



## Mathematical Approaches to Quantifying Energy in Chemical Reactions

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### Abstract:

*Mathematics plays an integral role in understanding and quantifying energy changes in chemical reactions. This article delves into mathematical methods, particularly linear algebra, that underpins the analysis of chemical kinetics and energy transformations. It emphasizes the application of stoichiometry, mass conservation laws, and rate equations to evaluate reaction rates and predict feasible reaction pathways. The discussion highlights Bowen's contributions to mathematically describing chemical reactions, using conservation principles to identify independent reactions in a mixture. Theoretical concepts such as enthalpy, Gibbs free energy, and activation energy are explored, alongside practical applications in thermodynamics, biochemistry, and industrial kinetics. For instance, energy calculations aid in optimizing catalytic processes, analyzing metabolic pathways, and enhancing reaction efficiencies. These mathematical approaches bridge experimental observations with theoretical models, enabling a deeper understanding of chemical processes and their energy dynamics. By incorporating rigorous mathematical frameworks, the study advocates for a broader adoption of these methods in chemical research and engineering. This comprehensive perspective illustrates how integrating mathematics with chemistry not only enhances precision but also opens avenues for innovation in scientific and industrial applications.*

**Keywords:** Kinetics, Reaction Rate, Independent Reactions, Dimensionality Reduction, Stoichiometry.

### Introduction:

Chemical kinetics is a field of chemistry where mathematical principles play a significant and dynamic role. Mathematics is not only essential for analyzing kinetic data but also for understanding broader theories at both microscopic (molecular) and macroscopic (phenomenological) levels. For decades, mathematicians have recognized that key concepts in stoichiometry and mass-action kinetics, developed through empirical observations, can be systematically described using linear algebra. Despite this, the physicochemical community has largely overlooked the potential of this precise mathematical approach. On the other hand, chemical reaction engineering has made greater strides in leveraging mathematics to optimize chemical plant design. This disparity may be attributed to a lack of practical examples showcasing the advantages of mathematical methods in chemical kinetics.

To establish the foundation for this work, a brief—though perhaps redundant—review of the core principles of chemical kinetics is presented.

The concept of a reaction rate is widely accepted in chemistry, though it cannot be measured directly. Instead, it is inferred from changes in the quantities or concentrations of reaction components over time. In flow-through systems, it is determined under specific steady-state conditions, such as flow rates. Measured component rates are then used to develop reaction rate expressions, as reaction rate definitions are inherently tied to component rates. To substantiate these ideas, a selection of textbooks on physical chemistry, chemical kinetics, and reaction engineering will be examined.

Silbey et al. (2005) describe reaction rate in terms of the extent of the reaction, defined by changes in the amount of any component within the reaction mixture. They explain that reaction rates are derived by observing how concentrations change over time. Similarly, Berry et al. (2000) highlight that concentrations of reactants and products are key factors influencing reaction rates. They note that the rate of change for any species is the cumulative effect of all processes involving that species and emphasize the importance of identifying significant reactions and conducting measurements to distinguish them. They state that the rate at which a species like  $[B]$  changes is the sum of all rates affecting it, with  $[B]$  representing the concentration of that species.

Pilling and Seakins (1996) do not explicitly define reaction rates but reference Wilhelmy's early work on sucrose hydrolysis, which established that reaction rates are proportional to the first power of the sucrose concentration. Such findings, alongside other experimental data, underpin the rate laws that relate the time derivative of a reactant's concentration to the product of specific powers of reactant concentrations.

Mortimer and Taylor (2002) argue that understanding reaction rates necessitates an experimental approach. They begin by discussing the rate of change of a reactant or product concentration over time and define reaction rate as the concentration's time derivative divided by its stoichiometric coefficient, assuming constant volume. Metiu (2006) initially considers using the time derivative of mole numbers to define reaction rate but ultimately prefers using the time derivative of the reaction's extent.

Smith (1981) defines the rate of a homogeneous reaction as the change in moles of a reactant or product per unit time and volume due to reaction. He describes how concentration-time profiles are experimentally obtained to derive rate equations. Similarly, Missen et al. (1999) differentiate between extensive and intensive reaction rates, the former being the observed rate of species formation and the latter normalized by reaction volume or catalyst mass. They emphasize that reaction rates are determined by measuring concentrations of reaction components.

Davis and Davis (2003) define reaction rate using the time derivative of the extent of reaction, applicable to homogeneous, closed systems under uniform conditions. They acknowledge that practical reactor conditions often deviate from these ideals, making direct measurement of reaction rates infeasible in such systems. Instead, rates are inferred from changes in composition over time or steady-state conversion rates in flow-through reactors.

In kinetic studies, measurements typically focus on the concentrations or concentration changes of individual components, or at least one key species in the mixture. Positive component rates indicate production, while negative rates signify consumption during the reaction. These rates are fundamental to determining and calculating overall reaction rates. Chemical intuition, often supported by computational studies of potential energy surfaces, guides the identification of the reactions taking place. These insights are formalized as reaction schemes (networks of reactions describing transformations in the mixture) or mechanisms

(sequences of elementary reactions). Reaction rates are then expressed using the kinetic mass-action law, involving rate constants and concentrations raised to specific powers.

It is important to recognize that component and reaction rates are mathematical entities, particularly when used to model concentration profiles or reactor dynamics. These rates must conform to the principle of atom conservation, ensuring consistency with mass conservation. Bowen (1968) demonstrated that reaction rates arise as mathematical consequences of atom conservation, which is governed by linear algebra. This connection highlights that reaction rates are not only a product of chemical reasoning but also a mathematical outcome of stoichiometric principles. Mathematics, therefore, serves as a powerful tool for identifying potential reactions in a mixture, complementing chemical insights.

The goal of this work is to explore the role of linear algebra in describing reaction kinetics through explicit examples of chemically reacting mixtures and to draw attention to Bowen's valuable yet underutilized contributions within the chemical community.

### **Purpose of the Study:**

The author seeks to:

1. Investigate the role of linear algebra in describing reaction kinetics.
2. Illustrate these concepts with concrete examples of reacting mixtures.
3. Advocate for a greater adoption of mathematical approaches in chemical kinetics.

In essence, this discussion emphasizes the importance of using mathematical tools, such as linear algebra, to enhance the understanding of chemical kinetics. It shows how these tools can bridge the gap between experimental findings and theoretical models, paving the way for more rigorous scientific inquiry.

### **Theoretical Methods:**

This section provides a summary of the foundational ideas behind Bowen's analysis (Bowen, 1968; Pekař and Samohýl, 2014). A list of symbols is available at the end for reference.

The principle of mass conservation in chemical reactions can be expressed as:

$$\sum_{i=1}^n m_i = 0, \quad (1)$$

Where  $m_i$  represents the rate of mass change (per unit volume and time) for component  $i$ . This conservation is derived from the fact that the total number of atoms in the system remains constant (excluding nuclear reactions). By introducing molecular weights  $w_i$  and molar rates of change  $R_i$  for components, the mass conservation equation can be reformulated as:

$$\sum_{i=1}^n R_i w_i = 0, \quad (2)$$

This equation resembles a dot product of two vectors, implying orthogonality between them in an  $n$ -dimensional vector space. These vectors can be expressed in terms of the basis vectors  $e_i$  of the component space  $U$ :

$$R = \sum_{i=1}^n R_i e_i, \quad W = \sum_{i=1}^n w_i e_i, \quad (3)$$

Where R is the vector of molar rates, and W is the vector of molecular weights. The conservation law (2) can also be written using atomic weights:

$$w_i = \sum_{j=1}^z A_j N_{ji}, \quad (4)$$

Where  $A_j$  represents the atomic weight of atom j,  $N_{ji}$  is the number of atoms j in component i, and z is the total number of atomic types. Substituting (4) into (2) gives:

$$\sum_{i=1}^n R_i w_i = \sum_{j=1}^z A_j = \sum_{i=1}^n N_{ji} R_i = 0. \quad (5)$$

Since the conservation of mass applies to each type of atom individually,

$$\sum_{i=1}^n N_{ji} R_i = 0 \quad \text{for } j = 1, 2, \dots, z. \quad (6)$$

This results in a homogeneous system of linear equations for  $R_i$ , with the coefficient matrix  $\|N_{ji}\|$ . For chemical reactions to occur ( $R_i \neq 0$ ), the rank r of this matrix must be less than n, implying  $n - r > 0$ . This simplifies the system to:

$$\sum_{i=1}^n S_{ji} R_i = 0 \quad \text{for } j = 1, 2, \dots, r, \quad (7)$$

Where  $\|S_{ji}\|$  is a reduced matrix derived from  $\|N_{ji}\|$  by eliminating linearly dependent rows. Molecular weights can then be expressed as:

$$w_i = \sum_{j=1}^r B_j S_{ji} \quad (8)$$

Where  $B_j$  represents pseudoatomic weights. The vector W is thus:

$$W = \sum_{j=1}^r B_j f_j \quad (9)$$

Where  $f_j$  are basis vectors of a subspace W with dimension r. Subspace W determines an orthogonal complementary subspace V with dimension  $n - r$ . Since  $R \cdot W = 0$ , the molar rate vector R lies in V.

To identify the coordinates of R in V, basis vectors  $d_k$  of V are defined as:

$$d_k = \sum_{i=1}^n P_{ki} e_i \quad (10)$$

Where  $\|P_{ki}\|$  is a matrix of rank  $n - r$  satisfying:

$$f_j \cdot d_k = 0.$$

The vector R in V is then expressed as:

$$R = \sum_{k=1}^{n-r} Q_k d_k, \quad (11)$$

Where  $Q_k$  are the rates of  $n - r$  independent reactions. Substituting into the component rates gives:

$$R_i = \sum_{k=1}^{n-r} Q_k P_{ki}. \quad (12)$$

Equation (12) shows that the rates of individual components ( $R_i$ ) are determined by the rates of  $n - r$  independent reactions ( $Q_k$ ). These independent reactions are defined by their consistency with mass conservation, as represented by:

$$\sum_{i=1}^n P_{ki} W_i = 0 \quad \text{for } k = 1, 2, \dots, n - r. \quad (13)$$

In this framework,  $\|P_{ki}\|$  represents the stoichiometric matrix, and  $Q_k$  are the independent reaction rates. These rates are mathematically sufficient to describe the transformations observed in kinetic experiments, providing a rigorous foundation for analyzing chemical reactions.

This linear algebraic approach demonstrates that reaction rates are direct consequences of mass conservation and atomic permanence. It also highlights that only independent reactions, as defined mathematically, are necessary to describe chemical systems. While traditional kinetics often relies on empirical mass-action expressions, this methodology ensures consistency with conservation laws and provides deeper insights into the mathematical structure underlying chemical processes.

## Applications of Energy Calculations

### 1. Thermodynamics

Enthalpy and Gibbs free energy calculations are essential for evaluating reaction feasibility. For example, in industrial processes like ammonia synthesis (Haber process), these calculations ensure optimized conditions for maximum yield.

### 2. Kinetics

Activation energy calculations help in designing catalysts to lower the energy barrier and accelerate reactions. In pharmaceutical chemistry, this principle is crucial for drug synthesis and stability.

### 3. Biochemistry

In metabolic pathways, Gibbs free energy calculations reveal whether a reaction can proceed under physiological conditions. ATP hydrolysis, for instance, is driven by a significant negative  $\Delta G$ .

## Conclusion:

Mathematics provides the tools necessary to understand and predict energy changes in chemical reactions. From enthalpy and Gibbs free energy to activation energy, these calculations are indispensable in research and industry. By applying mathematical principles, chemists can design efficient processes, develop new materials, and explore the fundamental mechanisms of chemical transformations.

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**Citation:** Sinha. Dr. J., Sinha. Dr. A. & Khawas. Dr. K., (2024) “Mathematical Approaches to Quantifying Energy in Chemical Reactions”, *Bharati International Journal of Multidisciplinary Research & Development (BIJMRD)*, Vol-2, Issue-11, December-2024.