

# A generalized solid state kinetic expression for reaction interface-controlled reactivity

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## ABSTRACT

The ICTAC-recommended approach was used to characterize the gasification of high-purity, highly crystalline, large natural graphite flakes in oxygen. The average activation energy was found to be  $157.7 \pm 4.2 \text{ kJ mol}^{-1}$ . The graphite properties and the simple gasification reaction taking place make this an ideal material for the study of reaction interface-controlled reactivity. Based on simple structural and geometrical observations, it was expected that the conversion function would be that of a shrinking disc. However, the experimental conversion function exhibited a behaviour which could not be linked to any of the commonly established reaction models.

A factor contributing to this disconnection is the use of an arbitrary scaling procedure in classic solid state kinetics. A more integrated approach has recently been proposed in the literature with the potential for reconciling disparate models into a single comprehensive scheme. A generalization of the classic solid state kinetic expressions for interface-controlled reactivity is proposed which fits into the integrated approach. It is based on fundamental considerations for the subset of reactions in which reactivity is controlled by the reaction interface alone. The fundamental nature of the approach yields an expression for which all the variables are directly measurable, without any assumptions regarding the conversion function.

The generalized conversion function will always start at a value of one, making interpretation and direct comparison of any active surface area (ASA) progression possible. Visual observations indicate the growth of defect structures within the macro graphite flakes, leading to an increase in ASA. This leads to a behaviour resembling nucleation and growth, despite the interface-controlled reaction taking place on a disc-shaped solid. The random nature of the oxidized flake microstructure makes it difficult to develop representative analytical models for this behaviour.

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## 1. Introduction

The solid state kinetic approach has been widely applied to the thermal decomposition of solids [1]. These reactions are fundamentally different from classic homogeneous reactions. For example, the concept of concentration is usually not applicable to the solid reactant. Crystalline solids contain defective or boundary regions which are more susceptible to chemical change than identical material elsewhere within the solid. This leads to heterogeneous reaction behaviour in which the kinetics are usually not determined by the amount of reactant available.

These reactions frequently occur only within a thin contact zone, the reaction interface, which advances into the remaining reactant. The zone undergoing reaction may be the total surface area, as in

the case of a sphere, or a specific surface region, as in the case of a disc reacting only at the edges, or even, in the case of a porous solid, the pore surface area. For the purpose of this investigation, all three will be referred to as the active surface area (ASA). Thus the reaction rate is fundamentally determined by geometrical variations of the ASA, under the assumption that the surface is homogeneous and the material is isotropic.

However, in most solid state decompositions other complex phenomena are also occurring, such as melting, sintering, etc. The situation is further complicated by the presence of different crystal defects and impurities. The solid state approach has also been applied to other solid transitions, such as crystallization or crystallographic transitions, and autocatalytic reactions, such as the thermal decomposition of potassium permanganate [2]. These reactions are subject to other rate-controlling factors such as nucleation and growth, or in some cases where a product barrier layer is formed, diffusion through this layer.

Graphite is a solid reactant with a well-known crystal structure that reacts directly with gaseous oxygen to produce gaseous carbon

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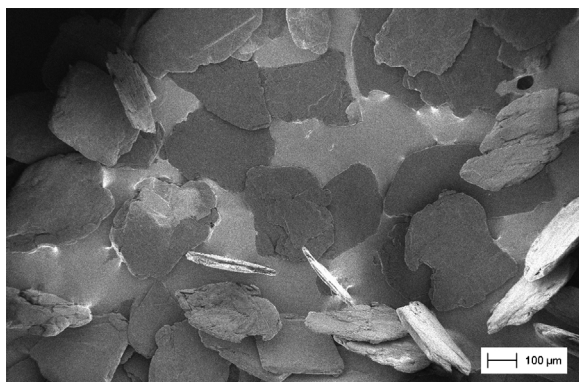


Fig. 1. Graphite flake shapes.

dioxide or carbon monoxide, depending on conditions. In general, graphite materials can have a very high purity and secondary reactions are limited with virtually no ash generation. Therefore graphite represents an ideal starting material for investigating the reaction at a solid interface, where only gaseous reaction products are formed and the reaction rate is governed solely by the reactive interface.

Due to its industrial significance, a large number of the studies on graphite are focused on bulk synthetic graphite materials. Natural graphite flakes are expected to have far larger crystallites and superior graphitic order compared with synthetic graphite [3]. Furthermore, due to the manufacturing process, synthetic graphite has a very complex microstructure and porosity [4]. These properties make this type of graphite very difficult to model easily from the perspective of solid state kinetics. Instead it was decided here to focus on the simpler, flake-type natural graphite. These particles represent a solid reactant, with no porosity, which should be easily characterized by the solid state kinetic approach.

The approach recommended by the ICTAC (International Confederation for Thermal Analysis and Calorimetry) [5] was applied to the natural graphite to determine its kinetic parameters. However, these flakes exhibit a conversion behaviour that is difficult to reconcile with the classic solid state kinetic models. A modified form of the solid state kinetic rate equation is proposed which is more general in its applicability to solid reactants where reactivity is governed solely by the progression of the reaction interface. Finally, the observed conversion function is represented analytically, in terms of directly observed microstructural effects.

## 2. Theory

### 2.1. Classic solid state kinetic expression for reaction interface-controlled reactivity

When the graphite flakes are examined under a scanning electron microscope (SEM), they appear to have a simple structure. As can be seen from Fig. 1, they are roughly disc-shaped, with some irregularities along the edges.

The flakes are solid with a very high aspect ratio. The structure of ideal graphite is layered, planes of hexagons forming a honeycomb structure, due to the  $sp^2$  hybridisation of the carbon atoms. Adjacent layers are weakly bonded to each other by van der Waals forces [4]. This can be seen schematically in Fig. 2.

When the particles are examined more closely, as in Fig. 3, the layered structure becomes clear and the edges can be seen to be fairly uniform and flat without porosity. This is consistent with expectations for highly crystalline graphite flakes. The slight roughness which is apparent on the upper flake surface is a very thin layer

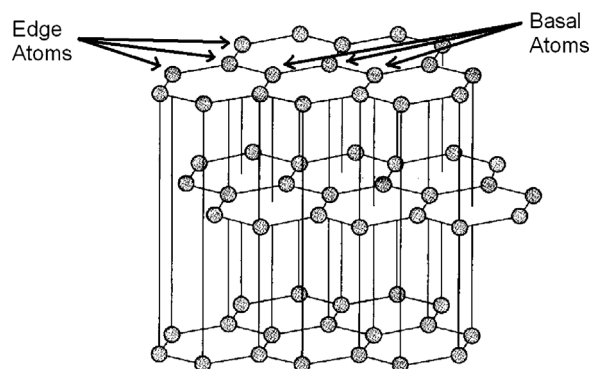


Fig. 2. Ideal graphite structure.

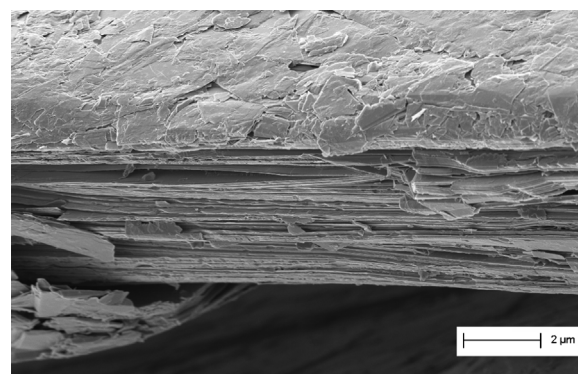


Fig. 3. Graphite flake edge.

of damaged structure which is created during beneficiation. On the whole, the flake is homogeneous and non-porous.

Natural graphite flakes are generally considered more consistently crystalline across the entire particle compared with synthetic materials. Due to the strong, in-plane covalent bonding, the basal plane of graphite, i.e. the flat flake surface, is considered to be comparatively inert [6]. Thus attack by oxygen is only possible at the edge atoms shown in Fig. 2, except at extreme temperatures. Nucleation is instantaneous and the reaction proceeds simultaneously at all active sites. A very slight difference exists between the reactivity of armchair and zig-zag edge sites [7]. However, since a distribution of both sites is expected to be present, it may be assumed that a single, average reactivity prevails. Hence, the most applicable reaction model from the table of common models given by Vyazovkin et al. [5] would appear to be that of a contracting cylinder or disc, shown schematically in Fig. 4.

This model is derived from the assumption that the reaction interface proceeds at a uniform velocity,  $v$ , towards the centre of the particle [8]. On an atomic level, this assumption is not strictly correct, since atoms will be removed at random from the surface and this will produce molecular irregularities on the surface. Statistically, these irregularities will be more likely to react and thus they will be preferentially removed, eventually leading to the development of a pseudo steady state. Thus on a macro scale it is assumed that the edge recession rate is a constant, averaged value and the reaction rate is governed only by the geometrical progression of

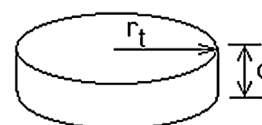


Fig. 4. Ideal natural graphite flake.

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