THE THERMAL DECOMPOSITION OF POTASSIUM PERMANGANATE.

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The thermal decomposition of solids conforms to certain general laws, *e.g.*, sigmoid curves with the same characteristics are invariably obtained.[1] There has not appeared, however, any comprehensive theory which provides a solution to the many problems which have arisen. The "chain" theory of Garner [2] is an attempt in this direction, but certain difficulties arise in its application, *viz.*, the type of branching would seem to account for a small fraction of the total reaction, and there appears no sound reason why such branching should occur, or why it should persist. These objections have been overcome to a great extent by Macdonald,[3] but only by postulating a specialized mechanism which is not expected to be of general validity. Since a large number of diversified gaseous reactions have been co-ordinated in the general theory of chains of various types, there appears no reason why a similar broad and flexible concept should not be applicable to solid decompositions. This paper is an attempt to explain the kinetics of the decomposition of $KMnO_4$ in a form which, when suitably modified, can be applied to other similar reactions. Potassium permanganate was used in this study because (*a*) considerable cracking, which is a complicating factor from the viewpoint of many previous theories, occurs during decomposition; (*b*) there is definite evidence that the end products catalyze the reaction; [4] (*c*) previous work is in disagreement with regard to the kinetics; [5] and suggests that any determination of the activation energy is impossible.

Experimental.—The effect of variation in initial concentration, rate of cooling and evaporation, time of growth, etc., was investigated in order to obtain the conditions for the production of crystals of good form and convenient size. Finally, 12 g. A.R. $KMnO_4$ were dissolved in 100 ml. dust-free, distilled water at 60° C.; after rapid filtration through glass wool to remove any MnO_2, the filtrate was placed in an enclosure at 25° C. for 6 hours in the dark, since when exposed to light superficial decomposition takes place causing the original bronze brown crystals to acquire a steel-blue lustre.[6] The supernatant liquid was then decanted, the crystals rapidly dried, and selected by hand under a microscope.

The apparatus consisted of a pumping system, two Macleod gauges with a pressure range 10^{-1} to 10^{-5} cm. Hg., a calibrated bulb for use in the determination of the volumes of the various systems, and a constant temperature vessel in which the decomposition took place and which was held in position by two ground glass joints. The latter allowed the vessel to be detached for cleaning and other purposes. The pumping system comprised a one-stage mercury diffusion pump backed by a Hyvac oil pump, and was in connection with the apparatus through a trap immersed in solid CO_2 and alcohol followed by a P_2O_5 tube. A similar trap between the gauges and the decomposition chamber prevented mercury vapour

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[1] Garner, *Trans. Faraday Soc.*, 1938, **34**, 940.

[2] Garner and Hailes, *Proc. Roy. Soc., A*, 1933, **139**, 576.

[3] Macdonald, *J.C.S.*, 1936, 832 and 839.

[4] Roginsky and Schulz, *Z. physik. Chem. A*, 1928, **138**, 21.

[5] Roginsky, *Trans. Faraday Soc.*, 1938, **34**, 959. Hinshelwood and Bowen, *Phil. Mag.* (6), 1920, **40**, 569; *Proc. Roy. Soc., A*, 1921, **99**, 203. Moles and Crespi, *Z. physik. Chem.*, 1922, **110**, 337. Roginsky and Schulz, [4].

[6] Brude and Fester, *Z. angew. Chem.*, 1922, **35**, 527.

from coming into contact with the decomposing crystal. Difficulty was experienced in obtaining constancy of temperature to 0·1° C. in the range 200-225° C. due to the absence of a constant D.C. supply and the fluctuations in the A.C. mains. Liquid baths, the boiling-points of which could be altered by pressure variation, were therefore used. Various designs were investigated; that finally employed consisted of a glass tube, closed and flattened at its lower end and internally sealed into a glass bulb which contained the boiling liquid (and garnets) sufficient in volume to cover the lower part of the inner tube. Near the internal seal was a T-joint which led to a spiral air condenser, into a large bulb and then, through fine capillaries, either to the oil pump or to a N_2 cylinder. The heat of ebullition was supplied by an electric furnace provided with a thick cylindrical core of copper, and which was hand regulated to ± 3° C. The temperature required to give rapid and regular boiling without superheating was 100° C. above that of the B.Pt. of the liquid. The furnace and vessel were finally enclosed in an asbestos box to avoid effects of draughts, etc. Various pure liquids, *e.g.*, ethyl salicylate, bromo-naphthalene, etc., were used, but over the period of the longer runs (12-16 hours) polymerization and decomposition were evident causing a temperature drift unless compensated by variation of pressure. Use was therefore made of a commercial paraffin from which the unsaturated compounds were removed by continuous treatment with conc. H_2SO_4, and which was then repeatedly fractionated. Since peroxides catalyze polymerizations, 0·1 % diphenylamine was added to the oil and the air over it replaced by N_2 during any run. A sample could then be used over a period of months before refractionation was necessary. The temperatures were measured by a mercury thermometer placed in the inner vessel of the decomposition chamber, being in such a position that the mercury bulb was symmetrically placed with respect to, and touching the side of, the Pt bucket containing the crystal. The thermometer, which had been previously calibrated in the range 190-250° C. under the same conditions, remained in position during all runs. A calibrated curve (V.P./B.Pt.) was constructed to give the pressure corresponding to the desired temperature and could be used to obtain a quick adjustment should self-heating effects be evident during decompositions. The plot served as a useful secondary measure of the temperature differences required in the determination of activation energies.

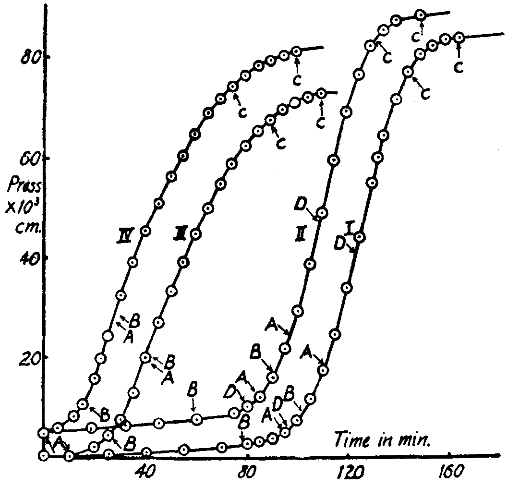

FIG. 1.

The bucket was provided with a lid and attached by a Pt hook to thin Pt wire, the other end of which was fixed to a winch sealed into a ground glass joint. Rotation of the winch allowed the bucket to be lowered from the region at room temperature to that at the decomposition temperature. The volumes of the various systems were 348, 459 and 695 c.c., the one used depending on the amount of oxygen liberated in the reaction. A second decomposition chamber similar to the above allowed visual observation of the crystal.

In any run, the decomposition vessel was removed at the two joints, the bucket cleaned with acidified KI and distilled water, dried and finally raised to red heat for 10 min. The required amount of $KMnO_4$ was weighed directly into the bucket, which was then attached to the Pt. wire and the winch rotated to raise it. The vessel was replaced, the furnace and box placed in position, the pressure adjusted over the paraffin for the desired B.Pt., and evacuation commenced. The crystal was left *in vacuo* for 12 hours, during which time thermal equilibrium in the reaction chamber was well established. The pumps were then cut off, the bucket lowered, and pressures recorded at suitable times. The final pressure (p_f) was recorded one hour after the apparent end-point had been attained.

Results.

In solid decompositions, strictly reproducible results are rarely obtained because of the difficulty of preparing crystals completely free from imperfections. This was expected to be particularly marked here since the tendency of the crystal to crack is well known. Experimentally, using carefully selected crystals, the reproducibility of the p/t plots was good and the agreement of the derived constants of decomposition, the constants in the equations derived by Garner [2] were calculated. These, together with others, including those obtained by a subsequent analysis (k_1, c_1, etc.), are collected in Table I, both for the whole crystals (each of 6·2 mg.) and samples of a quantity ground in an agate mortar. The agreement allows confidence to be placed in the activation energies derived later from such constants. The region of validity of the equations

TABLE I.

Equation.	Whole Crystal.		Ground Crystal.	
Temp. 224° C.	I.	II.	III.	IV.
k in $\log p = kt + c$	$3{\cdot}73 \times 10^{-1}$	$3{\cdot}78 \times 10^{-1}$	$4{\cdot}43 \times 10^{-1}$	$4{\cdot}41 \times 10^{-1}$
k in $\log (dp/dt) = kt + c$	$4{\cdot}00 \times 10^{-2}$	$3{\cdot}43 \times 10^{-2}$	$4{\cdot}19 \times 10^{-2}$	$4{\cdot}15 \times 10^{-2}$
k in monomolecular decay . . .	$6{\cdot}81 \times 10^{-2}$	$7{\cdot}65 \times 10^{-2}$	$3{\cdot}23 \times 10^{-2}$	$3{\cdot}21 \times 10^{-2}$
Max. vel. in cm./min.	$2{\cdot}08 \times 10^{-3}$	$1{\cdot}99 \times 10^{-3}$	$1{\cdot}60 \times 10^{-3}$	$1{\cdot}68 \times 10^{-3}$
$k_3 : k_1$ in equ. (1) .	4·61	4·68	6·14	6·13
$k_4 : k_2$ in equ. (1) .	6·59	6·62	2·92	2·90

(*a*) $\log p = kt + c_{(AA)}$;
(*b*) $\log (dp/dt - dp_o/dt) = kt + c_{(BB)}$;
(*c*) the monomolecular decay (CC) ; and
(*d*) $dp/dt = kt^n{}_{(DD)}$

is indicated on the plots and shows that these do not adequately represent the characteristics of the curves.

The final products of the decomposition are uncertain,[7] but all agree that MnO_2 is one of them. Table II summarizes the % decomposition

TABLE II.

Ground Crystal.			Whole Crystal.		
Mass (mgr.).	**Temp. °C.**	**% decompn.**	**Mass (mgr.).**	**Temp. °C.**	**% decompn.**
2·2	215	96·5	1·9	220	93
4·5	215	108·5	3·5	220	95·5
5·9$_4$	215	106	4·0	220	98·5
6·6$_6$	215	107	5·0	220	103
8·4	215	109·5	7·0	220	104
9·8$_2$	215	106·5	9·1$_4$	220	98·5
8·4	200	97·5	4·0	200	107
8·4	205	106	4·0	205	107·5
8·4	210	106	4·0	210	90·0
8·4	215	110·5	4·0	215	91
8·4	220	106	4·0	220	95·5
8·4	225	106	4·0	225	102

Average (const. T) = 105·7.
Average (const. mass) = 105·1.

Average (const. T) = 98·8.
Average (const. mass) = 98·8.

in terms of the equation $2KMnO_4 = MnO_2 + K_2MnO_4 + O_2$ for varying mass of ground and whole crystals at constant temperature, and at varying temperature for constant mass. There is no specific variation with mass or temperature over the limited range studied, but some dependence on particle size. The complexity of the chemical changes involved suggests the possible production of effective intermediates. If these were comparatively stable, but changing at a high rate because of the rapid acceleration, the decomposition might proceed by chains with degenerate branching;[8] but the interruption of the reaction by sudden cooling and subsequent reheating after 16 hours to the initial temperature gave no new induction period and the velocity was the same as that found at the moment of cooling.

Some disagreement exists as to whether the decomposition products and MnO_2 have catalytic effects; Roginsky and Schulz[4] show that not only MnO_2, but a series of other oxides (Ni, Cu, Co, Fe, etc.), have marked acceleratory influences, and this is confirmed by Moles and Crespi[9] for the residue. However, Hinshelwood[5] found that MnO_2 is ineffective. In the present work, using ground $KMnO_4$, both the residue and MnO_2 cause a shortening of the induction period and a slight increase of acceleration subsequently. These effects will be more marked during decomposition since, in mixing, simple contact is obtained, whereas when the residue is produced *in situ*, the surface energy associated with the common interface will be large, as discussed later.

In order to obtain more information, observations were made during the whole process through a low power microscope, pressure readings being simultaneously recorded. Crystals possessing good form and surface, and those in a badly ridged and chipped condition, were used at various temperatures, but the conclusions obtained at corresponding

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[7] Mellor, *Comprehensive Treatise on Inorganic Chemistry*, vol. 12, p. 307 *et seq*.

[8] Semenoff, *Chain Reactions*, 1935.

[9] Moles and Crespi, *Z. physik. Chem.*, 1922, **100**, 337.

points on the plots were the same. A series of crackings and splinterings occurred during the very early stages; these were sporadic and irregular except that splintering along the length of the crystal was preferred. As the reaction progressed, the sequence of events followed more quickly, and with the approach of the acceleratory period in the p/t plot the disintegration rate markedly increased. The acceleration continued until about 5 min. before the maximum velocity of oxygen evolution was attained, at which stage there was a complete absence of any large fragments. Some two minutes later, there was a marked decrease in the frequency of cracking, and disintegration ceased completely at the inflexion point of the p/t plot. The particles now appeared to be of uniform size and shape, and did not undergo any further change during the subsequent decay period. There was no visual evidence suggesting that the reaction was favoured at corners and edges; in fact, a corner of the original crystal retained its sharpness after a considerable degree of disintegration. There is, however, a marked parallelism between the rate of disintegration and the percentage decomposition.

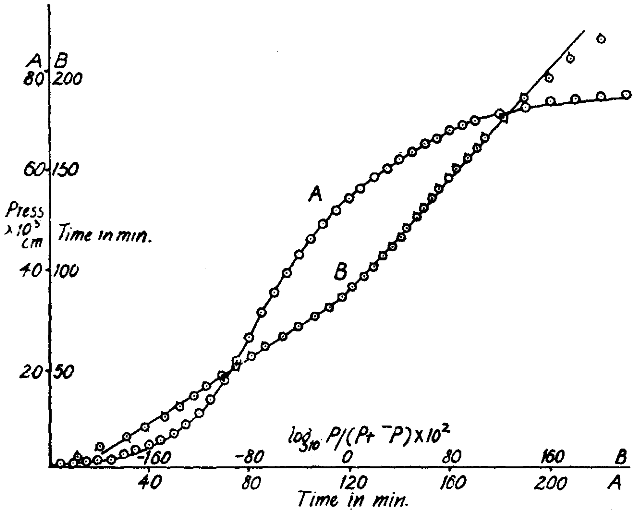

FIG. 2.

With ground crystals, the induction period was shorter, the acceleration more rapid, and the maximum velocity higher, the effects being increased with the degree of grinding. No measure of the total external surface area was attempted since there was a wide distribution of particle size. Such measurements would probably be of little value, since, in grinding, local heat effects would cause some decomposition and yield particles which would therefore decompose more rapidly.[10] Crushing, as distinct from grinding, effects a loss of "sharpness" in the induction period, *i.e.* the velocity during this time was higher but the subsequent acceleratory effect less than with whole crystals; a similar conclusion was obtained by Garner.[2]

The analyses of the plots were undertaken without reference to previous equations, which differed widely.[5] The resemblance of the plots to the hyperbolic function, tanh, suggested the expression

$$(p - p_1)/p_2 = \tanh (k/2(t - t_{\text{max.}})),$$

where the point of inflexion has co-ordinates (p_1, $t_{\text{max.}}$), p is the pressure

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[10] Parker, *J.C.S.*, 1914, **105**, 1504; 1918, **113**, 396.

at time t, and $p_2 = p_t - p_i$. With ground and whole crystals, $t_{\max}$ approximates to the time of 50 % of decomposition, hence

$$e^{k(t - t_{\max.})} = p/(p_f - p) \; ; \text{ or}$$
$$\log (p/(p_t - p) = kt \,.\, c \qquad . \quad . \quad . \quad . \quad (1)$$

where $c = kt_{\max.}$. The plot of the log term/t should be a straight line of gradient k which is constant throughout the reaction if the plot has symmetry about the inflexion point. In general, two constants are necessary because of asymmetry. Plots are given in Fig. 2 (ground) and Fig. 3 (whole) where the experimental readings are shown with the theoretical curve calculated from equation (1). The equation is not valid during the induction period (whole crystals); the origin has thus to be transferred to the end of this period—this is discussed later. The agreement is good—slight divergences are most marked at the end of the decay period.

The equation of Moles and Crespi (after the induction period) is $dx/dt = kx/a(a - x)$, and reduces to (1) where $a = p_f$ and $x = p$. The difference is that k and c have different values in equation (1), and not the same as suggested by them, after the inflexion point, since the plots are always asymmetrical. Similarly, if the exponential term in (1) is large compared with unity, then the equation (1) can be written $p = p_f e^{kt-c}$, or $\log p = kt + c^1$, where $c^1 = -c + \log p_f$, which is the equation of Garner[2] based on the same assumption. Thus, an analysis of one of the plots obtained with mercury fulminate shows that equation (1) is in good agreement.

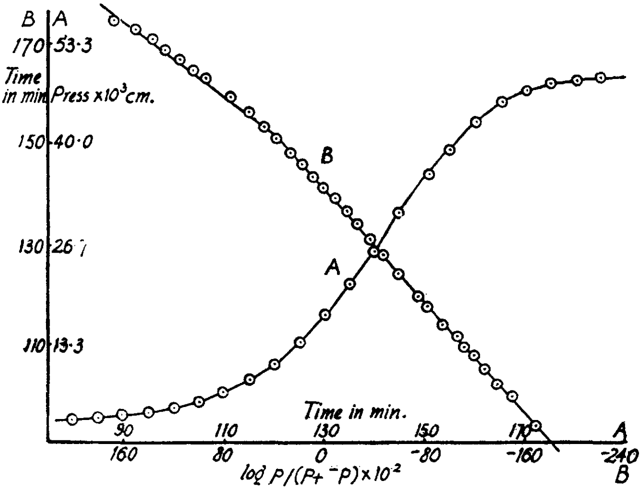

FIG. 3.

The constants, k_1, k_2 and c_1, c_2 (ground at 215° C.) and k_3, k_4 and c_3, c_4 (whole at 220° C.) for varying mass, and constant mass at varying temperature are shown in Table III. All constants are independent of mass and c_1, c_2, c_3, c_4 show no specific variation with temperature, whereas k_1, k_2, k_3, k_4 increase regularly. Plots of $\log k/^1/_T$ are given in Fig. 4, from which the activation energies, $E_1 = 34{\cdot}5$; $E_2 = 33{\cdot}1$; $E_3 = 38{\cdot}5$; $E_4 = 38{\cdot}8$ Kcal. can be obtained. The agreement of E_1 with E_2, and E_3 with E_4 suggests that the same chemical process occurs in the acceleratory and decay periods. The difference between ground and whole crystals is unexpected, since the estimated accuracy is 1·5 Kcal. It is probably due to the fact that the temperature of the decomposing crystal is not accurately recorded by the thermometer because of self heating. This latter,

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TABLE III.

Ground Crystals.

Mass (mgr.).	Temp. °C.	$k_1 \times 10^{+2}$ min.$^{-1}$.	$k_2 \times 10^{+2}$ min.$^{-1}$.	c_1.	c_2.
2·2	215	2·05	1·39	1·83	1·22
4·5	215	2·49	1·38	2·35	1·29
5·9$_4$	215	2·48	1·39	2·28	1·24
6·6$_8$	215	2·49	1·38	2·33	1·29
8·4	215	2·48	1·38	2·27	1·27
9·8$_2$	215	2·42	1·37	2·28	1·29
8·4	200	0·796	0·518	2·21	1·45
8·4	205	1·13	0·720	2·12	1·33
8·4	210	1·76	1·06	2·27	1·38
8·4	215	2·48	1·38	2·28	1·27
8·4	220	3·47	2·22	2·27	1·45
8·4	225	5·00	2·92	2·24	1·31

Whole Crystals.

Mass (mgr.).	Temp. °C.	$k_3 \times 10^{+2}$ min.$^{-1}$.	$k_4 \times 10^{+2}$ min.$^{-1}$.	c_3.	c_4.
1·9	220	3·15	5·96	3·95	7·93
3·5	220	3·65	6·29	4·63	8·40
4·0	220	3·63	5·79	5·09	8·48
5·0	220	3·72	5·91	4·74	7·88
7·0	220	3·73	5·80	4·77	7·78
9·1$_4$	220	3·71	5·79	4·75	7·80
4·0	200	0·672	0·956	4·01	6·12
4·0	205	1·09	1·64	4·57	7·22
4·0	210	1·57	2·96	4·07	8·20
4·0	215	2·65	4·05	4·91	7·78
4·0	220	3·63	5·79	5·09	4·48
4·0	225	5·48	9·74	5·32	8·86

which would be greater for whole than ground, is bigger the higher the temperature ; thus the recorded temperature would be proportionally lower than the true one. Such an effect would qualitatively account for the discrepancy.

Discussion.

The decomposition of solids is governed by the formation and growth of nuclei ; these have often been observed and photographed ;[11] they are formed on the external surface, and to a lesser extent within the mass of the crystal.[12] In some cases, clustering occurs,[12] and may mean that centres are formed from each other ; in others, the appearance of rows of nuclei [13] suggest that there are favoured places, such as along surface cracks or lines of strain, where formation is preferred. The reaction is mainly initiated on the external surface, and leads to the formation of an array of product molecules which in general have a unit cell differing in geometric form and in dimensions. Thus, although the chemical nature of the products with $KMnO_4$ is uncertain, MnO_2 is one of these. It has a body centred tetragonal cell of edge 4·44 A. and an axial ratio of 0·651 for

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[11] Kohlschütter, *Kolloid-Z*, 1927, **42**, 254. Coppeck, Colvin and Hulme, *Trans. Faraday Soc.*, 1931, **27**, 283. Garner *et alia*, *J.C.S.*, 1935, 1705 ; 1934, 1873 ; 1937, 1565 ; *Trans. Faraday Soc.*, 1936, **32**, 1739.

[12] Harvey, *Trans. Faraday Soc.*, 1933, **29**, 653.

[13] Wischin, *Proc. Roy. Soc., A*, 1939, **172**, 314.

c/a, where a is 4·38 A,[15] whereas $KMnO_4$ has an orthorhombic unit cell with $a = 9{\cdot}99$; $b = 5{\cdot}72$; and $c = 7{\cdot}41$ A.[16]

The surface layer, in as far as the MnO_2 molecules are concerned, will be different from that originally present, with a consequence that the interfacial region will be one of high energy, particularly since the process of reorganization in the immediate neighbourhood of the decomposing molecule will not necessarily lead to the rapid completion of the new lattice. Thus the reaction progresses (*a*) by an outward growth along the surface and (*b*) by a penetration into the mass of the crystal, in preference to the creation of further isolated nuclei. Thus Garner and Maggs [14] find that the activation energy of the interface reaction is smaller than that of the initial surface decomposition. In the simplest case, that of an isotropic body, the reaction zone spreads spherically into the solid and the rate of reaction is proportional to $p^{2/3}$ initially, as found [4] for $KMnO_4$, and to $(p_f - p)^{2/3}$ finally, where there will be volumes of unreacted $KMnO_4$ between coalescing spheres of products. Some plots obtained here can be fitted over a limited region by such expressions, but the agreement appears to depend fortuitously on the physical state of the $KMnO_4$ and not to be of general validity.

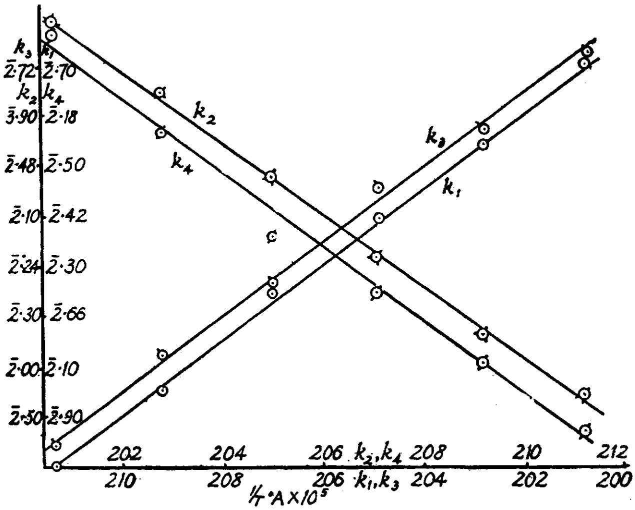

FIG. 4.

Equation (1) in the form $dx/dt = kx/a(a - x)$ represents a modified autocatalytic expression. In liquid or gaseous systems where there is perfect mixing of reactants and products, the interpretation is easy, but in the case of solids, the products may be considered to be stationary. This difficulty can be surmounted by assuming that ions and/or electrons are mobile (except when trapped in lattice discontinuities), *e.g.* by postulating an intercrystalline or intermolecular transference of electrons from an oxygen atom in $KMnO_4$ to the positive reducing ion ($K^{\cdot}$). This would explain why effective catalysts for this reaction are often coloured, para-magnetic, and possess strongly deformed, or deformable, electronic structures.[4] A similar hypothesis has been used with success by Garner in the more recent work on the alkaline earth azides, and can lead to a simple power law, $dp/dt = kt^n$; this latter arises from the dependence of the rate on the increase in number and the three dimensional growth of the nuclei.[17]

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[14] Garner and Maggs, *Proc. Roy. Soc., A*, 1939, **172**, 299.

[15] St. John, *Physic. Rev.*, 1923, **21**, 389.

[16] Mooney, *ibid.*, 1931, **37**, 1306.

With whole $KMnO_4$, the value of n is between 5 and 6 over a limited range (Fig. 1, DD), approaching the higher value with increase of temperature, as was found with azides. There are, however, certain obvious difficulties in the application of this hypothesis to the present decomposition. In the same way, a chain mechanism in the molecular sense has been proved to be improbable. The following theory is therefore suggested.

There are assumed to be n_0 nuclei originally in the crystal. Such nuclei in the widest sense are molecules of reactant whose decomposition is highly favoured, *i.e.* is attended by a lower activation energy than that associated with the majority of reactant molecules. They are present mainly on the surface, but some can be present within the mass. In each case, they are situated at lattice imperfections. Now, it is well known that the lattice constant of the two dimensional surface of any heteropolar crystal is about 5 % less than that of the corresponding three dimensional system [18]—lateral strains are therefore set up which are ultimately relieved by the formation of Smekal cracks.[19] The effect of a surface array of product molecules will be similar, but the magnitude will be much greater. At the mouths of such cracks, nuclear formation will be favoured; the reaction can therefore spread into the crystal down these crevices. The result will be that the inner surfaces of these latter will be progressively covered (as the reaction proceeds) with product molecules of different dimensions. This new surface array will again set up lateral strains leading ultimately to further cracking, "perpendicular" to this inner surface—the reaction will penetrate still further into the crystal and the phenomenon is repeated. The oxygen evolved finds free passage out through such crevices. There will thus occur a series of "branchings" similar to those envisaged by Garner and Macdonald, but such branchings will not be determined solely by the anisotropy of the crystal nor by the presence of ultimate Smekal blocks or crystallites.[2] The mechanical strain set up by this inhomogeneous deformation may result in the actual mechanical disruption of the crystal, as with $KMnO_4$, but this latter is a consequence and not the cause of branching. We therefore imagine the production of planes of strain or deformation, to be brought about by the surface array of product molecules —along these planes, the deformation effect of the product on the electronic structure of an adjacent molecule of $KMnO_4$ will be a maximum, and decomposition is favoured. Such deformation can be transmitted over short distances by induction so that there will be a number of potentially reactive reactant molecules associated with such planes, and there will be, on an average, a certain time interval between the creation of these conditions for reaction and the actual decomposition of the molecule. The depth of such planes can be regarded as being of fairly constant length, at least in the initial stages, since they will be extended at the forward edge at the same rate as the reaction proceeds at its rear.

The rate of increase of potentially reaction $KMnO_4$ molecules is thus:

$$dn/dt = n_0 + \alpha n/\delta t, \qquad (2)$$

where n is the number of such molecules existing at the time t, δt is the average time interval between production and decomposition, and α is the probability of branching. This branching proceeds unhindered initially, but since there are many initial centres from which the branching can originate, there will be considerable interference of such effects as the reaction progresses. Thus, when a plane of product molecules reaches a surface, either internal or external, where decomposition has already taken place, its effect in the continuance of the reaction ceases. If β represents the probability of interruption, the equation (2) can be written:

$$dn/dt = n_0 + (\alpha - \beta)n/\delta t. \qquad (3)$$

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[17] Mott, *Proc. Soc., A*, 1939, **172**, 325.
[18] Lennard-Jones and Dent, *Proc. Roy. Soc., A*, 1928, **131**, 247.
[19] Smekal, *Physik. Z.*, 1925, **26**, 707; *Roy.* 1927, **45**, 869.

There must clearly exist a relation between these two probabilities, since in origin they are fundamentally the same. In the simplest case $\beta = \alpha\phi$, and the solution of the differential equation depends on the nature of ϕ. Certain boundary conditions of ϕ are known, *e.g.* at $t = 0$, it is zero (since there is no interference), and is unity at the point of inflexion since after this the value of $(\alpha - \beta)$ must reverse its sign. This is satisfied by the quotient x/x_1, where x_1 is the extent of decomposition at the point of inflexion. Since the interference is regarded as a meeting of planes of decomposed molecules, the probability of mechanical disruption will be high, and thus there will be a parallelism between the rate of disruption and the extent of decomposition, as has been observed experimentally.

Since n_0 may be considered small, and because the velocity of the reaction $dx/dt = n/\delta t$, then equation (3) becomes

$$dn/dt = \alpha(1 - x/x_i)n/\delta t = dn/dx \,.\, dx/dt,$$

i.e.

$$dn/dx = \alpha(1 - x/x_1),$$

or

$$n = \alpha(x - x^2/2x_1).$$

As before, $2p_i = p_f$, so that since the pressure of oxygen is proportional to the extent of decomposition, this becomes

$$dp/dt = kp(1 - p/p_f) \quad . \quad . \quad . \quad . \quad (4)$$

where $k = \alpha/\delta t$, and is a constant, if the time interval between production and decomposition of active $KMnO_4$, and the probability of branching α are constant during this period. Equation (4) has a meaning when integrated within limits, since the term n_0 has been neglected. Thus, if $t_{max.}$ is the time when $p = p_i = \frac{1}{2}p_f$, then we have

$$k(t - t_{max.}) = \int_0^{p_f/2} p_f \,.\, dp/(p(p_f - p))\ ; \text{ or}$$

$$p/(p_f - p) = e^{(kt - t)_{max.}} \quad . \quad . \quad . \quad . \quad (5)$$

which is the relation found experimentally.

This mechanism will break down with the approach of the maximum velocity as is emphasized in the visual observations where it was noted that the disintegration process ceases at t_{max}. After this, the rate controlling factor becomes the number of unreacted $KMnO_4$ molecules remaining, which is proportional to $(p_f - p)$. Not all these molecules are favourably situated for decomposition since this requires that a molecule of product be adjacent to an unreacted $KMnO_4$ molecule, because contiguity facilitates decomposition. Therefore the rate of reaction is :

$$dp/dt = k'(p_f - p)\gamma,$$

where γ denotes the probability of this favoured situation. From geometric considerations based on the type of branching postulated here, it is reasonable to assume that γ is determined by the fraction of the number of product molecules to the total number of all molecules present, *i.e.* by p/p_f—this has the desired property of approaching unity as p tends to p_f. Thus, during the decay period $dp/dt = k'(p_f - p)p/p_f$, which on integration between limits, reduces to equation (5) except that k is replaced by k'.

Grinding will greatly increase n_0 but will not essentially alter the main acceleratory process, and thus we find that the acceleratory coefficients k_1, k_2 for ground and whole have the same value. With ground crystals, because n_0 is large, *i.e.* there are many initial points from which the branching can originate, and because the particle is small, so that interference takes place very early in the reaction, equation (5) is expected to hold almost from $t = 0$. With the whole crystal, however, branching is not important and interference is absent at the commencement—thus the rate should be at first fairly constant and be proportional to the rate of penetration of the planes. With the onset of branching, the rate should be initially described by a simple exponential function of time (*cp.* Garner), because interference is rare. This is shown to be the case in the plots given in Fig. 1. The difference found in the decay coefficients k_2, k_4 for ground and whole crystals is believed to be due to structural differences, because the residue from the whole appears black and crystalline and the particle size smaller than with the ground, where the residue is brown and amorphous.

The physical interpretation given here is similar to that of Garner, but differs in two respects: (*a*) the explanation of the decay period in terms of crystallites, or Smekal blocks, is not necessary, and thus the branching in terms of occasional bridgings of the unorganized material around these units, which could account for a small fraction of the decomposition, has been replaced by branching due to the covering of the surface by product molecules; and (*b*) there was no account taken in the previous theory of the effects of interference on the branching process. The theory put forward here has been greatly simplified, but a fuller and more rigorous development, which embraces the induction period found with whole crystals, is being worked out.

Summary.

The thermal decomposition of whole and ground crystals of $KMnO_4$ has been studied in the temperature range 200-225° C., and activation energies for both acceleratory and decay coefficients have been calculated. An equation, which has the form of a modified auto-catalytic expression, was found applicable and a theory has been postulated which leads to the correct relation.

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