

## Assessment of the apparent activation energies for gas/solid reactions — carbonate decomposition

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**Abstract:** The guidelines for assessing the apparent activation energies of gas/solid reactions have been proposed based on the experimental results from literatures. In CO<sub>2</sub> free inlet gas flow, CaCO<sub>3</sub> decomposition between 950 and 1250 K with thin sample layer could be controlled by the interfacial chemical reaction with apparent activation energy  $E = (215 \pm 10)$  kJ/mol and  $E = (200 \pm 10)$  kJ/mol at  $T = 813$  to 1020 K, respectively. With relatively thick sample layer between 793 and 1273 K, the CaCO<sub>3</sub> decomposition could be controlled by one or more steps involving self-cooling, nucleation, intrinsic diffusion and heat transfer of gases, and  $E$  could vary between 147 and 190 kJ/mol. In CO<sub>2</sub> containing inlet gas flow (5%-100% of CO<sub>2</sub>),  $E$  was determined to be varied from 949 to 2897 kJ/mol. For SrCO<sub>3</sub> and BaCO<sub>3</sub> decompositions controlled by the interfacial chemical reaction,  $E$  was  $(213 \pm 15)$  kJ/mol (1000-1350 K) and  $(305 \pm 15)$  kJ/mol (1260-1400 K), respectively.

**Key words:** assessment; activation energy; decomposition; carbonate

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To apply the reported apparent activation energy data to the kinetic evaluations and process optimizations, the assessments of these data are quite necessary and favorable. As a part of the work in developing the intellectualized database management system on kinetics of metallurgy (IDMSKM) involving kinetic prediction of gas/solid reactions (KinPreGSR) [1-3], the assessment of apparent activation energies were carried out for some gas/solid reactions. In this paper, the guidelines of the assessment are introduced and the assessment for some decomposition reactions of carbonates is described.

### 1 Guidelines of the assessment of gas/solid reactions

A gas/solid reaction often involves some of the following steps:

(1) The external mass transfer of the gaseous reactant or product to or from the surface of the solid particle;

(2) The internal diffusion of the gaseous reactant or product through the pores in the solid matrix;

(3) The interfacial chemical reaction at the interface between the solid product and reactant;

(4) Nucleation;

(5) The heat transfer.

The complexity of the reaction kinetics may indicate the necessity to correlate the apparent activation energy and other kinetic parameters with the experimental conditions mentioned above. The variation of the experimental conditions may be the most important reason resulting in the diverse of the kinetic parameters. The other reason could be the difficulties in the dynamic measurements at high temperature. The preceding discussion suggests that this assessment must be based on an extensive data accumulation from kinetic literature, and the work must proceed under reasonable scientific guidelines. According to the authors' practice, the following guidelines should be obeyed.

(1) The kinetic data should be published in the worldwide acknowledged scientific journals or well-known Chinese journals.

(2) If the experimental results (and the mechanism analysis) are provided without the necessary experimental conditions, the publication should not become the data source.

(3) The kinetic data should be measured using ac-

curate techniques with better reproducibility.

(4) Grouping the apparent activation energy data should be based on the reaction mechanism (rate controlling step(s)). Since the influences of the experimental conditions, the corresponding experimental parameters should also be grouped accordingly.

## 2 Assessments of the apparent activation energy

The present authors took the decomposition of alkaline earth carbonates as the first attempt. In the reaction, the carbonates decompose to produce the alkaline oxides and carbon dioxide.

### 2.1 The decomposition of CaCO<sub>3</sub>

Based on guidelines (1)-(3), thirteen references [4-16] have been selected from more than thirty papers on the CaCO<sub>3</sub> decomposition kinetics. The apparent activation energy data with the corresponding mechanism descriptions (the rate controlling step(s)) and key experimental parameters are listed in **tables 1** and **2**. According to the rate controlling step(s), the data have been divided into three groups, groups I to III. Group I involves the data at lines 1-8. The common features in those experiments were as follows: the relatively small (1-100 mg) sample mass, resulting in thin sample layer; CO<sub>2</sub> free in inlet gas flow, interfacial chemical reaction controlling (CR). Group II consists of the data at lines 9-13 in tables 1 and 2. In the relevant experiments, all sample mass ( $\geq 290$  mg) and CO<sub>2</sub> free in inlet gas flow were used. The overall rates in those processes may be controlled by the steps: the self-cooling, internal diffusion of gaseous species, heat transfer (HT) from the surface of solid particles to the chemical reaction interface, the nucleation as well as the interfacial chemical reaction jointly. Group III comprises some data obtained in the decomposition experiments carried out in CO<sub>2</sub> containing inlet gas flow (see lines 14 to 18). For the sake of brevity, the rate-controlling steps and experimental conditions are denoted using a couple of alphabets in the tables of this paper, which are listed in **table 3**. Also the adjective 'apparent' will be removed from now on in the text.

In group I, the activation energy values are ranged from 190 to 230 kJ/mol when the reaction is controlled by the interfacial chemical reaction step. At lines 1-3, the experimental temperature is somewhat lower than that at lines 4-8. Therefore, the activation energy values in Group I are classified into two sub-groups to improve the precision. In the temperature range of 950-1250 K, the values vary within (215 $\pm$ 10) kJ/mol, while between 813 and 1020 K, it takes the

values of (200 $\pm$ 10) kJ/mol. The temperature effect can be attributed to the slightly higher CO<sub>2</sub> partial pressure caused by high decomposition temperature. This will increase the activation energy significantly. The consideration is further confirmed by the data given in Group III. The partial overlap in activation energy values and experimental conditions for the two sub-groups is considered to be reasonable.

**Table 1** The samples for CaCO<sub>3</sub> decomposition

No.	<i>m</i> / mg	Geometry of particle(s)
1	1-12	Pellets, <i>D</i> =20-60 $\mu$ m, <i>d</i> =1.6 $\mu$ m
2	4	Powder, <i>d</i> = 20-44 $\mu$ m
3	40-65	Single crystal, <i>a</i> = 0.5-1 mm
4	228	Single crystal, <i>a</i> = 1.4-1.8 mm
5	10	Powder
6	100	Powder
7	12	Powder
8	12	Powder
9	500	Powder
10	429 & 315	Pellet, <i>D</i> = 4.5 or 3.8 mm
11	455	Pellet
12	290	Powder
13	1000	Pellet or powder
14	4	Powder, <i>d</i> = 20-44 $\mu$ m
15	4	Powder, <i>d</i> = 20-44 $\mu$ m
16	2-32	Powder
17	1-16	Powder
18	329	Pellet, <i>D</i> = 4.0 mm

Greater apparent activation energy values, 564-3824 kJ/mol, in group III show that the CO<sub>2</sub> content significantly affects the activation energy. With the extracted activation energy values from the decomposition experiments (lines 14-16), it can be concluded that the activation energy for the calcium carbonate decompositions in CO<sub>2</sub> containing gas (>5%) ranges from 950 to 3000 kJ/mol. More experiments are required to quantify how the apparent activation energy varies with the CO<sub>2</sub> content in the inlet gas. The activation energy data listed in lines 17 and 18 fall far beyond this range. The NTGA technique with just a single rising temperature run and unclear description of experimental conditions may rise doubt on the precision and accuracy. For this reason, those results have not been taken into consideration.

The mechanisms listed in lines 14-16 were regarded by the authors [5, 16] as to be heat transfer step controlling. The experimental basis was that the rates of the decomposition of CaCO<sub>3</sub> in different gases were proportional to the thermal conductivity of the gases. While Smith *et al.* [17] suggested that they were determined by mass transfer of the evolved CO<sub>2</sub>. It seems that further studies are needed to identify the

mechanism.

**Table 2** The kinetic data for CaCO<sub>3</sub> decomposition

No.	Experimental Technology	T / K	Atmosphere	E / (kJ/mol)	Controlling step(s)	Reference
1	ITGA	880-981	O <sub>2</sub>	190-208	CR	4
2	ITGA	813-1018	Ar	201	CR	5
3	ITGA	934-1013	Vaccum	205	CR	6
4	ITGA	910-1110	Vacuum	209±12.5	CR	7
5	NTGA 10 K/min	1063 -1250	N <sub>2</sub>	210-212	CR	8
6	NTGA	—	Air	216	CR	9
7	NTGA 10-20 K/min	950-1150	Ar	220-223	CR	10
8	DTA	950-1150	Ar	213-228	CR	10
9	ITGA	993-1053	Vaccum	147-176	CR&GID&NF	11
10	ITGA	987-1090	N <sub>2</sub>	173	HF	12
11	ITGA	1023-1173	Air	170	GID	13
12	NTGA	793-1273	Air	163	—	14
13	NTGA	873-1173	—	180-192	—	15
14	ITGA	813-1053	5%CO <sub>2</sub> + 95% Ar	949	HT	5
15	ITGA	813-1179	CO <sub>2</sub>	2000	HT	5
16	ITGA	1173-1223	CO <sub>2</sub>	2216-2897	HT	16
17	NTGA	—	CO <sub>2</sub>	564-3824	HT	16
18	NTGA 0.58 K/min	1000-1040	CO <sub>2</sub> 10 mm	167	HF	12

**Table 3** List of symbols

Symbol	Meaning
CR	Interfacial chemical reaction
GID	Gaseous internal diffusion
SID	Solid ion diffusion
NF	Nuclei formation
HF	Heat flow in solid
TT	Thermal transport
ITGA	Isothermal thermogravimetric analysis
NTGA	Non-isothermal thermogravimetric analysis
DTA	Differential thermal analysis
—	The data have not been found in the literature
E	Apparent activation energy
X	Fractional conversion

The activation energy values in group II (at lines 9-13) of tables 1 and 2 are between 147-190 kJ/mol lower than those in group I. The relatively large activation energy variation could be due to the thicker and varying layer of the solid samples in group II, 290-1000 mg, which would rise resistances for the diffusion, heat transfer of the gaseous species (including self-cooling effect), and perhaps of nucleation. As separating the effects of the above steps is sometimes difficult, we may simply regard that the overall CaCO<sub>3</sub> decomposition with the thick sample layer in CO<sub>2</sub> free inlet flow is controlled by mixed steps mentioned above. And the corresponding activation energy could

be assessed between 145 and 190 kJ/mol with the mass of 290-1000 mg for the process performed in standard commercial general thermogravimetric analysis units.

Linghai *et al.* [18] compared the decomposition kinetics of nano-particles of CaCO<sub>3</sub> (40 nm in diameter) with the powder containing particles of 5-20 μm in diameter in N<sub>2</sub> inlet gas flow using non-isothermal DTA technique. They found that the activation energy for the former was 120.5 kJ/mol, much lower than that of the latter, 207.8 kJ/mol. The difference could be due to the higher surface free energy, the stress and distortion on the nano-particles. This indicates that the

above assessed activation energies for groups I, II and III may not be used for the nano-particle calcite.

### 3.2 The decomposition of SrCO<sub>3</sub> and BaCO<sub>3</sub>

The kinetic data of SrCO<sub>3</sub> and BaCO<sub>3</sub> decompositions reported in the previous investigations are respectively listed in tables 4 and 5 [19, 22]. Compared with the data for CaCO<sub>3</sub>, there are much less publications that make our assessment difficult. In addition, it

has been reported that two phase transformations may occur during the decomposition of BaCO<sub>3</sub> [21], the transformation of orthorhombic to hexagonal at 1079 K, hexagonal to cubic at 1273 K. The eutectic reaction may proceed at high temperature. According to the phase diagram [23] for BaCO<sub>3</sub> decomposition, the eutectic point is at 1333 K and 0.661 kPa. So in the BaCO<sub>3</sub> decomposition studies, the phase transformations and eutectic reaction must be taken into account.

**Table 4 The kinetic data for SrCO<sub>3</sub> decomposition**

No	Sample	Experimental Technology	T / K	Atmosphere	E / (kJ/mol)	Controlling step(s)	Reference
1	10 mg, powder of 5 μm	NTGA, 10-20 K/min	1000-1350	Ar	203-218	CR	19
2	13.2 mg, pressed flakes with thickness less than 0.5 mm	NTGA	1000-1350	Ar	223	CR	19
3	200-1000 mg, powder	ITGA	1173-1273	—	288	SID	20

**Table 5 The kinetic data for BaCO<sub>3</sub> decomposition**

No	Sample	Experimental Technology	T / K	Atmosphere	E / (kJ/mol)	Controlling step(s)	Reference
1	10 mg, powder	NTGA, 7-15 K/min	1260-1400	Ar	305	X<0.15, CR	21
2	200-1000 mg, powder	ITGA	1323-1443	—	230	NF	20
3	Single crystal with 1 mm in thickness	NTGA	1162-1220	Vacuum 10 <sup>-2</sup> Pa	225.9	SID or desorption of CO <sub>2</sub>	22

From tables 4 and 5, the following viewpoints could be drawn.

(1) The activation energy data in lines 1 and 2 of table 4 are close. In the relevant experiments, the argon flow and internal diffusion rates were high, and the consequent interfacial chemical reaction was rate controlling. For the better reproducibility, the activation energy could be recommended to be (213±15) kJ/mol under conditions of interfacial chemical reaction controlling between 1000 and 1350 K.

(2) Corresponding to line 3 of table 4, a higher activation energy of 288 kJ/mol was attained, which may suggest a solid-diffusion step controlling mechanism. However, as the large sample mass adopted, the situation could be complex. To quantify resistances of transport steps on the rate of the decomposition, more experimental work is required.

(3) The experimental data in line 1 of table 5 were obtained with shallow bed powder and a high argon flow rate. Thus the resistances of the mass transfer of CO<sub>2</sub>, the heat transfer from the gas stream to the reaction interface were neglected. The decomposition were carried out at 1260-1400 K, the influences of the phase transformations could also be avoided. The experimental data at the earlier stages ( $X < 0.15$ ), when the amount of liquid due to the eutectic reaction was

very little, were used to extract the activation energies to ensure the reaction was controlled by the interfacial chemical reaction. The non-isothermal experiments were formed with very strictly controlled parameter. So, the reported activation energy for the decomposition controlled by interfacial chemical reaction step at 1260-1400 K could be confirmed to be (305±15) kJ/mol. Some relevant ITGA measurements at similar condition are expected to complete the assessment.

(4) The sample mass used for the BaCO<sub>3</sub> decomposition experiment listed in line 2 of table 5, 200-1000 mg, was higher and varied considerably. The measurement was carried out at 1323-1443 K. During the course, eutectic reaction would happen influencing on the mechanism. However, the activation energy was extracted and the mechanism was evaluated by fitting the experimental data from the initial to the later stages using different kinetic equations [20]. From the viewpoint of the present authors, more experimental data are desirable.

(5) The decomposition described at line 3 in table 4 was performed below the temperatures of the phase transformations and the eutectic reaction. According to reference [22], the decomposition of BaCO<sub>3</sub> with a thick sample in vacuum or CO<sub>2</sub> free gas flow may be controlled by solid phase diffusion or a surface step prior to desorption. This conclusion should be testified

by further isothermal TGA measurements.

It should be pointed out that the above conclusions regarding the SrCO<sub>3</sub> and BaCO<sub>3</sub> decompositions are tentative, for the less relevant data in literatures. More experiments are required to provide more accurate assessment on the activation energies of the decompositions.

### 3 Conclusions

(1) The decomposition of small amount of CaCO<sub>3</sub> powder in CO<sub>2</sub> free inlet gas flow from 813 to 1250 K could be controlled by interfacial chemical reaction and the activation energy could be (215±10) kJ/mol between 950 and 1250 K, and (200±10) kJ/mol from 813 to 1020 K. The decomposition with thicker sample layer in CO<sub>2</sub> free atmosphere ranging from 793 to 1273 K might be controlled by one or the mixed steps of the interfacial chemical reaction, self-cooling, nucleation, internal diffusion and heat transfer of gaseous species jointly. The apparent activation energy could vary from 147 to 190 kJ/mol. The activation energy of the decomposition in CO<sub>2</sub> containing gas (5%-100%) could be very high, 564-3824 kJ/mol.

(2) The activation energy of SrCO<sub>3</sub> decomposition controlled by the interfacial chemical reaction between 1000-1350 K could be in a range of 203-233 kJ/mol. For the decomposition controlled by diffusion in solid reactants between 1173-1273 K, it could be as much as (288±15) kJ/mol.

(3) Between 1260-1400 K, the *E* value of BaCO<sub>3</sub> decomposition under interfacial chemical reaction controlling mechanism could be as much as (305±15) kJ/mol. Under solid-state diffusion or desorption controlling, the value could be (226±15) kJ/mol.

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