Thermochimica Acta, 30 (1979) 273–280

THE APPEARANCE OF A COMPENSATION EFFECT IN THE THERMAL DECOMPOSITION OF MANGANESE(II) CARBONATES, PREPARED IN THE PRESENCE OF OTHER METAL IONS

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(Received 22 May 1978)

ABSTRACT

In this study, a compensation effect is observed for the thermal decomposition of manganese(II) carbonates, prepared in the presence of Al^{3+} and Na^{+} ions. This compensation effect is described by the equation $\log A = aE + b$, and the parameters are shown to be $a = 0.1$ and $b = -2.9$. The mechanism of decomposition was found to follow first order kinetics.

Both A, the pre-exponential function, and E, the energy of activation, depended on the concentration and type of metal ion present in the carbonate preparation, and on the experimental method used to obtain Arrhenius parameters. In the rising temperature experiments, more than one Arrhenius plot was obtained over different temperature ranges.

INTRODUCTION

The compensation effect

The significance in physical terms of the compensation plot has been the subject of extensive discussion[1-6]. In some cases, authors have considered it to be purely an indication of the experimental technique, and to be without any real physical meaning[7, 8]. The compensation effect was first applied in heterogeneous catalysis[9] to explain the fact that the activation energy changed with differing treatment of the catalysts but without actually altering the rate of reaction.

The Arrhenius equation relates the specific rate constant with the energy of activation, viz.

$$k(T) = Ae^{-E/RT} \tag{1}$$

where, $k(T)$ = specific rate constant (temperature dependent only); A = pre-exponential function; E = energy of activation; R = Gas constant; T = Absolute temperature.

A natural consequence[5] of using this equation in heterogeneous reactions is the appearance of the so-called compensation effect[10, 11]. Reactions which show this effect obey the equation

$$\log A = aE + b \tag{2}$$

where a and b are constants.

Care has to be taken in quoting values of a and b as the nomenclature employed in the literature is not consistent. This equation has been quoted as $\log A = B + eE$[12], or often with the A being replaced by Z[5, 6, 10]. It has also been printed as $\log A = a + bE$[13, 14].

The compensation plot of log A vs. E will then yield two parameters, firstly (referring to eqn. (2)) a, the gradient, and secondly b, the intercept. It is these two parameters that provide a more generalised picture of the characteristics of a series of related reactions[15]. A lack of physical significance not only exists for A, E and n (the order of reaction)[6, 16, 17], but there is considerable doubt as to the complete situation suggested by eqn. (1)[17], and it's applicability to heterogeneous reactions[18, 19].

Garn[5] states that a compensation effect is unavoidable if, when eqn. (1) is written in an alternative form, viz.

$$\log A = \frac{E}{2.3\,RT} + \log k \tag{3}$$

T is almost constant. Gorbachev[20] states that the only criterion for a compensation plot (log A vs. E) is the existence of an "iso-kinetic" temperature, where the rate constant is identical for all processes concerned, which may, or may not be experimentally accessible. From the Arrhenius plots in this report, it does not appear that an isokinetic point is obtainable. Zmijewski and Pysiak[21] however, show plots of similar shape, and still obtain an "iso-kinetic" point.

Zsako[16] gives a short review of the problems of deriving kinetic parameters from TG curves. Although agreeing with Garn[5] that kinetic parameters obtained from TG curves may have little physical meaning for a series of TG curves, he states that in the interpretation of kinetic parameters, the kinetic compensation effect must always be taken into account, since for a series of TG curves (e.g. varied heating rate, etc.) the kinetic parameters obtained may vary for each individual curve, whilst the compensation parameters, a and b, will always be the same for the whole series[6].

A compensation plot has been previously observed for the decomposition of manganese(II) carbonate[22], from results published earlier (refs. 2 and 3 from ref. 22). The compensation parameters were given as $a = 0.3$ and $b \sim 0$.

Manganese(II) carbonate

The actual process of thermal decomposition of manganese(II) carbonate may be affected by such things as heating rate[23, 24], purity of the sample[25, 26], nature of the sample[27, 28] etc., so it is not surprising that results published by different workers are not in good agreement[29–31].

It is, however, the activation energy that is of most importance to this report. For the decomposition of precipitated manganese(II) carbonate, Razouk et al.[27]

gave the activation energy (E) as 94.2 kJ mole^{-1}, and estimate that of rhodochrosite (a mineral containing mostly $MnCO_3$) as 243 kJ mole^{-1}. Tonge[32] found a value of 222 kJ mole^{-1} for precipitated $MnCO_3$ whilst Brill[33] reported an activation energy of 98.4 kJ mole^{-1} also for precipitated $MnCO_3$.

The techniques used to obtain data to produce a compensation plot were two-fold. Initially, classical isothermal techniques were employed, and secondly, programmed temperature rise experiments were performed. The disadvantage of the latter is that since not one, but many kinetic expressions may describe the course of the reaction, there is no method which will easily allow for the presence of several expressions whilst the decomposition is proceeding. Various methods have been proposed to obtain kinetic parameters from rising temperature techniques[34-39].

In this study data for a compensation plot is obtained from Arrhenius type plots using the specific reaction rate constant, obtained from a first order decay expression, as the isothermal studies indicated that this relationship gave a satisfactory fit.

EXPERIMENTAL

Materials

Standard laboratory reagent (S.L.R.) $MnCl_2 \cdot 4H_2O$ was used to make up the initial solutions of manganese(II) ions. S.L.R. NaCl or $AlCl_3 \cdot 6H_2O$ introduced the Na^+ or Al^{3+} ions into the initial solution. S.L.R. Na_2CO_3 as a solution was used to precipitate out manganese(II) carbonate in the presence of the foreign ions.

Equipment

All thermal decompositions, whether isothermal or non-isothermal, were carried out on a Stanton-Redcroft TG 750 thermobalance. This has a temperature programmer capable of heating rates from 1 to 100°C min^{-1} and an isothermal control between 0 and 1000°C, with an accuracy of ± 0.1 °C.

Procedure

All manganese(II) carbonate samples were prepared by precipitation in the presence of foreign ions. Seven samples were prepared in all, namely, six manganese(II) carbonate precipitates were brought down in the presence of sodium and aluminium as the foreign ions, in amounts of 1, 5 and 10% on a mole basis, referring to the decomposition to Mn_2O_3; the seventh sample was pure manganese(II) carbonate, prepared in an analogous manner, so as to avoid inconsistency when comparing results.

It was of course noted that in the case of sodium, the Na^+ ions would not actually appear in the final carbonate precipitate, but might influence the physical nature of the final product.

When a homogeneous solution was obtained containing Mn^{2+} and Al^{3+} or Na^+ ions, a solution of Na_2CO_3 was added in excess to precipitate manganese(II) carbonate, in the presence of foreign ions. The final precipitate was filtered through a vacuum pump, washed with distilled water and dried in an oven at 110°C for 24 h. It is noteworthy that although sodium carbonate in excess was used to precipitate the carbonates the initial presence of sodium ions in the original chloride solution influenced the manner in which the precipitated products decomposed.

Isothermal experiments were carried out at temperatures of 365, 390 and 420°C. Rising temperature experiments were run at a constant heating rate of 1.2°C min^{-1}. The makers state that because of the design of the furnace, there is little or no noticeable buoyancy effect over the entire temperature range, even on maximum sensitivity[40]. A slight increase in weight was observed, but was within the accuracy of the experiment. Between 6–8 mg of solid was used for the decompositions, which were carried out in air flowing at 30 ml min^{-1}.

RESULTS

The Arrhenius plot of log *k* vs. 1/*T* for isothermal data is shown in Fig. 1. The rate constant *k*, is obtained from first order decay expressions of isothermal

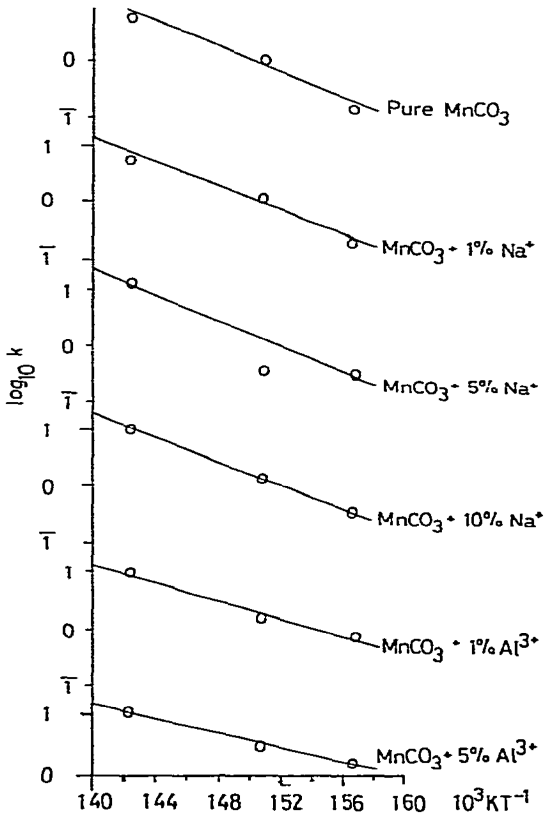

Fig. 1. Arrhenius plot for isothermal data.

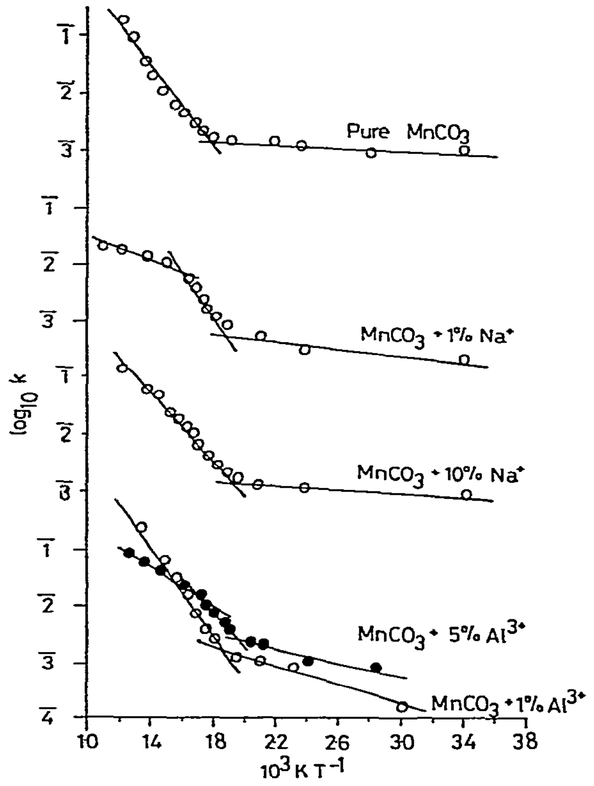

Fig. 2. Arrhenius plot for TG data.

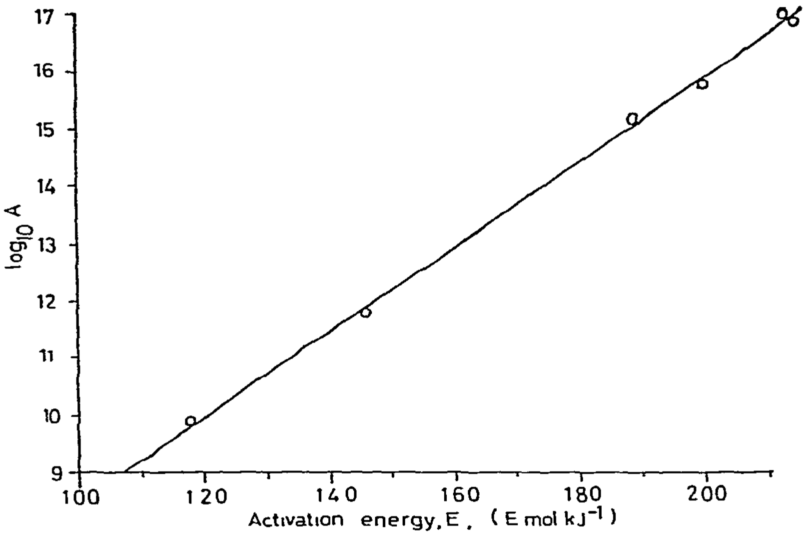

Fig. 3. Compensation plot for isothermal data.

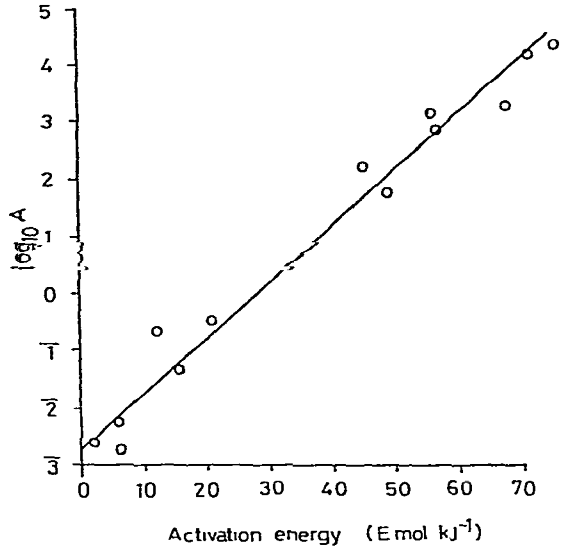

Fig. 4. Compensation plot for TG data.

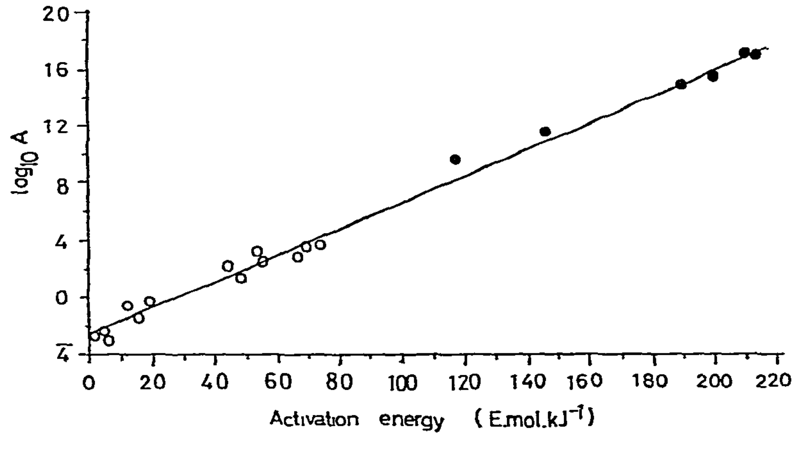

Fig. 5. Compensation plot for impure $MnCO_3$. ○, Data from TG experiments; ●, data from isothermal experiments.

experiments, T is the absolute temperature. A similar plot for rising temperature (TG) data is shown in Fig. 2. The scales have been displaced for clarity.

Compensation parameters obtained from these two plots are then plotted according to eqn. (2) and are shown in Figs. 3 and 4, for isothermal and TG experiments, respectively.

These compensation plots were replotted on a different scale to fit the two sets of data onto the same axes, this is shown in Fig. 5. The gradient of slope obtained by a method of least squares was 9.56×10^{-2} mole kJ^{-1}, and the interception was -2.89.

DISCUSSION

The rate of decomposition may be written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,\mathrm{f}(\alpha) \qquad (\alpha = \text{fraction decomposed}) \tag{4}$$

where $k(T)$ is only temperature dependent, $\mathrm{f}(\alpha)$ is a function of the fraction decomposed, i.e. a function of the phase composition of the reacting system at any one moment.

If eqn. (4) is now rearranged and integrated

$$\frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} = k(T)\mathrm{d}t \tag{5}$$

The left-hand side of this equation is given the function $\mathrm{g}(\alpha)$ and tables of the value of this function are available in the literature[34]. Since

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\mathrm{d}\alpha}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}T} \tag{6}$$

and

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta = \text{heating rate}$$

then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}T}\beta \tag{7}$$

If this is now incorporated into eqn. (5) it follows

$$\mathrm{g}(\alpha) = \frac{k(T)\mathrm{d}T}{\beta} \tag{8}$$

If the value for $k(T)$ from eqn. (1) is now substituted into eqn. (8), we get

$$\mathrm{g}(\alpha) = \frac{A}{\beta}\,\mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{9}$$

Integration of the exponential in eqn. (9) is impossible as it stands. Approximate methods for its evaluation and so, methods of obtaining kinetic parameters from it, are available. A good review of these methods is given by Wendlandt et al.[34].

In an attempt to obtain kinetic parameters other than by a direct use of eqn. (9), and the subsequent approximations, the following method was used. It must be noted beforehand that this method is only approximate in the calculation of $d\alpha/dT$, but this can be improved by the use of computor methods of evaluating the slope to a line.

In the differential form of eqn. (8)

$$\frac{d\alpha}{f(\alpha)} = \frac{k(T)\,dT}{\beta} \tag{10}$$

rearranging

$$k(T) = \frac{d\alpha/dT\,\beta}{f(\alpha)} \tag{11}$$

It was found from isothermal data that the solid decomposes following a first order decay law. This was assumed to be correct and substituted as $f(\alpha)$ into eqn. (11), this can be regarded as the first approximation. The second was in the calculation of $d\alpha/dT$, which was calculated manually, from the actual α–T trace obtained from the chart recorder. When these values are placed in eqn. (1) $k(T)$ can be found. The log of this value is then plotted against reciprocal temperature to obtain an Arrhenius plot. The gradient and interception of which (as shown in Figs. 1 and 2) can be identified with the energy of activation and preexponential function, respectively, (cf. eqn. (1)).

Cremer[41] has shown that for a model involving two types of active sites, each of a different activation energy, then a compensation effect will be seen, i.e., the overall rate will be influenced by the rates on the two types of site. This involves only two types of site, whilst in a real system there may be a graduation of sites producing composite effects. The concept has however been generalised[9,41,42] to include the involvement of n sites and thus describe more complex systems. An examination of a simple cubic structure demonstrates the existence of various sites which could be expected to possess individual Arrhenius parameters dependent upon their location. These sites would be three types of site located in the faces of the cube, edge-atoms and corner atoms making a total of five, and this number would increase with the complexity of the crystal structure. This would be further increased by the existence of deformities and non-stoichiometry induced in this study by altering the conditions of preparation.

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