

Reaction Kinetics for the Synthesis of Lithium-TITANATE (Li_2TiO_3) By Solid State Reaction

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ABSTRACT

Fusion of deuterium and tritium is being considered to produce energy to meet the future energy demand. Deuterium is available in nature whereas, tritium is not. Tritium may be produced by the nuclear reaction of neutron with lithium-6 (Li^6) isotope and for this, lithium-based ceramics, enriched by Li^6 isotope are considered. Lithium titanate (Li_2TiO_3) is one such Li-based ceramic material considered for tritium generation for future thermonuclear fusion reactors. Li_2TiO_3 will be used in the form of spherical pebbles with some specific properties. Sol-gel, solution-combustion and wet process have been developed to synthesize and fabricate Li_2TiO_3 pebbles. The common drawback of all these process is that the effluents or off gases produces in these processes may contain Li^6 , which is not acceptable. A solid state reaction process has been developed in which Li_2TiO_3 is synthesized by reacting lithium carbonate with titanium dioxide, pebbles are fabricated by using extrusion and spherodization and finally, pebbles of desired specifications are obtained by sintering. For large scale production; the process must to be optimized with respect to reaction parameters; for which the required kinetic data are not available. In a previous study the thermo-gravimetric and differential thermal analysis (TG-DTA) was used to study the reaction parameters. In the present study, the kinetic parameters have been determined from the reported TG-DTA data.

Keywords: Solid state reaction, TG-DTA, lithium-titanate, fusion reaction, reaction kinetics.

1. INTRODUCTION

In the near future the most difficult problems our peaceful world will face in finding the 'secured, safe, clean and economical energy source'. The world population has grown up excessively, from 1 billion in 1930 to 8 billion in 2010 and it is expected to cross 10 billion in 2060 (www.worldometers.info/world-population, geography.about.com/od/obtainpopulationdata/a/worldpopulation.htm). The per capita energy consumption has gone up from 6 BOE (barrel equivalent of oil) per person per year in 1960 to 11 BOI per person per year (Energy, Electricity and Nuclear Power Estimates for the Period up to 2030, Reference Data Series No.1, IAEA, 2009, Helium-3 Fusion Reactors – A Clean and Safe Source of Energy in the 21st Century, A Technical Report, Wisconsin Centre for Space Automation and Robotics, 1993). To meet this energy demand, we have to explore possible various alternative energy sources and fusion reaction is one such energy source.

Lithium-containing ceramics viz., lithium oxide (Li_2O), lithium aluminate (LiAlO_2), lithium-titanate (Li_2TiO_3), lithium ortho-silicate (Li_4SiO_4) and lithium zirconate (Li_2ZrO_3) are considered as tritium producing materials for fusion reactors (Johnson et al., 1988, Van Der Laan et al., 2000). Li_2TiO_3 is considered one of most suitable tritium producers due to its chemical inertness, thermal stability, low tritium solubility etc. (Mikkelsen and Pseudobinary, 1980; Miller et al., 1994; Ying et al., 2007,).

Li_2TiO_3 is not available in nature. Hence, it needs to be synthesized. It can be synthesized by using lithium

oxide (Li_2O) and titanium dioxide (TiO_2) (Kataoka et al., 2009; Kleykamp, 2001). The system $\text{Li}_2\text{O-TiO}_2$ contains four stable phases: Li_4TiO_4 , Li_2TiO_3 , $\text{Li}_5\text{Ti}_5\text{O}_{12}$ and $\text{Li}_2\text{Ti}_3\text{O}_7$, and one metastable phase, H. Li_2TiO_3 undergoes an order-disorder phase transition at 1488 K. Li_2TiO_3 forms an extensive range of solid solution between ~ 44 and 66 mole % TiO_2 and a limited range of solid solution between ~ 47 and 51% TiO_2 (Kataoka et al., 2009; Kleykamp, 2001). Mikkelsen (1980) determined the pseudo binary phase diagram of $\text{Li}_2\text{O-TiO}_2$ system with 50 to 100 mol % TiO_2 by DTA, microscopy, and X-ray analysis and found that a solid solution formed based on Li_2TiO_3 from 50 to 65 mol % TiO_3 at > 1203 K. Kataoka et al. (2009) successfully produced a single crystal of Li_2TiO_3 of size : 5.0 mm x 5.0 mm x 0.5 mm by a flux method. Kleykamp (2001) determined the enthalpy, heat capacity and transformation of different phases of Li_2TiO_3 .

Till date, much work has been done in the synthesis and fabrication of Li_2TiO_3 pebbles, characterization; tritium release behavior and database for properties are reported (Renoult et al., 1995). Various investigators proposed different methods for the synthesis of Li_2TiO_3 . The most commonly adopted methods are, solution combustion, wet and sol-gel process (Renoult et al., 1995; Izquierdo and West, 1980; Deptuła et al., 2009; Xiangwei et al., 2008; Xiangwei et al., 2009). In all these process high purity Li_2TiO_3 may be produced. But, there are some disadvantages in all these processes. One major drawback in these processes is that high volume of liquid or gaseous waste is generated which contains Li^6 isotope. Recovery of Li^6 from the waste stream is a difficult task,

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which prevents all these methods to effectively utilize resources (Xiangwei et al., 2008).

Mandal et al. have developed the solid state reaction process to synthesize Li_2TiO_3 (Mandal et al. (2010, Mandal et al., 2012). In this process equimolar Li_2CO_3 and TiO_2 are reacted at 1023 K to produce single phase Li_2TiO_3 . No waste, except carbon dioxide gas is generated, which is free from Li^6 .

Generally, the kinetics of solid state reactions cannot be assumed to follow simple rate laws that are applicable to liquid or gas phase reactions. However, the study of reaction kinetics is important for two reasons. First of all it will help in fixing process parameters and the secondly to investigate the reaction mechanisms. One of the fundamental tenets of chemical kinetics is that no reaction mechanism can ever be proved on the basis of kinetic data alone. One may demonstrate a proposed mechanism with kinetic data. However, kinetic analysis may not be the most efficient means of determining a reaction mechanism (Maciejewski and Reller, 1987); though the kinetic data are extremely useful to draw reasonable mechanistic conclusions (Vyazovkin, 1996; Vyazovkin and Sbirrazzuoli, 1996).

The most common experimental techniques employed to study reaction kinetics of thermally activated reactions are Thermogravimetry (TG), Differential Scanning Calorimetry (DSC), and Differential Thermal Analysis (DTA) (Vyazovkin and Wight, 1997). These techniques are widely applicable to many reactions but are not chemically specific in their means of detection. In TG analysis, mass loss is measured from a sample due to gas formation as a function of time and (or) temperature during a specified heating rate. The overall reaction rate may be determined by TG corresponds to the rate of gas formation. This technique has been utilized in determining the rate of reaction. This technique has been adopted to determine the kinetic data for the synthesis of Li_2TiO_3 by solid state reaction. The experimental details and results are discussed in this paper.

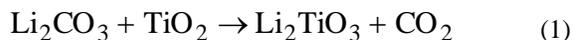
2. MATERIALS AND METHODS

2.1 Materials

- Analytical grade titanium dioxide (TiO_2) was obtained from SD Fine Chemicals, Mumbai, India.
- Lithium carbonate (Li_2CO_3) of 99.8% purity was purchased from Merck and Loba Chemicals, Mumbai, India.

2.2 Methods

Reactions between Li_2CO_3 and TiO_2 take place at the surface of their particles. So, very small particle size ($< 45 \mu\text{m}$) of both Li_2CO_3 and TiO_2 is desirable. Li_2CO_3 and TiO_2 were taken in stoichiometric (1:1 mole) ratio and milled in a planetary ball mill for 5 h. The intensely mixed and milled powders were classified in a vibratory sieve shaker. Particles (size $< 45 \mu\text{m}$) were separated and oversized particles were re-cycled to the ball mill. The mixed powders were put in alumina crucibles and small quantity of absolute methanol was added to make a paste and kept overnight. The crucibles containing a homogeneous mixture were kept in a muffle furnace. The temperature was increased to 1023 K in 2 h and constant temperature was maintained for 6 h for the reaction of Li_2CO_3 and TiO_2 to produce Li_2TiO_3 and CO_2 according to Reaction 1.



The product was cooled and milled (particles size $< 45 \mu\text{m}$) in ball mill.

Thermo-Gravimetric (TG) and Differential Thermal Analysis (DTA) techniques were used to study the decomposition of pure Li_2CO_3 and reactivity of intimately mixed powders of Li_2CO_3 and TiO_2 . The experiments were carried out in Netzsch TG-DTA (Model STA-409- PC/PG) and rate of temperature increase was set at 10 K per minute.

3. RESULTS AND DISCUSSION

3.1 TG DTA Analyses

Figure 1 shows the TG-DTA of pure Li_2CO_3 . It is observed that pure Li_2CO_3 does not have any significant weight loss until 1013 K. The sudden dip in the DTA curve indicates one endothermic peak corresponding to 1013.9 K and beginning of decomposition of Li_2CO_3 into Li_2O and CO_2 . Most of the decomposition reaction is completed by about 1423 K by which the mass loss reaches a plateau.

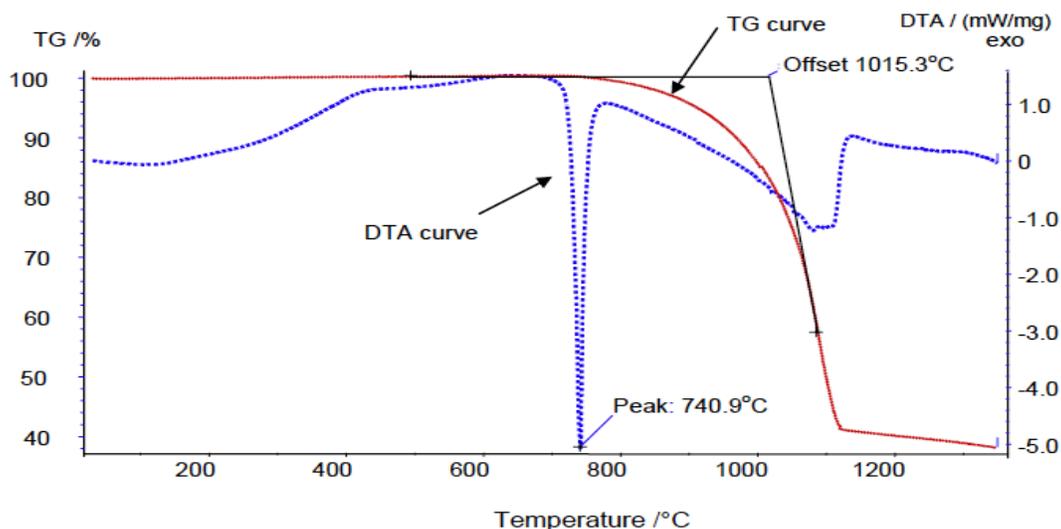


Fig 1: TG-DTA of Li_2CO_3 (30-1300°C). The temperature was ramped at 10°C per minute.

Figure 2 shows TG and DTA curves of the $\text{Li}_2\text{CO}_3\text{-TiO}_2$ system (1: 1 mole ratio). The TG-curve shows that the reaction of $\text{Li}_2\text{CO}_3\text{-TiO}_2$ mixtures starts at 803 K.

This reaction precedes the decomposition of pure Li_2CO_3 by about 413 K. Hence, Li_2CO_3 reacts with TiO_2 , before its decomposition. From the TG-DTA analysis, it was observed that the reaction is completed at 1073 K.

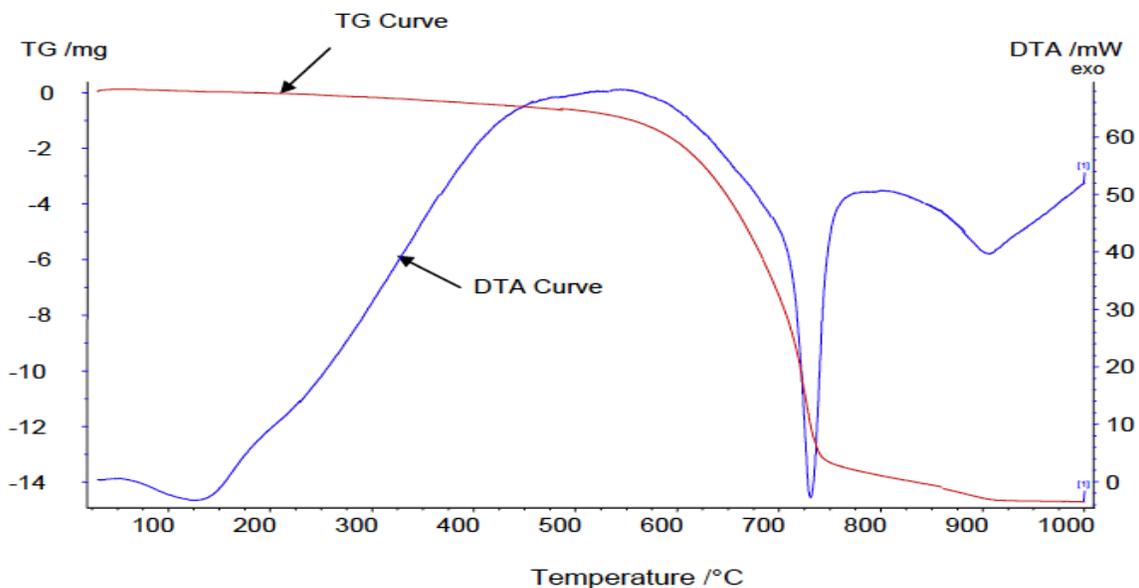


Fig 2: TG-DTA curves of $\text{Li}_2\text{CO}_3\text{-TiO}_2$ system. The temperature was ramped at 10°C per minute.

3.2 Heat of Formation

DTA provides qualitative as well as quantitative information about the formation solid Li_2TiO_3 . Figure 2 shows the DTA curve of $\text{Li}_2\text{CO}_3\text{-TiO}_2$ system. It is seen that reaction starts at 803 K and completed at 1073 K. The

information about reaction kinetics can be determined for the TG and DTA analysis.

The standard state heat of formation (ΔH_f°) of Li_2TiO_3 from Li_2TiO_3 and TiO_2 is estimated as 1670.671 kJ

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mole⁻¹. ΔH_f° of Li₂TiO₃, TiO₂ and CO₂ were taken from NIST-JANAF Thermo chemical Tables (NIST-JANAF Thermo chemical Tables).

3.3 Heat of Reaction

From TG-DTA analysis of an equimolar mixture of Li₂CO₃-TiO₂ (Figure 2), it is observed that the reaction is started at temperature at 803 K and completed at 1073 K. Area under curve within 803-1073 K has been estimated for DTA graph, which represents the energy consumed for reaction. The energy consumed by reaction was 16.972 J. The number of moles Li₂TiO₃ formed in reaction was 0.3115. So, the heat of reaction is 54.49 kJ mole⁻¹.

3.4 Rate Equation

Usually the change in extent of reaction (α) is used to study the solid state reaction kinetics:

$$\alpha = \frac{m_o - m_t}{m_o - m_\infty} \quad (2)$$

where, m_o , m_t and m_∞ are initial mass of Li₂CO₃ and TiO₂ mixture, reactant mass at time t and the mass of the product at the end of reaction.

Using the extent of reaction, the rate of reaction can be represented by,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

In Eq. (3), t represents time, T is the temperature, $k(T)$ is the temperature-dependent rate constant media and $f(\alpha)$ is a function called reaction model. In case of gas and liquid reactions $f(\alpha)$ would be simply the concentration of reactants and or products which remain same in the media at any instance, whereas in case of solid media it represent the local concentration where the reaction takes place, because in solid phase reaction molecular motion is highly restricted. Thus the reaction model $f(\alpha)$, usually plays the role of an empirical function (Vyazovkin and Wight, 1997). Several first-order, second-order, higher order and different other order reaction models are available in literature for solid phase reactions (Vyazovkin and Wight, 1997; Khawam, D. R. Flanagan, 2005).

Eq. (3) is often used in its integral form and for isothermal conditions it can be re-written as shown in Eq (4).

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha = \int_0^t k(T) dt = k(T)t \quad (4)$$

The explicit temperature dependence of the rate constant may be introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (5)$$

and

$$g(\alpha) = A \exp\left(\frac{-E_a}{RT}\right) t \quad (6)$$

where, A (preexponential factor) and E_a (activation energy) are the Arrhenius parameters, t is the time (minute), T is the temperature (K) and R is the universal gas constant (J mole⁻¹ K⁻¹).

Under non-isothermal condition, in which a sample is heated at a constant rate, the explicit temperature in Eq. (5) is eliminated through the trivial transformation:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (7)$$

Upon integration Eq. (7) gives

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) dT \quad (8)$$

where, β is a rate of increase in temperature [K min⁻¹] and A is the pre-exponential factor.

As there is no analytical solution of Eq. (8), according to the Coats-Redfern approximation (Coats and Redfern, 2009) it may be written as,

$$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (9)$$

From TG analysis (Figure 2) we can estimate α at different T and t . Figure 3 represents the variation of α with T . The nature of the curve is in agreement with the data simulated by Ebrahimi-Kahrizangi and Abbasi (Ebrahimi-Kahrizangi and Abbasi, 2008) for heating rate

10 K per minute on the basis of the Geometrical Contracting Sphere Model. As per this model,

$$g(\alpha) = 1 - (1 - \alpha)^{1/3} \quad (10)$$

Plotting left hand side of Eq. (9) versus $1/T$ the values of E_a and A have been estimated, these are 37.725 kJ mole⁻¹ and 1.496 minute⁻¹ respectively. Reaction rate can be calculated at different temperature.

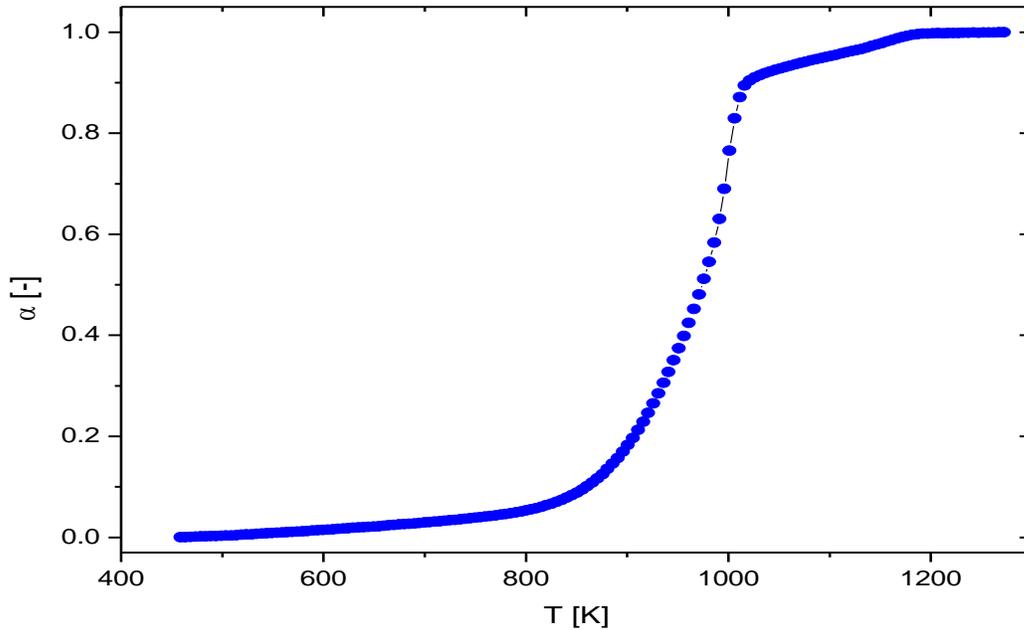


Fig 3: Variation of α with temperature.

3.5 XRD Analysis

Since wave diffraction occurs when the dimensions of the diffracting object are of the same order of magnitude as the wavelength of the incident wave, X-rays are ideally suited to probe crystal lattice structures. XRD-analysis of the synthesized Li_2TiO_3 powder and the powder from the grounded sintered pebbles were carried out. The X-ray data were taken at 2 θ scanning at the rate of 1 degree per minute

on an automated XRD unit with $\text{CuK}\alpha$ radiation and graphite monochromator, operated at 40 kV and 40 mA. Comparing the XRD results as shown in Figure 4, with the known standards in the JCPDS Powder Diffraction File (JCPD, 1986) it is confirmed the formation of Li_2TiO_3 crystals from the Reaction 1. No presence of un-reacted TiO_2 and Li_2O were found. This confirms that the Reaction 5 is completed at 1073 K.

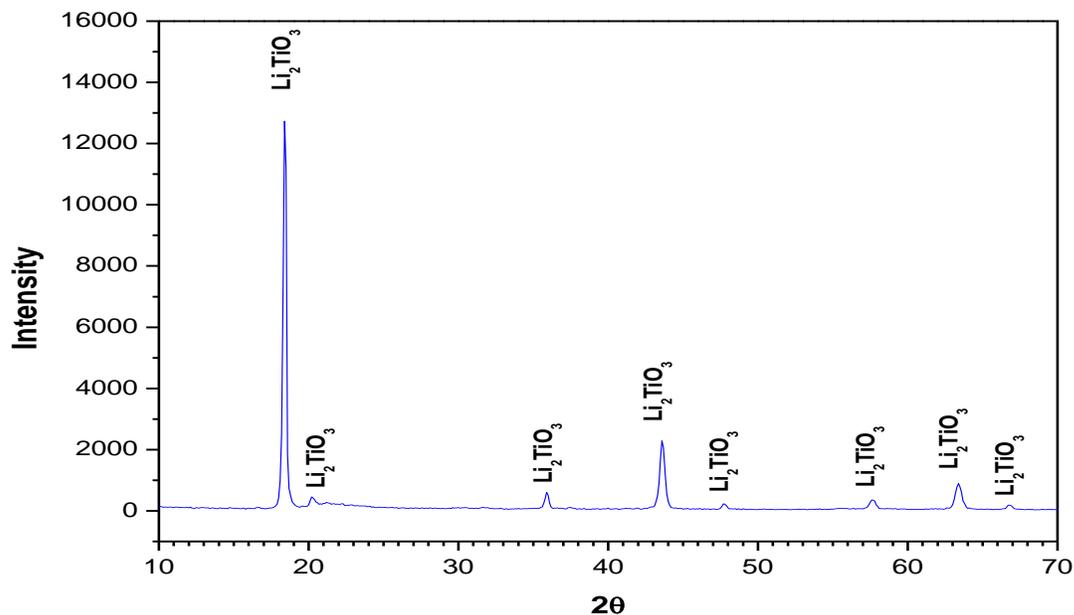


Fig 4: The XRD pattern of synthesized Li_2TiO_3 powder

4. CONCLUSIONS

In the present study the kinetic data have been determined for the solid state reaction process for the synthesis of Li_2TiO_3 by reacting TiO_2 to with Li_2CO_3 . Thermo gravimetric analysis indicates that the reaction starts before decomposition of Li_2CO_3 and is completed at 1073 K. From TG-DTA analysis kinetic parameters for the Li_2TiO_3 formation have been estimated. The XRD analysis confirmed the formation of single phase of Li_2TiO_3 .

The determined kinetic data for the formation of Li_2TiO_3 are useful for the optimization of process parameters and also for the design of a large scale or

continuous synthesis facility. As the solid state reaction process straight forward with 100 % resource utilization and no waste (except carbon-dioxide gas which is free from Li^6) is produced, the process may be considered for large scale production of Li_2TiO_3 these kinetic data are very useful.

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Glossary

| Symbols | |
|---------|--|
| A | pre-exponential factor $[(\text{mol m}^{-3})^{1-n} \text{ s}^{-1}]$ n is the order of reaction |
| E | activation energy $[\text{kJ mol}^{-1} \text{ K}^{-1}]$ |
| f | a function, (e.g., $f(x)$ is a function of x) [-] |
| g | a function (e.g., $g(y)$ is a function of y) [-] |
| k | rate constant $[(\text{mol m}^{-3})^{1-n} \text{ s}^{-1}]$, n is the order of reaction, $k(T)$ is the temperature-dependent rate constant |

| | |
|---------------|--|
| m | mass (suffix o stands for initial, t for mass at time t , and ∞ for after infinite time) [kg] |
| R | universal gas constant [$\text{kJ mol}^{-1} \text{K}^{-1}$] |
| t | time [s] |
| T | temperature [K] |
| Greek letters | |
| α | extent of reaction, defined in Equation 2 [-], $f(\alpha)$ is a function called the reaction model [-] |
| β | rate of increase in temperature [K s^{-1}] |

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