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THE APPEARANCE OF A COMPENSATION EFFECT IN THE RISING TEMPERATURE DECOMPOSITION OF A SERIES OF PURE CARBONATES

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ABSTRACT

In this study, a compensation effect is observed for the rising temperature decomposition of a series of pure carbonates. This compensation effect is described by the equation

$$\ln A = aE + b$$

and the parameters are shown to be $a = 0.22$ and $b = -4.16$. The mechanism of decomposition was found to follow first order kinetics.

An isokinetic point was found in the experimental region but, since one of the samples has a different decomposition mechanism, this criterion for a genuine compensation effect is obviously unsound. A model involving a distribution of active sites on a reacting solid has been discussed.

INTRODUCTION

Most solid state decompositions obey the Arrhenius equation which expresses the variation of the specific reaction rate, k, with temperature T

$$k = A e^{-E/RT} \tag{1}$$

where A is the pre-exponential function, R is the gas constant and E is the energy of activation. The compensation effect is a compensating change in the activation energy corresponding to an increase in the pre-exponential function. Thus for a series of reactions exhibiting this compensation effect the following equation is found

$$\ln A = E + b \tag{2}$$

Comparison of eqns. (1) and (2) shows that $a = (RT)^{-1}$ [1]. T, obtained from such a plot is the so-called "isokinetic temperature" [2], where the rate constant is identical for all processes concerned. This temperature may, or may not, be experimentally accessible.

It is the ability of the Arrhenius equation to produce straight lines for both $\ln k$ vs. $1/T$ and $\ln A$ vs. E data which suggests that the compensation effect is real and has a physical explanation. However, workers in this field do have doubts about the reality of the effect and indeed none of the expla-

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nations, reviewed by Galwey [3], are mutually exclusive and few provide convincing arguments in favour of one explanation in preference to all others. The compensation effect may simply arise, not from any kinetic properties of a system, but as an experimental artifact.

The Arrhenius equation has been criticised for being incomplete [4,5], and meaningless for heterogeneous reactions, where little significance can be attached to A, E and n (the so-called order of reaction). Garn [6], whilst agreeing with many of these ideas, states that the Arrhenius equation is incomplete but often possible variables are excluded in the choice of reaction systems. For example, if the series of reactions being studied all occur within the same temperature interval, then if either A or E varies, appropriate values of k are only possible if there is a measure of compensation [7,8]. Garn, in examining many reports of compensation behaviour, found that the reactions involved have a feature in common — a principle reaction in which some parameter changes the temperature variation without changing the general nature of the reaction.

Gorbachev [9] argues that when the existence of a true compensation effect in non-isothermal kinetics is in doubt, then the isokinetic temperature will serve as a criterion. If the isokinetic point can be found in the graph of $\ln k$ vs. $1/T$ then he argues that the compensation effect is real and has a physical significance. In this study the appearance of a compensation effect in the kinetic data obtained from rising temperature decompositions of a series of carbonates is discussed.

EXPERIMENTAL

Materials

All the carbonates used were standard laboratory reagent (SLR) grade, except aluminium carbonate which was only available in technical form.

Equipment

The instrument used was the Stanton Redcroft TG750 microbalance. This is a very low furnace mass instrument allowing heating rates of 1—100°C min^{-1}, with a cut-out switch at 1000°C, measuring the temperature with an accuracy of ±0.1°C.

The balance is an electronic microbalance with a switched range of sensitivities from 1 to 250 mg full-scale deflection (FSD). The sensitivity used in these experiments was 10 mg FSD, an average weight of 8.5 mg being used. It is stated [10] that because of the design of the furnace there is no noticeable "buoyancy effect" on the sample over the entire temperature range. This was found not to be totally true, but the slight decrease in weight was insignificant within the accuracy of the experiments.

The thermobalance was run at a constant heating rate of 1.2°C min^{-1} using an atmosphere of nitrogen with a flow rate into the furnace of 25 cm^3 min^{-1}.

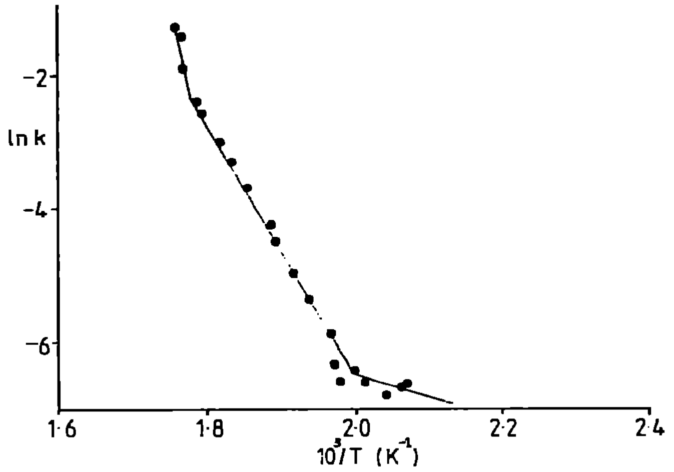

Fig. 1. Graph of ln k vs. $1/T$ for $CuCO_3$.

RESULTS

The Arrhenius plots of ln k vs. $1/T$ for all six carbonates are shown in Figs. 1—6. Before the kinetic parameters were calculated the contribution due to the loss of water was eliminated from the data. This was achieved by extrapolating both sections of the decomposition curve of weight loss against temperature and taking the mid-point as $\alpha = 0$ for the main carbonate reaction. The rate constant, k, was obtained from the following equation

$$\frac{d\alpha}{dT} \cdot \beta = k f(\alpha) \tag{3}$$

where $d\alpha/dT$ is the rate of change of the fraction decomposed, α, with temperature, T, β is the heating rate; and $f(\alpha) = (1 - \alpha)$. $d\alpha/dT$ was obtained by a graphical method.

Compensation parameters obtained from the ln k vs. $1/T$ plots were then

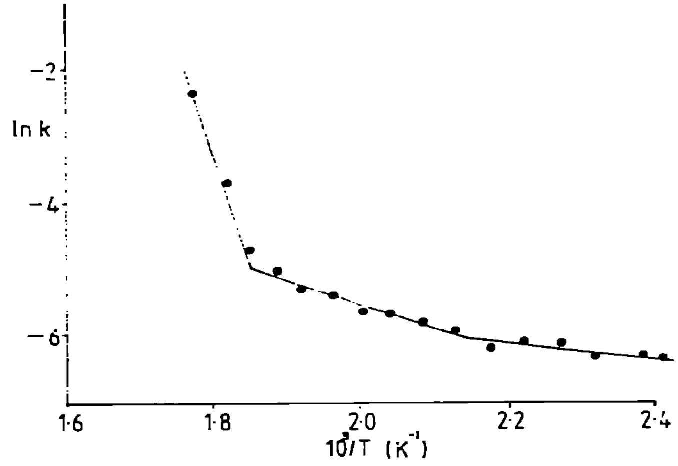

Fig. 2. Graph of ln k vs. $1/T$ for $AlCO_3$.

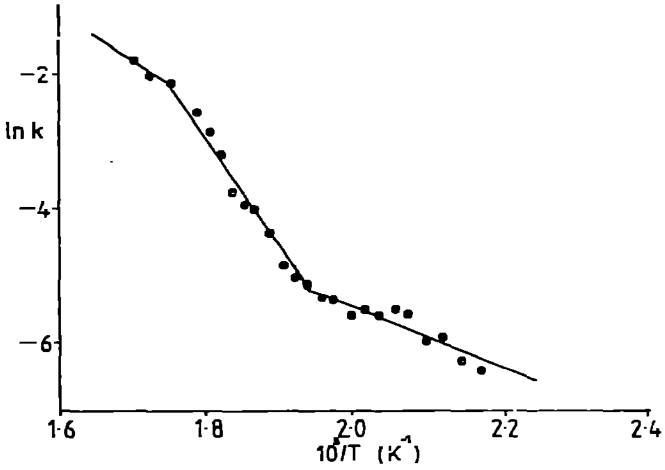

Fig. 3. Graph of ln *k* vs. 1/*T* for $CrCO_3$.

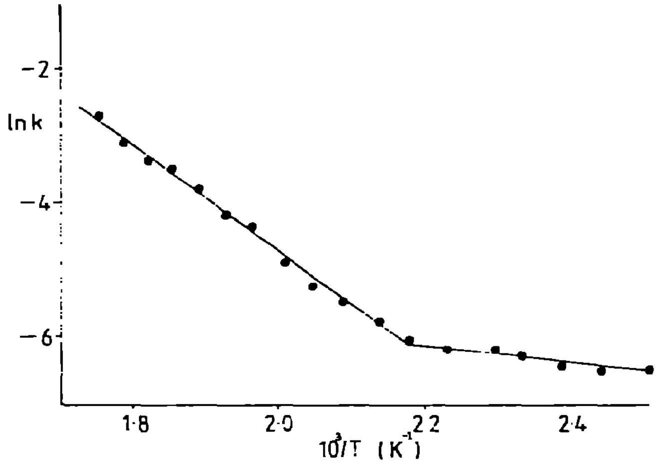

Fig. 4. Graph of ln *k* vs. 1/*T* for $CoCO_3$.

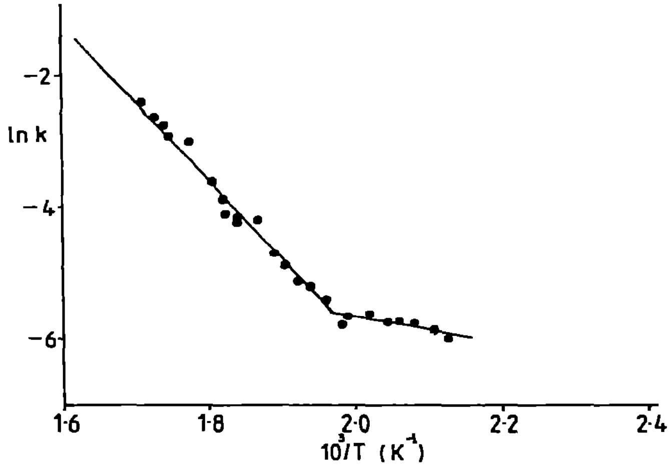

Fig. 5. Graph of ln *k* vs. 1/*T* for $NiCO_3$.

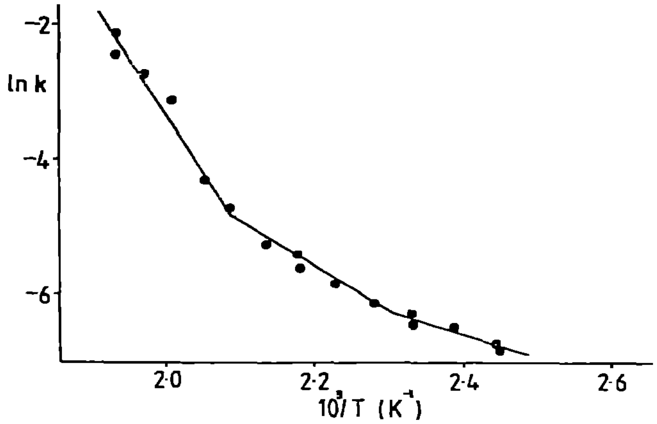

Fig. 6. Graph of ln *k* vs. 1/*T* for $ZnCO_3$.

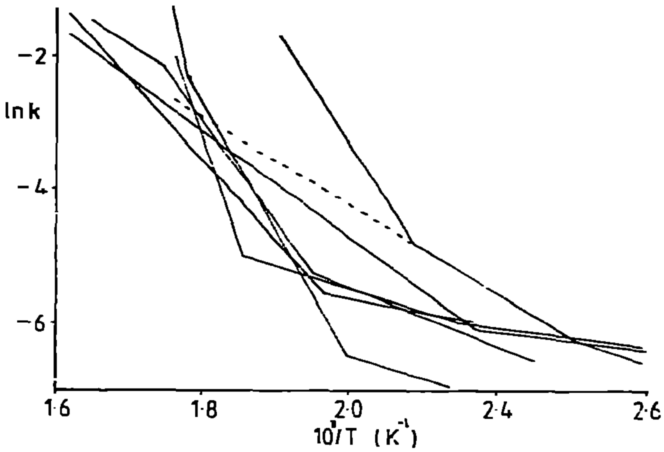

Fig. 7. Graph of ln *k* vs. 1/*T* to test obeyance to the compensation effect.

TABLE 1

Kinetic parameters obtained from rising temperature experiments

Compound	Temp. range (K)	*E* (kJ mole^{-1})	*A* (s^{-1})	ln *A*
Copper carbonate	470—500	27.114	1.04	0.040
	510—560	165.640	1.673×10^{14}	32.751
	564—568	420.670	1.153×10^{40}	92.246
Aluminium carbonate	410—460	9.661	2.735×10^{-2}	—3.599
	460—530	31.171	6.652	1.895
	540—560	268.233	3.655×10^{23}	54.256
Chromium carbonate	460—510	37.876	1.949×10^{3}	7.575
	515—580	136.241	2.189×10^{11}	26.112
	580—590	61.483	5.583×10^{4}	10.930
Cobalt carbonate	400—450	12.060	5.157×10^{-2}	—2.965
	460—580	66.864	7.104×10^{4}	11.171
Nickel carbonate	470—505	13.240	7.739×10^{-2}	—2.559
	510—585	102.731	9.271×10^{7}	18.345
Zinc carbonate	400—430	29.447	6.172	1.820
	430—470	55.528	7.406×10^{3}	8.910
	480—520	141.345	1.267×10^{13}	30.170

plotted according to eqn. (2) and are shown in Fig. 7 and Table 1. The resultant plot shows a linear relationship between ln A and E and thus obeyance of eqn. (2). The gradient of the line obtained by a method of least squares was 0.2196 $\mathrm{kJ^{-1}}$ mole, giving an isokinetic temperature of 548 K. The intercept was found to be —4.1629, and hence k at T_s was calculated as $1.556 \times 10^{-2}\ \mathrm{s^{-1}}$.

DISCUSSION

The values of k covered a larger range for each reaction than those obtained in previous non-isothermal studies of carbonate systems using nitrogen or carbon dioxide atmosphere. Ln k varied with a typical range of —2 to —6.5 and a maximum of —1.3 to —6.9 for copper carbonate. The largest literature range found was 0 to —4 for a cadmium carbonate/CO_2 system under isothermal conditions [12].

The presence of two or more linear regions on the ln k vs. $1/T$ plots for rising temperature experiments has been reported extensively in the literature. Zmijkewski and Pysiak [13], in a paper on the compensation effect, shows several plots exhibiting multiple Arrhenius values for carbonate/CO_2 systems. However, care must be taken in interpolating ln k vs. $1/T$ plots as a small spread of results can lead to erroneous extra A and E values.

Figure 8 shows all the ln k vs. $1/T$ data on one plot. From this it can be seen that sections of the lines do intersect at approximately 548 K. However, since all three sections of each individual plot do not intersect for each single carbonate then, using Gorbachev's [9] criteria, there is no genuine compensation effect between different sections of a carbonate decomposition.

The sudden inflections in the ln k vs. $1/T$ plots are indicative of a sudden

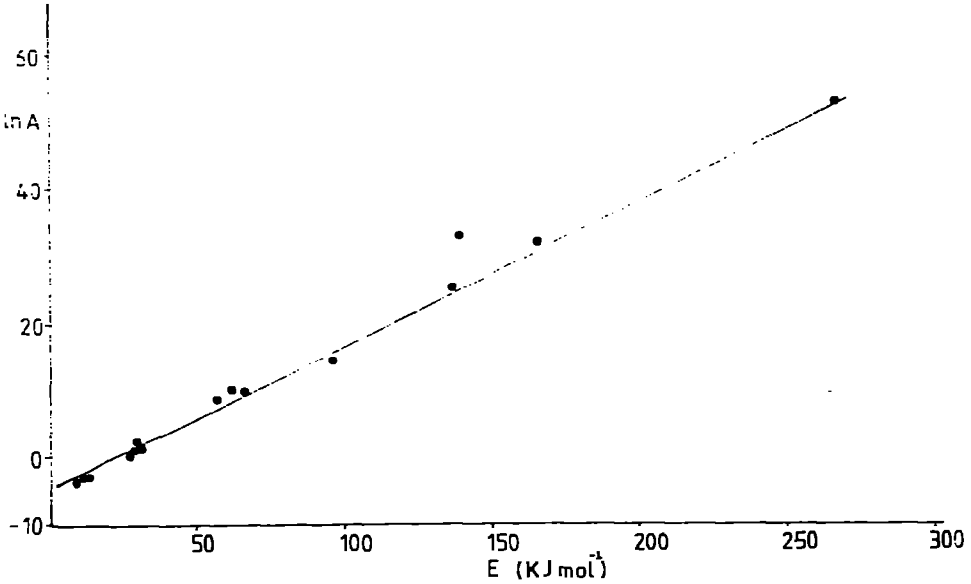

Fig. 8. Compensation plot of ln A vs. E for a series of carbonate decompositions.

change [14] in the energy site distribution. This may be due to a sintering mechanism or other physical process which with a decomposition reaction would not lead to a change in reaction mechanism. Thus, since the kinetic expression is the same in each case [$f(\alpha) = 1 - \alpha$] and the decomposition is unlikely to follow a different chemical process at different points, the criterion appears doubtful.

As indicated by Garn [6], the compensation plot may be due to the temperature range of the reactions considered. Of the carbonates tested here, aluminium carbonate is unusual in that it is not a true carbonate, having the formula $(Al_2(OH)_5)_2CO_3H_2O$. Thus the decomposition mechanism is probably different although the geometrical progression of the interface may be the same. Thus, although the criterion for a genuine compensation effect has been satisfied, it is unlikely that aluminium carbonate is part of this. We thus suggest that further studies are made using reactions which are known to follow different mechanistic pathways.

The compensation effect may thus be a genuine physical effect or it may be due to the experimental system selected [7,8], experimental error [15], or a particular function of the reactions studied [16]. Of the explanations given for a genuine effect [3] a model involving a distribution of active sites on the reacting solid appears to be a more general explanation than others. Consideration of the distribution of the activation energy on different sites was initially due to Constable [17] but has since been developed by others [18].

Let E_1 and E_2 be the lower and upper limits of the energy of activation E on an interface; the number of reaction centres having an energy of activation lying between E and $E + \delta E$ is given by

$$\delta n = F(E)\,\delta E \qquad (4)$$

Hence the total number of reaction centres is

$$n = \int_{E_1}^{E_2} F(E)\,\delta E \qquad (5)$$

The rate, r, of the reaction is given by

$$r = k \sum_i n_i \exp(-E_i/RT) \qquad (6)$$

where n_i = number of sites of energy E_i.

Assuming a continuous Gaussian distribution of energy sites, eqn. (2) can be integrated to give

$$n_i = a \exp(E_i/b) \qquad (7)$$

where a and b are constants, and so

$$r = \frac{ka}{g}(\exp - gE_1) - \exp(-gE_2) \qquad (8)$$

where $g = (1/b) - (1/RT)$. Cremer found that the second term of eqn. (8)

could be ignored and so, substituting back in for g gives

$$r = \frac{ka}{g} \exp(E_1/b) \exp(-E_1/RT) \tag{9}$$

This shows that the reaction must be proceeding almost exclusively on the most active sites. Since the activation energy has appeared in an exponential term in the pre-exponential factor with a positive sign, then for a related reaction an increase in E will cause an increase in A.

This explanation assumes, however, that the distribution of energy sites remains constant throughout the reaction. This may not be the case, especially if sintering and other physical processes occur during the reaction which may lead to a compensation effect for a multiple stage Arrhenius plot.

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