chem. physics*, 1938.

However, at higher temperatures the reaction proceeds with a sufficiently large velocity ; but instead of following the relation $V = Kt^2$, the relations are expressed by an equation of a higher order involving a second member,

$$v = k_1t^3 - k_2t^4. \quad . \quad . \quad . \quad . \quad (12)$$

According to our scheme this must be due to increased supersaturation, which, as pointed out above, must enlarge j, and provoke the appearance of a member with $(j + 1)$. The newly formed interface may, however, also be spoiled by the oil, the probability of which is proportional to $\gamma(t - \theta)$. Therefore

$$v = \int_t^0 A(t - \theta)^2 d\theta - \int_t^0 A(t - \theta)^2\gamma(t - \theta)d\theta.$$

This is equivalent to (12).

The examples considered show that in general the conclusions drawn from the considerations developed above are confirmed by experiment.

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