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The Kinetic Compensation Effect In The Decomposition Of Calcium Carbonate

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Abstract

Some specific factors that cause the kinetic compensation effect during the decomposition $CaCO_3$ are identified. The role of the CO_2 equilibrium pressure is examined in relation to the kinetic compensation effect. This investigation also shows why non – iso thermal experiments have some time necessarily to yield value of activation energy different from the value obtained from isothermal experiments.

Introduction

The technological application of calcium carbonate are diverse and require the preparation of materials with different physical and chemical properties .It is know that the experimentally determined value of activation energy depends on several factors associated with experimental technique and sample characteristics, especially when kinetic experiments are carried out under rising temperature conditions (1). It has been noted that the variation between log k and 1/T to determine values of E and A, This is called the kinetic compensation effect. this effect has been the subject of several investigations (2-8). The aim of the present work is to re-examine the origins of the kinetic compensation effect critically, identify some specific factors and then show why non-isothermal experiments must sometimes necessarily to yield a value of activation energy significantly different from the value obtained from isothermal experiments.

Table(1) Weight rate of equilibrm mixture at different temperatures . wo % $CaCO_3$=1

T (K°)	Equilibrium mixture	
	We % $CaCO_3$	W% CO_2
973	0.966	0.034
998	0.933	0.067
1023	0.900	0.100
1048	0.850	0.150

Table(2) The value of K and € at different temperatures

T (K°)	€ X 10^{-2}	K x 10^{-3}	Log K	(1/T) x 10^{-3}(1/K°)
973	3.519	4.667	-2.330	1.027
998	7.181	13.607	-1.866	1.002
1023	11.111	26.189	-1.581	0.977
1048	17.647	52.419	-1.280	0.954

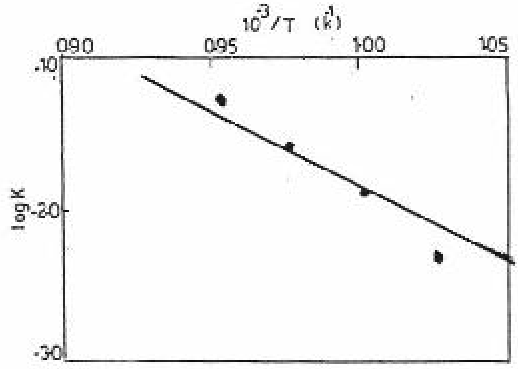

Fig.(1) The Arrhenins plot

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rate constant K by equation [2] and listed the values of Є and K in table (2). The Arrhenius plot of log K Against 1/T as in fig. (1) yields a straight line, the slope of which is –E/R and the intercept on the Y-axis is log A. However the value of E in this investigation amach smaller value equal to 191 KJ/mole as compard to the value 397 KJ/mole was obtaind by the analysis of isothermal data of the method of Rao (12). Then by intercept in fig. (1) the value of A is 0.47 X^{-4} min^{-1}.

The Arrhenius parameters A and E assumed constant. During actual reaction, such as the decomposition of $CaCO_3$. The particle size as well as the thermodynamic driving force is described in terms of the concentration of CO_2 in the ambient atmosphere and the equilibrium concentration of CO_2 at gas/solid interface where thermodynamic equilibrium for decomposition prevails, the exact fore of the equation being dependent on the reaction mechanism . The values of E equal to 191.KJ/mole and E by Rao (12) equal to 397 KJ/mole show why one may get a different value of activation energy from the analysis of non – is othermal data. The data for table (2) assume that A is constant , if there is aching in the size distribution of the particles and therefore, the average size during the course of heating , then this condition will be no longer hold . This of course will introduce some scatter of the data in the compensation plot .

Conclusions

It is shown that the kinetic compensation effect can be explained if one taking proper account of the various factors which influence the rate constant of a decomposition reaction one must consider amongst other factors the dynamic driving force, it is Also found that if one takes into account the variation of the equilibrum CO_2 pressure during the heating of $CaCO_3$, then one can show that the apparent value of the activation energy for decomposition would be different from the true value determined from isothermal experiments . Also the results of A= 0.47x-4 min^{-1} and E= 191 KJ/mole which were obtained in this investigation by differential thermal analysis (DTA) then by Arrhenius equation are very consistent and in good agreement with those obtained by Elder and Reddy.

Kinetic parameters of Arrhenins Equation

The Arrhenius expression for variation of the rate constant with temperature is written as (9):

$$K=A.\exp(-E/RT). \ldots[1]$$

Where K is the rate constant and A and E are Arrhenius parameters. We can also write K as (10)

$$K=\sqrt{\frac{\epsilon^3 P}{2}} \ldots\ldots\ldots\ldots[2]$$

The parameter P represents the constant atmospheric pressures and ϵ is the equilibrium constant which was obtained from the relation

$$\epsilon=\frac{W_o\%}{W_e\%}-1 \ldots\ldots\ldots\ldots\ldots[3]$$

Where W_o is the weight rate of the original mixture and W_e is the weight rate of the equilibrum mixture. For the theory outlined above to be valid, the following conditions must apply (2):

-The rate of reaction must be small at the lowest temperature of the DTA trace;

-The reaction must go to completion before the highest temperature of the DTA trace;

-The reaction must be accompanied by a measurable heat effect;

-The temperature in the holders must be uniform;

-Heat must be transferred to the holders by conduction only;

-The heat tranfer coefficient, K, must be the same for both holders;

-The heat capacity, C, of the material in the holders must be the same;

-K, C and E must be constant throughout the temperature rang of the DTA peak;

-The activation energy of reaction must be independent of temperature.

Results and Discussion

From differential thermal analysis DTA curves for $CaCo_3$ (11) used weight rate in table (1) to calculate the equilibrium constant ϵ by equation [3] for any temperature and used these results to calculate the

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تأثير معادلة الحركة في تفكك كاربونات الكالسيوم

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الخلاصة

تم تحديد بعض العوامل التي تسبب تأثير معادلة الحركة خلال التحليل الحراري لكاربونات الكالسيوم .وتم دراسة تأثيرضغط الاتزان لثاني اوكسيد الكاربون بعلاقة تأثير معادلة الحركة .وتم بيان لماذا تعطى التجارب التي تتم بدرجة حرارة غير ثابتة طاقة تفاعل تختلف عن تلك التي يتم الحصول عليها من التجارب التي تتم بدرجة حرارة ثابتة .