



# **Kinetics of Solid-Gas Reactions and Their Application to Carbonate Looping Systems**

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**Abstract:** Reaction kinetics is an important field of study in chemical engineering to translate laboratory-scale studies to large-scale reactor conditions. The procedures used to determine kinetic parameters (activation energy, pre-exponential factor and the reaction model) include model-fitting, model-free and generalized methods, which have been extensively used in published literature to model solid-gas reactions. A comprehensive review of kinetic analysis methods will be presented using the example of carbonate looping, an important process applied to thermochemical energy storage and carbon capture technologies. The kinetic parameters obtained by different methods for both the calcination and carbonation reactions are compared. The experimental conditions, material properties and the kinetic method are found to strongly influence the kinetic parameters and recommendations are provided for the analysis of both reactions. Of the methods, isoconversional techniques are encouraged to arrive at non-mechanistic parameters for calcination, while for carbonation, material characterization is recommended before choosing a specific kinetic analysis method.

**Keywords:** kinetics; solid-gas reactions; carbonate looping; calcium looping; thermochemical energy storage; carbon capture and storage

# 1. Introduction

Reaction kinetics is essential to study a wide variety of processes. The main objectives are to obtain information about the reaction mechanism and determine kinetic parameters (such as activation energy and pre-exponential factor). Identifying the reaction mechanism can prove useful in modifying the course of the reaction or predicting the behavior of similar reactions, while calculating kinetic parameters may allow reaction rates to be obtained at different experimental conditions [1]. This is of particular value during the scale-up of thermal processes from laboratory to reactor scale [2].

Common methods of kinetic analysis (such as model-fitting and model-free methods) are applicable to numerous chemical processes, including the thermal decomposition of solids, thermal degradation of polymers and crystallization of glasses [3]. However, throughout the practical application of kinetic analysis to heterogeneous reactions (such as solid-gas reactions), concerns have been raised about the suitability of some kinetic methods, disparity in calculated kinetic parameters and the quality of experimental data [1].

This review will comprehensively evaluate the methods used in solid-gas reactions, including model-fitting, model-free and generalized methods, and discuss the advantages and disadvantages of each of them. At the end of the review of solid-gas kinetic methods, example studies for the carbonate looping cycle will be discussed. This review analyses the disparity in results and provides recommendations for the application of kinetic methods.

#### 2. Carbonate Looping Technologies

Carbonate looping technologies are based on the equilibrium reaction of a metal oxide (MeO) with its related metal carbonate (MeCO<sub>3</sub>) and CO<sub>2</sub>. This equilibrium is expressed by the following equation:

$$MeCO_3 (s) \rightleftharpoons MeO (s) + CO_2 (g)$$
 (1)

where pairs of MeCO<sub>3</sub>/MeO are commonly CaCO<sub>3</sub>/CaO [4–6], MgCO<sub>3</sub>/MgO [7–9], SrCO<sub>3</sub>/SrO [4,10], BaCO<sub>3</sub>/BaO [9], CaMg(CO<sub>3</sub>)<sub>2</sub>/CaMgO<sub>2</sub> [11] and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>/La<sub>2</sub>O<sub>3</sub> [12]. In particular, the CaCO<sub>3</sub>/CaO system, referred to as calcium looping (CaL), consists of the following reversible reaction [5]:

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$$
 (2)

where the reaction enthalpy at standard conditions is -178.4 kJ mol<sup>-1</sup>. Generally, CaL systems show high adaptability in fluidized bed applications and possesses suitable adsorption and desorption kinetics [13]. For these reasons, CaL has been extensively studied for carbon capture and storage technologies (CCS) [4,14–16] and thermochemical energy storage (TCES) [4,5,17,18].

In the CaL-CCS system, CaO is used as a regenerable sorbent subjected to a flue gas stream (pre-combustion/post-combustion) from a coal combustion power plant [19,20]. Other industrial plants, such as cement manufacture, iron/steel making or natural gas treatment could also be coupled with CaL-CCS [19]. Many laboratory-scale studies include the use of inert supports, particularly calcium aluminates, which is widely documented to decrease sintering with thermal cycling [21,22]. An alternative to CCS is the utilization of CO<sub>2</sub>, referred to as CCS+U, which includes using the captured and stored CO<sub>2</sub> as a technological fluid, for fuel production or for energy generation and storage [19]. Several CaL demonstration projects have also been tested in recent years [18,23–25] and some have been coupled with solar thermal energy [26].

Reaction kinetics is a key consideration in the design of reactors for CaL systems, for which several system configurations exist. A typical configuration consists of two interconnected circulating fluidized beds: a calciner and carbonator [27–30]. In the case of solar-driven CaL, the calciner and carbonator reactors are generally separated and several solar-driven reactors have been proposed [26,31,32]. Carbonation typically uses a fluidized bed reactor and kinetic reaction models suitable for the conditions of interest in CaL have been specifically studied [28,33–35], as well as single particle models, which consider kinetics, thermal transport and mass transfer [36,37]. Models such as these have helped in the design of carbonator reactors [27,29,30,38–40].

As well as CCS+U, the CaL systems can also be used as TCES integrated with concentrating solar thermal (CST) power plants to increase their efficiency and reduce their costs [4]. While calcination proceeds in a similar way to CCS, in TCES the released heat from the carbonation reaction (Equation (2)) is used to drive a power cycle [41]. Various TCES systems have been explored using equilibrium reactions from hydroxide looping, metal oxides based on reduction-oxidation reactions and chemical-looping combustion [4,42]. Recently, CaL-TCES has been shown to be promising in terms of cost and compatibility with efficient power cycles [4]. It has large energy storage densities [4,5,17,18] and has been modelled for the MW-scale [17].

# 3. Kinetics of Solid-Gas Reactions

Solid-gas reactions involve the transformation of one solid into a gas and another solid, and vice versa [43]. Figure 1 shows a schematic of a solid-gas reaction.



**Figure 1.** Schematic of a solid-gas reaction, i.e.,  $A(s) \rightarrow B(s) + C(g)$ . *AB* is the reactant-product interface.

The way in which these processes occur (fast, slow, linear, and non-linear) is expressed by the variation of conversion with time, X(t). The nature of the solid-gas reactions involves the release or absorption of a gas and, therefore, X(t) can be obtained by using weight changes. X(t) is frequently described using the fractional weight change, which is obtained using the initial mass ( $m_0$ ), the mass at time t ( $m_t$ ) and the final mass ( $m_f$ ) [21]. Different expressions of X(t) will be used depending on whether the process involves decomposition (weight loss) or product formation (weight gain):

$$X(t) \begin{cases} \text{weight loss } m_0 > m_t \to \frac{m_0 - m_t}{m_0 w} \\ \text{weight gain } m_0 < m_t \to \frac{m_t - m_0}{m_f w} \end{cases}$$
(3)

where *w* is the weight fraction of the mass of the solid effectively contributing to the reaction. As X(t) may not necessarily reach unity, (which would indicate reaction completion), the extent of conversion ( $\alpha$ ) is commonly used in the analysis of solid-gas reaction kinetics.  $\alpha$  is obtained from Equation (3), where *w* is assumed to be unity. The mass is normalized by the maximum weight obtained in the process to obtain values in the range of 0 to 1, regardless of the maximum X(t):

$$\alpha \begin{cases} \text{weight loss } m_0 > m_t \to \frac{m_0 - m_t}{m_0 - m_f} \text{ for } m_0 = m_{\max} \\ \text{weight gain } m_0 < m_t \to \frac{m_t - m_0}{m_f - m_0} \text{ for } m_f = m_{\max} \end{cases}$$
(4)

These values of X(t) and  $\alpha$  usually change over the course of the reaction with respect to time and can have characteristic shapes [44]. Solid-gas kinetic models are used to understand these shapes and relate them to different mechanisms involved [45]. The reaction rate ( $d\alpha/dt$ ) of a solid-gas reaction is commonly described by the equation:

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

where k(T) is the temperature-dependent reaction rate constant, expressed in min<sup>-1</sup>;  $f(\alpha)$  is the reaction model describing the mechanism; and h(P) is the pressure dependence term. The Arrhenius equation is often used to describe k(T):

$$k(T) = A \exp\left(\frac{-E_a}{RT}\right) \tag{6}$$

where *A* is the pre-exponential or frequency factor  $(\min^{-1})$ ,  $E_a$  is the activation energy (J mol<sup>-1</sup>), *R* is the universal gas constant (J mol<sup>-1</sup> K<sup>-1</sup>) and *T* is the temperature (K). Substituting Equation (6) into (5) leads to the differential form of  $d\alpha/dt$ :

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) h(P) f(\alpha) \tag{7}$$

The pressure dependence term h(P) is rarely used in most kinetic methods, but depending on the atmosphere, may have a significant effect as the reaction progresses [3]. A recent work suggests that the equilibrium pressure,  $P_0$  (kPa), of the gaseous product has a significant influence on  $d\alpha/dt$  and the effective  $E_a$  for decomposition reactions under temperature swing cycling [46]. Various forms of the pressure dependence term (also known as the accommodation function) have been derived and used in solid-gas systems [47,48]. The following h(P) function is derived by considering the contribution of the reverse reaction (e.g. product pressure) in the overall reaction rate and accounts for the influence of  $P_0$  and the total pressure P(kPa) [49]:

$$h(P) = \left(1 - \frac{P}{P_0}\right) \tag{8}$$

If a solid-gas reaction is reversible such as in Equation (1), then  $P_0$  is equal to the equilibrium constant  $K_{eq}$  [49,50] leading to:

$$P_0 = K_{eq} = \exp\left(-\frac{\Delta G_r^0}{RT}\right) \tag{9}$$

where  $\Delta G_r^0$  is the Gibbs free energy (kJ mol<sup>-1</sup>).

An alternative form of the accommodation function was developed by Koga et al. after finding that the conventional function (Equation (8)) did not universally describe various reaction induction period processes in the thermal decomposition of solids [47]. A generalized form was proposed to describe kinetic behavior under different pressure conditions:

$$h(P) = \left(\frac{P_S}{P}\right)^a \left[1 - \left(\frac{P}{P_0}\right)^b\right]$$
(10)

where *a* and *b* are constants and  $P_S$  (kPa) is the standard pressure (introduced to express all pressure terms in the same units) [47].

Methods of solid-gas kinetic analysis are either differential, based on the differential form of the reaction model,  $f(\alpha)$ ; or integral, based on the integral form  $g(\alpha)$ . The expression for  $g(\alpha)$  is obtained by rearranging Equation (7) and then integrating, leading to the general expression of the integral form:

$$g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = A \int_{0}^{t} \exp\left(\frac{-E_{a}}{RT}\right) h(P) dt$$
(11)

Experimentally, the solid-gas reactions can be performed under isothermal or non-isothermal conditions. An analytical solution to Equation (11) can be obtained for isothermal experiments because the integrand is time independent [51]. However, the accuracy of isothermal techniques has been questioned because the reaction may begin during the heating process. Furthermore, the range in temperature where  $\alpha$  is evaluated is much smaller, which exaggerates errors in the calculation of the kinetic parameters [52]. For these reasons, non-isothermal experiments are preferred over isothermal experiments. Non-isothermal experiments employ a heating rate ( $\beta$  in K min<sup>-1</sup>), which is constant with time. Equation (11) is therefore transformed to express  $\alpha$  as a function of temperature, Equation (12a) [53]. Equation (12b) is the starting equation for many integral methods of evaluating non-isothermal kinetic parameters with constant  $\beta$ :

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) h(P) f(\alpha) \tag{12a}$$

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) h(P) dT$$
(12b)

Similarly, to Equation (11), Equation (12b) has no analytical solution under non-isothermal conditions and algebraic expressions must be used as approximations. Commonly used kinetic methods can be classified depending on the type of approximations used and/or assumptions made:

- Model-fitting methods, where expressions of  $f(\alpha)$  and  $g(\alpha)$  are approximated to defined linear or non-linear expressions dependent on  $\alpha$  and the order of reaction n. These methods provide global values of  $E_a$  and A corresponding to kinetic mechanisms [3].
- Model-free methods assume that the dα/dt at a specific value of conversion is only a function of temperature [54] and do not fit experimental data to assumed reaction models [55]. The model-free methods often begin with Equation (12b), which is linearized to obtain *E<sub>a</sub>*. This method, however, cannot obtain independent values of *A* without making assumptions about *f*(*α*). A posteriori application of a model fitting method of *f*(*α*) can be applied to obtain *A* [3].
- Generalized kinetic models allow for the reaction to consist of a simultaneous combination of multiple steps. In the case of simultaneous multi-step reactions, neither model-free nor model-fitting methods can be used to determine *E*<sub>a</sub> and *A*. Therefore, a specific physicochemical model should be applied for the reaction in question [56]. These methods have the benefit of combining mass and heat transfer effects into a single model. However, they can be complicated to implement [57], leading to long simulation times. In addition, these methods are purely based on other empirical parameters (e.g., porosity, bulk density, void fraction) that may vary with synthesis conditions.

As mentioned at the beginning of this section, solid-gas kinetics ultimately rely on measuring the changes in weight of a solid sample to obtain the values of  $\alpha$  required to solve Equations (7), (11) or (12b). Thermogravimetric analysis (TGA) is a popular means of obtaining quantitative weight changes [58]. One of the critical issues is to obtain good quality data from the TGA. Experimental factors such as particle size, sample mass and gas flow rate must be controlled to reduce the influence of external and internal mass transfer limitations [59,60]. Reducing particle sizes and dispersing particles can minimize inter-particle mass transfer limitations, while adopting high gas flow rates can minimize external mass transfer limitations. The choice of the gas flow rate is commonly limited by the type of TGA analyser used.

It has been suggested that  $g(\alpha)$  methods are better suited to analyzing integral data collected by TGA, and  $f(\alpha)$  methods better suited to data collected using differential scanning calorimetry (DSC) [3]. This is because differentiating integral data tends to magnify noise. However, modern thermal analysis equipment usually employs good numerical methods with enough data points to reduce noise [3]. Therefore, modern kinetic methodologies can use either  $f(\alpha)$  or  $g(\alpha)$  methods depending on the desired results. The following sections (Sections 4–6) will describe the theoretical expressions of  $f(\alpha)$  and  $g(\alpha)$  leading to different approximations of Equations (7), (11) and (12b) commonly used in kinetic analysis of solid-gas reactions.

#### 4. Model-Fitting Kinetic Reaction Models

Model-fitting methods are based on fitting experimental data to various known solid-state reaction models and in this way obtaining  $E_a$  and A [3]. The general principle is to minimize the difference between the experimentally measured and calculated data for the given reaction rate expressions in Table 1 [3].

<b>Reaction Model</b>	Code	$f(\alpha)$	g(a)
Zero-order	F0	1	α
First-order	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order	F2	$(1 - \alpha)^2$	$\frac{1}{(1-\alpha)} - 1$
Third-order	F3	$(1 - \alpha)^3$	$\frac{1}{2}\left[(1-\alpha)^{-2}-1\right]$
Avrami-Erofeyev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avrami-Erofeyev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avrami-Erofeyev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout-Tompkins	B1	$\alpha(1-\alpha)$	$\ln[\alpha(1-\alpha)] + c^{\alpha}$
Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Contracting area	R2	$2(1-\alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
Contracting volume	R3	$3(1-\alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
1-D diffusion	D1	$1/(2\alpha)$	$\alpha^2$
2-D diffusion	D2	$-\ln(1-\alpha)$	$((1-\alpha)\ln(1-\alpha)) + \alpha$
3-D diffusion	D3	$\frac{3(1-\alpha)^{2/3}}{2-(1-\alpha)^{1/3}}$	$(1 - (1 - \alpha)^{1/3})^2$
Ginstling-Brounshtein	D4	$\frac{3}{2} \frac{1}{(1-\alpha)^{-1/3}-1}$	$1 - (2/3)\alpha) - (1 - \alpha)^{2/3})$

Table 1. Classification of model-fitting kinetic expressions for reaction mechanisms [45].

Table 1 categorizes kinetic models for reaction mechanisms and provides the algebraic functions for  $f(\alpha)$  and  $g(\alpha)$ . The general expression for  $g(\alpha)$  is given when  $f(\alpha)$  is approximated as  $(1 - \alpha)^n$  [61]:

$$g(\alpha) = [1 - (1 - \alpha)^{1 - n}] / (1 - n)$$
(13)

for all values of n except n = 0, which corresponds with the zero-order model (F0), and for n = 1, which corresponds with the first-order model (F1):

$$g(\alpha) = -\ln(1-\alpha) \tag{14}$$

In order-based models (F0–F3), the reaction rate is proportional to  $\alpha$ , the conversion degree, raised to a power, which represents the reaction order. These types of models are the simplest of all the kinetic models and are similar to those used in homogeneous kinetics [45]. Figure 2 depicts the functions  $f(\alpha)$  and  $g(\alpha)$  over  $\alpha$  for the order-based methods.



**Figure 2.** Order-based reaction models: (a)  $f(\alpha)$  plots; (b)  $g(\alpha)$  plots.

The Avrami-Erofeyev (A2–A4) models are referred to as nucleation-based models (see Figure 3). Nucleation models describe the kinetics of many solid-state reactions, including crystallization, crystallographic transition, decomposition and adsorption [45]. These methods are frequently applied

to solid-gas reactions. They are described by the general Equation (15) and vary depending on the order, described by the exponent *n*:

$$g(\alpha) = \left[-\ln(1-\alpha)\right]^{1/n} \tag{15}$$



**Figure 3.** Formation and growth of nuclei of reaction products: (**a**) nucleation sites; (**b**) first nuclei formed; (**c**) growth and further nucleation; (**d**) overlap of nuclei; (**e**) ingestion of a nucleation site; (**f**) continued growth.

Note that the first order model (F1) corresponds to the case when n = 1 in Equation (15) [45]. For Avrami nucleation, the graph of  $\alpha$  versus time is sigmoidal with an induction period at the beginning of the reaction (see Figure 4). Orders of nucleation are classified as either A2, A3 or A4 to reflect the exponential terms in the reaction models (see Table 1). When *n* is equal to 4, the reaction mechanism is often interpreted as autocatalytic nucleation [43]. This occurs if nuclei growth promotes a continued reaction due to the formation of defects such as dislocations or cracks at the reaction interface. Autocatalytic nucleation continues until the reaction begins to spread to material that has decomposed [45].



**Figure 4.** Nucleation-based reaction models: (a)  $f(\alpha)$  plots; (b)  $g(\alpha)$  plots.

A schematic of nucleation and growth in Avrami models is shown in Figure 3. The Avrami models identify that there are two restrictions on nuclei growth. After the initial growth of individual nuclei (Figure 3a–c), the first restriction is driven by the ingestion (Figure 3d,e) [1]. The ingestion facilitates the elimination of a potential nucleation site by growth of an existing nucleus. The second is coalescence (Figure 3e,f), the loss of the reactant-product interface when two or more growing nuclei merge or ingestion occurs [1,45].

A non-Avrami based nucleation and isotropic growth kinetic model was developed specifically for the decomposition of  $CaCO_3$  in powder form by Bouineau et al. [62]. This model was based on one first proposed by Mampel [63] and assumes that the rate-limiting step of growth occurs at the internal interface between CaO particles. The model of Bouineau, however, does not assume that the extent of conversion of the powder is identical to that of a single particle. The extent of conversion can be obtained by the following expression

$$\alpha(t) = 4\pi r_0^2 \gamma \int_0^t \alpha_t \exp\left(-4\pi r_0^2 \gamma t\right) dt$$
(16)

where  $\gamma$  is the number of nuclei that appear (m<sup>2</sup> s<sup>-1</sup>)

The Prout-Tompkins model (B1) also assumes a sigmoidal relationship between  $\alpha$  and time, like the Avrami-Erofeyev models. It assumes that nucleation occurs at the same rate as "branching", which occurs during autocatalysis if nuclei growth promotes a continued reaction due to the formation of defects at the reaction interface [45]. The power law model (P2) is employed for a simple case where nucleation rate follows a power law and nuclei growth is assumed to be constant [45].

The geometric contraction (R2-R3) models assume that nucleation occurs rapidly on the surface of the solid. The reaction is controlled by the resulting reaction interface progressing towards the center. If the solid particle is assumed to have a cylindrical shape, the contracting area (R2) model is used, while if a spherical or cubical shape is assumed, the contracting volume (R3) model is employed (see Figure 5).



**Figure 5.** Geometric models, where *r* is the radius at time *t* and  $r_0$  is the radius at time  $t_0$ : (**a**) cylinder (R2); (**b**) sphere (R3); (**c**) cube (R3).

As the mathematical derivation of the geometric models involves the radius of the solid particle, k(T) will be a function of particle size, which will also be the case for the diffusion models (see next) [45]. Reaction functions for geometric models are depicted in Figure 6.



**Figure 6.** Geometry-based reaction models: (a)  $f(\alpha)$  plots; (b)  $g(\alpha)$  plots.

Diffusion often plays a role in solid-state reactions because of the mobility of constituents in the systems. While reactant molecules are usually readily available to one another in homogeneous systems, solid-state reactions often occur between crystal lattices. In these lattices, motion can be restricted and may depend on lattice defects. A product layer may form and increase in thickness where the reaction rate is controlled by the movement of the reactants to, or products from, the reaction interface. In diffusion processes,  $\alpha$  decreases proportionally with the thickness of the product layer.

The one-dimensional (D1) diffusion model is based on the rate equation for an infinite flat plate that does not involve a shape factor (see Figure 7).



**Figure 7.** Schematic of 1D diffusion through a flat plate, where *A* and *B* are reactants, *AB* is the product interface, *l* is the thickness of the product layer, and *x* is the distance measured from interface *Q* into *AB*.

The two-dimensional diffusion model (D2) assumes that the solid particles are cylindrical, and that diffusion occurs radially through a cylindrical shell with an increasing reaction zone. The three-dimensional diffusion model is known as the Jander equation (D3) and assumes spherical solid particles. It is derived from a combination of the parabolic law which reflects the one-dimensional oxidation of models, reformulated taking spherical geometry into consideration [64]. McIlvried and Massoth argue that the expression in Table 1 is only a good approximation at very low extents of conversion [64] and should instead be correctly expressed as:

$$g(\alpha) = 3 - 3(1 - \alpha)^{2/3} - 2\alpha \tag{17}$$

The Ginstling-Brounshtein model (D4) is a three-dimensional diffusion model based on a different mathematical representation of the product layer thickness [45]. The reaction model consists of a sphere of component A with a homogeneous matrix of component B and the formation of a number of intermediate phases in a concentric layer [65]. Diffusion-based reaction models are depicted in Figure 8.



**Figure 8.** Diffusion-based reaction models: (a)  $f(\alpha)$  plots; (b)  $g(\alpha)$  plots.

# 4.1. Integral Approximation

Integral approximations are commonly employed in non-isothermal kinetic analyses [53]. Integral approximations are based on Equation (11) and generally omit the pressure dependency term h(P). The integral from Equation (12b) can be approximated by replacing *x* with  $E_a/RT$  [53]:

$$\int_{0}^{T} \exp\left(\frac{-E_{a}}{RT}\right) dT = \left(\frac{R}{E_{a}}\right) T^{2} \exp\left(\frac{-E_{a}}{RT}\right) Q(x)$$
(18)

where Q(x) is a function which changes slowly with x and is close to unity [53]. It can alternatively be expressed in terms of p(x):

$$\int_{0}^{T} \exp\left(\frac{-E_{a}}{RT}\right) dT = \left(\frac{E_{a}}{R}\right) p(x)$$
(19)

where p(x) is used to transform the integration limits from *T* to *x* [53]:

$$p(x) = \int_{x}^{\infty} \left(\frac{1}{x^2}\right) \exp(-x) \, \mathrm{d}x \tag{20}$$

The following relationship between p(x) and Q(x) can be obtained by equating Equations (18) and (19) and rearranging for p(x):

$$p(x) = \left(\frac{1}{x^2}\right) \exp(-x)Q(x)$$
(21)

An expression for  $g(\alpha)$  can then be obtained by substituting Equation (21) into Equation (19) and then into Equation (12b):

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT = \left(\frac{A}{\beta}\right) \left(\frac{E_a}{R}\right) p(x) = \left(\frac{AE_a}{\beta R}\right) \left(\frac{1}{x^2}\right) \exp(-x)Q(x)$$
(22)

As Q(x) has no analytical solution, many approximations are available, including the Agarwal and Sivasubramanium (A&S) [66] and the Coats-Redfern (CR) approach [53]. The CR method utilizes the asymptotic series expansion and approximates Q(x) to be  $\frac{(x-2)}{x}$ , leading to the following expression of  $g(\alpha)$ :

$$g(\alpha) = \frac{AR}{E_a\beta}T^2 \exp\left(\frac{-E_a}{RT}\right)\frac{(x-2)}{x}$$
(23)

Therefore, plots of  $\ln[g(\alpha)/T^2]$  versus 1/T (Arrhenius plots) will produce a straight line for which the slope and intercept allow an estimation of  $E_a$  and A [61]:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln\left[\frac{AR}{E_a\beta}\right]\left(1 - \frac{2RT_{av}}{E_a}\right)$$
(24)

 $T_{av}$  is the average temperature over the course of the reaction [55]. One pair of  $E_a$  and A for each mechanism can be obtained by linear data-fitting and the mechanism is chosen by the best linear correlation coefficient. However, careful considerations should be taken as selecting the best expression of  $g(\alpha)$  that produces the best fit could lead to wrong conclusions. As for all model-fitting methods, CR should not be applied to simultaneous multi-step reactions, although it can adequately represent a multi-step process with a single rate-limiting step [3].

## 4.2. Master Plots

Master plots are defined as characteristic curves independent of the condition of measurement which are obtained from experimental data [67]. One example of a master plot is the  $Z(\alpha)$  method, which is derived from a combination of the differential and integral forms of the reaction mechanism, defined as follows:

$$Z(\alpha) = f(\alpha)g(\alpha) \tag{25}$$

An alternative integral approximation for  $g(\alpha)$  to the CR approximation in Section 4.1 is  $\frac{\pi(x)}{x}$ , where  $\pi(x)$  is an approximation made by a polynomial function of x ( $E_a/RT$ ) [68–70]:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}$$
(26)

By including  $\pi(x)$  and x in Equation (12b) and integrating with respect to temperature, we can obtain an approximation to the integral form of  $g(\alpha)$ :

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT = \frac{A}{\beta} \frac{E_a}{RT} T\left(\exp(-x)\frac{\pi(x)}{x}\right) = \frac{A}{\beta} \left(\frac{T^2}{T} \exp(-x)\pi(x)\right)$$
(27)

If Equation (7) is rearranged to produce:

$$f(\alpha) = \frac{1}{A \exp(-x)} \frac{\mathrm{d}\alpha}{\mathrm{d}t}$$
(28)

the expression used for the  $Z(\alpha)$  method is obtained by substituting Equations (27) and (28) into Equation (25):

$$Z(\alpha) = \frac{\mathrm{d}\alpha}{\mathrm{d}t} T^2 \left[ \frac{\pi(x)}{\beta T} \right]$$
(29)

For each of the reaction mechanisms, theoretical  $Z(\alpha)$  master plot curves (Equation (25)) can be plotted using the approximate algebraic functions in Table 1 for  $f(\alpha)$  and  $g(\alpha)$ , as shown in Figure 9. A plot of experimental values can be produced with Equation (29). The experimental values will provide a good fit for the theoretical curve with the same mechanism. As the experimental points have not been transformed into functions of the kinetic models, no prior assumptions are made for the kinetic mechanism.

F0 1.4 F1 **F2** 1.2 F3 A2 1.0 A3  $(\alpha)_{Z(\alpha)}^{0.8}$ A4 **B**1 **P1** 0.6 R2 **R3** 0.4 D1 0.2 D2 D3 D4 0.0 0.2 0.4 0.6 0.0 0.8 1.0 α

**Figure 9.**  $Z(\alpha)$  theoretical master plot for reaction mechanisms in Table 1.

# 5. Model-Free Methods of Kinetic Analysis

Model-free methods calculate  $E_a$  independently of a reaction model and require multiple data sets [71] and assumptions about a reaction mechanism are avoided. Another benefit of these methods is that multi-step processes can be identified [3]. The kinetic parameters ( $E_{\alpha}$  and  $A_{\alpha}$ ) depend on the values of  $\alpha$  and are typically obtained over the range of 0.05 <  $\alpha$  < 0.95. Model-free methods include differential and integral isoconversional methods and the Kissinger method [3].



#### 5.1. Differential Isoconversional Methods

Differential isoconversional methods draw on the differential form of the kinetic equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) h(P) f(\alpha) \tag{30}$$

If the pressure dependence has been considered in the kinetic analysis, the differential form of the kinetic equation will be:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta} \exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) \frac{(P_0 - P)}{P_0} f(\alpha) \tag{31}$$

The isoconversional principle is based on the temperature dependence of the reaction rate, which can be used to evaluate the isoconversional  $E_a$  related to a given  $\alpha$ . Following this principle, the Friedman isoconversional model is carried out by taking the logarithmic derivative of the reaction rate:

$$\ln\left(\beta_{i}\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha,i} = \ln[f(\alpha)A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$
(32)

At each value of  $\alpha$ , the value of  $E_{\alpha}$  is determined from the slope of a plot of  $\ln(d\alpha/dT)_{\alpha,i}$  against  $1/T_{\alpha,i}$  as in Equation (32). For non-isothermal experiments, *i* represents an individual heating rate and the  $T_{\alpha,i}$  is the temperature at which the extent of conversion is reached in the temperature program [3]. In this method, the h(P) term could be negligible or included as a pressure correction in the following expression [49]:

$$E_{\alpha(P)} = E_{\alpha} + \Delta H_{\rm r} \frac{P_0}{(P_0 - P)}$$
(33)

where  $E_{\alpha}$  and  $E_{\alpha(P)}$  denote the activation energy before and after applying the pressure correction, respectively.  $\Delta H_r$  is the standard enthalpy (kJ mol<sup>-1</sup>) over the temperature range of the reaction and can be evaluated using the van't Hoff equation:

$$\ln K_{eq} = -\frac{\Delta H_{\rm r}}{RT} + \frac{\Delta S_{\rm r}}{R} \tag{34}$$

where  $\Delta S_r$  is the entropy change (J mol<sup>-1</sup> K<sup>-1</sup>) of the system and  $K_{eq}$  is the equilibrium constant of the solid-gas reaction, which is equal to  $P_0$  in stoichiometric reactions as per Equation (1) (see Section 3).  $A_{\alpha}$  can be obtained using the compensation effect (see Section 6).

# 5.2. Integral Isoconversional Methods

Integral isoconversional methods apply the same linearization principle as differential isoconversional methods to the integral equation (Equation (11)). The general form is now:

$$\ln\left(\frac{\beta_i}{T^B_{\alpha,i}}\right) = Const - C\left(\frac{E_\alpha}{RT_\alpha}\right)$$
(35)

where B (in  $T^B_{\alpha,i}$ ) and C are the parameters determined by the type of temperature integral approximation. Several approximations can be applied and one is the Flynn and Wall and/or Ozawa (FWO) equation [72] that approximates B = 0 and takes the form:

$$\ln(\beta_i) = Const - 1.052 \left(\frac{E_\alpha}{RT_\alpha}\right)$$
(36)

Numerical methods of solving the integral approximation have since been developed which display greater accuracy [3].

#### 5.3. Kissinger Method

The Kissinger method, a multi-heating rate method, has been applied extensively to determine  $E_a$  because of its ease of use. The basic equation of the method is derived from Equation (7) under the condition of maximum reaction rate:

$$\frac{\mathrm{d}^{2}\alpha}{\mathrm{d}t^{2}} = \left[\frac{E_{a}\beta}{RT_{max}^{2}} + Af\prime(\alpha_{m})\exp\left(-\frac{E_{a}}{RT_{max}}\right)\right] \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{max} = 0$$
(37)

where  $f'(\alpha) = df(\alpha)/d\alpha$  and the subscript *max* refers to the maximum value. After differentiating and rearranging, the Kissinger equation is obtained:

$$\ln\left(\frac{\beta}{T_{m,i}^2}\right) = \ln\left(-\frac{AR}{E_a}f\prime(\alpha_m)\right) - \frac{E_a}{RT_{m,i}}$$
(38)

The limitations of the method are that an accurate value of  $E_a$  requires  $f'(\alpha_{max})$  to be independent of the heating rate  $\beta$ , which is not fulfilled in some reaction models and hence violates the isoconversional principle. Another limitation is that the Kissinger method (unlike Friedman and FWO) produces a single value of activation energy, regardless of the complexity of the reaction [49]. Additionally, the use of approximations mean that FWO and Kissinger methods are potentially less accurate than differential methods (Friedman) [3].

#### 6. Combination of Model-Fitting and Model-Free Methods

Model-free methods allow  $E_{\alpha}$  to be evaluated without determining the reaction model. However, it is possible to determine the reaction model (and *A*) by combining the results of a model-free method and a model-fitting method. The reaction can be reasonably approximated as single-step kinetics if  $E_{\alpha}$  is nearly constant with  $\alpha$ . However, if  $E_{\alpha}$  varies with  $\alpha$ , the reaction can be split into multiple steps and model-fitting can be carried out for each step [3].

In this combination of model-fitting and model-free methods, the Friedman method is first performed, which gives a range of values of  $E_{\alpha}$  over the extent of reaction  $\alpha$ . Then, if the value of  $E_{\alpha}$  does not vary considerably with  $\alpha$ , an average value  $E_0$  can be calculated. A corresponding value of  $A_0$  can then be determined using the compensation effect [3]. The compensation effect assumes a linear correlation  $E_a$  and A. Therefore, values of  $E_a$  and A obtained from model-fitting (denoted as  $E_i$  and  $A_i$ ) can be used to determine the constants a and b [3]:

$$\ln A_i = aE_i + b \tag{39}$$

Different functions of  $f(\alpha)$  produce widely different values of  $E_i$  and  $A_i$ , however, they all demonstrate a strong linear correlation based on the parameters *a* and *b* [3]. Therefore, the average value  $E_0$  can be used to determine the model-free estimate of the pre-exponential factor,  $A_0$ , using the *a* and *b* constants:

$$\ln A_0 = aE_0 + b \tag{40}$$

The integral form of the reaction model can then be reconstructed by substituting  $E_0$  and  $A_0$  into Equation (12b), which can then be plotted and compared with the theoretical  $g(\alpha)$  curves (see Table 1) to suggest a reaction mechanism [3]:

$$g(\alpha) = \frac{A_0}{\beta} \int_0^{T_\alpha} \exp\left(\frac{-E_0}{RT}\right) dT$$
(41)

# 7. Generalized Kinetic Models

Some solid-gas reactions display an ever-changing mixture of products, reactants, and intermediates [73]. These can consist of multiple reactions occurring simultaneously, and in these cases, using model-fitting and model-free methods will produce erroneous kinetic parameters and lead to mistaken conclusions about the reaction mechanisms [54]. Additionally, model-fitting and model-free methods do not consider any of the morphological properties in the reacting sample that could be relevant to the reaction kinetics [56]. For example, nucleation and growth are reduced to Avrami relationships, (which assume that nucleation occurs in the bulk of the solid) without taking into account the fact that nucleation also occurs at the surface [56].

In light of these challenges, Pijolat et al. describe the use of a "generalized approach," which is useful for modelling gas-solid reactions, regardless of its individual morphological characteristics and the type of reaction [56]. Unlike the models in Sections 4 and 5, these morphological models do not assume that the k(T) varies with temperature through an Arrhenius dependence, or that there is an  $f(\alpha)$  dependence on  $\alpha$  [56]. This generalized approach leads to a rate equation with both thermodynamic "variables" (e.g., temperature and partial pressures) and morphological variables. The physical models that determine the variation in the reaction rate with time are referred to as geometrical models.

If the rate-determining step is a reaction such as adsorption, desorption or an interfacial reaction, its kinetic rate is described by the following equation, where  $d\xi/dt$  refers to the absolute speed of reaction (mol s<sup>-1</sup>):

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}(\text{surface or interface}) = v_s S \tag{42}$$

where *S* (m<sup>2</sup>) is the surface area of the reactional zone where the rate-determining steps takes place and  $v_s$  is the rate for a rate-determining step located at the surface or an interface (mol m<sup>-2</sup> s<sup>-1</sup>) [56].

If the rate-determining step is a diffusion step,  $v_s$  is replaced with the diffusion flux *J*:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t}(\mathrm{diffusion}) = JS = D\Delta CG_D S \tag{43}$$

where D (m<sup>2</sup> s<sup>-1</sup>) is the diffusion coefficient of the diffusing species,  $\Delta C$  (mol m<sup>-3</sup>) is the difference in concentrations of the diffusing species at both interfaces and  $G_D$  (dimensionless) is the function of the particle symmetry (equal to 1 in the case of a surface or interfacial rate-determining step). *J* depends only on the thermodynamic variables, while both  $G_D$  and *S* depend on morphological variables which vary as a function of time [56].

The reaction rate can be expressed in terms of the geometrical models (see next section) which vary depending on assumptions of nucleation, growth, particle symmetry and rate-determining step localization. The rate is then expressed in terms of fractional conversion, where  $\phi$  is a function (mol m<sup>-2</sup> s<sup>-1</sup>), which depends only on thermodynamics and  $S_m$  (m<sup>2</sup> mol<sup>-1</sup>) on both kinetic and geometrical assumptions (taking into account nucleation, growth and morphological features) [56]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \phi S_m \tag{44}$$

In contrast to model-fitting and model-free methods, generalized kinetic models are specific to the reaction system considered. In the next section, the application of these models to carbonate looping systems will be explained in detail.

#### 8. Generalized Kinetic Models Applied to Carbonate Looping Systems

In the carbonate looping systems, the calcination reaction commonly follows a thermal decomposition process that can be approximated by model-fitting and model-free methods. However, carbonation reactions involve several mechanisms such as nucleation and growth, impeded CO<sub>2</sub> diffusion or geometrical constraints related to the shape of the particles and pore size distribution of the

powder [74]. Therefore, instead of using a purely kinetics-based approach for analysis of carbonation, functional forms of  $f(\alpha)$  have been proposed to reflect these diverse mechanisms. Numerous studies suggest that the carbonation reaction takes place in two stages: an initial rapid conversion (kinetic control region) followed by a slower plateau (diffusion control region) [60]. These studies have been performed for the CaL system and studies on the carbonation of other metal oxides have not been carried out. Many works examined the deactivation and sintering of CaO through CaL [33,75–78], although these studies are beyond the scope of this review.

The kinetic control region of the carbonation reaction occurs by heterogeneous surface chemical reaction kinetics. The driving force for this kinetic control region is generally seen to be the difference between the bulk CO<sub>2</sub> pressure and equilibrium CO<sub>2</sub> pressure [59]. This region is generally described by the kinetic reaction rate constant  $k_s$  (m<sup>4</sup> mol<sup>-1</sup>s<sup>-1</sup>), which is an intrinsic property of the material. Intraparticle and transport resistances [16] may mean that the kinetic analysis determines an effective value instead of an intrinsic property.

Following this initial stage, the diffusion control region takes place because a compact layer of the product CaCO<sub>3</sub> develops on the outer region of the CaO particle (at the product-reactant interface, see Figure 1) [79]. The diffusion region is described by the product layer diffusion constant D (m<sup>2</sup> s<sup>-1</sup>) (see Equation (43)). A schematic of product layer formation during the reaction cycles is shown in Figure 10.



a) CaO particle b) Carbonation c) Calcination

**Figure 10.** Schematic representation of a CaO particle undergoing carbonation-calcination cycling reactions.

The formation and growth of the  $CaCO_3$  product layer is often considered to be the most important rate-limiting reaction step. The layer of  $CaCO_3$  impedes the ability of  $CO_2$  to further diffuse to the bulk and will also result in the plugging of the porous structure [80].

There are four major groups of generalized models which describe how the particles change during the carbonation of CaL system (see Figure 11). The shrinking core model is a form of the simple homogeneous particle model and separates the surface chemical reaction from the product layer diffusion reaction. Pore models assume that the initial reaction stage is driven by the filling of small pores, before a diffusion process takes over. Grain models focus on how grain size distribution changes as the reaction progresses, while the nucleation and growth model represents the reaction through the nucleation of product CaCO<sub>3</sub>. A simplified generalized model (the apparent model) has also been developed for the carbonation reaction, which does not consider morphological properties. These models are described in detail in the following sections.



**Figure 11.** Solid gas reaction models: (**a**) Shrinking core model; (**b**) Pore model; (**c**) Grain model; (**d**) Nucleation and growth.

#### 8.1. Shrinking Core Model

The shrinking core model (SCM) is derived from the homogeneous particle model [13] and was first introduced by Yagi and Kunii [81], with further zone-reaction models proposed by authors such as Ishida and Wen [82]. The SCM describes the particle as a non-porous sphere [83] and discriminates between product layer diffusion and reaction at the surface of the unreacted core as possible rate-determining steps [84].

The equations governing the kinetic and diffusion control regions are described by the following equations respectively [13,85]:

$$t = \frac{\rho r}{k_s C} \Big[ 1 - (1 - X(t))^{1/3} \Big]$$
(45)

$$t = \frac{\rho r^2}{6DC} \Big[ 1 - 3(1 - X(t))^{2/3} + 2(1 - X(t)) \Big]$$
(46)

where *r* is the radius of the CaO particle,  $\rho$  is the density of CaO (kg m<sup>-3</sup>),  $k_s$  is the kinetic reaction rate constant (m<sup>4</sup> mol<sup>-1</sup> s<sup>-1</sup>), *D* is the product layer diffusion constant (m<sup>2</sup> s<sup>-1</sup>), *C* is the molar concentration of CO<sub>2</sub> (mol m<sup>-3</sup>), *X*(*t*) is the extent of carbonation conversion (see Equation (3)) and *t* is the time (s).

# 8.2. Pore Models

The pore models focus on the evolution of the voids (pores) in the particle, and consider the solid form to be the continuous phase [13]. The random pore model (RPM) correlates the reaction behavior with the internal pore structure [21] and was developed by Bhatia and Perlmutter [86]. Applied to carbonation, the RPM considers structural parameters and  $CO_2$  partial pressure to be the driving forces for the reaction. It is proposed that the carbonation reaction in the kinetic region is governed by the filling of small pores, while in the diffusion region the reaction continues in larger pores with a much smaller specific surface area [86]. The following expressions were developed to describe the kinetic and diffusion control regions respectively [13,86]:

$$\frac{1}{\psi} \left[ \sqrt{1 - \psi \ln(1 - X(t))} - 1 \right] = \frac{k_s S_0 t(C_b - C_e)}{2(1 - \varepsilon_0)} \tag{47}$$

$$\frac{1}{\psi} \left[ \sqrt{1 - \psi \ln(1 - X(t))} - 1 \right] = \frac{S_0 \sqrt{\frac{M_{CaO}DCt}{4.352\rho}}}{2(1 - \varepsilon_0)}$$
(48)

where  $k_s$  is the kinetic reaction rate constant (m<sup>4</sup> mol<sup>-1</sup> s<sup>-1</sup>) and *D* is the product layer diffusion constant (m<sup>2</sup> s<sup>-1</sup>).  $C_b$  and *Ce* are the bulk and equilibrium concentrations of CO<sub>2</sub>, while *C* is the concentration of the diffusing species on the pore surface.  $M_{CaO}$  is the molar mass of CaO (kg mol<sup>-1</sup>), X(t) is the conversion and  $\rho$  is the density of CaO (kg m<sup>-3</sup>).  $\psi$  is a structural parameter, related to  $S_0$ , the initial surface area per unit volume (m<sup>2</sup> m<sup>-3</sup>),  $\varepsilon_0$ , the initial porosity of the sorbent, and  $L_0$ , the pore length per unit volume (m m<sup>-3</sup>), as described by Equation (46):

$$\psi = \frac{4\pi L_0 (1 - \varepsilon_0)}{S_0^2}$$
(49)

Although the RPM has been shown to predict carbonation kinetics well, the requirement of structural parameters makes it complex to use [13]. A number of modifications have also been made to the RPM [13], including simplifications [87] and extensions to take into account CO<sub>2</sub> partial pressure, carbonation temperature and particle size [35].

#### 8.3. Grain Models

The grain models assume that the material is composed of non-porous solid grains of CaO, randomly located in the particle and dispersed in gas, and are based on the modelling studies of

solid-gas reactions by Szekely and Evans [88]. A CaCO<sub>3</sub> product layer is formed on the outside of each CaO grain during carbonation [13,21]. The gas is the continuous phase instead of the solid phase as considered in the pore models. Grain models also consider convection heat transfer in the surface of the particle versus heat conduction in the particles [21] and numerical models have been developed to model conversion and reaction rates [36,37]. The changing grain size (CGS) model considers the system composed by a set of particles as non-porous spherical grains of uniform initial radius which change as the reaction progresses [83]. This model considers the grain size distribution and the overlapping effect of grains.

The overlapping grain model (OGM) also takes into account the structural changes in the particles. The kinetic control region is described by:

$$\frac{dX}{dt(1-X(t))^{2/3}} = 3k$$
(50)

where *k* is the grain model reaction rate (min<sup>-1</sup>), which is assumed to be constant over the kinetic control region [59] and X(t) is the conversion. In integral form, the reaction rate can be expressed as:

$$\left[1 - (1 - X(t))^{1/3}\right] = kt \tag{51}$$

#### 8.4. Nucleation Model (Rate Equation Theory)

A rate equation was derived by Li et al. to replace the assumption of a critical product layer [80]. In this model, nucleation and growth describes the kinetic behavior of the reaction which display a sigmoidal relationship for conversion versus time [80]. Nucleation involves the development of product "islands", which is generally not discussed in other carbonation models [13]. The kinetic and diffusion control regions are described as follows:

$$F_n = k_n (C_b - C_e) N_{molecular}$$
<sup>(52)</sup>

$$D_i = D_{0i} \exp\left(-\frac{E_i}{RT}\right) \tag{53}$$

where  $F_n$  is the chemical reaction rate for nucleation (mol m<sup>3</sup> s<sup>-1</sup>),  $k_n$  is the chemical reaction rate constant for nucleation (m<sup>3</sup> s<sup>-1</sup>),  $N_{\text{molecular}}$  is Avagadro's number,  $D_i$  (m<sup>2</sup> s<sup>-1</sup>) is the diffusion constant at temperature *T* and  $D_{0i}$  (m<sup>2</sup> s<sup>-1</sup>) is the initial diffusion constant.

#### 8.5. Apparent Model

The simplest form of model for a solid-gas reaction is the apparent model. This model employs a simple rate expression which may include the maximum carbonation conversion, the reaction rate constant and the average  $CO_2$  concentration (the difference between the bulk and equilibrium concentrations) [80].

Apparent models provide a simple description of reaction kinetics using a semi-empirical approach and avoiding the need for morphological measurements. A simple model equation to describe the apparent kinetics of CaO-carbonation was provided by Lee [57]:

$$X(t) = X_u \left[ 1 - \exp\left(-\frac{k}{X_u}t\right) \right]$$
(54)

$$X(t) = \frac{X_u t}{(X_u/k) + t}$$
(55)

where  $X_u$  is the ultimate conversion of CaO to CaCO<sub>3</sub> and *k* is the reaction rate (min<sup>-1</sup>).

#### 9. Calcination of Carbonate Looping Systems

The calcination of carbonate looping systems has been carried out using a variety of model-fitting and model-free methods. The vast majority of experiments are carried out for the calcination of CaCO<sub>3</sub> (one of the most well-studied solid-gas reactions [60]), although other metal carbonates have also been studied. To obtain the experimental data needed to perform a kinetic analysis, TGA experiments are conducted under an atmosphere of either N<sub>2</sub>, air, Ar, CO<sub>2</sub> or a mixture of N<sub>2</sub> and CO<sub>2</sub>. Experiments which have been carried out using alternative methods to TGA, including the use of differential reactors [89] and single crystal studies using an electrobalance [90] are outside the scope of this review. Table 2 shows the result of calcination experiments, including experimental conditions (atmosphere and temperature range), method of kinetic analysis, the kinetic parameters obtained and the suggested mechanism.

Several major rate-limiting mechanisms have been identified, although a consensus has not been reached on which are most important. Table 2 gathers possible reaction mechanisms for the processes of calcination and carbonation, including [80]:

- Heat transfer (thermal transport) through the particle to the reaction interface
- External mass transfer through the particle
- Mass transport of the CO<sub>2</sub> desorbed from the reaction surface through the porous system (Internal mass transfer or CO<sub>2</sub> diffusion inside the pore)
- CO<sub>2</sub> diffusion through the product layer
- Chemical reaction

Material & Ref.	Atmosphere	Initial Sample Size (mg) Particle Sizes	Decomposition Range (°C)	Method	$E_a$ (kJ mol <sup>-1</sup> )	A (s <sup>-1</sup> )	Reaction Order or Model
CaCO <sub>3</sub> [61]	N <sub>2</sub>	NS	NS	CR	180.1212	$1.18\times 10^7$	R2
CaCO <sub>3</sub> [69]	NS	NS	~640–900	CR	187.1	NS	R3
CaCO <sub>3</sub> [66]	N <sub>2</sub>	NS	400-960	CR	190.46	$3.4  imes 10^7$	F1
CaCO <sub>3</sub> [51]	N <sub>2</sub>	NS	400-960	A&S	224.46	$3 \times 10^4$	D2
CaCO <sub>3</sub> [46]	N <sub>2</sub>	17	~550-800	Friedman	171–147 Average: 164	$2.5 \times 10^{5}$ - $2.9 \times 10^{5}$	NS
CaCO <sub>3</sub> [91]	Air	NS	~600–810	FWO & model-fitting (method NS)	FWO: 205 (for α < 0.2) 176 (for α > 0.2) Model-fitting: D1: 203 F1: 180	D1: $8.02 \times 10^7$ F1: $3.98 \times 10^7$	$\alpha < 0.2 \text{ D1}$ $\alpha > 0.2 \text{ F1}$
CaCO <sub>3</sub> [92]	N <sub>2</sub> /CO <sub>2</sub> mixture (5–90% CO <sub>2</sub> )	NS	830–900 isothermal	Data fitting of α vs t curves from XRD CaCO <sub>3</sub> /CaO wt%	150	NS	B1/A2-A4
CaCO <sub>3</sub> (pellets) [93]	Air/ CO <sub>2</sub> (0–100% CO <sub>2</sub> )	455 Particle diameters <56 μm	790–850	General rate equation: $r_0\rho_0 f = kt$ where $f =$ fractional thickness of reacted material	169.9	NS	R3 Double interface decomposition mechanism
L (type A and B) [28]	Air/ CO <sub>2</sub> (0–10% CO <sub>2</sub> )	NS Particle diameters < 300 μm	820-910	RPM	A (CaCO3 $\varepsilon$ = 0.044): 112.4 B (CaCO <sub>3</sub> $\varepsilon$ = 0.02): 91.7	NS	Chemical reaction
L [94]		0.4–1.3 Mean particle diameters: 7.5, 57 & 90 μm	780 isothermal	Modified RPM	NS	NS	Chemical reaction and mass transport
CaCO <sub>3</sub> (spheres) [95]	N2/CO2 (0-21% CO2	NSParticle diameters: 2,5 & 7mm	700, 800, 900 isothermal	SCM	152.5–163.7	179–529 kg m <sup>-1</sup> s <sup>-1</sup>	Chemical reaction (assumed first order)
ML, SAD & BL [83]	N <sub>2</sub> /CO <sub>2</sub> (0-80% CO <sub>2</sub> )	2 Particle diameters: 50–75 μm	775–960 isothermal	CGSM for ML & SAD SCM for BL	ML: 131 SAD: 114 BL: 166	NS	Chemical reaction and mass transport

**Table 2.** Classification of kinetic models for reaction mechanisms. NS = not specified. For Coats-Redfern (CR)/Agarwal and Sivasubramanium (A&S) methods, kinetic parameters are average values from all heating rate experiments.

Material & Ref.	Atmosphere	Initial Sample Size (mg) Particle Sizes	Decomposition Range (°C)	Method	$E_a$ (kJ mol <sup>-1</sup> )	A (s <sup>-1</sup> )	Reaction Order or Model
CaCO <sub>3</sub> 4 types of L [62]	CO <sub>2</sub>	5	700isothermal	Modified Mampel model	NS	NS	Nucleation & growth
CL PL (spheres) [96]	N <sub>2</sub>	0.1–0.5 g (Fluidized bed experiments) Particle diameters: CL: 1.4–1.7 mm PL: 0.7–0.81 & 1.4–1.7 mm	750, 850, 875, 900 isothermal	Pore model/experimentally determined function	CL: 175 PL: 186	NS	CL: Chemical reaction PL: <825°C: Chemical reaction >825 °C: Mass transport
CaCO <sub>3</sub> [97]	Air/CO <sub>2</sub> (pp. CO <sub>2</sub> 1.3–20 kPa)	25	~700–900	Model fitting	187	$4.43  imes 10^7$	Assumed R3
CaCO <sub>3</sub> [98]	CO <sub>2</sub>	4	906 isothermal	CR	2104.6	10 <sup>90</sup>	<i>n</i> = 2
CaCO <sub>3</sub> [52]	CO <sub>2</sub>	16	~700–977	CR	1037.6	$3.98\times10^{40}$	n = 2/3 R3
CaCO <sub>3</sub> [46]	CO <sub>2</sub>	17	~900–980	Friedman	530–171 Average: 307	$6.63 \times 10^{32} - 6.2 \times 10^2$	NS
D [11]	N <sub>2</sub>	NS	~687-840	CR	123.684	$5.53 \times 10^5$	<i>n</i> = 0.15
SrCO <sub>3</sub> [66]	N <sub>2</sub>	NS	810-1000	CR	238.32	$7.3 \times 10^{7}$	F1
SrCO <sub>3</sub> [51]	N <sub>2</sub>	NS	810-1000	A&S	238.32	$5.9  imes 10^4$	D4
SrCO <sub>3</sub> [99]	Ar	10	727–1077	Non-mechanistic integral approx.	210	$2.17 \times 10^6$	<i>n</i> = 0.42
SrCO <sub>3</sub> [100]	Air	30	875-1250	Kissinger	$\alpha$ -phase: 255 $\beta$ -phase: 227	α: 15.8 × 107 β: 8.4 × 107	$\alpha$ : R3 $\beta$ : chemical reaction, n = 1/3
BaCO <sub>3</sub> [66]	N <sub>2</sub>	NS	930–1155	CR	292.98	$1.4 \times 10^8$	F1
BaCO <sub>3</sub> [51]	N <sub>2</sub>	NS	930–1155	A&S	292.98	$1.4\times 10^5$	D2
MgCO <sub>3</sub> [66]	N <sub>2</sub>	NS	510–750	CR	140.16	$2.0 \times 10^{6}$	F1
MgCO <sub>3</sub> [51]	N <sub>2</sub>	NS	510-750	A&S	181.16	$2.1 \times 10^3$	D2

# Table 2. Cont.

Acronyms: ML: Mequinenza limestone; SAD: Sierra de Arcos dolomite; BL: Blanca limestone; L: Limestone; D: Dolomite; CL: Compostilla limestone; PL: Purbeck limestone; SCM: Shrinking core model; CGSM: Changing grain size model; *α*-phase: orthorhombic phase of SrCO<sub>3</sub>; β-phase: hexagonal phase of SrCO<sub>3</sub>.

#### Comparison of Calcination Kinetic Analysis

Although the calcination of CaCO<sub>3</sub> has been extensively studied, a consensus on the reaction mechanism has not been established. The intrinsic chemical reaction is considered to be the rate-limiting step by most authors (see Table 2). However, another work considered the initial diffusion of CO<sub>2</sub> as a rate-limiting step [91] and some studies indicate that mass transport is significant [83,94,96]. Experiments conducted in CO<sub>2</sub> show that decomposition of CaCO<sub>3</sub> occurs more rapidly in an atmosphere with the highest thermal conductivity, which implies that the mechanism of decomposition is thermal transport [98]. This is because thermal transport is more effective at higher temperatures due to the T<sup>4</sup> dependence involved in the radiation effects. However, in more recent studies, most authors do not consider heat transfer to be the rate-limiting step [83].

Most analyses employed integral approximation model-fitting methods (CR or A&S; see Section 4.1) to obtain kinetic parameters. Using the CR approximation, calcination of commercial or synthetic CaCO<sub>3</sub> or natural limestone generally produced  $E_a$  values ranging from 180–190 kJ mol<sup>-1</sup> (see Table 1). Using the A&S approximation resulted in a slightly higher  $E_a$  of 224.5 kJ mol<sup>-1</sup> [51]. The suggested reaction mechanisms were predominantly R2/R3, although F1 [66] and D2 [51] were also suggested.

Another integral approximation, although model-free (FWO; see Section 5.2), was used by Rodriguez-Navarro et al. [91] and compared with an unspecified model-fitting method. Both methods suggested that the reaction was initially governed by D1 ( $E_a \sim 204 \text{ kJ mol}^{-1}$ ), before transitioning to a F1 mechanism ( $E_a \sim 178 \text{ kJ mol}^{-1}$ ). The transition in rate-changing mechanism is postulated to be due to the formation of macropores through which CO<sub>2</sub> can easily escape, which reduces resistance against CO<sub>2</sub> diffusion.

An alternative method was used by Valverde et al. [74]. The extent of conversion of the calcination reaction was evaluated by calculating the time evolution of the CaCO<sub>3</sub>/CaO weight fraction from the XRD analysis. The best-fitting reaction mechanism was found to be the Prout-Tompkins rate equation (B1) or Avrami equations (A2–A4). The authors suggest that this is due to the existence of an induction period and that the chemical reaction originates in structural defects, and a slightly lower activation energy of 150 kJ mol<sup>-1</sup> was obtained. Ingraham et al. studied die-prepared pellets of CaCO<sub>3</sub> and used a general rate equation which depended on the fractional thickness of the reacted product (see Table 2) [93]. The authors suggested that the reaction could follow a geometric contraction model (R3) or potentially a double interface decomposition mechanism.

García-Labiano et al. used morphological methods based on microscopy observations to examine two types of limestone and one type of dolomite [83]. The calcination of one limestone was modelled using a CGS model (see Section 8.3), while the other used a SCM (Section 8.1). Chemical reaction and mass transport in the particle system were the main rate-limiting factors in this study, and values of  $E_a$  were significantly lower than those obtained by the integral approximations (114–166 kJ mol<sup>-1</sup>). Lee et al. also used a SCM to determine the kinetic parameters of limestone particles with three different particle sizes, assuming first-order chemical reaction control [95]. Other studies which used morphological methods include those of Bouineau et al., which used a modified Mampel method [62] (see Section 4) and Martínez et al., which used the RPM to determine the kinetic parameters of two different types of natural limestone [28]. Khinast et al. used a modified RPM and examined the effects of experimental conditions on calcination reaction rates and mechanisms [94].

A novel approach was taken by Dai et al. to model the calcination of limestone, which had previously undergone CaL [96]. It used a pore model to describe intraparticle mass transfer of  $CO_2$  through the pores of limestone coupled with an experimentally-determined function to describe pore evolution as a function of conversion from CaCO<sub>3</sub> to CaO. This model produced excellent agreement with experimental results [96].

The model-fitting study by Criado et al. studied the effects of increasing concentrations of  $CO_2$  on the kinetic parameters on the kinetic parameters [97]. With increasing  $CO_2$  partial pressure, the calcination reaction shifts to higher temperatures and reaction rates decrease. However, sharper DTG peaks mean that the kinetic parameters can be overestimated if a pressure correction is not applied [97].

Applying a pressure correction (see Section 3), an average  $E_a$  of 187 kJ mol<sup>-1</sup> was obtained, similar to the studies under inert atmospheres. However, CO<sub>2</sub> partial pressures higher than 20 kPa were not studied.

A study by Fedunik-Hofman et al. used the Friedman isoconversional method to obtain a range of  $E_a$  [46] under two different atmospheres, N<sub>2</sub> and CO<sub>2</sub>. Under N<sub>2</sub>, an average activation energy of 164 kJ mol<sup>-1</sup> was obtained (see Figure 12), similar to other analysis methods and much closer to the enthalpy of reaction of the calcination reaction (~169 kJ mol<sup>-1</sup> [46]). Activation energies were much higher under CO<sub>2</sub>, despite the application of pressure correction and a much larger variation in  $E_a$  (see Figure 12) was calculated over the course of the reaction (170–530 kJ mol<sup>-1</sup>), which was attributed to the major morphological changes in the material under CO<sub>2</sub> [46].



**Figure 12.** Isoconversional values of  $E_{\alpha}$  for CaCO<sub>3</sub> calcination: (a) under N<sub>2</sub>; (b) under CO<sub>2</sub> [46].

In other studies carried out under 100% CO<sub>2</sub>, (which use the CR approximation), activation energies can reach up to 2000 kJ mol<sup>-1</sup>. Caldwell et al. attribute this to the fact that the temperature range of decomposition becomes higher and narrower as the percentage of CO<sub>2</sub> increases, resulting in a higher apparent activation energy [98]. They also suggest a possible change in reaction mechanism [98], although this is disputed by Criado et al. [97]. Additionally, no pressure correction appears to have been applied, so the activation energies may be overestimated. In another study carried out under 100% CO<sub>2</sub> by Gallagher and Johnson,  $E_a$  values were seen to increase as the heating rate and sample size decreased, supporting the theory of thermal transport controlled decomposition, although it is difficult to distinguish between the effects of thermal transport and mass transport [52].

For other alkaline earth metal carbonates,  $E_a$  was found to be proportional to molecular mass by Maitra et al., who utilized a different model-fitting approximation (A&S, see Section 4.1) [51]. Decomposition of all four carbonates (Ca, Sr, Ba and Mg) was observed to follow diffusion-controlled mechanisms, but the order of the diffusion varied among the carbonates (D2 and D4). On the microstructural scale, the migration rate of the strontium and barium oxides formed away from the reactant-product interface was relatively slow due to their higher molecular masses [51].

Activation energies ranging from 210–255 kJ mol<sup>-1</sup> were obtained for the decomposition of SrCO<sub>3</sub> [99,100], and there is no consensus for the reaction mechanism. The decomposition incorporates a phase transformation from  $\alpha$ -SrCO<sub>3</sub> (orthorhombic) to  $\beta$ -SrCO<sub>3</sub> (hexagonal), which occurs between 900 and 1000 °C [100]. This decreases the activation energy and changes the mechanism of the process in the study by Ptáček et al. [100], although another study does not report a change in reaction mechanism [99].

Kinetic parameters vary depending not only on the experimental atmosphere, but also on the different types of CaCO<sub>3</sub> used. For example, the different types of limestone studied by Bouineau et al. exhibited different reaction rates, which was attributed to the different impurities present in each

sample [62]. The differing porosities of the two types of limestone in the study of Martínez et al. [28] may also have influenced the activation energies. The disparity in results suggests that sample morphology plays an important role in determining decomposition kinetics.

Sample and particle sizes can also influence the reaction mechanism, as well as  $CO_2$  partial pressure. In a decomposition mechanism where the reaction advances inwards from the outside of the particle, smaller particles will decompose more quickly. Larger particles with a prolonged calcination time will begin to sinter, leading to decreased porosity, increased  $CO_2$  diffusional resistance and lower active surface areas [95]. It has been suggested that the slower calcination reaction rates at higher  $CO_2$  partial pressures mean that the reaction mainly depends on available active surface area, so chemical reaction control is dominant. At lower  $CO_2$  partial pressures, particle diffusion becomes more dominant. This would increase the influence of the sample size (interparticle transport) and individual particle sizes (intraparticle transport), meaning that the reaction could be mass transport controlled [94]. However, Martínez et al. found that particle size did not influence calcination rates, suggesting that internal mass transfer was negligible at the specified sizes (~60 µm) [28]. Dai et al. used larger particles (~0.8 mm diameters) and were able to conclude from the obtained kinetic parameters that the particles were not severely affected by intraparticle mass transfer for one form of limestone, although tests with another limestone with larger diameters (~1.7 mm) indicated mass transfer limitations on the reaction rate (see Table 2) [96].

Additionally, some of the studies suggest that there is a correlation between the method of kinetic analysis (type of approximation used) and the reaction mechanism obtained. For instance, all analyses performed by Maitra et al. using the CR integral approximation suggest that the reaction mechanism is F1 [66], while when the A&S approximation is used the suggested reaction mechanism is D2 or D4 [51], even for different alkaline earth metal carbonates.

### 10. Carbonation of CaO-Based Systems

Carbonation kinetics are typically evaluated by carrying out several experiments at different isothermal temperatures and/or under different  $CO_2$  partial pressures. Arrhenius plots are then produced using data points from different experimental conditions, and the kinetic parameters thus evaluated. Expressions can also be developed for the kinetic and diffusion rate constants using the models described in Section 8.

A summary of experimental conditions,  $E_a$  and reactions rates/constants are summarized for the CaO-based materials in Table 3. As kinetic and diffusion rate constants are a function of temperature, values are average rate constants over the carbonation isotherms are given or provided at specified temperatures. Alternatively, the order of the reaction is provided. For non-morphological analyses (Friedman and apparent models), reaction rates (min<sup>-1</sup>) are provided. The following sub-sections review the literature based on morphological reaction models and are followed by a comparative discussion of carbonation modelling of CaO-based materials.

Material & Ref.	Atmosphere	Initial Sample Mass (mg) Particle Sizes	Carbonation Temperatures (°C)	Method	Kinetic Region <i>E<sub>a</sub></i> (kJ mol <sup>-1</sup> )	k <sub>s</sub> , (m <sup>4</sup> mol <sup>-1</sup> s <sup>-1</sup> )/ Reaction Order/Kinetic Reaction Rate (min <sup>-1</sup> )	Diffusion Region $E_a$ (kJ mol <sup>-1</sup> )	D (m <sup>2</sup> s <sup>-1</sup> )/Reaction Order/Diffusion Rate (min <sup>-1</sup> )
CaO [86]	N <sub>2</sub> /CO <sub>2</sub> (0.2–0.4 atm)	1.3 Particle sizes: 81 & 137 μm	500-725	RPM	0	$\begin{array}{c} 5.95 \times 10^{-10} \ \mathrm{m^4 \ mol^{-1} \ s^{-1}} \\ \mathrm{CO_2} < 10\% : \ \mathrm{F1} \end{array}$	<961°C: 89 >961°C: 180	$0.0595 \text{ cm}^4 \text{ gmol}^{-1} \text{ s}^{-1}$
IL KL [35]	Air/CO <sub>2</sub> (0.01–0.1 MPa CO <sub>2</sub> )	5–20	550–750	RPM	IL: 21.3 KL: 19.2	$\begin{split} \text{IL:} & 5.559 \times 10^{-10} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1} \\ & \text{KL:} \\ & 5.293 \times 10^{-10} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1} \\ & \text{F1} (\text{pCO}_2 < 100 \text{ kPa}) \\ & \text{F0} (\text{pCO}_2 > 100 \text{ kPa}) \end{split}$	IL: 163 KL: 163	I: $3.37 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ K: $4.32 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
L [101]	CO <sub>2</sub> & O <sub>2</sub> /air mixture (5–85 kPa CO <sub>2</sub> )	3	650, 700 & 800	RPM	21.3	$3.335 \times 10^{-9} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$	140	$3.37 \times 10^{-5} \ m^2 \ s^{-1}$
Com. CaO [102]	N <sub>2</sub> /CO <sub>2</sub> (7–50% v/v CO <sub>2</sub> )	NS	550-700	RPM	46.42	CO <sub>2</sub> < 10%: F1 CO <sub>2</sub> > 10%: F0	137.7	$10^{-16} \mathrm{~cms^{-1}}$
L D [34]	N <sub>2</sub> /CO <sub>2</sub> mixture (25–80% v/v CO <sub>2</sub> )	2.9 Particle size: 38–45 μm	550-850	Pore model	-	-	L: 215 D: 187	F1 (pCO <sub>2</sub> < 10kPa) F0 (pCO <sub>2</sub> > 10kPa)
CaO/MY [21]	N <sub>2</sub> /CO, (0.005–0.015 MPa CO <sub>2</sub> )	10Particle size: 50–75 μm	500-700	RPM	28.4	$5.44 \times 10^{-6} \ \mathrm{m \ s^{-1}}$	88.7	$1.03\times 10^{-14}~{\rm m^2~s^{-1}}$
CaO/CA [87]	N2/CO2 (25%v/v CO2)	25	550-650	Simplified RPM	-	-	96.01	NS
L [16]	N <sub>2</sub> /CO <sub>2</sub> (0.002–0.01 MPa)	15	NS	Homogeneous particle model	NS	$3.2-8.9 \times 10^{-10} \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$	-	-
CaO [80]	N <sub>2</sub> /CO <sub>2</sub> , (14%v/v CO <sub>2</sub> )	8–10 Particle size: 20 μm	515–743	Rate (nucleation) model	NS	$1.33 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ (515 °C)	-	-
CaO [103]	He/ CO <sub>2</sub> , (2–30 kPa CO <sub>2</sub> )	10	650	Surface nucleation & isotropic growth model	Temperature coefficient: 23.15	$5.9\times 10^{-5}\ m^3\ s^{-1}$	-	-
CaO [79]	N <sub>2</sub> /CO <sub>2</sub> (1–11.7 atm)	3 Particle size: 15–20 μm	550-1100	Grain model	-	-	238	$6.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} (1000 ^\circ\text{C})$
L D [59]	N <sub>2</sub> /CO <sub>2</sub> mixture (25–80% <i>v</i> / <i>v</i> CO <sub>2</sub> )	2.9 Particle size: 38–45 μm	550-850	Grain model (intrinsic rate constants)	L: 29 D: 24	F1 (pCO <sub>2</sub> < 10 kPa) F0 (pCO <sub>2</sub> > 10 kPa)	-	-
CaO/MY [21]	N <sub>2</sub> /CO, (0.005–0.015 MPa CO <sub>2</sub> )	10 Particle size: 50–75 μm	500-700	OGM	32.3	$1.67\times10^{-5}~{\rm m/s}$	113.1	$2.74\times 10^{-13}\ m^2\ s^{-1}$
CaO [57] Data from [86] & [104]	N <sub>2</sub> /CO <sub>2</sub> (0.2–0.4 atm)	1.3 5–20	500-725	Apparent model		0.858 min <sup>-1</sup> (650°C)	$ \begin{array}{c} [86] \ 102.5 \\ A \ ({\rm s}^{-1}): \ 2.33 \times 10^5 [104] \\ 189.3 \\ A \ ({\rm s}^{-1}): \ 1.57 \times 10^{10} \end{array} $	0.375 min <sup>-1</sup> (650 °C)
CaO [46]	CO <sub>2</sub>	17	~890–720 (850 isotherm)	Friedman	573-414 Average: 350	$1\times 10^{-2}~{\rm min}^{-1}$	1237	$4 \times 10^{-3} \text{ min}^{-1}$
CaO [46]	N <sub>2</sub> /CO <sub>2</sub> (25 % <i>v</i> /v CO <sub>2</sub> )	17	~775–500 (650 isotherm)	Friedman	262–149 Average: 205	$8 \times 10^{-3} \mathrm{min}^{-1}$	269	$2 \times 10^{-3} \text{ min}^{-1}$

**Table 3.** Classification of kinetic models for reaction mechanisms. NS = not specified.

Acronyms: Com.: Commercial;  $k_s$  (kinetic control reaction rate constant); D (product layer diffusion constant); L: Limestone; D: Dolomite IL: Imeco limestone; KL: Katowice limestone; MY: Mayenite; CA: Calcium Aluminate.

#### 10.1. Pore Models, Homogeneous Particle Models and Rate Equation Theory

Bhatia and Perlmutter studied the effects of the product layer on carbonation kinetics and examined a range of experimental conditions, including temperature, gas composition and particle size [86]. The initial rapid chemical reaction was found to follow F1 at low CO<sub>2</sub> partial pressures ( $pCO_2 < 10\%$ ) and the  $E_a$  was established to be 0 kJ mol<sup>-1</sup>. Grasa et al. applied the RPM (see Section 8.2) to estimate the kinetic parameters for two types of limestone [35].  $E_a$  values of approximately 20 kJ mol<sup>-1</sup> were obtained and the reaction was found to be F1 up to  $pCO_2 = 100$  kPa.  $E_a$  of the diffusion region was approximately 160 kJ mol<sup>-1</sup> for both materials. A further study obtained the kinetic parameters under recarbonation conditions [101]. A simplified RPM was used by Nouri et al. to model carbonation of limestone [102], which showed a similar relationship between reaction order and  $pCO_2$  to Bhatia and Perlmutter [86], although  $E_a$  in the kinetic control region was larger(~47 kJ mol<sup>-1</sup>). Values of  $E_a$  in the diffusion region were calculated to be ~140 kJ mol<sup>-1</sup> [102].

Sun et al. proposed a new pore model to describe the entire carbonation period, tracing the pore evolution along with the reaction [34]. For both limestone and dolomite samples (see Table 3), intrinsic kinetic data from a previous study [59] were utilized. In this case, F0 was identified at  $pCO_2$  greater than 10 kPa.

Zhou et al. studied the kinetics of a synthetic CaO-based sorbent supported with 15 wt% mayenite  $(Ca_{12}Al_{14}O_{33})$  using the RPM and the results were compared with those obtained using the OGM [21]. For the RPM model, the conversion was also divided into the two typical regions: kinetic and diffusion control.  $E_a$  in the kinetic control region was similar to that of limestone (~28 kJ mol<sup>-1</sup>), but was much lower in the diffusion region (89 kJ mol<sup>-1</sup>). The model was used to simulate the extent of carbonation conversion/CO<sub>2</sub> uptake, and showed a good fit with experimental data. Compared to the limestone analyzed in the other studies, values of  $k_s$  were seen to be approximately one order of magnitude smaller. Values of *D* were significantly smaller compared to the limestone in other studies [35,101] (see Table 3). Jiang et al. used a simplified RPM to evaluate the kinetics of a calcium aluminate-supported CaO-based synthetic sorbent, and the diffusion region was also found to be lower than those of limestone/CaO [87].

Grasa et al. used a more basic model based on the homogeneous particle model to values of  $k_s$  with cycling, which was also a function of specific surface area [16]. The values determined for  $k_s$  were very similar to those calculated using the RPM by Bhatia and Perlmutter [86].

A nucleation model based on rate equation theory was used by Li et al. [80] to determine kinetic parameters, but the different underlying assumptions mean it cannot be directly compared with models such as RPM and particle models. Rouchon et al. developed a surface nucleation and isotropic growth kinetic model to determine the effects of temperature and  $CO_2$  partial pressure on the kinetic control region, which they described using several reaction steps [103]. They obtained a temperature coefficient which was a sum of the intrinsic activation energy and the enthalpies of reaction of two steps:  $CO_2$  adsorption on the CaCO<sub>3</sub> surface and the external interface reaction with the creation of an interstitial  $CO_2$  group in the CaCO<sub>3</sub> phase [103].

The effects of other gases on carbonation kinetics has also been examined (results are not included in Table 3). Nikulshina et al. tested the effects of water vapor on the kinetics of CaO carbonation as part of a thermochemical cycle to capture  $CO_2$  using CST [105]. Carbonation reaction kinetics were fitted using an unreacted shrinking core model which encompassed both the intrinsic chemical reaction followed by intra-particle diffusion. Kinetic parameters were determined with and without the presence of water vapor. No Arrhenius-based dependency was obtained for the diffusion region and hence kinetic parameters were not determined. Water vapor was found to enhance the carbonation of CaO, which results in a reaction rate which is 22 times faster than the dry carbonation of CaO [105]. Water vapor was also shown to enhance the carbonation rate in studies of mesoporous MgO [106].

Symonds et al. examined the effects of syngas on the carbonation kinetics of CaO in the kinetic control region by applying a grain model [107]. The presence of CO and  $H_2$  were found to increase the reaction rate by 70.6%, which was attributed to the CaO surface sites catalysing the water-gas shift

reaction and increasing the local  $CO_2$  concentration. Activation energies also increased from 29.7 to 60.3 kJ mol<sup>-1</sup>, which was postulated to be due to the formation of intermediate compounds [107].

# 10.2. Grain Models

Mess et al. studied product layer diffusion during the carbonation reaction, using microscopy to confirm the formation of a nearly homogeneous product layer [79]. The carbonation rate was described by a model where CO<sub>2</sub> pressure-independent grain boundary diffusion and diffusion through the carbonate crystals act in parallel. An  $E_a$  of 238 kJ mol<sup>-1</sup> was established for the diffusion region.

Sun et al. used a grain model to develop an intrinsic kinetic model for both limestone and dolomite sorbents with the aim of determining the  $E_a$  of the kinetic control region [59]. They argued that the zero activation energy proposed by Bhatia and Perlmutter [86] was unlikely. Values of  $E_a$  between 24–29 kJ mol<sup>-1</sup> were established. The reaction order was found to be dependent on the CO<sub>2</sub> partial pressure, and a shift in reaction order (from F1 to F0) was observed in the experimental results when the difference between total CO<sub>2</sub> pressure and at equilibrium exceeded 10 kPa. The authors also calculated a kinetic control  $E_a$  of 41.5 kJ mol<sup>-1</sup> using the equilibrium constant proposed by Baker et al. [108]. However, they suggest that the higher value is due to the assumption of chemical equilibrium at the initial point of carbonation being invalid [59]. Zhou et al. used an OGM (see Section 8.3) to study a synthetic CaO-based sorbent supported with 15 wt% mayenite and compared the results with the RPM [21] (see Section 10.1). For the OGM model, both the kinetic and diffusion control region were considered as a whole using an adaptation of the method of Szekely and Evans [88]. Both the RPM and OGM modelled the carbonation of the sorbent accurately. An  $E_a$  of ~32 kJ mol<sup>-1</sup> was calculated in the kinetic control region, similar to that of limestone/CaO. In the diffusion control region, a lower value of ~113 kJ mol<sup>-1</sup> was calculated [21]. Values of  $k_s$  and D were approximately one order of magnitude higher when calculated with the OGM.

Modelling extent of conversion is also a focal point of carbonation kinetics, specifically for carbon capture applications. Butler et al. used a modified grain model for  $CO_2$  adsorption modelling through pressure swing cycling [109]. They found that extent of conversion in the kinetic control region to be influenced by  $CO_2$  pressure, while reaction rates in the diffusion region were independent of pressure and temperature [109]. Yu et al. also modelled extent of conversion using an adapted CGS model for the carbonation of a synthetic CaO-based sorbent supported by a framework of 25% MgO [110]. Conversion was found to be dependent on reaction temperature and morphology, and heat transfer due to convection in the particles was significant [110]. Liu et al. investigated the kinetics of  $CO_2$  uptake by a synthetic CaO-based sorbent supported with mayenite using an OGM, which was found to be accurately account for changes in rate and extent of reaction [111]. As these studies used kinetic parameters from previous literature studies, they are not included in Table 3.

#### 10.3. Apparent and Isoconversional Models

Lee used an apparent (semi-empirical) model for carbonation using literature-reported data [86,104] for CaO carbonation conversion [57]. A kinetic analysis was carried out for both the kinetic control and diffusion regions. The carbonation conversion was found to be dependent on k, indicating that k can be regarding as the intrinsic chemical reaction rate constant [57] as well as the reaction constant in the diffusion region, although the different units mean that it cannot be directly compared with  $k_s$  for pore models and grain models.  $E_a$  values in the kinetic control region were somewhat larger than the results in the literature (~72 kJ mol<sup>-1</sup>). This was attributed to intra-particle diffusion limitations due to the relatively low temperatures of carbonation and hence low carbonation conversion [57]. Diffusion  $E_a$  of one of the limestones (using [86]) was found to be lower than average (~100 kJ mol<sup>-1</sup>), while the other had a more typical value of  $E_a$  (~190 kJ mol<sup>-1</sup>). It was postulated that this was due to the microporous material's susceptibility to pore plugging, which would limit diffusion [104].

Fedunik-Hofman et al. used an isoconversional (Friedman) method to determine kinetic parameters and reaction rates over the course of the carbonation reaction under two different

experimental atmospheres (see Table 3 and Figure 13) [46]. The gradient of the curve of  $E_{\alpha}$  vs  $\alpha$  suggests that the reaction is initially controlled by surface chemical reaction kinetics, before becoming diffusion controlled [44]. Under 100% CO<sub>2</sub>, the  $E_a$  ranged from 573–414 kJ mol<sup>-1</sup> in the kinetic control region, while a peak activation energy of 1237 kJ mol<sup>-1</sup> was obtained for the diffusion region. Under an atmosphere of 25% v/v CO<sub>2</sub>,  $E_a$  values between 262–149 kJ mol<sup>-1</sup> were calculated for the kinetic control region.  $E_a$  reaches a maximum of 269 kJ mol<sup>-1</sup> around the transition to diffusion control. These values are much higher than typical. An overestimation of the  $E_a$  could be the result of the incomplete conversion of the carbonation reaction, as a significant percentage of the material is unutilized CaO which does not participate in the carbonation reaction [46]. As for calcination in N2, the  $E_a$  is found to be closer to the enthalpy of reaction due to greater morphological variation [46]. Reaction rates were 1–3 orders of magnitude smaller than those of Lee et al. [57], indicating slower reaction kinetics.



**Figure 13.** Isoconversional values of  $E_{\alpha}$  for CaCO<sub>3</sub>: (**a**) carbonation: under 100 v/v% CO<sub>2</sub>. (**b**) under 75 v/v% N<sub>2</sub>/ CO<sub>2</sub> [46].

## 10.4. Comparison of Carbonation Kinetic Analysis

In the kinetic control region,  $E_a$  has been reported to be independent of material properties, while morphological effects have a greater influence in the diffusion control region, leading to a greater disparity in diffusion activation energies [13]. For the kinetic control region, activation energies of ~20 [35] –29 kJ mol<sup>-1</sup> [59] were obtained using the morphological models for natural limestone, while for commercial CaO a larger value of 46 kJ mol<sup>-1</sup> [102] is obtained. Synthetic sorbents supported with calcium aluminate mostly indicate  $E_a$  of ~30 kJ mol<sup>-1</sup> [21,59]. This indicates that material properties in fact exhibit an effect on values of  $E_a$  in the kinetic control region.

The studies which show significantly greater  $E_a$  values used apparent and isoconversional methods [57]. This can be attributed to an overestimation of  $E_a$  due to morphological variations in the material. In particular, a 100% CO<sub>2</sub> atmosphere accelerates the sintering of particles [15], which could exacerbate the morphological changes in the study by Fedunik-Hofman et al. [46]. It is also possible that the rapid nature of the kinetic control region is not accurately modelled by these methods due to data fitting limitations. The rapid reaction leads to consistently high values of  $d\alpha/dT$  over the short reaction. For the Friedman method, this results in a high gradient in graphs of  $\ln(\beta \ d\alpha/dT)$  versus *T*, and hence higher  $E_a$  values [46].

Lower  $E_a$  values are generally determined for dolomite, which is attributed to structural differences in the materials. MgO in dolomite could act as an impurity and reduce strain energy between grains and in this way reduce effective activation energy [59]. For synthetic CaO/calcium aluminate lower values of ~90 [21] to 113 kJ mol<sup>-1</sup> [21] are reported. A possible explanation for the lowered  $E_a$  in the supported materials is that the introduction of the calcium aluminate introduces defects through which the diffusing species can travelling, reducing effective  $E_a$ .

There is some disagreement regarding the reaction order for the kinetic control region. Some studies find the reaction to be F1 up to a  $pCO_2$  of 10 kPa [59,86,102]. However, Grasa et al. report that the carbonation reaction is F1 up to 100 kPa, before transitioning to F0 at higher CO<sub>2</sub> partial pressures [35]

For diffusion,  $E_a$  values range between ~100 [57] and ~270 kJ mol<sup>-1</sup> [57] for CaO and natural limestones. Not only is there a disparity in  $E_a$ , there is also a lack of consensus on the diffusion mechanism (gas or solid state diffusion), as well as the diffusing species (CO<sub>2</sub> gas molecules, CO<sub>3</sub><sup>2-</sup> ions or O<sup>2-</sup> ions) [60]. It is also suggested that the diffusion mechanism may change depending on whether the sample is porous or non-porous. If the sample material is porous CaO, the kinetic analysis tends to produce higher values of  $E_a$  and the suggested mechanism is CO<sub>2</sub> gas diffusing through the CaCO<sub>3</sub> product layer [60], while when the sample is non-porous CaO, this suggests that the reaction is governed by the diffusion of CO<sub>2</sub> on grain boundaries [60]. The mechanism may also change with temperature. At low temperatures (< 515 °C), Bhatia and Perlmutter conclude that the diffusion process cannot be governed by the diffusion of the CO<sub>2</sub> gas molecules, but instead by solid-state diffusion of the CO<sub>3</sub><sup>2-</sup> anion [86].

The effect of different experimental conditions on the kinetic parameters should also be considered. Sample mass has been found to have an influence on experimental TGA curves and hence on kinetic parameters due to heat and mass transfer effects [112,113]. Initial sample sizes less than 10 mg have therefore been recommended by Koga et al. for decomposition of CaCO<sub>3</sub> using TGA [114]. However, undesired effects due to diffusion resistance through the CaCO<sub>3</sub> samples became apparent only using initial samples masses ~40 mg [114]. Hence, the studies in Table 3 using initial sample sizes <25 mg should not be discounted. Particle sizes will also be influential due to mass transport effects (see Section 9). It has been suggested that if particle size is sufficiently small, the carbonation reaction will theoretically be completed within the chemical reaction control region and no diffusion region will take place [115], which has not been observed in these literature experiments. Several studies reported that varying particle sizes within the ranges specified did not appreciably affect reaction kinetics [21,86] and Sun et al. found that limiting particle sizes to smaller than 53–63 µm eliminated the effects of intraparticle mass transfer [59].

## 11. Recommendations and Conclusions

Kinetics of solid-gas reactions are reviewed here together with their application to carbonate looping reactions used in CCS and TCES. The different methods were reviewed, and the following recommendations can be made:

- Quality of the measured data is critical to obtain reproducible results and lead to similar conclusions. It is important that TGA analysis is performed carefully for kinetic analysis and experimental errors should be detailed.
- Different kinetic methods should be performed in parallel and compared against each other. In particular, it has been found to be very useful to perform model-free methods (e.g., Friedman) before model-fitting methods (integral approximations or master plots). This combination should be considered for further studies of solid-gas reactions showing a single step. This recommendation is supported by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee, which recommends the use of multi-heating rate experiments over single heating-rate experiments [2].
- If the previous methodology cannot reproduce the experimental results, then a generalized method should be performed. In addition, the generalized methodology should be considered when the kinetic analysis is performed on particles instead of powder form samples and where simultaneous multi-step reactions are applicable, as the previous methods will lead to the wrong conclusions.

After the kinetics review, a revision of kinetic methods applied for carbonate looping systems has been given, comprehensively comparing the different methodologies. For both calcination and carbonation reactions, disparate results have been observed and the following recommendations can be made to reduce future inconsistency:

- For calcination reaction studies the disparity in results suggests that sample morphology plays an important role. Overall, the use of a multiple heating-rate isoconversional methods, such as Friedman, should be carried out to validate the model-fitting methods. This will allow comparison of the average values of  $E_i$  from model-fitting with isoconversional values of  $E_{\alpha}$ , which could reveal several reaction steps. The model-free method of determining a reaction mechanism can then be employed, which could reduce the disparity in reaction mechanisms observed.
- For carbonation reaction studies, generalized models show better representation of the phenomena shown in the two reaction regions. For the kinetic control region, it is recommended that morphological methods of kinetic analysis such as pore models and grain models are recommended, as opposed to apparent or isoconversional methods. For the diffusion region, the kinetic parameters obtained are seen to vary considerably based on material properties. Therefore, material characterization such as porosimetry and scanning/transmission electron microscopy is recommended prior to the kinetic analysis. Nonporous materials evidently will not suit the use of pore models, while microporous materials may be better suited to the use of an apparent model rather than pore models.

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# Nomenclature

Α	Pre-exponential factor, min <sup>-1</sup>
$A_i$	Model-fitting estimate of pre-exponential factor, min <sup>-1</sup>
$A_0$	Model-free estimate of pre-exponential factor, min <sup>-1</sup>
С	Concentration of diffusing gases, mol m <sup>-3</sup>
$C_b$	Bulk concentration of diffusing gases, mol m <sup>-3</sup>
Ce	Equilibrium concentration of diffusing gases, mol $m^{-3}$
D	Product layer diffusion constant, m <sup>2</sup> s <sup>-1</sup>
Ea	Activation energy, kJ mol <sup>-1</sup>
$E_{\alpha}$	Isoconversional activation energy (function of $\alpha$ ), kJ mol <sup>-1</sup>
$E_i$	Model-fitting estimate of activation energy, kJ mol <sup>-1</sup>
$E_0$	Model-free estimate of activation energy, kJ mol <sup>-1</sup>
$F_n$	Chemical reaction rate for nucleation, mol $m^3 s^{-1}$
$G_D$	Function of the particle symmetry, dimensionless
$\Delta H_r$	Reaction enthalpy, kJ mol <sup>-1</sup>
J	Diffusion flux, mol m <sup><math>-2</math></sup> s <sup><math>-1</math></sup>
k(T) or k	Reaction rate constant, min <sup>-1</sup>
<i>k</i> <sub>n</sub>	Chemical reaction rate constant for nucleation, $m^3 s^{-1}$
$k_s$	Kinetic reaction rate constant, m <sup>4</sup> mol·s <sup>-1</sup>
$L_0$	Pore length per unit volume (m $m^{-3}$ )
М	Molar mass, g mol <sup>-1</sup>
$m_0$	Initial sample mass, g

$m_f$	Sample mass after reaction completion, g
$m_t$	Sample mass at time t, g
N <sub>molecular</sub>	Avogadro's number
Р	Total pressure, kPa
$P_0$	Equilibrium pressure, kPa
r	Particle radius, m
R	Universal gas constant, kJ mol <sup><math>-1</math></sup> ·K <sup><math>-1</math></sup>
S	Surface area of the reactional zone, m <sup>2</sup>
$S_m$	Kinetic and morphological parameter, m <sup>2</sup> mol <sup>-1</sup>
S <sub>0</sub>	Initial specific surface area of the reactional zone, $m^2 m^{-3}$
$\Delta S_r$	Reaction entropy, kJ mol <sup>-1</sup> K <sup>-1</sup>
t	Time, s
Т	Temperature, K
w	Mass fraction of solid contributing to reaction, dimensionless
X(t)	Carbonation conversion after t time, dimensionless
$X_u$	Ultimate carbonation conversion, dimensionless
Greek letter	5
α	Exent of conversion, dimensionless
β	Heating rate, K min <sup>-1</sup>
$d\alpha/dt$	Reaction rate, s <sup>-1</sup>
dξ/dt	Absolute speed of reaction, mol s <sup>-1</sup>
ε	Initial sorbent porosity, dimensionless
ρ	Density, kg m <sup>-3</sup>
φ	Thermodynamic parameter mol $m^{-2} c^{-1} P_{aaction}$ rate for surface reaction mol $m^{-2} c^{-1}$
$v_s$	mermouynamic parameter, morini s Reaction rate for surrace feaction, morini s
ψ	Structural parameter, dimensionless

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