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*In celebration of the $60^{th}$ birthday of Dr. Andrew K. Galwey*

# OLD AND NEW STUDIES OF THE THERMAL DECOMPOSITION OF POTASSIUM PERMANGANATE

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## Abstract

The overall chemical equation representing the thermal decomposition of potassium permanganate up to ≈300°C is given approximately by: 10 $KMnO_4 \rightarrow 2.65\ K_2MnO_4 + [2.35\ K_2O\cdot 7.35\ MnO_{2.05}] + 6O_2$, the bracketed material being δ-$MnO_2$. The experimental mass loss in air is ≈ 12% and the enthalpy of decomposition is ≈10 kJ/mol of $KMnO_4$. Analysis of published kinetic studies of the decomposition show that most of the results can be represented by the Prout-Tompkins equation $\ln (x/(1-x)) = k_T t$ + constant, and insertion of the rate constants into the Arrhenius equation gives an activation energy for decomposition of ≈150 kJ/mol of $KMnO_4$. Although the kinetic studies have always been interpreted in terms of a single type of chemical decomposition, with the different rates encountered during the course of the decomposition ascribed to physical effects, X-ray diffraction studies by Boldyrev and co-workers have shown that the reaction actually occurs in two stages, with essentially all the $KMnO_4$ transformed into $K_3(MnO_4)_2$, δ-$MnO_2$ and $O_2$ in the first stage, and the $K_3(MnO_4)_2$ then decomposing into $K_2MnO_4$ and more δ-$MnO_2$ and $O_2$ in the second stage. We have confirmed the Boldyrev diffraction results and extended them by measuring the kinetics of the appearance and disappearance of $K_3(MnO_4)_2$ by an X-ray diffraction method. Our earlier isotope studies have shown that the oxygen molecules come from oxygen atoms produced by breaking Mn–O bonds in different permanganate ions i.e. the decomposition mechanism is interionic. We conclude by summarising what is, and is not, currently known about the thermal decomposition of potassium permanganate up to ≈300°C.

**Keywords**: decomposition mechanism, kinetics, potassium permanganate

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## Introduction

The study of the thermal decomposition of inorganic permanganates is an attractive field of study for solid state chemists; a useful survey of the literature on oxomanganese compounds up to 1975 is given in Gmelin [1]. The alkali metal permanganates $MMnO_4$ ($M = NH_4$, K, Rb, Cs) form an isomorphous group with the barite ($BaSO_4$) structure ($KMnO_4$ [2], $NH_4MnO_4$ [3], $RbMnO_4$ [4] and $CsMnO_4$ [5]), with $BaMn^{VI}O_4$ (barite structure [6]) presenting intriguing similarities and differences. $Ba(MnO_4)_2$ could also be an interesting subject for further study, the crystal structure and kinetics of decomposition having been reported [7–9]. Although Li and Na permanganates crystallize as trihydrates at room temperature (the crystal structure of $LiMnO_4 \cdot 3H_2O$ [10] and kinetics of decomposition of both [11] have been reported), the anhydrous materials appear to be obtained on mild heating and could be used for comparative studies.

Although the decomposition of $AgMnO_4$ is sometimes compared to that of $KMnO_4$, this is not justified, because the two compounds are not isomorphous (crystal structure of $AgMnO_4$ by Boonstra [12]), and the first stage of the decomposition of $AgMnO_4$ (kinetics studied by Prout and Tompkins [13] and Prout and Sole [14]) gives a totally amorphous product [15, 16], quite different from those obtained from the alkali metal permanganates.

The thermal decomposition of potassium permanganate itself has probably received more attention from solid state chemists than any other comparable reaction. The reason is not clear – the decomposition reaction itself is not of overwhelming practical importance, although more than 40000 tons of $KMnO_4$ are produced annually, nor is it really simple enough for choice as an obviously rewarding subject for scientific study. Nevertheless, the reaction has attracted and retained attention for a period of almost two hundred years, and there is a large body of published work. In this paper we restrict ourselves to considering the behaviour of the system below 300°C; reactions occurring above this temperature concern the products of the first stage of the decomposition [17] and are not relevant here. Study of the first stage of the thermal decomposition of rubidium and cesium permanganates (i.e. up to $\approx 300^{\circ}C$) should be very relevant in the present context as the decomposition products appear to be analogous [17], and some information is available (kinetics of decomposition of rubidium and cesium permanganate [18]).

The main topics of study have been:

(i) establishment of the chemical equation representing the decomposition reaction,

(ii) experimental determination of the kinetics of the decomposition reaction as a function of temperature, and development of an equation relating degree of decomposition with time,

(iii) experimental determination of the effect of the physical state of the sample on the kinetics of the decomposition reaction (sample consisting of many small single crystals or of ground and/or crushed crystals have been compared; the effect of the degree and type of sample irradiation (e.g. light [19, 20]; nuclear [11]) has been studied),

(iv) experimental determination of the effect of chemical admixtures to the sample on the kinetics of the decomposition reaction,

(v) attempts to infer a chemical and crystallographic decomposition mechanism from these experimental results.

We plan to review the available experimental evidence on most of these topics, to present new experimental results and to suggest new lines of attack.

## The chemical nature of the products of the thermal decomposition of $KMnO_4$ below 300°C

If $KMnO_4$ is heated in a DTA or DSC apparatus, then an exothermic peak occurs at ≈ 250°C (Fig. 1; the actual temperature depends on the rate of heating and the physical nature of the sample). Measured values of the enthalpy of de-

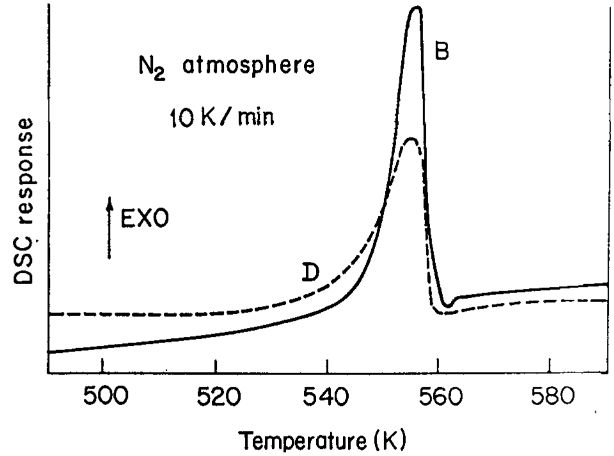


Fig. 1 Dynamic DSC curve for the thermal decomposition of $KMnO_4$. This figure is adapted from Fig. 1 of Brown, Sole & Beck [22], but we reproduce only the results reported for recrystallized AR $KMnO_4$ (B-sample composed of small single crystals, 6.49 mg; D-crushed sample, 5.86 mg)

composition have been reported as –10.5 kJ/mol of $KMnO_4$ [21] or –9.3(7) [22], both in nitrogen; –11.4(7) in oxygen [22]. The overall mass loss (Fig. 2 [17]) is 12.1% up to 250°C in air, or 13% in vacuum and is entirely due to the loss of molecular oxygen; these values agree well with those reported earlier [23, 24] and later (11.5(0.6)% in nitrogen, 10.3(1.1)% in oxygen [22]).

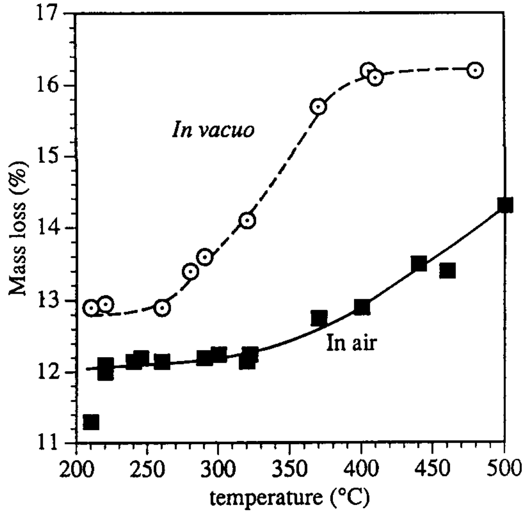


**Fig. 2** Mass loss during the heating of $KMnO_4$ to constant mass at the given temperatures. A mass loss of 12.15% corresponds to evolution of 6 moles of $O_2$/10 moles of $KMnO_4$ and is reached in air in the temperature range 200–300°C (mass losses of 14.2 and 16.2% correspond, respectively, to evolution of 7 and 8 moles of $O_2$/10 moles of $KMnO_4$). The additional $O_2$ lost at higher temperatures in air comes from the δ-$MnO_2$ phase as, presumably, does the extra 0.5 moles of $O_2$ lost in vacuum at 200°C. This figure shows that a temperature range of 200–300°C will give constant results for samples heated in air, but that 260°C should not be exceeded for samples heated in vacuum. Adapted from Herbstein, Ron and Weissman [17]

The solid product obtained after heating to 250–300°C consists of water-soluble $K_2MnO_4$ and a hygroscopic, water-insoluble material which we call for convenience δ-$MnO_2$ and define more closely below. The simple and obvious chemical equation

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

(first suggested more than 170 years ago [25] and still sometimes used [26]) is unsatisfactory for five reasons. Firstly, the calculated mass loss is 10.12%, significantly less than the measured values. Secondly, the product does not show the diffraction pattern of either of the crystalline polymorphic phases of stoichiometric $MnO_2$ (pyrolusite ($\beta$-$MnO_2$), ramsdellite ($\gamma$-$MnO_2$)). Thirdly, the $\delta$-$MnO_2$ phase contains appreciable amounts of potassium, as first shown by Rüdorf [27] (who, incidentally, decomposed his sample over a Bunsen burner). Fourthly, the measured enthalpy of the decomposition reaction is about one-half of the value calculated on the basis of the above equation (–39.7 kJ/mol of $KMnO_4$ [28]). Fifthly, only about half as much $K_2MnO_4$ is produced [17, 29] as is required by the above equation.

Our experimentally-determined approximate equation for the thermal decomposition of $KMnO_4$ in air at 250°C is [17]:

$$10\ KMnO_4 \rightarrow 2.65\ K_2MnO_4 + [2.35\ K_2O{\cdot}7.35\ MnO_{2.05}] + 6O_2.$$

The detailed form of this equation depends to some extent on how the decomposition experiment was executed, and particularly on temperature and ambient atmosphere. The closest predecessor to this equation is that of Rüdorf [27] $\{10\ KMnO_4 \rightarrow 3\ K_2MnO_4 + 2\ K_2O + 7\ MnO_2 + 6\ O_2\}$, especially if we combine his $K_2O$ and $MnO_2$ into one phase.

## The kinetics of the decomposition reaction as a function of temperature

Two experimental methods have been used to determine the kinetics of the decomposition reaction as a function of temperature-measurement of the pressure of released oxygen (employed by Prout and Tompkins [30] and also used by Boldyrev and Hill and their co-workers) and measurement of mass loss in a thermogravimetric balance, apparently first used by Booth, Dollimore and Heal [31]. Only isothermal studies are relevant here. The curves of fractional decomposition versus time all have the sigmoid shape characteristic of the logistic growth curve, which describes, for example, the growth in length of a beanstalk as a function of age [32] as well as many other features of growth in the real world. An excellent description has been given by Price [33]: ‘The logistic growth curve is limited by a floor – that is, by the base value of the index of growth, usually zero – and by a ceiling, which is the ultimate value of the growth beyond which it cannot go in its accustomed fashion. In its typical pattern, growth starts exponentially and maintains this pace to a point almost halfway between floor and ceiling, where it has an inflection. After this, the pace of growth declines so that the curve continues towards the ceiling in a manner symmetrical with the way in which it climbed from the floor to the midpoint.’

The details of the qualitatively similar curves of fractional decomposition versus time depend on the temperature of the experiment and on the form and history of the samples used [34]. We give in Fig. 3 a few of the experimental results found in the literature for samples composed of a number of small single crystals. Similar curves are found for powdered samples (crushed and/or ground), but the rates of decomposition are appreciably higher. This figure illustrates the effect of temperature on the *x-t* curves (214° 234° and 237°C), and the differences among the results reported by different groups of investigators (cf. the two curves given for 214°C).

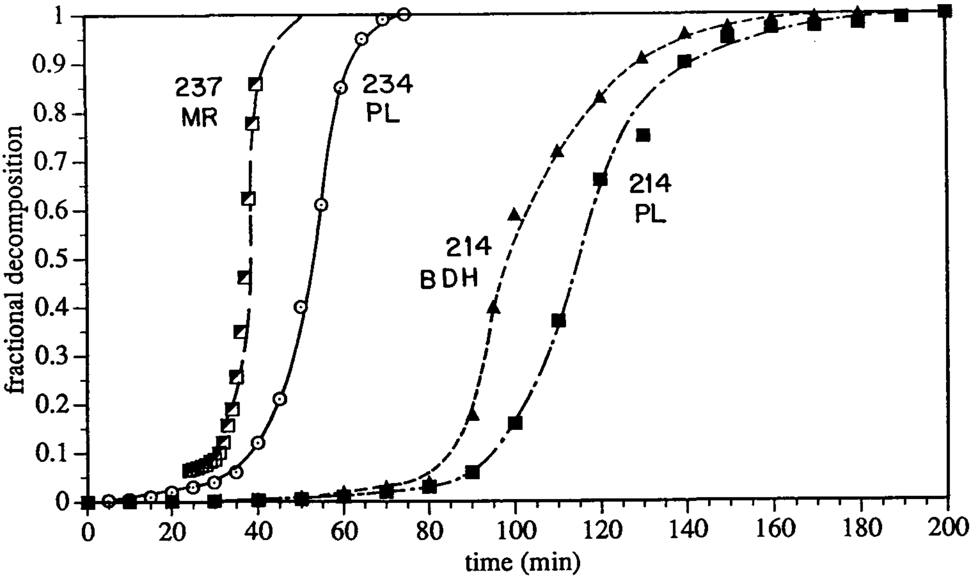


**Fig. 3** Fractional decomposition *vs.* time curves for multi-single crystal samples of $KMnO_4$ at various temperatures (°C) and from various sources (214PL and 234PL [35]; 214BDH [20]; 237MR [26]). The figure was constructed from enlargements of experimental curves given in these references; not all the points in our figure refer to actual experimental measurements

A convenient summary of the kinetic results can be obtained by plotting times for 50% decomposition ($t_{1/2}$) against temperature (Fig. 4). The values of $t_{1/2}$ are fairly consistent, especially when one considers that they come from seven groups of investigators using samples of different provenance. It is no surprise to note that $t_{1/2}$ is quite strongly inversely dependent on temperature, and more so for powdered than for multi-single crystal samples. The feasible temperature range for measurement by standard techniques is from ≈ 180 to ≈ 250°C and the convenient range ≈ 200 to ≈ 240°C. This figure can be used to estimate the time required for 50% decompositions at given temperatures, but the values obtained should be used with considerable caution.

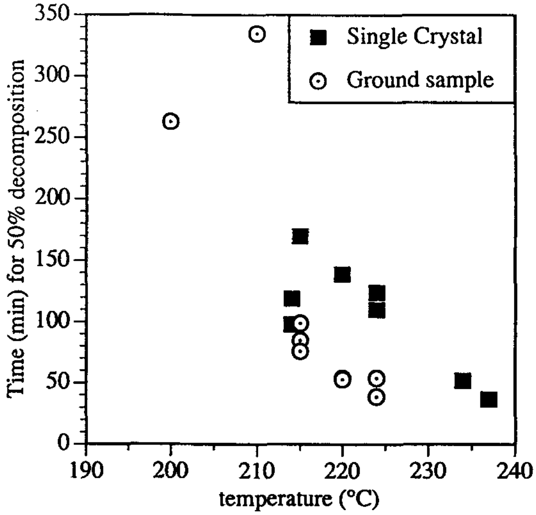


**Fig. 4** Times for 50% decomposition plotted against temperature for single-crystal and powdered samples. The values have been taken from our own work (isothermal gravimetry at 215°C for a powdered sample) and from Refs [26], [30], [31], [35], [36]

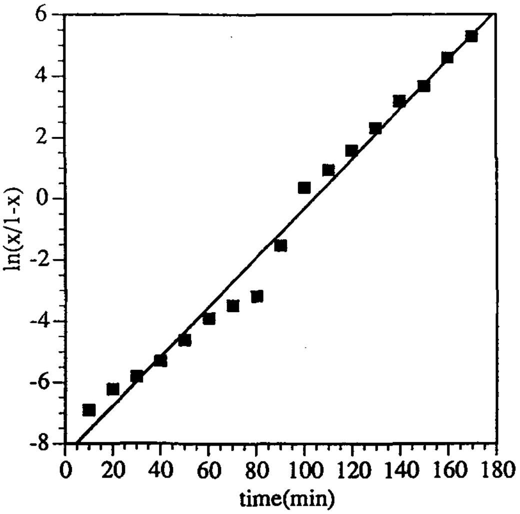


**Fig. 5** Prout-Tompkins plot of ln $(x/1-x)$ *vs.* time for a single-crystal sample decomposed at 214°C [31]. The fitted line has the form ln $(x/1-x) = 0.08061\, t - 8.639$, with $R^2 = 0.9847$

Decomposition–time curves such as those shown in Fig. 3 have been plotted to check whether the results conform to the Prout-Tompkins equation $\ln(x/1-x) = k_Tt + c$, where $x$ is the fraction decomposed after time $t$ at absolute temperature $T$ [30]. A typical graph is shown in Fig. 5. The Prout-Tompkins equation fits the experimental results for most samples well enough to make it possible to derive values of the rate constant $k_T$ at the temperatures of measurement. We emphasise that we use the Prout-Tompkins equation as a convenient function for curve fitting and not to imply a particular decomposition mechanism.

However, not all ln $(x/1-x)-t$ plots are as satisfactory as that of Fig. 5 and a typical deviant example, for a powdered sample, is given in Fig. 6. Here three rate constants are needed for the three different, approximately-linear, regions of the curve; in other examples only two rate constants are needed. There must be some inherent difference, the source of which is not clear at present, between obedient and deviant samples.

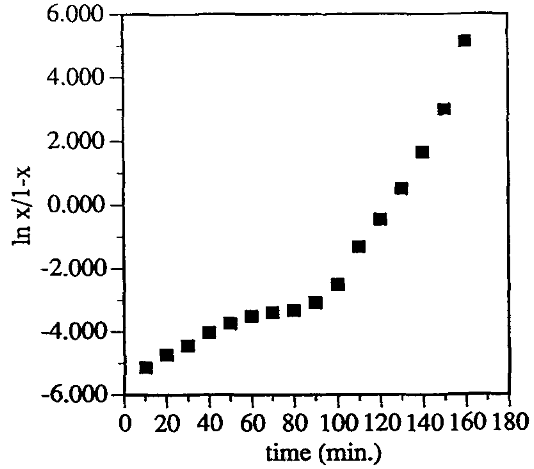


**Fig. 6** Unsatisfactory Prout-Tompkins plot for results for thermal decomposition of a powdered $KMnO_4$ sample at 200°C [31]. Here we have estimated a value of $k_T$ from the central, approximately linear, portion of the graph

Despite these difficulties, we have derived values of the rate constants ($k_T$) from part of the available experimental results and values of ln $k_T$ are plotted against $1000/T$ in Fig. 7, using the Arrhenius equation $k_T = A \exp(-E_a/RT)$, where $E_a$ is the energy of activation and $A$ the pre-exponential factor. We derive from Fig. 7 that $E_a$ (= –(slope) $X$ $R$ = 17195 $X$ 8.314 J/mol) = 143 kJ/mol (34.2 kcal/mol). It would be hazardous to estimate a reliable (as opposed to a formal) value of the estimated standard deviation of $E_a$ because of the systematic errors in the values of $k_T$. However, our value is similar to those given by earlier authors: for example, Prout and Tompkins [30] give four values (34.5, 33.1, 38.5, 38.8 kcal/mol), for the acceleratory and decay portions of the curves of powdered and multi-single crystal samples, which we average as 151 kJ/mol, and Hill, Richardson and Rodger [36] give 37.0(0.6) kcal/mol for exponential acceleration in isothermal reactions, 31.0(1.1) kcal/mol for reaction at an interface and approximately 50 kcal/mol for nucleation within grains. We have not included here 48 values of $k_T$ for the acceleratory and decay portions of the curves of powdered and multi-single crystal samples for the temperature range 200–225°C given in Table III of Prout and Tompkins [30] because these would overwhelm the other results; inclusion of the 'acceleratory' values gives an overall value of 180 kJ/mol (42.9 kcal/mol) for $E_a$.

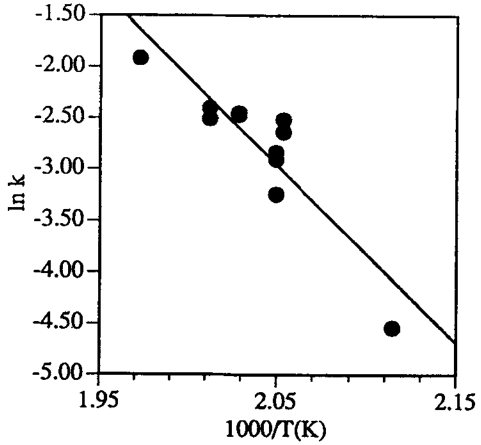


**Fig. 7** Arrhenius plot of ln $k_T$ *vs.* 1000/$T$ for multi-single crystal and powdered samples combined

For completeness, we note some other kinetic studies, which we have not been able to use. Hill and Welsh [28], who studied the decomposition at 221°C, only give information about the initial stages of the decomposition, as do Phillips and Taylor [37] ($\alpha \leq 0.1$).

All these studies are integral studies, where the amount of decomposition is measured at each point in the time range. However, one may also make differential measurements by measuring the rate of decomposition at each point in the time range. This method was introduced by Hill, Richardson and Rodger [36], who studied the decomposition over the extended temperature range 110–230°C; unfortunately not enough information is given to allow their results to be converted to our present integral form, although they do give one presentation (their Fig. 7; $t = 209.7^{\circ}C$) as a Prout-Tompkins plot. We have also made differential measurements, using a mass spectrometer to measure rate of oxygen production as a function of time [21] (see Section 5 below); our values are only semi-quantitative.

## Is the first stage composed of one or two chemical reactions?

Although some of the thermal decomposition–time curves can be divided into more than one stage (cf. the use of the terms 'induction period', 'acceleratory stage', 'decay stage'), this phenomenon has always been attributed to physical causes. This point of view has been clearly summarised by Prout and Herley [18]: 'The [Prout-Tompkins] equation has been derived theoretically on the basis of a branching mechanism for the [decomposition] reaction. In the acceleratory period the surface array of product molecules produces lateral strains which are relieved by cracks along which nuclear formation is favoured. The reaction therefore spreads into the crystal from these crevices and covers the inner surfaces with product molecules. The cracking process is repeated on these surfaces and the reaction proceeds through the solid by a system of branching planes of decomposed material. These ultimately interfere, and after the time of the maximum velocity the rate is controlled by the number of unchanged permanganate molecules which are contiguous to product molecules.'

An obvious alternative explanation – that there was a sequence of different chemical reactions – did not appear in the literature until about 1970, when Boldyrev and coworkers reported that $K_3(MnO_4)_2$ was an intermediate in the formation of $K_2MnO_4$ from $KMnO_4$ [38]. This innovative and strikingly unexpected result was met with indifference or disbelief. For example, we [39] were unable to confirm Boldyrev's results. The Russian group then repeated their work and reported it in greater detail [40]. Basing ourselves on this second report, we have now repeated the work of the Boldyrev group, using diffractometric in addition to film methods, and have completely confirmed their results, which we have extended by making a series of isothermal kinetic measurements. Although their crystal structures are different, the Debye-Scherrer patterns of $KMnO_4$, $K_2MnO_4$ and $K_3(MnO_4)_2$ are rather similar, with many overlapping lines and only a few resolved lines characteristic of the individual compounds. We have used the isothermal growth and decay of the integrated intensity of the $K_3(MnO_4)_2$ peak at $2\theta = 18.1^{\circ}$ ($CuK_{\alpha}$) to follow the thermal decomposition process (Fig. 8; sufficiently wide receiving slits were used to ensure that integrated intensity was measured). The temperatures used were 200, 210, 220 and 230°C for the growth process and 210, 220, 230 and 240°C for the decay process. We find that the amount of $K_3(MnO_4)_2$ reaches a maximum after 70 minutes at 210°C, and after 32 minutes at 220°C.

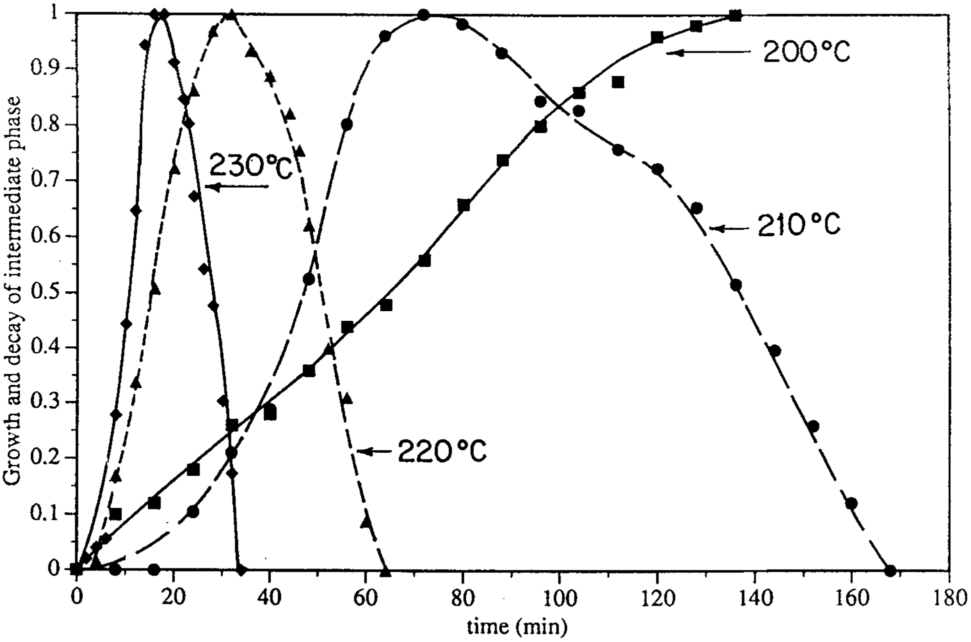


**Fig. 8** Growth and decay of the integrated intensity of the $K_3(MnO_4)_2$ peak at $2\theta = 18.1^\circ$ (CuK$\alpha$) during the thermal decomposition of $KMnO_4$; powdered samples at 200 (growth only), 210, 220, 230 and 240°C (decay only at 240°C)

The original $KMnO_4$ pattern has disappeared when the $K_3(MnO_4)_2$ peak reaches its maximum intensity. This is in essential agreement with the results of the Boldyrev group [34], who show patterns (their *e* and *f*, obtained after 52–59 minutes at 215°C) 'which are almost pure $K_3(MnO_4)_2$ with $KMnO_4$ and $K_2MnO_4$ as impurities...' Thus the decomposition proceeds in two separate stages; first $KMnO_4$ decomposes to $K_3(MnO_4)_2$ and $\delta$-$MnO_2$, with release of about half the total amount of oxygen, and then $K_3(MnO_4)_2$ decomposes to $K_2MnO_4$, with formation of more $\delta$-$MnO_2$, and release of the remaining oxygen. We do not have direct information on the amount of $K_3(MnO_4)_2$ formed, nor is the composition of the $\delta$-$MnO_2$ phase necessarily constant over the whole course of the reaction. The diffraction pattern of $K_3(MnO_4)_2$ is appreciably sharper than that of $K_2MnO_4$, indicating that the intermediate product is better crystallized than the final product.

A complete picture of the kinetics would require similar measurements of the disappearance of the $KMnO_4$ phase, and the growth of the $\delta$-$MnO_2$ and

$K_2MnO_4$ phases. Parallel isothermal diffractometric and thermogravimetric (or oxygen pressure) measurements on different aliquots of the same sample would be desirable. We also note that measurement of intensities of reflected peaks is not entirely satisfactory as the samples buckle and expand during the reaction and do not remain flat. Although we have mechanically flattened the samples held at temperature, some systematic errors must remain uncorrected. A transmission method would perhaps give better results.

Thus our diffraction results and those of the Boldyrev group show that there is no support for the suggestion of Booth *et al.* [31] that the so-called 'Boldyrev' and 'Herbstein' mechanisms 'exist side by side.' However, their comment that '...if...the viewpoint of Boldyrev is taken, then all the earlier studies of the thermal decomposition of $KMnO_4$ will have to be re-interpreted' is certainly correct. It is indeed remarkable that the possibility that two successive chemical processes occur during the decomposition reaction had not been seriously envisaged by earlier investigators, especially as it is known that $K_3(MnO_4)_2$ is stable with respect to disproportionation to $KMnO_4$ and $K_2MnO_4$ ([1], see p. 135). It is also salutary to remark that one of us [41] had noted, but not identified, the $K_3(MnO_4)_2$ powder patterns obtained from a ground sample of $K_2MnO_4$; the identification was made in Ref. [1], p. 135. One should therefore ask whether contrary evidence has been ignored. Hindsight could provide a chemical interpretation of some of the Prout-Tompkins plots, but the accepted physical explanations are not unreasonable; from their measured activation energies, Prout and Tompkins [30] concluded that 'the same chemical process occurs in the acceleratory and decay periods.' Some indication of two (or perhaps more) successive processes is provided by the isothermal DSC curve shown for

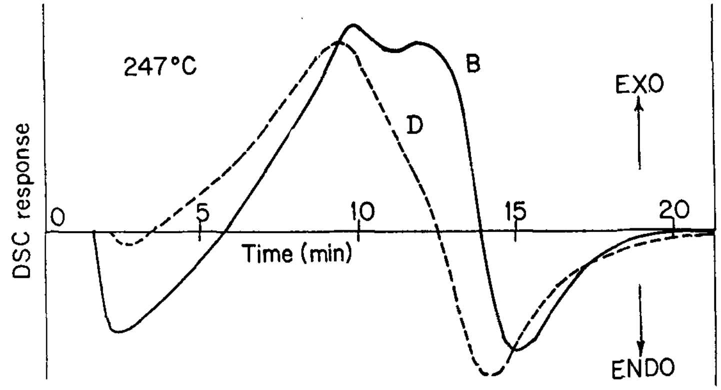


**Fig. 9** Isothermal DSC curve for the thermal decomposition of $KMnO_4$ at 247°C; B is a multi-single crystal sample and D a crushed sample, both of mass ≈ 10 mg. Adapted from Brown, Sole & Beck [22]

$KMnO_4$ at 247°C by Brown, Sole & Beck [22]. This temperature is unfortunately a little high for optimum resolution of the two processes, but the decomposition is divided into an earlier exothermal and a later endothermal part (Fig. 9), the initial behaviour being unclear. These could be the two stages of the reaction as described above, but additional studies at lower temperatures would seem to be needed.

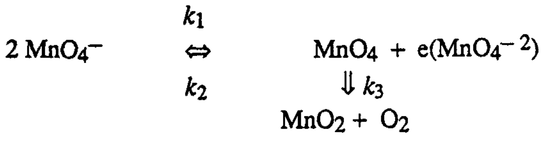
$K_3(MnO_4)_2$ was first reported in 1861 [42] and has the $A_3(XO_4)_2$ structure first described by Zacharaisen [43], with rapid electron exchange between permanganate and manganate ions. A displacive structural mechanism has been proposed for the mutual transformation of $K_3(MnO_4)_2$ and $K_2MnO_4$ [44] involving relatively small movements of atoms; it will be necessary to determine the crystallographic features of the transformation in order to establish whether this takes place by a displacive or nucleation-and-growth mechanism.

## Description of the overall decomposition process

In this section we describe the overall solid state decomposition reaction permanganate → manganate, and consider later what changes are needed when the two-stage nature of this process is taken into account.

The overall reaction is a redox process in which oxygen ($O^{II-}$) from permanganate is oxidized to molecular oxygen while manganese is reduced from $Mn^{VII}$ (in permanganate) to $Mn^{VI}$ (in manganate) and $Mn^{IV}$ (nominally) in the $\delta$-$MnO_2$ phase. In $KMnO_4$ at $\approx 250$°C Mn–O bonds are broken in about 3/4 of the permanganate ions, with two bonds broken in about half of these and one bond in the other half (we neglect the possibility of more than two Mn–O bonds being broken in a single $MnO_4^-$ ion). Electrons are transferred to about 1/4 of the permanganate ions, reducing them to manganate with little change in their tetrahedral shape ($d(Mn^{VII}–O) = 1.629(8)$Å [2]; $d(Mn^{VI}–O) = 1.659(8)$Å [46]).

Boldyrev [34], from studies of the thermal decomposition of permanganate ions in dilute solid solution in $KClO_4$, has concluded that 'the presence of pairs of permanganate ions in the lattice, indispensable for electron transition from one anion site to another, is a substantial factor in the elementary stages of the process of the thermal decomposition of permanganate. Accordingly, the process may be expressed as



$$\begin{tikzcd} 2\,MnO_4^- \arrow[r, Leftrightarrow, "k_1", "k_2"'] & MnO_4 + e(MnO_4^{-2}) \arrow[d, Rightarrow, "k_3"] \\ & MnO_2 + O_2 \end{tikzcd}$$

The implication is that the neutral $MnO_4$ 'molecule' is unstable and decomposes to $MnO_2$ and molecular oxygen, with the two atoms coming from the same $MnO_4$ 'molecule'. This is an intraionic decomposition scheme.

An alternative decomposition scheme has been proposed in terms of the manganese oxo species $MnO_4^{2-}$, $MnO_2$ and $MnO_3^{2-}$ [46], but the formulation in terms of individual ions and 'molecules' does not appear appropriate to reactions occurring in the solid state. However, the decompositions of unstable species here lead to evolution of oxygen atoms which presumably combine later to give molecules. Thus this is an interionic decomposition scheme.

Distinction between intra- and interionic decomposition schemes is open to experimental test by using isotopically-labelled permanganate ions. We have briefly reported the results of such experiments [21] and we now summarise the essential conclusions. However, we should note that the fact that only one Mn–O bond is broken in about one-half of the permanganate ions already means that the decomposition cannot be purely intraionic but must be at least about 50% interionic. In fact, the experiments show that the mechanism is wholly interionic.

The method used consisted of preparation of mixed crystals of ideal composition $KMnO_4^{16}\cdot KMnO_4^{18}$, with the differently labelled permanganate ions distributed at random in the structure, followed by mass spectrometric determination of the isotopic composition of the oxygen molecules produced during thermal decomposition. If the reaction is purely intraionic then only oxygens of mass number 36 and 32 will be observed, while mixed and interionic mechanisms will also give mass number 34. The proportion can be calculated, taking into account the fact that the $O^{18}$ used is only about 95% pure and that the composition of the mixed crystals may deviate from the ideal 1:1 ratio. Care must also be taken to avoid isotope exchange during preparation of the samples.

The rate of decomposition, as measured by the amount of oxygen (of the three possible isotopic compositions) produced per unit time interval (here 5 minutes) is shown in Fig. 10.

This figure is analogous to the rate curves shown in Fig. 1 (and other figures) of Ref. [36] and Fig. 2 of Ref. [26].

The direct experimental measurements of Fig. 10 are expressed as ratios of the intensities of pairs of mass numbers 32, 34 and 36 (R(36/32) and R(36/34)) and are plotted as functions of time in Fig. 11. R(36/34) is a more efficient discriminator between possible mechanisms than R(36/32) because it is not affected by the presence of residual air molecules in the mass spectrometer background. Under our conditions, R(36/34) tends to infinity for a purely intraionic mechanism, to 0.5 for a purely interionic mechanism and to intermedi-

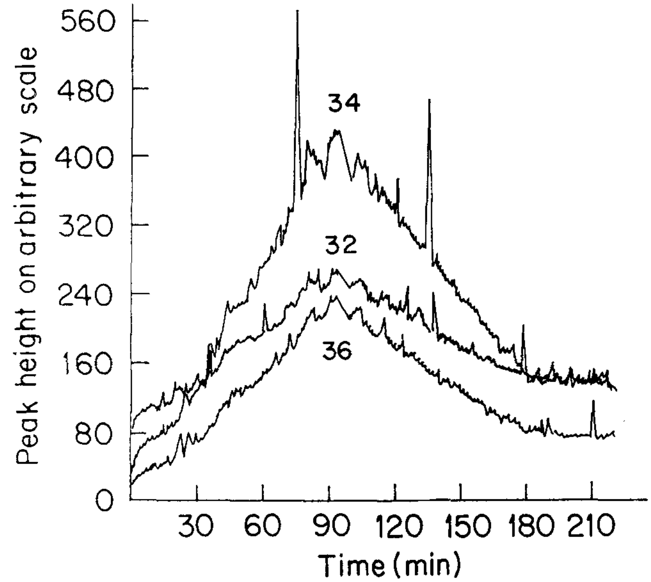


**Fig. 10** Mass-spectrometrically measured values of the intensities of the 36, 34 and 32 mass peaks as functions of time for the thermal decomposition of mixed crystals of $KMnO_4^{16} \cdot KMnO_4^{18}$; the estimated sample temperature is 215°C. Each experimental point represents an integration over a period of 5 minutes. The results have deliberately not been smoothed as the oxygen molecules are emitted in bursts. The background pressure was ≈ $5\times10^{-9}$ mm. Adapted from [21]

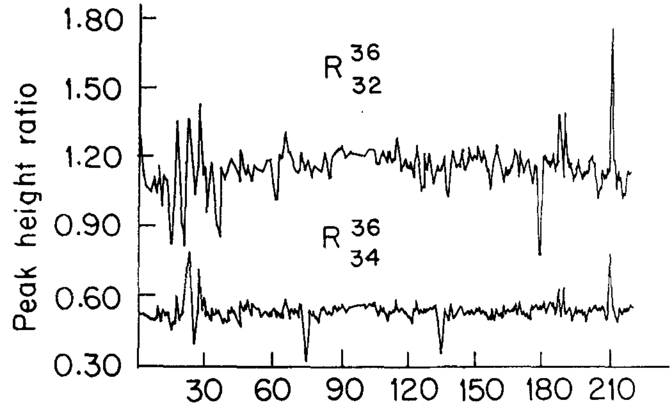


**Fig. 11** Mass-spectrometrically measured values of $R$(36/32) and $R$(36/34) as functions of time for thermal decomposition of mixed crystals of $KMnO_4^{16} \cdot KMnO_4^{18}$; the estimated sample temperature is 215°C. Adapted from [21]

ate values for a mixed mechanism. The results show that a purely interionic mechanism occurs. One caveat we have about this conclusion is that it does not take into account the possibility of further scrambling of the atoms in oxygen molecules after their initial formation, perhaps due to interchange reactions taking place on the active surfaces formed during the decomposition. If this interchange occurred, then it would obscure the difference between intra- and interionic mechanisms for those permanganate ions where two Mn–O bonds were broken; we have already noted that single Mn–O bonds are broken in about half the decomposing permanganate ions and the interionic mechanism must hold for these. However, such interchange reactions seem inherently unlikely, involving as they would initial intraionic formation of oxygen molecules, followed by break-up of these molecules to atoms and then subsequent recombination of the atoms to molecules in a simulated interionic mechanism.

## Description of the reaction mechanism in terms of a two-stage decomposition process

The two individual stages of the decomposition have not been described in the same detail as the overall process but a preliminary picture can be given. The principal difference seems to be that in the first stage (when $K_3(MnO_4)_2$ is formed from $KMnO_4$) the distinction between unreacted permanganate and manganate ions (i.e. those where no Mn–O bond has been broken) is not strictly maintained because of rapid electron exchange between them. In the second stage, non-exchanging manganate ions are formed.

At present it is not clear how the measured overall kinetics of the decomposition can be dissected into the contributions of two distinct stages - the initial decomposition of $KMnO_4$ to give $K_3(MnO_4)_2$, $\delta$-$MnO_2$ and $O_2$, and the subsequent decomposition of $K_3(MnO_4)_2$ to give $K_2MnO_4$ and more $\delta$-$MnO_2$ and $O_2$. It will be necessary to establish the quantitative details of the equation representing each stage.

## The nature of $\delta$-$MnO_2$

The potassium-manganese-oxygen system for $K/Mn \leq 1$ has been studied by Delmas and Fouassier [48]. Their work on the P3 phase of composition $K_xMnO_{2+y}$ $(0.45 \leq x \leq 0.67)$ is particularly relevant in the present context; in our notation the composition range is $K_{3.6-5.4}Mn_8O_{16+8y}$. The powder pattern given by Herbstein, Ron and Weissman [1] for anhydrous '$K_4Mn_7O_{16}$' at 650°C was indexed [47] in terms of a hexagonal unit cell with $a = 2.94$, $c = 19.26$ Å; the space group in R3m. The structure type is $K_{0.5}CoO_2$ [48], with layers of oxygens in AABBCC arrangement, the Mn in octahedral sites and the K intercalated between the $(MnO_2)_n$ layers in a prismatic environment. This is also the structure of δ-$MnO_2$ formed at ≈ 200–250°C, where it is not as well-crystallized as at higher temperatures.

## A programme for further study

Preparation of uniform and reproducible samples is essential for any experimental programme. A large freshly-recrystallized sample of $KMnO_4$, screened from light, should be divided into aliquots of uniform particle size for multi-single crystal samples, and some crushed in a standard way to provide powdered samples. Isothermal kinetic measurements should be carried out over the temperature range 180–250°C in dry air, or nitrogen atmospheres, or under vacuum. Thermogravimetry is probably the most convenient method. Parallel kinetic measurements, covering the behaviour of each of the individual phases, should be made by X-ray diffraction. Thus the decomposition of $KMnO_4$, the growth and decomposition of $K_3(MnO_4)_2$, and the growth of $K_2MnO_4$ and δ-$MnO_2$ would be determined by following the growth and/or decay of the integrated intensities of suitable diffraction peaks from polycrystalline samples at a range of temperatures. Measurements of peak shapes may give useful information about the physical state of the individual phases. A parallel study should be carried out for $K_3(MnO_4)_2$. The chemical equations of the two stages of the decomposition process will have to be determined.

The effects of extraneous physical and chemical factors on the kinetics of the decomposition reaction should logically be investigated only after the detailed nature of the decomposition of neat potassium permanganate has been established.

## Concluding summary

The following facts have been established by the research efforts of the last 170 years:

1. The thermal decomposition of potassium permanganate, heated to constant mass in air below 250–300°C, is represented by the following equation

$$10\ KMnO_4 \rightarrow 2.65\ K_2MnO_4 + [2.35\ K_2O \cdot 7.35\ MnO_{2.05}] + 6\ O_2.$$

2. The overall reaction consists of two stages–initial decomposition of $KMnO_4$ to give $K_3(MnO_4)_2$, δ-$MnO_2$ (the phase in square brackets in the above equation) and $O_2$, and subsequent decomposition of $K_3(MnO_4)_2$ to give $K_2MnO_4$ and more δ-$MnO_2$ and $O_2$. The chemical equations representing these two stages have not yet been determined.

3. The $O_2$ molecules are formed from oxygen atoms which arise from the breaking of Mn–O bonds in different permanganate ions, i.e. the reaction is interionic.

4. Many measurements have been made of the kinetics of the overall decomposition reaction in the temperature range 200–240°C, and these all show qualitatively similar sigmoid shapes characteristic of the logistic growth curve, but details are dependent on the temperature of the experiment and on the form and history of the samples used. The time for half-reaction falls sharply with increasing temperature, but the values reported in the literature show a considerable spread.

5. Many of the sigmoid curves of 'fraction reacted' ($x$) *vs.* 'time' ($t$) can be quantitatively described in terms of the Prout-Tompkins equation $\ln(x/(1-x)) = \text{constant} + k_T t$, with a single temperature-dependent rate constant $k_T$. Insertion of these rate constants into the Arrhenius equation $k_T = A \exp(-\Delta E_a/RT)$ gives an activation energy $E_a$ which lies in the range 140–180 kJ/mol.

6. The crystal structures of all the phases participating in the decomposition reaction are known.

7. The crystallographic mechanism of the decomposition reaction has been little investigated by modern microscopic techniques and is hardly understood [49].

* * *

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**Zusammenfassung** — Die Bruttoreaktionsgleichung für die thermische Zersetzung von Kaliumpermanganat bis etwa 300°C lautet ungefähr: $10\ KMnNO_4 \rightarrow 2.65\ K_2MnO_4 + [2.35\ K_2O{\cdot}7.35\ MnO_{2.05}] + 6O_2$, wobei der in Klammern angeführte Ausdruck für δ-$MnO_2$ steht. Im Experiment erfolgt in Luft ein Masseverlust von etwa 12% und die Enthalpie der Zersetzung beträgt 10 kJ/mol $KMnO_4$. Eine Auswertung der publizierten kinetischen Untersuchungen der Zersetzung ergaben, daß die meisten Resultate mit Hilfe der Prout-Tompkins-Gleichung $\ln(x/(1-x)) = k_T t$ + Konstante beschrieben werden können und Einsetzen der Geschwindigkeitskonstanten in der Arr-heniusschen Gleichung ergibt für die Zersetzung eine Aktivierungsenergie von etwa 150 kJ/mol $KMnO_4$. Obwohl die kinetischen Untersuchungen bereits als Einzeltyp einer chemischen Zersetzung interpretiert wurden, bei deren Verlauf aufgrund physikalischer Effekte verschiedene Geschwindigkeiten auftreten, zeigten Röntendiffraktionsuntersuchungen von Boldyrev und Mitarb., daß die Reaktion eigentlich in zwei Schritten verläuft, wobei im ersten Schritt alles $KMnO_4$ zu $K_3(MnO_4)_2$, δ-$MnO_2$ und $O_2$ umgesetzt wird, und im zweiten Schritt zersetzt sich dann $K_3(MnO_4)_2$ zu $K_2MnO_4$ und noch mehr δ-$MnO_2$ und $O_2$. Wir bestätigten Boldyrev's Diffraktionsergebnisse und erweiterten diese durch die Messung der Kinetik des Erscheinens und Verschwindens von $K_3(MnO_4)_2$ mittels einer Röntgendiffraktionsmethode. Unsere früheren Isotopenuntersuchungen zeigten, daß die Sauerstoffmoleküle aus Sauerstoffatomen entstehen, die aus der Spaltung von Mn–O-Bindungen unterschiedlicher Permanganationen stammen, d.h. es handelt sich um einen interionischen Zersetzungsmechanismus.