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The Prout–Tompkins rate equation in solid-state kinetics

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Abstract

In more than 50 years since its publication, a paper in the Transactions of the Faraday Society by Prout and Tompkins has been extensively cited in the literature. The paper dealt with the kinetics of the thermal decomposition of crystals of potassium permanganate, and suggested a rate equation, which has become known within the field as the Prout–Tompkins equation, for use in the kinetic analysis of solid-state reactions. This equation and its applications in a variety of different fields, including general kinetics of solid-state reactions; continuing work on $KMnO_4$; irradiation effects; pharmaceutical stability studies, and colloid and interfacial chemistry, are discussed. © 1997 Elsevier Science B.V.

Keywords: Autocatalysis; Kinetics; Potassium permanganate; Prout–Tompkins equation; Solid-state reactions

1. Introduction

It is more than half a century since a paper by Prout and Tompkins [1], dealing with the kinetics of the thermal decomposition of crystals of potassium permanganate ($KMnO_4$), appeared in the Transactions of the Faraday Society. The decomposition of $KMnO_4$ has received a lot of attention over the years. Herbstein [2] has discussed the almost 200-year old history of studies of this compound. He comments: "the decomposition reaction itself is not of an overwhelming practical importance, although more than 40 000 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 maintained attention..."

Even more important than its contribution to the accumulated information on the decomposition of $KMnO_4$, is the attention that the paper [1] focusses on a suggested rate equation, for use in the kinetic analysis of solid-state reactions. This equation has become known within the field as the Prout–Tompkins equation and its applications are discussed in more detail below.

2. Personal details

2.1. *Frederick C. Tompkins (1910–1995)*

Frederick Tompkins [3] (Fig. 1) was born and received his schooling in Yeovil, Somerset. He won a scholarship to Bristol University where he obtained his doctorate. After being a lecturer at King's College, London, he spent nine years lecturing at the University of Natal, Pietermaritzburg, South Africa. During this time the work [1] referred to in this paper was pub-

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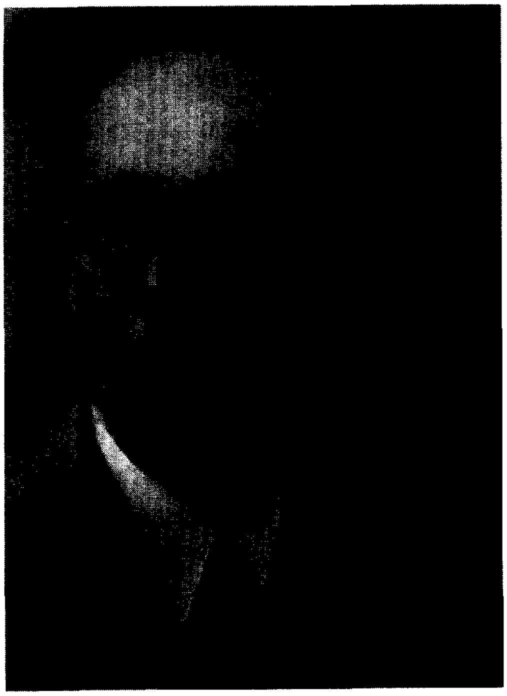

Fig. 1. Professor F.C. Tompkins, FRS (Courtesy of the Royal Society of Chemistry Library and Information Centre).

lished. (It is interesting to note that the Transactions of the Faraday Society, at the time, did not give the affiliations of the authors!).

In 1946, Dr. Tompkins spent a year as an ICI Research Fellow at King's College, London, before being appointed as a Reader in Physical Chemistry at Imperial College. During this time, he and Dr. P.W.M. Jacobs, a Lecturer at Imperial College at the time, contributed several chapters to the extremely influential book, 'Chemistry of the Solid State', edited by W.E. Garner [4].

Dr. Tompkins became a Fellow of the Royal Society in 1955 and Professor of Physical Chemistry in 1959. He remained at Imperial College until his retirement in 1977. From 1950 to 1977, he was Secretary and Editor of the Faraday Society (later the Faraday Division of the Royal Society of Chemistry). He died on 5th November 1995.

2.2. *Ernest G. Prout*

Ernest Prout (Fig. 2) was born in 1922 and went to school in Pietermaritzburg. He studied chemistry at the University of Natal, Pietermaritzburg, which was then a College of the University of South Africa. His postgraduate studies on decompositions of solids (including permanganates) under Dr. Tompkins led to the award of his PhD in 1945. It was during his doctoral studies that the influential paper [1] was published.

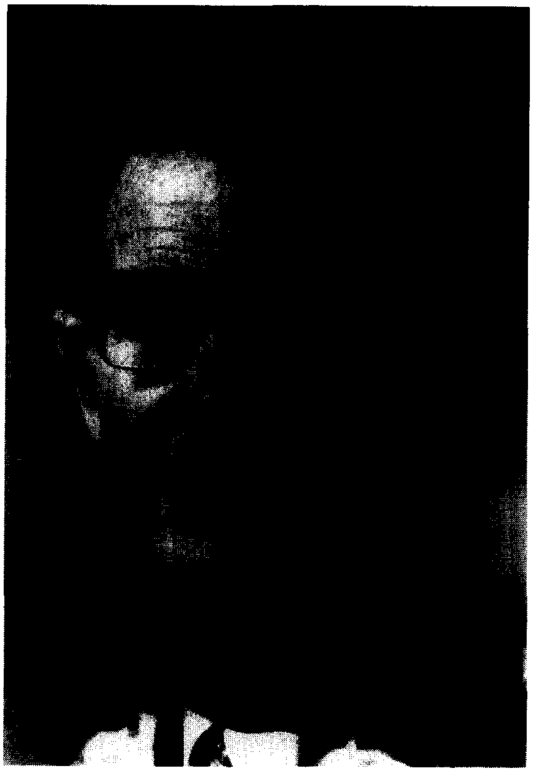

Fig. 2. Professor E.G. Prout.

Dr. Prout lectured at the Cape Technical College for five years and then became a Research Fellow in 1951, at Imperial College, London, with Sir Alfred Egerton, FRS. Two years of lecturing at the University of Cape Town was followed by two years at the Atomic Energy Research Establishment, Harwell.

He returned to South Africa in 1956 as Senior Lecturer at Rhodes University, Grahamstown, and was appointed as Professor of Physical Chemistry in 1962. In 1966 he moved with his research group to the University of Cape Town, was awarded a DSc in 1974 and retired in 1985. Following his retirement, he has become well-known in a different field – for his artistic pottery.

2.3. Citation record

A survey of Science Citation Index from 1966 to 1996 showed 150 citations of the original Prout and Tompkins paper. No ready method of determining the citation history between 1944 and 1965 was available. Only a very few of the citing papers included reference to the Prout–Tompkins equation (or model) in the title. Without reading every paper in detail, the significance of each citation cannot be definitely assessed, but at least four different reasons for citation were identified. These were in reference to:

1. the decomposition of potassium, or other permanganates;
2. the Prout–Tompkins equation (quantitatively), or more qualitatively to aspects of the model such as chain-branching, role of defects, etc;
3. the apparatus used for decomposition studies by Prout and Tompkins (also described by Prout and Herley in the Journal of Chemical Education [5]); and
4. the sources of the set of 'standard' models in general.

From the titles (and authors) of the 150 papers which cite reference [1], several different fields of interest can be distinguished:

- general kinetics of solid-state reactions;
- continuing work on the decomposition of $KMnO_4$ and other permanganates;
- the decomposition of other solids;
- solid-phase transitions and solid-solid reactions;
- solid–gas reactions and catalysis;
- irradiation effects;
- pharmaceutical applications;
- colloid and interfacial chemistry;
- miscellaneous.

These applications are further described in the following.

3. Rate equations in solid-state kinetics

The most important rate equations that have found application in solid-state kinetic analyses are so well known that they are usually referred to by a shorthand code. Full tables of equations of the derivative forms: $\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha)$ and integrated forms: $g(\alpha) = kt + c$, where α is the fractional extent of reaction, have been published repetitively [6]. These expressions are grouped according to the shape of the *isothermal* α–time curves as acceleratory, sigmoid or deceleratory. Among the rate equations which produce sigmoid α–time curves is the Prout–Tompkins equation (often referred to as B1, but, in this paper, as the P–T equation, or model):

$$\text{(derivative form)}\quad \mathrm{d}\alpha/\mathrm{d}t = k_{\mathrm{B}}\alpha(1-\alpha) \qquad (1)$$

which on integration (see below) gives:

$$\ln[\alpha/(1-\alpha)] = k_{\mathrm{B}}t + c \qquad (2)$$

The derivative form (1) shows clearly the dependence of the rate on both the amount of reactant left and the amount of product formed, known as autocatalysis.

Eq. (2) was found to describe the kinetics of isothermal decomposition of $KMnO_4$, but the results for the decomposition of silver(I) permanganate ($AgMnO_4$) [7] did not give very good agreement with Eq. (2). They were better fitted by:

$$\ln[\alpha/(1-\alpha)] = k_{\mathrm{B}}\ln(t) + c' \qquad (3)$$

which is referred to as the *modified* Prout–Tompkins equation.

A more general rate equation has been proposed [8–10] to include most of the familiar rate equations. This equation is often referred to as the *Sesták–Berggren* equation:

$$(\mathrm{d}\alpha/\mathrm{d}t) = k\alpha^m(1-\alpha)^n(-\ln(1-\alpha))^p \qquad (4)$$

Sesták [11] has suggested the epithet '*accommodation coefficient*' for the additional terms, other than $(1-\alpha)^n$, which are needed to modify the reaction order (RO)-type of equation for application to heterogeneous systems. (See also Koga [12].) When $m = n = 1$ and $p = 0$, the general equation becomes the Prout–Tompkins equation.

Ng [8] discussed the more limited expression

$$\mathrm{d}\alpha/\mathrm{d}t = k\alpha^m(1-\alpha)^n \qquad (5)$$

applied under isothermal conditions. The relative values of m and n determine relative contributions from the acceleratory and decay regions. Ng pointed out that the maximum rate is at $\alpha \equiv \alpha_m = m/(m+n)$. Hence, $m = an$, where $a = \alpha_m/(1-\alpha_m)$. Eq. (5) can be written in the form

$$\ln(\mathrm{d}\alpha/\mathrm{dt}) = \ln(k) + n[a\ln(\alpha) + \ln(1-\alpha)]$$

and since α_m is readily determinable from the decomposition curve, a plot of $\ln(\mathrm{d}\alpha/\mathrm{dt})$ against $[a\ln(\alpha) + \ln(1-\alpha)]$ can be used to obtain n, m and k. Ng also pointed out that the modified P–T Eq. (3) can be written as

$$(\mathrm{d}\alpha/\mathrm{dt}) = k\alpha^{1-(1/k)}(1-\alpha)^{1+(1/k)}$$

3.1. Models based on autocatalysis

The origin of an equation of the form

$$\ln[F/(1-F)] = kt \qquad (6)$$

where F is some fractional quantity between 0 and 1.0, would be difficult to trace. Casti [13] gives some non-chemical examples of applications of "what biologists call the *logistic curve*," to growth of bacterial colonies with a fixed amount of nutrient; the growth in the number of mainframe computers in Japan; and the cumulative production of Mozart's 35 major musical works.

Mata-Perez and Perez-Benito [14] have discussed the kinetics of autocatalytic reactions, using the oxidation of dimethylamine by $\mathrm{MnO_4^-}$(aqueous) as an example, and emphasized the need for an additional term in the rate equation to allow the reaction to start. Schwartz [15] has extended their analysis. Constantinou [16] has also contributed to the useful discussion on the kinetics of autocatalytic decompositions of both solids and liquids.

Austin and Rickett [17] in a (1939) study of the isothermal decomposition of austentite, did an empirical analysis of their kinetic results in terms of "the logistic, or autocatalytic, curve" (Eq. (6)), but found better agreement with

$$\log[F/(1-F)] = k\log(t) + c$$

(equivalent to Eq. (3)) since the curves of F against t were not symmetrical about the inflexion point.

Young [18] refers to the "Ostwald equation for autocatalysis of the second-type", and points out that equations of this type require that the entire solid product has to be able to catalyze all reactant particles equally, throughout the decomposition. He states (without reference) that "using the approach of Kolmogorov, it (the equation) can be written down directly."

Young also points out the serious defect of the P–T equation that, in application, it may require different rate constants (possibly with different temperature dependences) to describe the experimental data. He regards this as a suggestion that the assumptions made in its derivation could be at fault.

Hood and Murphy [19] reported on the early (1905) work of Lewis [20], on the thermal decomposition of silver(I) oxide. The autocatalytic equation was used; integrated to give the form equivalent to the P–T equation and the rate as a function of time was given as:

$$\mathrm{d}X/\mathrm{dt} = k/(\exp(kt'/2) + \exp(-kt'/2)) = (k/4)\,\mathrm{sech}^2(kt'/2)$$

Prout and Tompkins [1] say that analysis of their sigmoidal plots of evolved gas pressure, p, against time, at constant temperature, was "undertaken without reference to previous equations, which differed widely. The resemblance of the plots to the hyperbolic function, tanh (see Fig. 3), suggested the expression

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

where the point of inflexion has coordinates (p_1, $t_{\max}$)... and $p_2 = p_f - p_i$," where p_i is the initial pressure in the constant volume system.

An example of an α–time plot for the Prout–Tompkins model, i.e. $\alpha = [1 + \exp(-k(t - t_0))]^{-1}$ is shown in Fig. 4, using: $k = 0.07784\ \mathrm{min}^{-1}$ and $t_0 = 50$ min, so that $\alpha = 0.50$ at $t = 50$ min.

The effect of using two different values of k, i.e. $k = k_1$ at $\alpha \leq 0.50$ and $k = k_2$ at $\alpha > 0.50$ is shown in Fig. 5 for different ratios of $k_2 : k_1$. In practice, such a transition is likely to be more gradual.

Plots of the α–time curves derived from the more general autocatalytic rate Eq. (5), for different combinations of m and n, are shown in Fig. 6.

3.2. The Prout–Tompkins (P–T) model

Considerable early interest and controversy arose concerning whether the acceleratory period of the isothermal decomposition of $\mathrm{KMnO_4}$ was better described by an exponential or power law relationship

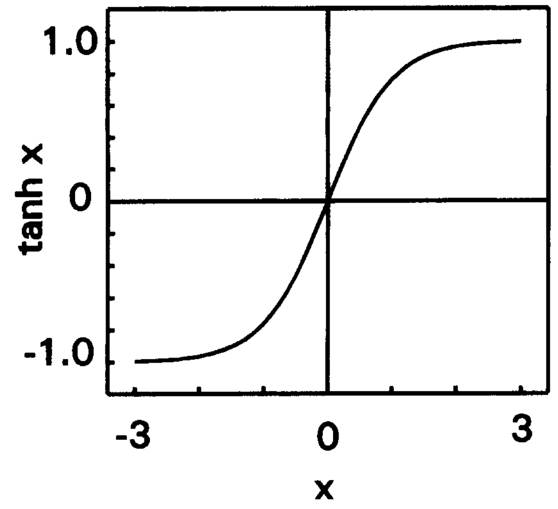

Fig. 3. Plot of tanh x against x.

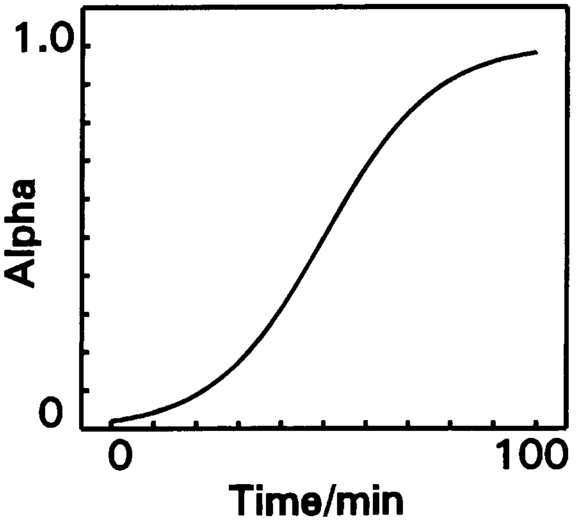

Fig. 4. Prout–Tompkins plot using $k = 0.07784\ \mathrm{min}^{-1}$ and $t_0 = 50$ min.

[18]. Garner's theory [4,18] of the exponential acceleratory period was formally identical with classical chain reaction theory, and his model led to a decay period describable by the first-order equation. Models based on a power-law acceleratory period [18] were followed by a contracting-volume decay.

The P–T equation was originally formulated [1] on the concept of 'nucleus branching', analogous to homogeneous chain reactions. Occurrence of 'branching', without restriction on multiplicative development or allowance for termination, would lead to an exponential dependence of α on t: $\alpha = k\exp(k_\mathrm{B}t)$, where k_B is the rate coefficient for nucleus branching. Acceleratory behaviour cannot be maintained

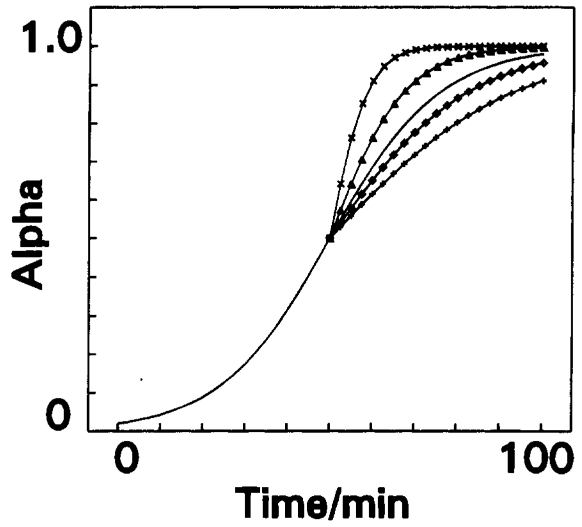

Fig. 5. Prout–Tompkins plots showing the influence of the ratio of $k_2 : k_1$. The solid line – $k_2 = k_1$; x – $k_2 = 3k_1$; △ – $k_2 = 1.5k_1$; ◇ – $k_2 = 0.8k_1$; and + – $k_2 = 0.6k_1$.

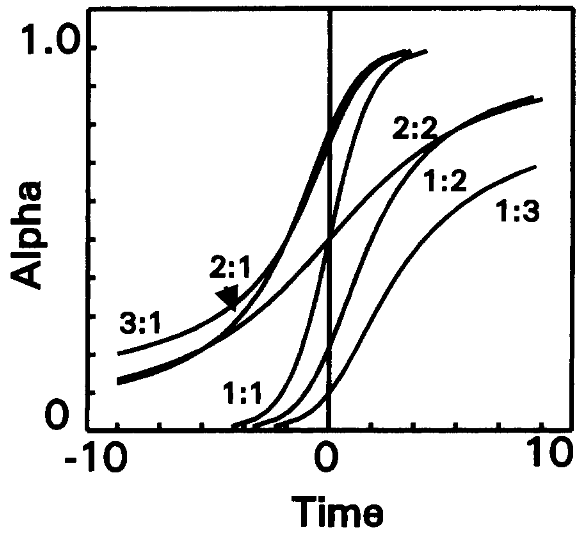

Fig. 6. Plots of the general autocatalytic function (Eq. (5)) showing the influence of values of m and n. ($m : n$ as labelled).

indefinitely in any real reaction and allowance for termination can be made by including a term $k_T(\alpha)$, so that:

$$dN/dt = k_N N_0 + N\{k_B - k_T(\alpha)\}$$

where k_T is a function of α. When k_N is large, all available sites (N_0) are rapidly exhausted. When k_N is very small,

$$\{k_B - k_T(\alpha)\} \gg k_N N_0, \text{ and } dN/dt = N\{k_B - k_T(\alpha)\}$$

If it is assumed that the rate of reaction ($d\alpha/dt$) is proportional to the numbers of participating nuclei (N), integration of this expression requires knowledge of the relationship between k_B, $k_T(\alpha)$ and α. Prout and Tompkins [1] considered the particular case of sigmoid α–time curves, with the point of inflection at $\alpha = 0.50$. This leads to Eq. (1) above, and, on integration, to Eq. (2).

Eq. (1) requires an additional term to represent the initiation of the nucleation that subsequently undergoes branching, to enable such reactions to start. If k_B varies inversely with time (i.e. there is a decrease in the effectiveness of branching as reaction proceeds), it follows that [7]:

$$\ln[\alpha/(1-\alpha)] = k_B \ln t + c$$

The energy chain theory on which this model was based is now regarded as unacceptable because energy quanta released from reaction are expected to be dispersed as thermal energy and not specifically transferred to potential reactant species. Product generation at branching nuclei promotes particle disintegration, exposing more surface on which decomposition proceeds. This model was clearly and graphically described by Prout and Tompkins [1]. However, observational support for this model could not be obtained in an examination of the reaction zone in $KMnO_4$ crystals [21].

Autocatalytic behaviour has also been ascribed [22] to the accelerated reaction proceeding in an increasing volume of melt. Galwey [23] has discussed the possible role of melting in thermal reactions of initially solid reactants, a fact not always considered in the interpretation of kinetic data and the formulation of reaction mechanisms.

3.3. *Distinguishability from other sigmoid models*

The sigmoid form of the α–time curve expressed by Eq. (5) is similar in shape to those derived from the Avrami–Erofeev equation [24] (also attributed to Johnson, Mehl and Kolmogorov, hence the JMAEK equation):

$$[-\ln(1-\alpha)]^{1/q} = k(t - t_0) \tag{7}$$

(Note that the exponent, q, is usually written as n and the model is referred to as An. q is used here, to avoid confusion with exponents in the other equations discussed above.) The differential form of the JMAEK equation [24] is:

$$d\alpha/dt = kq(1-\alpha)[\ln(1-\alpha)]^{1-(1/q)} \tag{8}$$

which may be rewritten as [24,25]:

$$d\alpha/dt = k(\alpha)^m(1-\alpha)^n$$

If q=2, then m=0.774 and n=0.500; if q=3, then m=0.700 and n=0.667; and if q=4, m=0.664 and n=0.750.

Distinguishing the fit of data to these alternative kinetic expressions is difficult [26,27]. In Fig. 7, the P–T function is compared with those of the A2, A3 and A4 models, calculated so that $\alpha = 0.50$ at $t = 50$ min. On this basis, the A3 function is closest to the P–T function. This similarity is re-inforced by

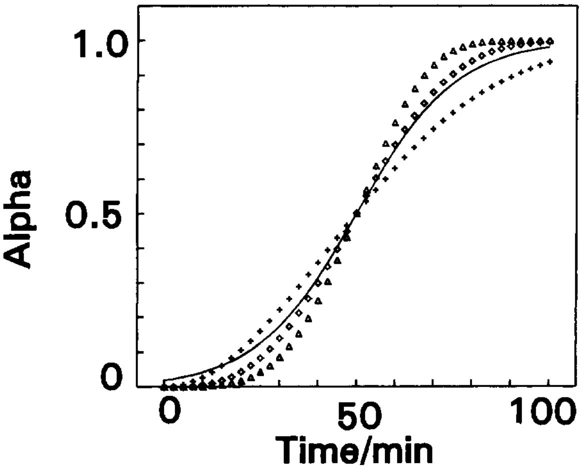

Fig. 7. Prout–Tompkins plot using $k = 0.07784\ \mathrm{min}^{-1}$ and $t_0 = 50$ min (solid line), compared with the plots for the A2 (+); A3 (◇); and A4 (△) models calculated so that $\alpha = 0.50$ at $t = 50$ min.

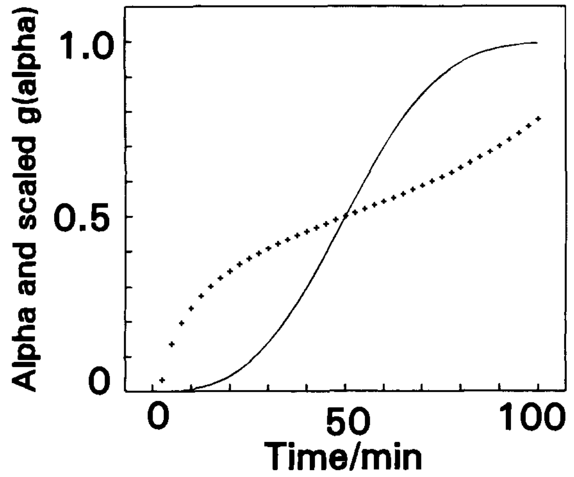

Fig. 8. The Avrami–Erofeev model A3 analyzed using the linear form of the Prout–Tompkins equation $g(\alpha)$. This function has been scaled: $(g(\alpha)/20) + 0.5$, for plotting on the same axes.

the plots shown in Fig. 8, where the α–time curve for the A3 model has been analyzed using the linear form of the P–T equation (suitably scaled for plotting on the same axes). The latter plot is approximately linear over a wide range of α (~0.05 to 0.95).

Criado et al. [28] have developed a rather complicated method specifically designed for identifying reactions following the Prout–Tompkins model under *programmed temperature* conditions. To simplify the kinetic analysis, the reactant is partially decomposed, to a set value α_0, under isothermal conditions, even before the heating programme begins. Details of the analysis are given [28], but this again emphasizes the difficulties of applying an equation which becomes indeterminate at the limits.

A comparison of kinetic results obtained from isothermal and programmed temperature experiments [29] showed that compounds whose isothermal decompositions were describable in terms of the P–T model over at least 90% of the decomposition, gave apparent first-order behaviour under non-isothermal conditions with excessively high E_a values.

4. Continuing work on $KMnO_4$ and other permanganates

Galwey [30] has pointed out that several of Tompkins' early papers [31–36] dealt with oxidations of organic compounds in solution by $KMnO_4$. One of these studies, the homogeneous oxidation of 2,4-dinitrophenol [31], showed a relatively unusual induction period due to the slow step, $MnO_4^- \rightarrow Mn^{4+}$. Tompkins' research direction appears to have moved gradually from the kinetics of homogeneous reactions to the heterogenous reactions. For example, the formation of MnO_2 was shown [33] to be accelerated by heterogeneous reaction on oxide surfaces.

Herbstein [2] provides a comprehensive history of studies on $KMnO_4$ up to the present. A recent electron microscopy study by Brown et al. [21] revealed a crystalline product of unusual texture that is formed early in the reaction. The solid products contain material that is inhomogeneous, poorly crystallized and possibly non-stoichiometric. The decomposition kinetics are satisfactorily described by the Avrami–Erofeev equation ($n = 2$) based on a nucleation-and-growth reaction model.

A method of non-isothermal kinetic analysis proposed by Urbanovici and Segal [37] suggests that the activation energy for the $KMnO_4$ decomposition increases significantly with the extent of decomposition. In a second paper [38], they report that the most appropriate rate equation for the non-isothermal decomposition of $KMnO_4$ is $d\alpha/dT = k(T)\alpha^{1.15}$.

Herley and Prout studied the decompositions of cesium [39] and rubidium [40] permanganates and found the P–T equation applicable to both. Recent re-examination of the $CsMnO_4$ [41] and $RbMnO_4$ [42] decompositions showed that for $CsMnO_4$, the maximum decomposition rate occurred at $\alpha = 0.7$ and the initial acceleratory period was described by the power law ($\alpha^{1/2} = kt$). P–T plots were satisfactory only up to the rate maximum. For $RbMnO_4$ [42], the rate maximum was slightly lower, $\alpha = 0.65$, and the initial acceleratory period was described by the power law ($\alpha^{1/3} = kt$) The textural changes accompanying decomposition suggested local melting which results in autocatalysis.

Nickel permanganate [43] decomposed (356 to 400 K) according to the JMAEK model (A2). Decomposition of the solid is more rapid than the breakdown of MnO_4^- in aqueous solution, which is not influenced by the presence of dissolved nickel ions. This is an example of an autocatalytic reaction proceeding more rapidly in the solid state than the comparable homogeneous reaction in solution.

Recent studies generally support Boldyrev's [44] proposed electron transfer decomposition mechanism, with little influence of the cation. For example, the activation energies for thermal decomposition of $KMnO_4$ and $AgMnO_4$ were compared [45] with the energy of the longest wavelength O → Mn charge transfer transition and a good correlation was found. Such a relationship can be valid when electron transfer is the rate determining step.

5. Thermal decompositions of other solids

Many solids, other than permanganates, decompose on heating under isothermal conditions to give a sigmoidal α–time curve [4,6,18], e.g. mercury(II) fulminate, lead oxalate, silver oxalate, nickel formate, silver oxide, barium and calcium azides, etc. In many such studies, as discussed earlier, it is difficult to decide whether the experimental results are best described by:

1. the P–T equation with a single k value; or
2. the JMAEK equation with an appropriate value of n; or
3. the P–T equation with two different k values; or
4. the application of separate models to the acceleratory and decay regions.

Some more recent examples of the possible application of the P–T equation in such studies are described below.

In a very thorough study of the thermal decomposition of bischofite, $MgCl_2{\cdot}6H_2O$, to periclase, MgO, in atmospheres of dry nitrogen, moist air and dry steam, Herbstein et al. [46] used TG and high-temperature in situ X-ray diffractometry to identify and determine the kinetics of the decomposition stages. Five decomposition stages were distinguished (see [46]) and some melting was observed. The P–T equation was applicable to all stages, except stage 5 in dry nitrogen, which was better described by a power law with exponent n between 0.82 and 0.87.

Cleaver and Davies [47] used Raman spectroscopy to study the kinetics of thermal decomposition of sodium and potassium dithionates to the corresponding sulphates. The decrease in intensity of the ν_s (SO_3) mode of $(S_2O_6)^{2-}$ with time was used as a measure of the extent of decomposition. The sodium salt decomposed according to the first-order kinetics and data for the potassium salt fitted the P–T equation. These results were in agreement with measurements of pressures of evolved SO_2. Structural information needed to explain the difference in behaviour of the sodium and potassium salts was not available.

The decompositions of some halates have also been described by the P–T equation, e.g. $Ba(BrO_3) \rightarrow BaBr_2 + 3O_2$, with two k values [48]. The kinetics of thermal decomposition of sulphate-doped potassium metaperiodate [49] were described by the P–T model ($0.1 < \alpha < 0.9$). Doping enhanced the decomposition rate, but E_a decreased only slightly. The mechanism was proposed to involve electron transfer leading to growth of nuclei.

A comprehensive review of the thermal behaviour of long chain metal carboxylates [50] mentions that the decompositions of even-chain Mn(II) carboxylates fit the P–T equation with two values of k. No account was taken of possible melting.

Phosphonium bromide decomposes [51] according to a P–T mechanism, described as "autocatalyzed nucleation of a freely migrating nucleus with an already reacted site." Phosphonium chloride, however, decomposed in a first-order process.

Thermal decomposition of polyvinylbenzyltriphenylphosphonium chloride takes place in two stages [52]. The first stage, which is loss of triphenylphosphine and HCl, was reported to fit the P–T equation, but no plots were illustrated, no ranges specified and no interpretation given.

Examination of the kinetics of volatilization of three cyclic phosphonates [53] showed that one reactant volatilized leaving no residue, the second decomposed in the solid state with P–T kinetics and the third decomposed in the melt. The same autocatalytic intermediate was identified for II and III, so that the chemical steps can be assumed similar, but the kinetics depend on the state of the reactant.

Isothermal decomposition of two different preparations (1a and 1b) of the (methanethiolato)zinc complex, $[Zn(SMe)2]_n$, led to the formation of β-ZnS [54] with different kinetics. Decomposition of 1a had autocatalytic (P–T type) kinetics and 1b had first-order kinetics. This behaviour was attributed to differences in surface areas of the particles of the two preparations. Preparation 1a had larger particles and an autocatalytic type of curve was believed to arise from influences of diffusion as discussed by Gafner [55].

The kinetics of thermal decomposition of ammonium carbamate [56] were measured under conditions where the carbamate remains partly solid. The P–T equation described the results and the product water, in contact with the solid product, was suggested to create nuclei for decomposition.

The solid-state thermal decomposition of azodicarbamide (470 to 479 K) is a strongly exothermic (-131 kJ mol^{-1}) and autocatalytic reaction [57] as shown by isothermal and programmed temperature DSC experiments. The complex temperature programme involved rapid heating to 460 K followed by switching to 5 K min^{-1}. Slow heating from lower temperatures did not produce the exotherm. The applicability of the P–T equation was interpreted in terms of collapse of the reactant crystal lattice into nucleation centres with critical dimensions.

6. Irradiation effects

In 1947, Prout and Tompkins studied the effects of electron bombardment on the subsequent thermal decomposition of mercury(II) oxalate [58]. Later, Prout [59] carried out an extensive study on the effects of pre-irradiation on the thermal decomposition of $KMnO_4$. The induction period, which is shortened by grinding of the reactant owing to the defects introduced, remained unaffected by exposure of the reactant to UV or to 20 kV electrons. Bombardment with thermal neutrons, or ^{60}Co γ-rays, or 145 MeV protons, all shortened the induction period and accelerated the main reaction. These effects were shown to be proportional to the dose of γ-irradiation. The results of similar studies on other reactants, including other permanganates, were surveyed in 1959 by Prout [60] who concluded that substances likely to be affected by pre-irradiation are those containing a simple metal cation and decomposing according to a branching chain mechanism. Irradiation nuclei produce strain which cracks the reactant and creates new reactive surfaces.

Some more recent studies of irradiation effects are described in the following.

The effects of gamma and neutron irradiation, and of addition of MnO_4^-, on the thermal decomposition of ammonium perchlorate were examined by Dedgaonkar and Chaudhari [61]. Data were analyzed according to the P–T equation by means of two equations with two different rate constants. The activation energy was lowered from 85 kJ mol^{-1} to 46 kJ mol^{-1} after a 10 Mrad dose of γ-irradiation. The irradiation effect was more pronounced than that of the addition of 2% of $KMnO_4$, $Ba(MnO_4)_2$ or NH_4MnO_4. The addition of NH_4MnO_4 alone decreased E_a (to 55 kJ mol^{-1}). Neutron irradiation did not change the decomposition characteristics.

The acceleratory and decay stages of the isothermal decomposition (613 to 653 K), of pure as well as Ba^{2+} doped, sodium bromate ($NaBrO_3$) [62] were analyzed according to the Prout–Tompkins and Avrami–Erofeev equations with two different rate constants, k(A) and k(D) in each case. ^{60}Co γ-irradiation, as well as doping, shortened the induction period and increased the rate and extent of reaction. The activation energy of the acceleratory period decreased and that of the decay stage increased with doping, but the values were unaffected by irradiation.

γ-Irradiation also increased the rate of decomposition of lead nitrate [63]. The P–T, first-order and contracting-volume equations all gave poor fits. Melting occurred so that the autocatalytic behaviour was attributed to the action of NO_2^- rather than to the defects of any kind.

Decomposition of pure $K_2Cr_2O_7$ [64] takes place in the melt (m.p. 398°C), but decomposition is catalyzed, below the melting point (330° to 360°C), by CdS, ZnS, CdO or ZnO (with reactivity in the order shown). γ-irradiation poisoned the catalyst and delayed decomposition. The P–T equation described the kinetics.

7. Solid-phase transitions and solid-solid reactions

The kinetics of the phase-transformation of $Na_4UO_2(SO_4)_3$, from glass to quasi-crystalline [65], showed an excellent fit with an autocatalytic (P–T) rate equation, and were interpreted in terms of nucleation, branching growth and termination. Larger values of the rate constant for the smaller crushed particles suggested that nucleation sites were located on the surfaces. Agreement between E_a values from independent conductivity and isothermal kinetic data led to the conclusion that the transformation step is linked to the mobility of Na^+ ion in the glass.

Several apparently solid–solid reactions gave reaction curves fitted by the P–T equation, e.g. CuCl+Ge [66] over the very limited range $0.15 < \alpha < 0.75$, and CuCl+Si [70] for $0.1 < \alpha < 0.9$. In their study of the preparation of Cu_3Si from Si and CuCl, Tamhankar et al. [67] obtained kinetic results which were interpreted as arising from simultaneous occurrence of an autocatalytic and a non-catalytic process. The P–T equation was modified to incorporate an additional rate constant, k_1 associated with the non-catalytic step:

$$\ln[(\alpha + k_1)/(1 - \alpha)] = k_2(t - t_i) + \ln k_1$$

where t_i is the induction period.

Thermal rearrangement of 4-methyl and 4-ethyl substituted, 4H-1,2,4-triazoles to the corresponding l-alkyl substituted triazoles [68], can take place either in the crystalline state or in the melts. Reaction rates were measured in both phases, by chemical analyses of quenched samples, and the activation parameters determined. The methyl substituted triazole reacted faster than the ethyl compound (methyl: $E_a = 104$ kJ mol^{-1}, ethyl: $E_a = 173$ kJ mol^{-1}). The results could be described by the P–T equation and were in agreement with a nucleophilic-type group transfer mechanism. The activation parameters for reactions in the solid state could be correlated with the interatomic distances between the I-N atoms of the triazole rings and the alpha-atom of the 4-alkyl groups in a neighbouring molecule.

8. Solid-fluid reactions and catalysis

Reduction of copper(I) oxides with hydrogen (69° to 111°C) was used [69] to prepare uniform copper particles. The reduction of fine copper(I) oxide particles took place through an autocatalytic process, which could be described by the P–T equation, while the reaction rates of rather coarse oxide particles were controlled by the diffusion of gaseous species through the copper layers formed.

The carbothermic reduction of nickel oxide [70] is an autocatalytic process with the Ni metal product acting as a catalyst. This product may undergo sintering and grain growth leading to decreased activity. Additives such as alkali metal carbonates melt and cover the metallic surface, hence, a deceleratory reaction. The kinetics were described by the modified P–T equation. The variation in the rate coefficient with time was attributed to the changes occurring in the metal phase. A calcium lignosulphonate catalyst was found which enhanced the rate of reduction by providing more active sites for the reaction: $CO_2(g) + C(s) \rightarrow 2CO(g)$.

Pattou and Perrin [71] have compared various models for the gaseous chlorination of phenols. The kinetics of chlorination of solid 4-chlorophenol were first-order for powdered reactant and describable by the P–T equation when single crystals were used. These results were interpreted as indicating that crystal defects played an important role in the mechanism.

Raney-nickel catalyst [72] is often prepared by leaching of a Ni–Al alloy with aqueous sodium hydroxide. The fractional leaching, α, of Al from 45 μm particles under isothermal conditions, was determined from Al analyses of the leaching solution. The deceleratory α–time curves were best described by the modified P–T equation and the activation energy was 57 kJ mol^{-1}. The leaching process is complex, involving several different Ni–Al phases. Alkali attack is believed to occur first at the grain boundaries of $NiAl_3$ with development, growth and branching of cracks.

The isothermal decomposition of (bulk) nickel formate was found [73] to be autocatalytic. The sigmoid α–time curves could be described by the P–T or A2 equations. E_a was 94 kJ mol^{-1}. The selectivity, S, defined as the $CO_2 : CO$ ratio in the gaseous products, ranged from 3.5 to 5.0 with the extent of reaction, α. These results were compared with the temperature-programmed decomposition of nickel formate and of formic acid pre-adsorbed on nickel powder, and with the steady-state catalytic reaction of HCOOH on Ni. Selectivities and estimated E_a values were similar for all processes and the formate ion was proposed as a common intermediate.

9. Pharmaceutical applications

Use of the Prout–Tompkins equation in the kinetic analysis of reactions of solid substances of pharmaceutical interest has been widespread and will be reviewed separately [74]. The influential and prolific publications by Carstensen (e.g. Ref. [75]) have played a major part in focussing attention in this field on the P–T equation.

Pharmaceutical studies of stability [75,76] are mainly concerned with initial degradation. Accelerated degradation studies have to be extrapolated to lower temperatures, with allowance for the possibility of phase changes, and taking the estimated errors in the kinetic parameters (E_a, A and $g(\alpha)$) into account. Behaviour of the pure drug is usually very different from that of a formulation. Monkhouse and Van Campen [76] have reviewed the factors which need to be considered. These include the presence of moisture and/or granulating solvent; the pH of the excipient surface; the volume of the container; differences in heat capacity of the drug and excipient; phase changes and chemical equilibria.

10. Colloid and interfacial chemistry

The chain nucleation processes described by Prout and Tompkins [1] have been modified for application in colloid and interfacial chemistry, a field rather different to the solid state for which the model was envisaged.

Monolayers and bilayers of surfactants on aqueous surfaces are useful models of biological systems [77]. The stabilities of such layers towards collapse to the bulk phase depend on many factors.

The mechanisms of collapse of monolayers to the bulk phase can be determined by kinetic studies [78]. Compression of the monolayers has to be done under carefully controlled conditions. The decrease of surface pressure with time at a fixed surface area (and temperature) may be used as a measure of the extent of collapse, $\alpha = (\pi_0 - \pi)/\pi$, where π and π_0 are the surface pressures at times t and 0, respectively. Alternatively, the surface pressure may be kept constant, by further compression of the monolayer, and the area (A) may be measured as a function of time [79]. At a surface pressure greater than the equilibrium spreading pressure, $\pi_{e'}$, monolayers may collapse by macroscopic film fracture, or by formation and growth of nuclei of bulk surfactant fragments. Vollhardt [80,81] has reviewed the theories of nucleation and growth in supersaturated monolayers. He considered (i) single-step nucleation and subsequent growth of the nuclei, (ii) the total transformation rate as convolution of nucleation rate and growth rate, and (iii) overlapping of the growing centres. The first model was for the limiting cases of nucleation and growth with assumed geometric shape, and the second model for nucleation according to the exponential law and the formation of lenticular centres from a supersaturated monolayer. He concluded [81] that adaptation of the P–T model is possible if overlapping of chains can be excluded, i.e. only over the initial stages of monolayer collapse. Adaptation of the Avrami model (which gives results very similar to those of the P–T equation, as described above) was also considered.

The modified P–T equation, with two different k values, was found to apply to experimental data for the collapse of monolayers of cellulose acetate [77]. Activation energies decreased with decreasing values of the surface area chosen for kinetic measurements. Entropies of activation, calculated from the pre-exponential factors, were negative. The initial step in the mechanism was suggested as a separation of some polymeric chains from the monolayer. These chains then grow by branching and hinder the separation of other chains. Interference increases with the degree of collapse. There is evidence of the existence of highly ordered structures in the collapsed phase.

A similar study on cholesterol monolayers [82], at temperatures below 40°C, gave data fitted by the modified P–T equation over the initial stage and second-order kinetics over the later stage. This second stage was suggested to be growth of nuclei formed as described above [77]. The activation energy for the first stage was comparable with the enthalpy of fusion of cholesterol in the bulk phase.

The effects of interactions between monoglycerides and solutes on monolayer stability were studied by Feria and Patino [79]. They are as follows: sugars or ethanol increase the instability of the monolayers; and temperature and surface pressure influence the loss of film molecules. Existing relaxation mechanisms were tested. There is a competition between the collapse and desorption mechanisms for monolayer destabilization as a function of the monoglyceride, subphase composition, temperature, and surface pressure.

11. Miscellaneous

A method [83] for the estimation of the 'time to achieve maximum rate under adiabatic conditions' for safety assessment of autocatalytic decompositions was based on competitive first-order and Prout–Tompkins kinetics. The method requires the heat release rates at the beginning of the reaction and at its maximum.

Burnham et al. [25] used a modified autocatalytic equation

$$d\alpha/dt = k(1-\alpha)(0.01+\alpha)^m$$

to describe the kinetics of isothermal pyrolysis of kerogens which showed sigmoid α–time curves and, hence, did not correspond to the usual parallel reaction, or single first-order model. This equation was referred to as the 'three-parameter model' (A, E_a and m) and the factor 0.01 eliminates the problems at $\alpha = 0$ and 1.0. The applicability of the equation was compared with the JMAEK equation and the Bouster equation [84]:

$$d\alpha/dt = k(1-\alpha)[1-(1-\alpha)^{2b}]^{1/2}$$

where $k = A_1\exp(-E_1/RT)$ and $b = A_2\exp(-E_2/RT)$. The differences in the predicted temperatures of geological oil formation, resulting from use of the different models, are discussed [25].

Nam and Seferis [85] have emphasized the need for an accurate description of polymer degradation kinetics in order to predict service lifetimes. Poly-ether–ether–ketone (PEEK) has been used as a model system. The kinetics of PEEK degradation have been studied with the help of isothermal and dynamic-heating experiments and various methods of kinetic analysis. A generally applicable rate equation was not found. Nam and Seferis [85] thus developed a more general rate equation capable of describing sigmoidal isothermal α–time curves of different types of symmetry. Several concurrent processes are combined with suitable weighting, e.g. $f(\alpha) = \sum y_i f_i(\alpha)$, where $\sum y_i = 1.0$, and $f_i(\alpha) = \alpha^{mi}(1-\alpha)^{ni}$. For example [86], if $f_1(\alpha) = (1-\alpha)$ is combined with $f_2(\alpha) = \alpha(1-\alpha)$ so that

$$d\alpha/dt = k[y_1(1-\alpha) + y_2\alpha(1-\alpha)]$$

integration gives

$$\ln[(\alpha + y_1/y_2)/(1-\alpha)] = \ln(y_1/y_2) + kt \tag{10}$$

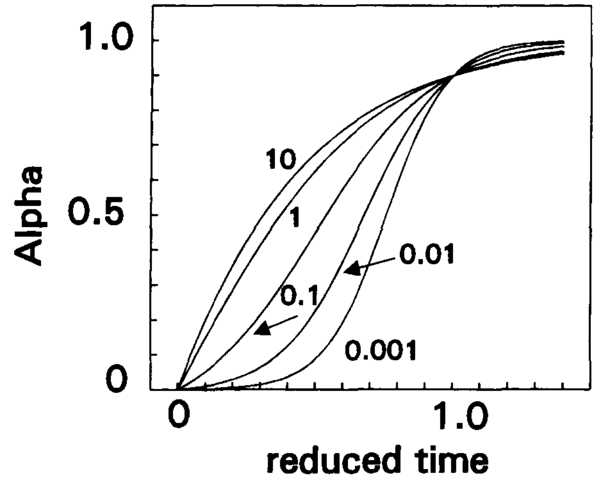

Fig. 9. Reduced-time plots, derived from Eq. (10), namely. $\alpha = c(\exp(kt_{\mathrm{red}}) - 1)/(1 + c(\exp(kt_{\mathrm{red}}))$, where $c = y_1/y_2$ and $k = \ln[(0.90 + c)/0.10c]$ for various values of c from 10 to 0.001 (based on Fig. 4 of Ref. [85]).

At the rate maximum, $d(d\alpha/dt)/d\alpha = 0$, hence $y_1/y_2 = 1 - 2\alpha_{\max}$.

Reduced-time plots of Eq. (10) for various values of y_1/y_2 (based on Fig. 2 of Ref. [85]) are shown in Fig. 9. As $y_1/y_2 \rightarrow 0$, the equation approaches the P–T equation with $\alpha_{\max} = 0.50$. As y_1/y_2 increases, the maximum rate decreases and $\alpha_{\max}$ decreases. When $y_1/y_2 \rightarrow \infty$, the maximum rate equation is at $\alpha = 0$ and the rate equation is of the first-order. The model equation derived [85] is thus capable of describing various types of degradation behaviour by adjustment of the y_1/y_2 ratio.

12. Conclusions

The Prout–Tompkins equation has achieved an interesting and unique status in solid-state kinetics. Although the mathematical form of the equation was not novel, the interpretation given to its application in solid-state reactions has led to developments in reaction models, including adaptation to fields outside the solid-state chemistry, such as colloid and interface science, as described above.

The equation is not particularly convenient for application in kinetic analysis because of its indeterminate nature at small and large extremes of the extent of decomposition, α. Its applicability is also not readily distinguishable from other rate equations which give sigmoidal α–time curves, i.e. the JMAEK equation. It is not usual to cite a specific reference to a kinetic model which **did not** apply to the reaction considered, unless the author is disputing an earlier claim of applicability, but several of the articles (e.g. [86]) cite Ref. [1] in indicating the difficulty of deciding between the P–T and the JMAEK equations.

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