

Jander Equation

The **Jander equation** is one of the most important kinetic equations used to describe diffusion-controlled solid-state reactions. It was proposed by **Wilhelm Jander** in 1927 to explain reactions in which diffusion of ions through the product layer controls the overall reaction rate.

As the reaction proceeds, a product layer forms around the unreacted core. This layer becomes progressively thicker, making diffusion more difficult. Consequently, the reaction rate decreases with time.

Definition

The Jander equation is a mathematical expression that relates the fraction of reaction completed with time for diffusion-controlled solid-state reactions involving spherical particles.

Assumptions of the Jander Equation

- The reactant particles are spherical.
- All particles have the same size.
- The reaction starts uniformly over the particle surface.
- A continuous product layer is formed.
- Diffusion through the product layer is the rate-controlling step.
- The diffusion coefficient remains constant during the reaction.
- The temperature remains constant throughout the reaction.

Concept of the Jander Model

Consider a spherical particle of initial radius R . The reaction begins at the outer surface and produces a layer of product around an unreacted core of radius r . The reactant ions must diffuse through this product layer before further reaction can occur.

Initially

- The entire particle is unreacted.
- The unreacted core radius is equal to the original radius R .
- The product layer thickness is zero.

During the Reaction

- The unreacted core radius decreases from R to r .

- The product layer thickness increases from zero to $R - r$.
- The diffusion path becomes longer.
- The reaction rate decreases with time.

Detailed Derivation of the Jander Equation

Notation

- α = Fraction of material reacted
- t = Reaction time
- D = Diffusion coefficient
- k = Rate constant
- R = Initial radius of the particle
- r = Radius of the unreacted core after time t

1. Relationship Between Conversion and Core Radius

The fraction reacted is equal to the fraction of the original volume that has been converted into product. Since the particle is spherical, the volume is proportional to the cube of its radius.

$$\text{Volume of unreacted core} = \frac{4}{3}\pi r^3$$

$$\text{Initial volume of particle} = \frac{4}{3}\pi R^3$$

The fraction remaining unreacted is therefore:

$$1 - \alpha = \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi R^3}$$

Cancelling the common terms gives:

$$1 - \alpha = \frac{r^3}{R^3}$$

Taking the cube root of both sides:

$$\frac{r}{R} = (1 - \alpha)^{1/3}$$

Hence,

$$r = R(1 - \alpha)^{1/3}$$

2. Thickness of the Product Layer

The thickness of the product layer is the difference between the original radius and the radius of the unreacted core.

$$x = R - r$$

Substituting the value of r :

$$x = R - R(1 - \alpha)^{1/3}$$

Taking R as a common factor:

$$x = R \left[1 - (1 - \alpha)^{1/3} \right]$$

Thus, the diffusion distance increases continuously as the reaction proceeds.

3. Diffusion-Controlled Rate Expression

According to Fick's law, the diffusion rate through the product layer is inversely proportional to its thickness.

$$\text{Rate} \propto \frac{D}{x}$$

Since the movement of the reaction interface is controlled by diffusion,

$$-\frac{dr}{dt} \propto \frac{D}{R - r}$$

Introducing the proportionality constant k ,

$$-\frac{dr}{dt} = \frac{k}{R - r}$$

Rearranging the equation gives:

$$(R - r) dr = -k dt$$

Integrating between the limits $r = R$ at $t = 0$ and $r = r$ at time t :

$$\int_R^r (R - r) dr = - \int_0^t k dt$$

After performing the integration and simplifying the mathematical expression, we obtain:

$$\left(1 - \frac{r}{R}\right)^2 = kt$$

From the relationship derived earlier,

$$\frac{r}{R} = (1 - \alpha)^{1/3}$$

Substituting this expression into the above equation gives:

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = kt$$

This equation is known as the **Jander equation**. It is one of the most widely used kinetic equations for diffusion-controlled solid-state reactions.

Meaning of the Equation

The Jander equation is expressed as:

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = kt$$

where:

- α = Fraction of reaction completed
- k = Diffusion-controlled rate constant
- t = Reaction time

The equation indicates that the square of the relative diffusion distance is directly proportional to the reaction time. As the reaction proceeds, the product layer becomes thicker, increasing the diffusion path and slowing the reaction.

Physical Significance

- Initially, the product layer is very thin and diffusion is rapid.
- As the product layer grows, ions must diffuse through a longer path.
- The increase in diffusion distance reduces the reaction rate.
- The reaction gradually slows until the reactants are completely consumed.

Graphical Representation

If a reaction follows the Jander equation, a graph of

$$\left[1 - (1 - \alpha)^{1/3}\right]^2$$

against reaction time t gives a straight line passing through the origin.

The slope of this straight line is equal to the diffusion-controlled rate constant k .

Applications

- Study of diffusion-controlled solid-state reactions.
- Preparation of ceramic materials.
- Solid-state synthesis of ferrites.
- Formation of spinel compounds.
- Oxidation of metals.
- Semiconductor material synthesis.
- Sintering and powder metallurgy.

Advantages

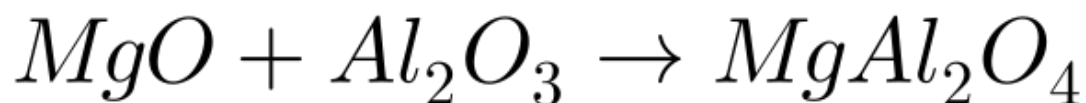
- Simple mathematical expression.
- Easy determination of diffusion rate constant.
- Provides a good description of many ceramic reactions.
- Useful for studying diffusion mechanisms.
- Widely accepted in solid-state chemistry.

Limitations

- Applicable only to diffusion-controlled reactions.
- Assumes spherical particles.
- Assumes uniform particle size.
- Assumes a constant diffusion coefficient.
- Not suitable for nucleation-controlled or interface-controlled reactions.
- Does not accurately describe reactions involving particle cracking or pore formation.

Example

During the preparation of magnesium aluminate spinel, the following solid-state reaction occurs:



A layer of magnesium aluminate forms between magnesium oxide and aluminium oxide. Magnesium and aluminium ions must diffuse through this product layer before further reaction can occur. Since diffusion is the slowest step, the reaction approximately follows the Jander equation.

Summary

The Jander equation is an important kinetic model for diffusion-controlled solid-state reactions. It is derived using the shrinking-core model and assumes spherical particles with a constant diffusion coefficient. The equation explains why the reaction rate decreases as the product layer grows thicker. It is extensively used in ceramic chemistry, metallurgy, materials science and solid-state synthesis.

Important Points for Examination

- Proposed by Wilhelm Jander in 1927.
- Applicable to diffusion-controlled solid-state reactions.
- Based on the shrinking-core model.
- Assumes spherical particles and constant diffusion coefficient.
- The integrated equation is:

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = kt$$

- A linear plot of $\left[1 - (1 - \alpha)^{1/3}\right]^2$ versus t confirms the applicability of the Jander model.
- The slope of the graph gives the diffusion-controlled rate constant k .
- Widely used for studying ceramic, ferrite and oxide formation reactions.