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THERMAL DECOMPOSITION OF AQUEOUS MANGANESE NITRATE SOLUTIONS AND ANHYDROUS MANGANESE NITRATE. PART 3. ISOTHERMAL KINETICS

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ABSTRACT

The kinetics of the thermal decomposition of aqueous manganese nitrate solutions and anhydrous manganese nitrate in air were established from isothermal experiments. By heating the solution, first most of the water evaporates to a composition of equimolar amounts of water and manganese nitrate; this concentrated solution then decomposes to γ-MnO_2, NO_2 and water, usually in two steps. The first step can be described best by the model $[-\ln(1-\alpha)]^{1/2} = 8.9 \times 10^{11} \exp(-121000/RT)t$, whereas the second step is described equally well by several models. The kinetic parameters of these models are quite similar, the average activation energy being 141 kJ mole^{-1}.

The decomposition of anhydrous $Mn(NO_3)_2$, which proceeds in a single step, can also be described with several similar models. In this case the average activation energy is about 92 kJ mole^{-1}.

INTRODUCTION

As part of a project directed at obtaining battery-grade manganese dioxide from manganese ore by thermal decomposition of an aqueous manganese nitrate solution, the mechanism and kinetics of the thermal decomposition of such solutions as well as anhydrous $Mn(NO_3)_2$ have been studied. In Part 1 [1] the decomposition mechanism was resolved, which was found to depend strongly on the presence of water. On heating an aqueous manganese nitrate solution most of the water evaporates to a composition of about 1 mole H_2O per mole $Mn(NO_3)_2$, then at 130—140°C the residual water is driven off and part of the $Mn(NO_3)_2$ decomposes due to the accelerating effect of water on the $Mn(NO_3)_2$ decomposition. The intermediate product formed consists of a mixture of γ-MnO_2 and anhydrous $Mn(NO_3)_2$. On further heating, the remainder of the $Mn(NO_3)_2$ decomposes. If water is completely removed prior to decomposition by applying vacuum, which results in $Mn(NO_3)_2$ anhydrate, the decomposition occurs in only one step.

Part 2 [2] of this series was concerned with the heat of reaction of the two decomposition steps of $Mn(NO_3)_2$ solutions and of the decomposition of anhydrous manganese nitrate. The results were compared to values obtained from thermodynamic data.

In the present paper the kinetics are discussed, again for both steps occur-

TABLE 1

Kinetic parameters found by Gallagher and Johnson [4]

Gas	First decomposition step		Second decomposition step	
	Activation energy (kJ $mole^{-1}$)	Pre-exponential factor (s^{-1})	Activation energy (kJ $mole^{-1}$)	Pre-exponential factor (s^{-1})
N_2	91	6.2×10^9	137	3.1×10^{12}
N_2/H_2O	105	1.9×10^9	86	5.4×10^6
O_2	88	2.0×10^7	122	1.3×10^{11}
O_2/H_2O	85	8.5×10^6	75	2.9×10^5

ring when decomposing aqueous manganese nitrate solutions and for the decomposition of anhydrous manganese nitrate. The data were obtained from isothermal measurements.

LITERATURE

Few literature data are available for the kinetics of the decomposition. Only Lumme and Raivio [3] and Gallagher and Johnson [4] measured the kinetics. Lumme and Raivio found the decomposition to occur in a single step, with an activation energy of 99 kJ $mole^{-1}$, whereas Gallagher and Johnson observed two decomposition steps. The latter tried to describe each reaction step by 18 different kinetic equations. Although more than one equation appeared suitable to describe each step, one equation was selected for each step, viz. $kt = [-\ln(1-\alpha)]^{1/4}$ for the first decomposition step and $kt = 1 - (1-\alpha)^{1/2}$ for the second. With these equations the activation energy and pre-exponential factor were calculated. The equations applied to reactions in oxygen and nitrogen with and without water vapour present. Unfortunately, the water vapour concentration in the gases is not mentioned in Gallagher and Johnson's work, the results of which are summarised in Table 1. The effect of water vapour on the second decomposition step is noteworthy.

EXPERIMENTAL

Equipment

A Cahn RG (TGS-1) thermobalance was employed for the measurements on the thermal decomposition of aqueous manganese nitrate solutions and a Stanton-Redcroft TG 750 balance for the experiments on anhydrous manganese nitrate. The decompositions were carried out in air, dried with molecular sieves, which normally flowed through the balances at a rate of 100 ml min^{-1}. Sample weights were between 1 and 3 mg.

Materials

The two aqueous solutions of reagent-grade manganese nitrate used were obtained from J.T. Baker Chemicals Corp. The compositions were 61.5 wt.% $Mn(NO_3)_2$, 2.4 wt.% HNO_3 and 36.1 wt.% H_2O for the first solution and 59.9 wt.% $Mn(NO_3)_2$, 2.7 wt.% HNO_3 and 37.4 wt.% H_2O for the second.

Procedures

The first solution was used to study the thermal decomposition of aqueous solutions of manganese nitrate [1]. First, most of the water was removed by heating the solution to 110—120°C. A constant weight loss was normally obtained, corresponding to a residual sample composition of approximately 1 mole of water per mole of manganese nitrate. The sample was then heated rapidly to the temperature where the first decomposition step occurred (144—185°C). After completion of the reaction the intermediate product [MnO_2 and $Mn(NO_3)_2$] was further heated to the temperature where the second decomposition step was measured (188—225°C). All this was carried out under an air flow of 100 ml min^{-1}.

Anhydrous manganese nitrate was prepared from the second solution by heating the sample to about 100°C at a rate of 15°C min^{-1}. When the weight had become constant, vacuum ($\simeq$3 kPa) was applied for 1 h. After raising the pressure to atmospheric and adjusting the air flow to 100 ml min^{-1}, the anhydrous manganese nitrate produced was rapidly heated (100°C min^{-1}) to a temperature where the decomposition occurred (190—256°C).

The nitric acid present in all samples was assumed to have been evaporated completely before the decomposition started [5]. Because neither the weight loss of the first decomposition step nor that of the second was constant, each decomposition step was analysed separately. In doing this, the weight loss observed for each step was taken as 100% conversion, and thus time—conversion curves were obtained for each decomposition (step).

MODELLING

Isothermal reactions can be described by equations relating conversion (α) to reaction time. Generally those equations are of the form

$$g(\alpha) = kt$$

where $g(\alpha)$ is a function of the conversion and depends on the reaction mechanism, k is the reaction rate constant (s^{-1}), and t is the reaction time(s).

In all, 23 different models were tested to describe measured time—conversion curves (see Table 2). This was done by plotting the $g(\alpha)$ function against the reaction time for three randomly selected experiments on each decomposition step. Those models which gave the best straight line on visual inspection were selected for further processing by computer.

The value of the reaction rate constant was obtained for every model by a computer programme by varying the value of the constant until the

TABLE 2

Kinetic models tested [6—8]

Models of the general form $g(\alpha) = kt$		Type
$\alpha = kt$		Zero order
$-\ln(1-\alpha) = kt$ (**; ***)		First order
$(1-\alpha)^{-1} - 1 = kt$		Second order
$1-(1-\alpha)^n = kt$	$n = 1/2$ (**), $1/3$ (**; ***)	Surface reactions
$[-\ln(1-\alpha)]^n = kt$	$n = 2$, $2/3$ (**; ***), $1/2$ (*; ***), $1/3$ (*), $1/4$ (*)	Avrami—Erofeev (nuclei growth)
$\ln \frac{\alpha}{1-\alpha} = kt$		Prout—Tompkins; (nuclei growth)
$1-(1-\alpha)^n = kt$	$n = 2, 3, 4$	Reaction order
$\ln \alpha = kt$		Exponential
$\ln(\alpha^2) = kt$		Exponential

Diffusion-type equations	Type
$\alpha^2 = kt$	One-dimensional, parabolic
$(1-\alpha)\ln(1-\alpha) + \alpha = kt$	Two-dimensional
$(1 - 2/3\alpha) - (1-\alpha)^{2/3} = kt$	Ginstling, Brounshtein
$(1-(1-\alpha)^{1/3})^2 = kt$	Jander
$\exp(\alpha^2) = kt$	One-dimensional, exponential
$\left[\left(\frac{1}{1-\alpha}\right)^{1/3} - 1\right]^2 = kt$	Zhuralev et al.
$\exp[1-(1-\alpha)^{1/3}]^2 = kt$	Kroger, Ziegler

* Model selected for first decomposition step.

** Model selected for second decomposition step.

*** Model selected for decomposition of anhydrous manganese nitrate.

minimum was reached in the following sum

$$\sum_{i=1}^{m} \left(\frac{t_{\text{theor}} - t_{\text{exp}}}{t_{\text{exp}}}\right)^2$$

where t_{exp} is the measured reaction time needed to reach a certain conversion, and t_{theor} is the theoretical reaction time necessary to reach the same conversion but now calculated by using the relevant model. The difference between the two times is divided by t_{exp} to decrease the emphasis otherwise placed on the end of the time—conversion curve. The number of conversions for which the sum is calculated is represented by m. To discriminate between different models, the variance was calculated which is defined as

$$v = \sum_{i=1}^{m} \left(\frac{t_{\text{theor}} - t_{\text{exp}}}{m-1}\right)^2$$

RESULTS AND DISCUSSION

A plot of most g(α) functions against time for the second decomposition step of one specific experiment is shown in Figs. 1 and 2. Most lines show a definite curvature. The models resulting in an approximately straight line were applied to calculate the reaction rate constant. The models selected for the different decompositions are indicated in Table 2 by *, ** or ***. None of the plots of a diffusion-type equation vs. t resulted in a straight line. Thus, only nuclei-growth-type equations or equations valid for surface reactions can describe the decomposition studied here.

First, the results from modelling the decomposition of the solution will be given. Table 3 contains the variances of the selected models for some experiments on the decomposition of aqueous solution of manganese nitrate. For the first decomposition step the model $[-\ln(1-\alpha)]^{1/2} = kt$ is better for all experiments, whereas for the second decomposition step each of the models selected sometimes had the lowest variance, depending on the experiment examined. Examples of the fit between a measured and a calculated time—conversion curve for the two decomposition steps are shown in Figs. 3 and 4. It is very clear that for the first decomposition step the model $[-\ln(1-\alpha)]^{1/2} = kt$ is best (Fig. 3) and that the second decomposition step is described equally well by all models (Fig. 4). To obtain the activation energies Arrhenius plots were made. For the first decomposition step only results from the model $[-\ln(1-\alpha)]^{1/2} = kt$ were used (Fig. 5), whereas for the second step results from all the models selected were plotted (example in Fig. 6). A relatively large scatter occurs in the reaction rates of both decomposition steps, probably due to differences in the development of the physical structure of each sample. The activation energies and pre-exponential factors calculated from the Arrhenius plots are shown in Table 4. Satisfactorily small differences occur between the kinetic parameters of the second decomposition step. It is impossible to state according to which mechanism the manganese nitrate decomposes. This applies to the first step, which may either proceed according to two-dimensional growth of a constant number of nuclei or to one-dimensional growth with a constant rate of new nuclei for-

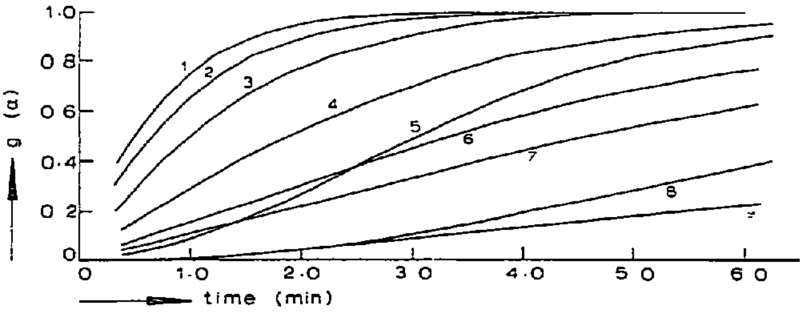


Fig. 1. Plot of several g(α) functions vs. time for the second decomposition step. T = 225°C. $g(\alpha) =$ (1) $1-(1-\alpha)^4$; (2) $1-(1-\alpha)^3$; (3) $1-(1-\alpha)^2$; (4) α; (5) α^2; (6) $1-(1-\alpha)^{1/2}$; (7) $1-(1-\alpha)^{1/3}$; (8) $\{1-(1-\alpha)^{1/3}\}^2$; (9) $1-2/3\,\alpha-(1-\alpha)^{2/3}$.

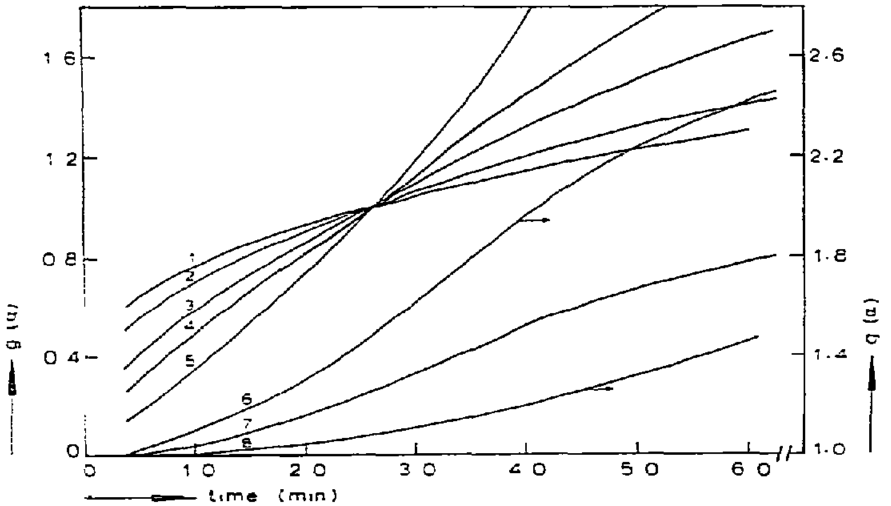


Fig. 2. Plot of several g(α) functions vs. time for the second decomposition step. T = 225°C. g(α) = (1) $[-\ln(1-\alpha)]^{1/4}$; (2) $[-\ln(1-\alpha)]^{1/3}$; (3) $[-\ln(1-\alpha)]^{1/2}$; (4) $[-\ln(1-\alpha)]^{2/3}$; (5) $-\ln(1-\alpha)$; (6) $\exp(\alpha^2)$; (7) $(1-\alpha)\ln(1-\alpha)+\alpha$; (8) $\exp[(1-(1-\alpha)^{1/3})^2]$.

mation. For the second decomposition step even more possibilities arise (cf. Table 2). For details about the different equations for certain mechanisms see refs. 6, 8—10.

The activation energy for the first decomposition step is higher than the value found by Gallagher and Johnson [4]; however, Gallagher and Johnson used a different model to calculate the kinetic parameters. For the second step the values agree more closely. The activation energy obtained is lower for the first decomposition step than for the second, which is probably

TABLE 3

Variances of tested models for some experiments on decomposition of manganese nitrate solution

Step	Variances for models:			d.f.	Temp. (°C)
	$[-\ln(1-\alpha)]^{1/4}$	$[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{1/2}$		
1	1.0×10^{-1}	4.7×10^{-2}	1.4×10^{-3}	15	185
1	1.3	6.9×10^{-1}	4.3×10^{-2}	19	170
1	2.1×10^{2}	1.5×10^{2}	5.1×10^{1}	19	150
1	5.6	3.0	2.5×10^{-1}	18	160
	$-\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{2/3}$	$1-(1-\alpha)^{1/3}$		
2	7.2	9.1	1.4	17	200
2	1.9×10^{-1}	4.0×10^{-1}	1.2×10^{-2}	19	225
2	7.6	2.6×10^{-2}	2.3	18	210
2	5.0×10^{1}	8.6×10^{2}	3.4×10^{2}	19	188

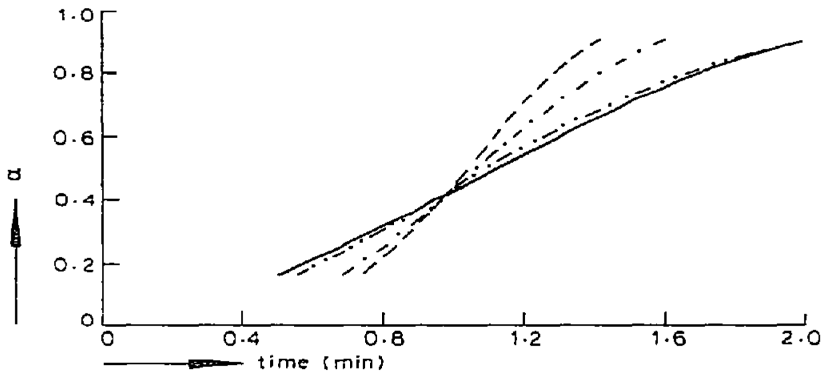


Fig. 3. Measured and calculated time—conversion curves for the first decomposition step. (——— Measured; (— — —) $g(\alpha) = [-\ln(1-\alpha)]^{1/4}$; (· — · — ·) $g(\alpha) = [-\ln(1-\alpha)]^{1/3}$; (— · · —) $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$.

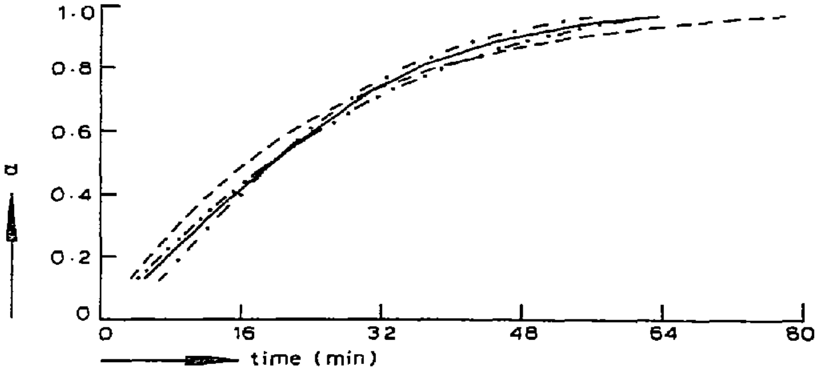
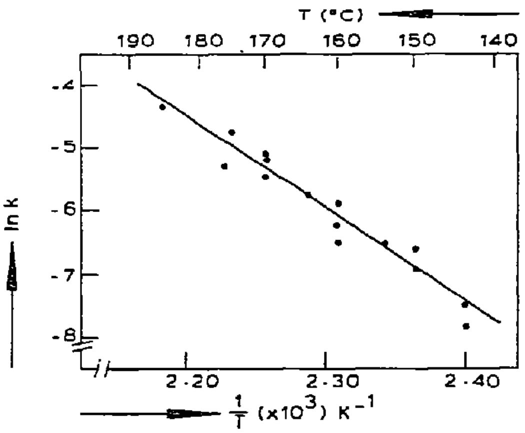


Fig. 4. Measured and calculated time—conversion curves for the second decomposition step. (———) Measured; (— — —) $g(\alpha) = -\ln(1-\alpha)$; (· — · — ·) $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$; (— · ·) $g(\alpha) = 1-(1-\alpha)^{1/3}$.



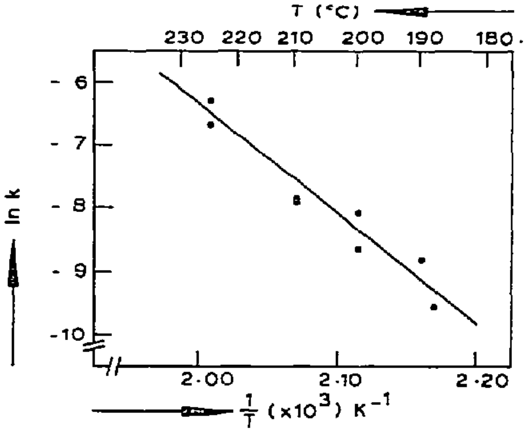


Fig. 5. Arrhenius plot for the first decomposition step. Results from the model $[-\ln(1-\alpha)]^{1/2} = kt$.

Fig. 6. Arrhenius plot for the second decomposition step. Results from the model $1-(1-\alpha)^{1/3} = kt$.

TABLE 4

Kinetic parameters for decomposition of aqueous solutions

Model	Pre-exponential factor (s^{-1})	Activation energy (kJ $mole^{-1}$)
First decomposition step		
$[-\ln(1-\alpha)]^{1/2}$	8.9×10^{11}	121
Second decomposition step		
$-\ln(1-\alpha)$	6.5×10^{12}	143
$[-\ln(1-\alpha)]^{2/3}$	2.0×10^{12}	139
$1-(1-\alpha)^{1/2}$	8.6×10^{11}	140
$1-(1-\alpha)^{1/3}$	1.6×10^{12}	143

caused by water vapour. Gallagher and Johnson [4] found that water vapour markedly reduces the activation energy of the second decomposition step. As is stated in Part 1 of this series [1], the second decomposition step is actually the decomposition of unreacted anhydrous $Mn(NO_3)_2$ remaining after the first step. It was further reported in ref. 1 that the first decomposition step consists of the removal of water plus decomposition of part of the $Mn(NO_3)_2$, the latter being accelerated by the presence of water (vapour), which thus probably also causes the lower activation energy.

Results for the decomposition of anhydrous manganese nitrate were obtained in essentially the same way. Table 5 contains the variances of the models selected for some experiments. The models $[-\ln(1-\alpha)]^{2/3}$ and $1-(1-\alpha)^{1/3}$ appear to describe the reaction well, though the first usually gives slightly better fits. However, it was noticed that the correspondence between a measured and a calculated time—conversion curve depended strongly on the choice of the position of the time axis. As is known, the problem with isothermal experiments is that it takes some time for the sample to reach the reaction temperature, during which time some decomposition already occurs. Therefore, the exact position of the point $t = 0$, at which the isothermal reaction is supposed to start, is never known. What happens when a

TABLE 5

Variances of models tested (anhydrous $Mn(NO_3)_2$)

Variances for models:				Temp. (°C)
$-\ln(1-\alpha)$	$[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/2}$	$1-(1-\alpha)^{1/3}$	
2.6×10^{-1}	4.1×10^{-4}	1.1×10^{-1}	7.1×10^{-2}	223.5
1.4×10^{-1}	1.1×10^{-3}	3.8×10^{-2}	2.5×10^{-2}	241.5
2.6×10^{-1}	2.5×10^{-3}	1.6×10^{-1}	4.8×10^{-2}	232.5
1.1×10^{1}	1.6×10^{1}		9.3×10^{-1}	190.0
1.7	3.0×10^{-2}		4.8×10^{-1}	212.5
3.9×10^{-1}	1.3×10^{-1}		3.1×10^{-2}	215.0
2.5×10^{-1}	1.2×10^{-2}		5.7×10^{-2}	240.0

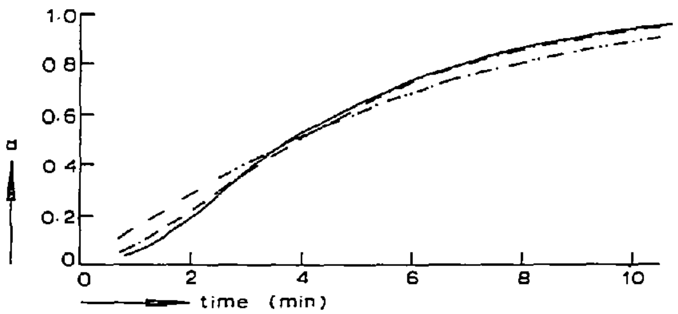
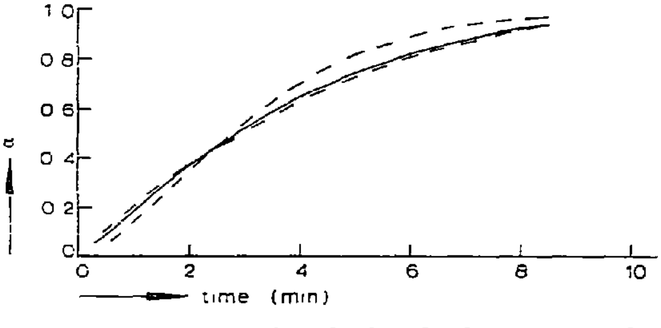


Fig. 7. Measured and calculated time—conversion curves for the decomposition of anhydrous manganese nitrate. (———) Measured; (· — · — ·) $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$, variance 3.0×10^{-2}; (— · · —) $g(\alpha) = 1-(1-\alpha)^{1/3}$, variance 4.8×10^{-1}.

slightly different position of the $t = 0$ point is assumed is shown in Figs. 7 and 8. Figure 7 shows a measured time—conversion curve and two curves obtained by fitting this curve with the two models giving the lowest variances (Table 5). In Fig. 8 the same measured time—conversion curve is shown with the time axis shifted backwards by about 1 min. This was fitted to the same models; in Fig. 7 the model $[-\ln(1-\alpha)]^{2/3}$ gives the best fit, whereas in Fig. 8 the model $1-(1-\alpha)^{1/3}$ results in the best fit; moreover, it was established that the fit to the model $-\ln(1-\alpha)$ improves appreciably (data not shown). Shifting the time axis forward would probably have resulted in a better fit of a model like $[-\ln(1-\alpha)]^p$, with $p < 2/3$. Because no specific model could be selected as being best, Arrhenius plots were made for both models as well as for the model $-\ln(1-\alpha) = kt$. As an example, Fig. 9 shows



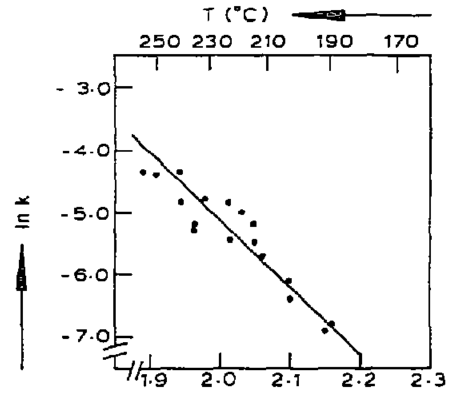


Fig. 8. Measured and calculated time—conversion curves for the decomposition of anhydrous manganese nitrate; time axis shifted about 1 min backwards. (———) Measured; (· — · — ·) $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$, variance 4.1×10^{-1}; (— · · —) $g(\alpha) = 1-(1-\alpha)^{1/3}$, variance 2.4×10^{-2}.

Fig. 9. Arrhenius plot for the decomposition of anhydrous manganese nitrate. Results from the model $[-\ln(1-\alpha)]^{2/3} = kt$.

TABLE 6

Kinetic parameters for decomposition of anhydrous manganese nitrate

Model	Pre-exponential factor (s^{-1})	Activation energy (kJ $mole^{-1}$)
$-\ln(1-\alpha)$	2.6×10^7	93
$[-\ln(1-\alpha)]^{2/3}$	1.4×10^7	90
$1-(1-\alpha)^{1/3}$	1.1×10^7	94

the plot for $[-\ln(1-\alpha)]^{2/3} = kt$. The pre-exponential factors and activation energies obtained from those plots are given in Table 6. The kinetic parameters are in close agreement, the activation energy being about 92 kJ $mole^{-1}$.

Several possibilities are open regarding the mechanism according to which the decomposition occurs. The same is true for the second step of the decomposition of an aqueous manganese nitrate solution. Although both reactions are in fact decompositions of anhydrous manganese nitrate, large differences in kinetic parameters result, whereas the difference in the reaction rate constant (k) is relatively small in the temperature range investigated (Table 7). The difference in the kinetic parameters must be caused by the completely different physical structure of the sample at the onset of decomposition. For the second decomposition step MnO_2 is distributed randomly in the $Mn(NO_3)_2$ and the material is voluminous and porous (swollen) [1]. The "anhydrous $Mn(NO_3)_2$" consists of tiny particles which seem to have no, or almost no, porosity. To acquire more information about the exact mechanism according to which both reactions proceed, non-isothermal experiments have been performed, the results of which will be described elsewhere.

TABLE 7

Reaction rate constant (k) of the second decomposition step and of the decomposition of anhydrous $Mn(NO_3)_2$ at several temperatures

Second decomposition step		Decomposition of anhydrous $Mn(NO_3)_2$
Pre-exponential factor (s^{-1}): 2.7×10^{12} Activation energy (kJ $mole^{-1}$): 141 000		1.6×10^7 92 000 } Average values
T (K)	k (s^{-1})	k (s^{-1})
450	1.1×10^{-4}	3.2×10^{-4}
475	7.9×10^{-4}	1.2×10^{-3}
500	4.7×10^{-3}	3.8×10^{-3}
525	2.4×10^{-2}	1.1×10^{-2}

CONCLUSIONS

On decomposition of an aqueous manganese nitrate solution in air, a first decomposition step occurs above about 130°C, which can be described by the equation $[-\ln(1-\alpha)]^{1/2} = kt$, with $k = 8.9 \times 10^{11} \exp(-121000/RT)$. A second decomposition step starts at about 180°C; this step can be described by several equations (Table 4), with an average activation energy of 141 kJ mole^{-1}.

The decomposition of anhydrous manganese nitrate in air can also be described by more than one model for which the kinetic parameters are about equal. The average activation energy in the temperature range 190—256°C was found to be 92 kJ mole^{-1}. No definite answer can be given about the mechanism according to which the reactions proceed.

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