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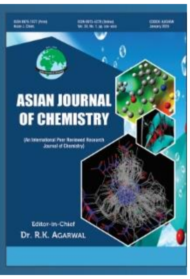

REVIEW

From Equilibrium to Emergence: The Physical Foundations of Chemical Order – A Conceptual Framework Linking Thermodynamics, Quantum Mechanics and Systems Chemistry

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Chemistry has evolved from empirical pattern recognition to a unified, physics-informed science governed by universal principles. This perspective traces the conceptual progression of chemical thought from Mendeleev's periodic classification to thermodynamics, quantum mechanics and the emerging systems view of self-organisation and complexity. By dividing this trajectory into four historical phases *viz.* (i) thermodynamic and kinetic universality, (ii) nonideal solution theory and ionic interactions, (iii) quantum-mechanical interpretation of matter and bonding, and (iv) self-organisation in far-from-equilibrium systems. Each phase contributed to a deeper understanding of matter-energy relationships and strengthened the theoretical foundations of chemistry. Emphasis is placed on the interplay between the macroscopic laws and microscopic models, with recurring themes of order, symmetry and energy flow serving as unifying principles across both equilibrium and non-equilibrium phenomena. This conceptual synthesis illustrates the natural convergence of thermodynamics, statistical mechanics, and quantum theory, giving rise to systems chemistry and the modern study of emergent behaviour. Beyond its historical narrative, the work asserts that an analysis of chemistry through its evolving paradigms reveals a coherent scientific continuum integrating atomic theory, information and complexity, thereby positioning chemistry as a central discipline for elucidating organisational principles in natural systems.

Keywords: History of chemistry, Quantum mechanics, Chemical bonding and Oscillations, Patterns, Origin of life.

INTRODUCTION

The establishment of the periodic table by Dmitri Mendeleev in 1869 marked a decisive transformation of chemistry from an empirical discipline into a theoretically grounded science [1-3]. Initially constructed from observed periodicities in elemental properties, Mendeleev's framework implied the existence of deeper, unifying principles that would later find explanation in thermodynamics and quantum mechanics. The systematic ordering of the elements became the first macroscopic reflection of an underlying microscopic regularity, a notion that has guided chemical inquiry for more than 150 years.

This perspective examines the evolution of chemical principles across successive scientific paradigms, highlighting the progressive integration of physical laws and mathematical structure to explain and predict the behaviour of matter [4,5]. The history of this evolution can be meaningfully divided into four conceptual phases.

Phase I (1869-1915) made the universality of thermodynamics and kinetics of chemical change by linking macroscopic observables (heat, work, entropy, *etc.*) to reaction rates, probabilities and feasibility. Phase II (1915-1950s) extended the theoretical characterisation of real systems through nonideal solution theory and ionic interactions, reflected by the Debye-Hückel model [6] that quantified electrostatic effects in electrolyte solutions. The subsequent quantum revolution in the 1920s and 1950s (Phase III) also dealt with the tensions in classical theory, introducing the microscopic architecture of atomic structure, molecular bonding and spectroscopy [4,5,7,8]. Phase IV (post-1950) expanded the conceptual scope of chemistry to include open systems, self-organisation and complexity and introduced new links between chemical kinetics, information flow and biological organisation. This evolution indicates a widening of the explanatory potential. Thermodynamics revealed the universality of energy conservation and transformation. Whereas, statistical mechanics bridged macro-

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scopic behaviour to molecular probability distributions and quantum mechanics unveiled the discrete, probabilistic nature of matter itself. Each framework, while overcoming the limitations of the previous one, has preserved its core principles. This shows that the advance of chemistry is not only gradual progress but also a hierarchy in which each new layer converges with and reframes the preceding one.

By emphasizing these inter-relationships, the current perspective aims to transcend historical and conceptual barriers within and across disciplines, with chemistry serving as a link between the physical sciences, from classical to quantum and from equilibrium to non-equilibrium descriptions. Moreover, recurring motifs of symmetry, feedback and self-organisation observed across multiple scales, from atoms to biological systems, indicate that chemistry provides a fundamental language for describing the emergence of structure and function in the natural systems [9-11].

By traversing the conceptual scheme and the respective paradigms of chemical theory, this project constructs an intellectual continuum that links the knowledge of the periodic law [12] with systems chemistry and supramolecular complexity [10]. This conceptual framework not only clarifies the logical organisation of chemical understanding but also highlights its significance for modern advancements like materials engineering, molecular computing and synthetic biology. An appreciation of this intellectual lineage deepens the contemporary perspectives on chemistry's role, positioning it not merely as an applied extension of physics but as the discipline fundamentally concerned with structured matter and emergent complexity.

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Phase I (1869–1915): Universal laws of thermodynamics and kinetics:

Birth of thermodynamic principles: The years from 1869-1915 were significant in the building of thermodynamics and its basis role in the formulation of universal laws of chemistry [13-15]. Thermodynamics is the study of the relations among the diverse properties of matter. It gained prominence during and after the Industrial Revolution (1760-1830) [16,17]. James Watt, a pivotal figure in this era, patented the steam engine in 1775 and this invention turned thermal energy into mechanical work, a work of early thermodynamics in action.

Interest in the efficiency of engines was aroused during the Industrial Revolution, which eventually lead the laws of thermodynamics. The first law linked the concepts of heat, work and internal energy (ΔE) *via* the primary regulation. The 2nd law added entropy (S) and opened one of the paths for a comprehension of chemical feasibility, which explained through free energy ($F = E - TS$) [16-18]. Carnot made the ideal engine and placed limits on efficiencies [19-21]. Helmholtz defined the free energy as a measure of useful work. The basic idea of thermodynamics is the conversion of heat into work and the corresponding change in internal energy of a system. This relationship is included in the basic eqn. 1:

$$Q = W + \Delta E \qquad (1)$$

In which, Q is the heat supplied; W is the work done by the system; and ΔE is the change in the system's energy. Usually, heat causes the material medium to expand and mechanical work follows. This idea is illustrated in a simplified version in a toy engine with rubber band spokes flowing from one temperature reservoir to the other, T_1 and T_2 (Fig. 1). Heat flows from high temperature source T_1 and subsequently expands and performs work before releasing heat to low temperature T_2. The cyclic process between two temperatures is quasi-static, occurring sufficiently slowly that the system remains effectively in equilibrium throughout, resulting in an equilibrium state at the completion of each cycle. Such an approach to thermodynamics is foundational for modern physical chemistry and brings to light some of the universal principles in science to encompass conservation and transformation of energy.

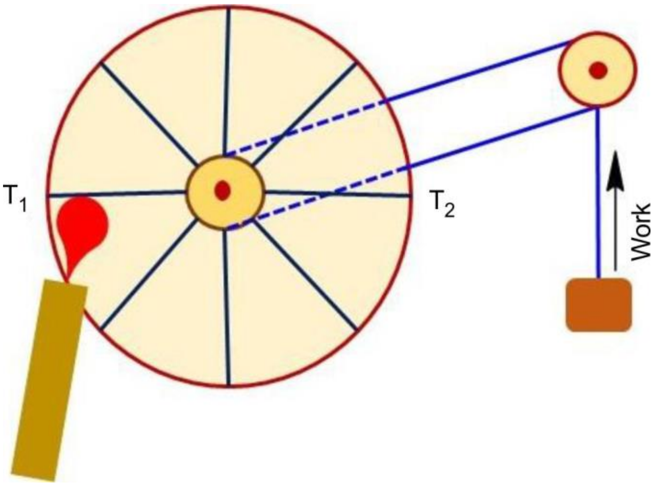


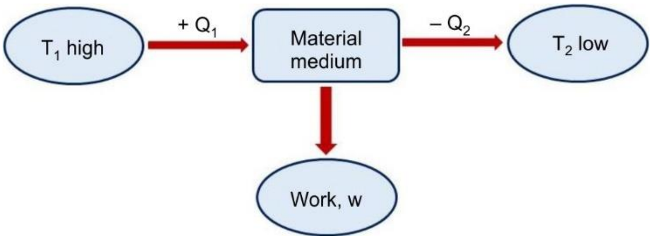
Fig. 1. Understanding the thermodynamic work cycle using a schematic of toy engine

The history of thermodynamics illustrates the emergence of abstract mathematical principles from practical and technological challenges, particularly in the optimisation of steam engine efficiency. The combination of scientific real-world engineering issues and theoretical formal arguments of Carnot, Clausius and Helmholtz that helped set the stage for a comprehensive approach to heat, work and energy conservation. This development turned sensible questions on efficiency into foundational principles of entropy, free energy and spontaneity, ideas that have persisted within the study of physical description of chemical processes.

The foundation of thermodynamic analysis in physical and chemical systems rests on understanding both ideal and real processes. An ideal engine is a theoretical construct for engine design, such as a Carnot engine (eqn. 2) that travels between two thermal reservoirs, T_1 (high temperature) and T_2 (low temperature), without any thermal energy dissipation (**Scheme-I**). In such a theory, a novel thermodynamic quantity, entropy (eqn. 3), becomes the essence of the study of heat transfer and the efficiency of energy.

Ideal engine (Carnot engine):

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \qquad (2)$$



Scheme-I: Schematic representation of heat and work interactions in a thermodynamic system. Heat Q_1 is absorbed from a high-temperature reservoir (T_1); part is converted into work W and the rest (Q_2) is rejected to a low-temperature reservoir (T_2)

A new quantity:

$$\frac{Q}{T} = S \text{ (Entropy)} \tag{3}$$

For an ideal, reversible process, the change in entropy is zero: $\Delta S = 0$.

However, for real engines or natural (irreversible) processes, energy dissipation leads to an increase in entropy: $\Delta S > 0$ [22]. In ideal thermodynamic systems, entropy changes (ΔS) govern the directionality of natural processes and chemical feasibility. Clausius' formulation $\Delta S \geq 0$ in real systems was pivotal in understanding irreversibility and disorder [23].

The term TS represents the dissipated portion of energy in a system (eqn. 3). This relationship quantitatively expresses the energy that is no longer available to perform useful work. Accordingly, it introduces the concept of free energy, which denotes the fraction of energy available for work after accounting for entropy-related losses, as defined by eqn. 4.

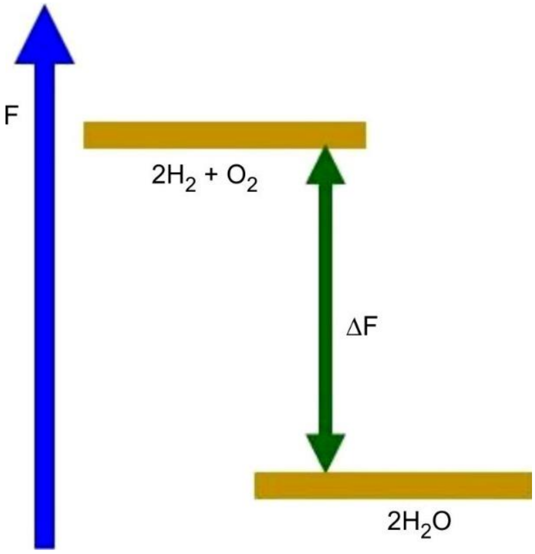
$$F = E - TS \tag{4}$$

where F is the Helmholtz free energy available to do work; E is the total internal energy of system; and TS represents the dissipated energy. For spontaneous processes or chemical reactions at constant temperature and volume, the Helmholtz free energy change must be negative ($\Delta F < 0$) [15,16].

This condition determines whether a natural process or chemical reaction is thermodynamically possible. For example, the reaction between hydrogen and oxygen to produce water: $2H_2 + O_2 \rightarrow 2H_2O$ is a natural and spontaneous process as it causes a negative change in free energy (**Scheme-II**). Conversely, a process with $\Delta F > 0$ is not feasible under the same conditions, since it would need external input to succeed.

Reaction kinetics and activation energy barriers: In this review, we delve into the basic idea of the rate law in chemical kinetics and the thermodynamic motivation behind reaction barriers, with a general expression for the reaction rates. By introducing the concept of an activation barrier and tracing the historical and theoretical development of the Arrhenius equation [24], the integration of macroscopic measurements, such as rate constants, with microscopic kinetic behaviour is highlighted [25]. The statistical mechanical foundations established in the first half of the twentieth century are also highlighted, providing a rigorous framework for expressing this universal rate [26].

The rate of a chemical reaction is determined not only by the reactants themselves but also by the energetic landscape through which they must traverse. Treating reactants and products as distinct thermodynamic states requires a conceptual and energetic separation, an activation barrier that prevents spontaneous interconversion in the absence of sufficient energy input. This framework is fundamental to connecting thermodynamic principles with reaction kinetics [15].



Scheme-II: Free energy change (ΔF) associated with the formation of water from hydrogen and oxygen

Activation barrier and reaction dynamics: A chemical reaction such as $A + B \rightarrow C$ does not occur instantaneously upon mixing of reactants. Instead, it usually proceeds through a high-energy intermediate state. As shown in the energy profile (Fig. 2), the system must overcome an energy barrier that is ΔE_0 before the reaction can proceed. This energy barrier is the activation energy, a crucial notion introduced to understand the slow rate of certain reactions in spite of favourable thermodynamics [27]. The existence of this barrier means that the reactant (A + B) and the product (C) states will be treated as independent thermodynamic entities, each with its own energy well.

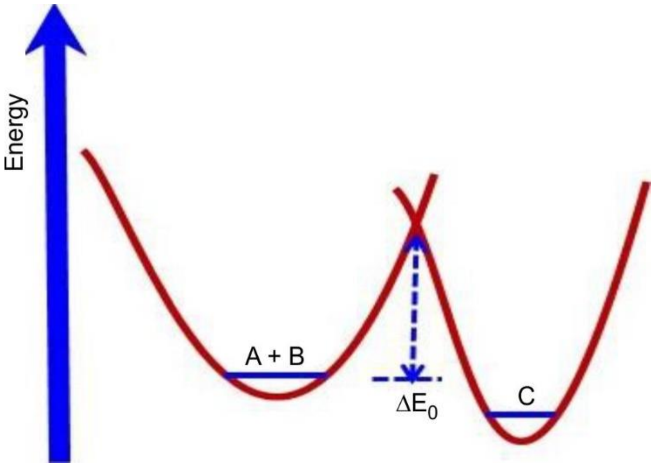


Fig. 2. The energy profile diagram shows how the reaction, $A + B \rightarrow C$ must climb an activation energy barrier (ΔE_0). The reactants first pass through a high-energy transition state before settling into the more stable, lower-energy product state (C)

Universal rate expression: The Arrhenius law: Svante Arrhenius (1887) proposed a mathematical form (eqn. 5) for the rate constant k of a reaction, which can be formulated as follows:

$$k = A\exp\left(-\frac{\Delta E_o}{k_B T}\right) \tag{5}$$

where A is the pre-exponential factor, which is associated with molecular collisions and orientation, ΔE_o is the activation energy, k_B is Boltzmann's constant and T is the absolute temperature. This expression (eqn. 5) describes the exponential sensitivity of reaction rates to the temperature and is the basis of the classical chemical kinetics [24,25]. The Arrhenius equation evolves fundamentally from empirical kinetics to molecular interpretation. Combined with the transition-state theory and statistical mechanics, this approach transformed the previously empirical temperature dependence of reactions into a quantitative framework for analyzing reaction kinetics at the molecular level. This evolution demonstrates the progression of phenomenological models in chemistry into physically grounded formulations, in which macroscopic rate laws are directly connected to microscopic energy distributions.

Statistical mechanical justification: Although Arrhenius's formula was phenomenological, its theoretical basis was later based on statistical mechanics and kinetics. Between 1930 and 1940, scientists such as Eugene Wigner, Henry Eyring and Hans Kramers provided rigorous interpretations of reaction dynamics through transition state theory and reaction rate theory [28-31].

The transition state theory of Eyring (TST) focused on an activated complex in equilibrium with reactants. Whereas, Kramers' work is based on the principle of stochastic processes in reaction rates, which respond to the effects of friction and noise. These models connected the macroscopic rate law with microscopic particle behaviour, justifying the form of the Arrhenius equation using molecular energy distributions and the concept of thermal activation [28,29].

The universal rate law illustrated by the Arrhenius equation captures the close connection between energy landscapes and processes of chemical kinetics [24,32]. The concept of an activation barrier not only enforces the separation of thermodynamic states but also provides a mechanistic basis for explaining the role of thermal energy in driving chemical transformations. This universal law, more firmly established from the principles of statistical mechanics that entered the discipline in the early 20th century, became the microscopic basis of chemical science and one of its most enduring principles.

Phase II (1915-1950): Ionic solutions deviations from ideality: A historical and theoretical review: Solution chemistry first developed in the early 20th century and marked a significant milestone in understanding complex systems that did not behave ideally. Until 1915, solution chemistry was largely based on the postulation of ideal behaviour, a state where solutes did not interact. However, the empirical data especially from electrolytic solutions increasingly contradicted these assumptions. Phenomena such as freezing point depression, osmotic pressure anomalies and electrical conductivity variations prompted the search for new models incorporating interionic forces and long-range Coulombic interactions.

Emerging between 1915 and the 1950s, this period, often designated as Phase II in the development of solution chemistry, established the foundation for theories and models describing nonideal solutions [33-36]. A major focus of this era was the study of ionic solutions, in which the interplay among electrostatic interactions**,** the ionic atmosphere and deviations from ideal thermodynamic behaviour became the subject of intensive theoretical analysis. This review also focuses on the historical development, major contributors and theoretical foundations, especially the fundamental contributions of Debye and Hückel, to understanding the properties of ionic solutions, their structure and thermodynamic features.

Importantly, the shift from ideal to non-ideal reflects a crucial transformation in the scope of validity of the physical laws. These systematic deviations between theoretical predictions and experimental data observed in electrolyte solutions highlighted the requirement for new theoretical perspectives. The Debye-Hückel theory became the first quantitative treatment of ionic interactions in dilute solutions, uniting thermodynamics with electrostatics and statistical mechanics. By introducing the pivotal parameters such as ionic strength and activity coefficients, this framework changed solution chemistry from a purely empirical field to a scientific one governed by molecular-scale electrostatic principles. The resulting synthesis of theory and experiment not only advanced the physics of electrolytes but also exemplified the broader evolution of chemistry toward predictive, quantitatively grounded models of real systems.

Historical context and scientific milestones: Several overlapping developments during 1915-1950s reshaped solution theory focusing on non-ideal behaviour:

Ionic solutions (Ghosh (1918) and later Debye & Hückel (1923)): Marked by the development of the ionic atmosphere theory and quantitative electrostatic models [6,37].

Colloids (1920s – Thomas Graham): Investigation into large molecular assemblies in suspension, crucial for early polymer science and surface chemistry [38-40].

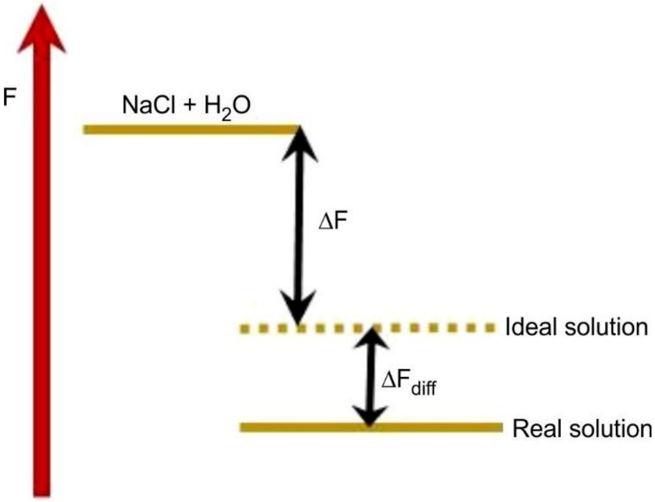
Polymers (1940s – Paul Flory): Statistical mechanics began to explain the thermodynamic behaviour of long-chain molecules, known as the molecule thermodynamics [41].

Micelles (1950s – McBain): Supramolecular structures studied for their role in self-assembling surfactant aggregates in aqueous media and solubilisation [42-44]. Of these, ionic solutions were among the earliest to reveal clear deviations from ideal behaviour, sparking the development of new physical models.

Thermodynamic perspective: Ionic solutions and non-ideality: The electrolyte, such as NaCl dissociates into Na^+ and Cl^- ions in aqueous solution. In an ideal solution, these ions would behave independently; however, in reality, they show remarkable electrostatic interactions, resulting in deviations from ideality.

Free energy changes and non-ideality: Let the free energy change upon dissolution be denoted by ΔF (**Scheme-III**). For a real ionic solution, the free energy deviates from the ideal case due to interionic interactions. The difference: $\Delta F_{diff} = \Delta F_{real} - \Delta F_{ideal}$ is a measure of non-ideality. These deviations are not random but arise from predictable electrostatic interactions governed by Coulomb's Law [15,45].

The shift from ideal to non-ideal models illustrates the recognition that scientific laws have specific areas of validity.



Scheme-III: Free energy change (ΔF) for the dissolution of NaCl in water, showing how real ionic solutions deviate from ideal behaviour due to different interionic interactions (ΔF_{diff})

Differences between ideal solution predictions and experimental measurements show the inadequacy of simplified assumptions and stimulate a process of theoretical refinement. This conceptual progression reflects the self-correcting nature of scientific inquiry, in which models evolve to provide increasingly realistic descriptions of molecular interactions.

Electrostatic interactions: Debye-Hückel theory

Coulombic interaction and free energy: Coulomb's law dictates that the interaction energy between two charged particles is inversely proportional to the distance between them (eqn. 6). In the context of ionic solutions, the electrostatic contribution to free energy is approximated as:

$$\Delta F_{diff} = -\frac{Ne^2}{2\bar{l}} \tag{6}$$

where N is Avogadro's number, *e* is the elementary charge; $\bar{l}$ is the average distance of interaction between ions. This equation implies that as ions come closer (smaller $\bar{l}$), the electrostatic stabilisation increases (more negative free energy) [6,46].

Structural interpretation: Ion atmosphere: The concept of an ion atmosphere, a statistical cloud of oppositely charged ions surrounding each ion in solution (Fig. 3), was introduced by Debye and Hückel [6]. This structural idea decreases the electrostatic potential, influence ionic mobility and modify colligative and thermodynamic properties. This type of organisation elucidates for the higher freezing point depression and boiling point elevation of the electrolyte solutions relative to non-electrolytes [47,48].

The ion atmosphere plays an important role in understanding the structure of ionic solutions. Every ion is wrapped by a surrounding layer of oppositely charged ions, collectively forming a locally neutral region. This arrangement influences both the transport properties (like conductivity and diffusion) and the thermodynamic properties (like activity coefficients and osmotic pressure).

These molecular-level observations provide a rationale for macroscopic phenomena such as freezing point depression, boiling point elevation and variations in colligative properties.

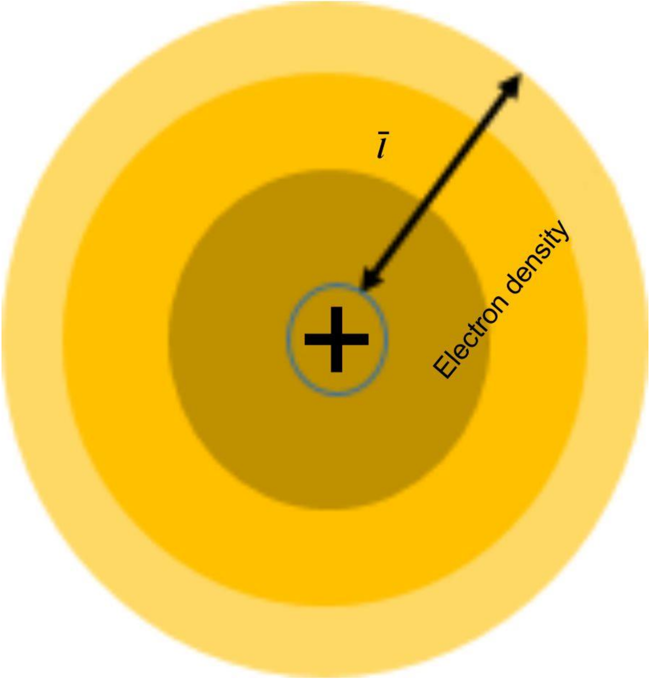


Fig. 3. Illustration of the ion atmosphere described by Debye-Hückel theory, showing how a central ion in solution surrounded by a statistical cloud of oppositely charged ions

Activity coefficients and ionic strength: It has been shown that electrolytes depress the freezing point and raise the boiling point more than non-electrolytes. For this work, two concepts are used to measure the deviation from the ideality *viz.* activity coefficient and ionic strength [49,50]. The historical development of these concepts was also examined, briefly elucidating their theoretical roots with particular emphasis on Debye-Hückel theory, exploring the practical applications in physical chemistry and biochemistry, and highlighting selected contemporary approaches. In real chemical systems, however, solute behaviour, especially in electrolyte solutions, often deviates from the predictions of ideal solution laws. Such deviations are vital for accurate predictions of equilibrium, solubility, pH and electrochemical potentials. In thermodynamic equations, a species 'concentration' is replaced with the corresponding 'activity' and account for non-ideality using the activity coefficient (γ). The concept of ionic strength serves as a key parameter affecting these coefficients [51,52].

For a solute A, the activity a_A is given by:

$$a_A = \gamma_A \cdot [A]$$

where γ_A = activity coefficient of species A; [A] = molar concentration of A

Ideal behaviour assumes γ = 1; deviations arise in the real solutions.

The total concentration and ionic charge of a solution measure the ionic strength of that solution (eqn. 7):

$$I = \frac{1}{2}\sum_i C_i Z_i^2 \tag{7}$$

C_i and Z_i denote the molar concentration and charge of the *i*-th ion, respectively. Consequently, higher ionic strength results in stronger interionic interactions, leading to greater deviations from the ideality.

Although the concepts such as ionic strength and activity coefficient are clearly mathematically formal and they can be illuminated more spontaneously by relating them to the history of Debye-Hückel theory. It not only provides the conceptual background but also integrates thermodynamics, electrostatics and statistical mechanics into a coherent learning experience.

Debye-Hückel limiting law: Peter Debye and Erich Hückel laid the cornerstone of ionic solution theory in 1923 [6]. They derived the limiting law for dilute electrolyte solutions and proposed that the average interaction length $\bar{l}$ (eqn. 8) is inversely related to the square root of ionic concentration:

$$\bar{l} \propto \frac{1}{\sqrt{C}} \tag{8}$$

This relationship allowed the derivation of the Debye-Hückel limiting law (eqn. 9) for the activity coefficients γ of ions in dilute solutions, which quantifies deviation from ideal behaviour:

$$\log \gamma = -\frac{Az^2\sqrt{I}}{1+Ba\sqrt{I}} \tag{9}$$

where z is the ionic charge; I is the ionic strength; A, B and a are the constants dependent on the solvent and temperature. The theory introduced the concept of the ion atmosphere, a statistical cloud of opposite-charge ions surrounding a given ion, reducing its effective electrostatic potential. This formulation laid the foundation for modern electrolyte theory [53-56]. In case of highly dilute solutions, the limiting law in its simplified form is expressed in eqn. 10.

$$\log_{10} \gamma_i = -Az_i^2\sqrt{I} \tag{10}$$

The development of ionic solution theory had far-reaching impacts across multiple disciplines, including (i) colloid and interface science through the understanding of charged particle stability in suspensions, (ii) polymer solution theory through Flory-Huggins lattice models, (iii) biophysics through insights into ionic screening in DNA, proteins and cell membranes, and (iv) electrochemistry by informing electrode kinetics and electrolyte modelling. Even today, the Debye-Hückel theory remains a critical component of physical chemistry curricula and is instrumental in modelling ionic interactions in diverse fields including pharmaceutical science, biophysics and environmental chemistry [57-59].

Phase II in the historical development of chemical thought marked a major shift from simplified, idealised ideas toward more rigorous, physics-grounded models, which could explain and predict the behaviour of real chemical systems. The Debye-Hückel theory is rooted in electrostatics and statistical mechanics. It was among the first to successfully connect microscopic ion behaviour with macroscopic thermodynamic observables. It remains one of the foundational ideas in solution chemistry and continues to shape modern approaches to understanding ionic environments.

Phase III (1920-1950s): From classical radiation to microscopic matter waves: Quantum emergence in chemistry: Quantum mechanics ushered in a new era of unprecedented insight into matter and energy. It not only resolved long-standing contradictions in classical physics but also introduced the core principles and constants that chemistry continues to rely on today. The transition from radiation studies to wave mechanics set the stage for understanding atomic and molecular behaviour, chemical bonds and, eventually, the structure of matter itself.

Quantum mechanics revolutionised the understanding of the micro-world, especially in the realm of chemical phenomena. Classical models could not account for black-body radiation, atomic stability and the structure of chemical bonds; quantum mechanics offered a coherent and predictive foundation [60-62]. Presenting landmark quantum discoveries chronologically helps interpret the quantum mechanics. Educators can foster appreciation for science's investigative nature by framing quantum principles not as abstract postulates, but as necessary solutions to experimental puzzles, thereby illuminating its problem-solving essence.

Black-Body radiation: Birth of Planck's constant

Blackbody radiation and Maxwell theory: In 1962, Maxwell's classical electromagnetism succeeded in defining light as an electromagnetic wave. However, this theory failed to explain blackbody radiation (Fig. 4), especially the observed spectral distribution of emitted radiation from the hot objects [63-65].

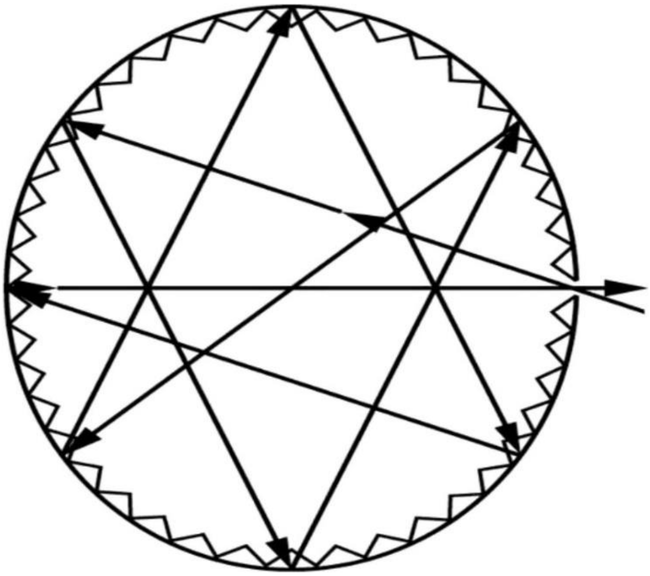


Fig. 4. Schematic illustration of a black body: a hollow cavity with a small hole in its wall, allowing radiation to enter and undergo multiple reflections, resulting in nearly perfect absorption

Everyday experience: Empirical observations: As metals are heated, their colour visibly shifts from red to yellow and ultimately to white, providing a simple yet powerful indication of increasing emitted energy; scientists also recognised that a substance's capacity to radiate heat and light is closely linked to its ability to absorb heat. In other words, good emitters are also good absorbers. This insight, arising the from radiation research, eventually helped pave the way for Wien's displacement law, which can be written as:

$$\lambda_{max} T = \text{Constant} \tag{11a}$$

$$\frac{ck_B T}{\nu_{max}} = \text{Constant} \tag{11b}$$

These equations (11a-b) suggest that there is a new fundamental constant that the classical physics has not yet acknowledged. This constant was later identified as Planck's constant, h. A theoretical expression of Wien's displacement law (λ_{max} T = b, where b is Wien's displacement constant) also yields the spectral energy density distribution of black-body radiation [66], as shown in Fig. 5, which represents the blackbody radiation energy density spectra (ρ_λ *vs.* λ for two temperatures T_1 and T_2 ($T_2 > T_1$), demonstrating both the shift of the emission peak toward shorter wavelengths and the increase in total emitted energy with rising temperature.

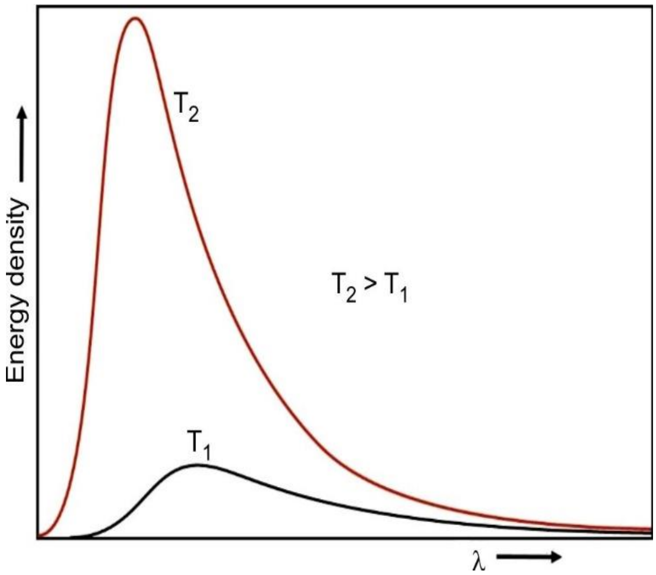


Fig. 5. Illustration of Wien's displacement law (λ_{max} T = constant) and the temperature dependence of blackbody radiation energy density distribution

Universality of black-body radiation: Quantum hypothesis: Black body radiation is a universal phenomenon that occurs regardless of the material of the emitting body, indicating that classical parameters such as mass or charge do not affect it. Consequently, the governing constant cannot depend on such quantities [66]. Instead, it must correspond to a new fundamental constant, given by eqn. 12:

$$\frac{k_B T}{\nu_{max}} = \text{Constant} = \frac{\text{Constant}}{c} \Rightarrow h \qquad (12)$$

Planck's quantum hypothesis (1900): To resolve the ultraviolet catastrophe (Fig. 6), Planck proposed that the oscillators in the cavity walls of blackbody exchange energy with standing modes of the cavity only in discrete quanta of hν [63,67]. Emission and absorption of radiation by matter is therefore discrete, E = hν.

Einstein's photon concept (1905): Einstein advanced the idea that light is composed of energy quanta called photons, which formed the basis for the photoelectric effect, where electrons are released from a metal surface when exposed to light [68], highlighting the dual nature of light. His photon theory effectively explained two phenomena *viz.* (i) only photons with energy greater than the work function (ϕ) of the metal could eject electrons; and (ii) the kinetic energy (K.E.) of the emitted electrons is as: K.E. = $h\nu - \phi$.

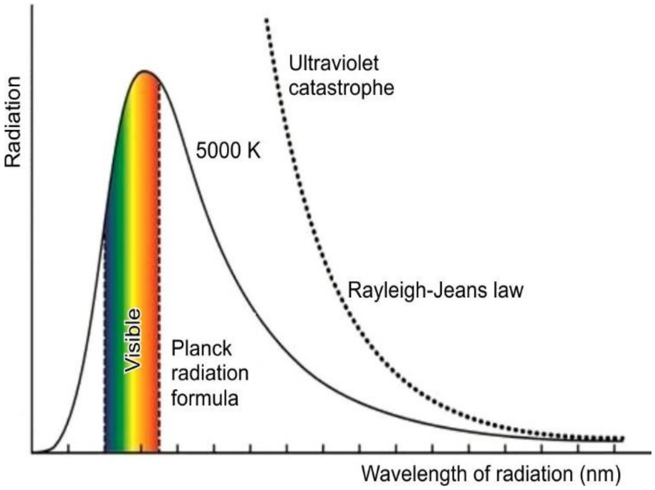


Fig. 6. Blackbody radiation: classical Rayleigh–Jeans law (dashed) diverges at short wavelengths ("ultraviolet catastrophe"), while Planck's quantum model (solid) accurately fits experimental data

This work introduced a ground-breaking concept in physics, for example, the wave-particle duality of light. It revealed that light is not solely one form and behaves like a wave, producing patterns of interference and diffraction, and like a particle, arriving in small energy packets that trigger the photoelectric effect. This unexpected dual nature of light eventually became a fundamental principle of quantum mechanics [69].

Einstein's major breakthrough came from explaining the photoelectric effect through the concept of photons, demonstrating that light consists of real, measurable energy packets. His 1921 Nobel Prize in Physics was awarded not for relativity but for this explanation, which confirmed the particle nature of light and marked one of the earliest and most decisive successes of quantum theory.

Atom and Planck's constant: Bohr's quantisation rule: In 1913, Niels Bohr introduced a revolutionary atomic model that successfully explained the hydrogen atom's line spectrum, a problem that had long eluded classical physics [70]. To realize this, Bohr integrated Planck's constant into atomic theory to develop the idea of quantised angular momentum. Bohr stated that an electron around a nucleus could only travel along a certain permitted orbit if its angular momentum is an integer multiple of h/2π (also $\hbar$) as in eqn. 13:

$$mVr = n\frac{h}{2\pi} \qquad (13)$$

Despite its success, Bohr's quantisation rule was not derived from a complete theoretical framework; rather, it was introduced ad hoc, guided by experimental observations, to reproduce the notable spectral lines of hydrogen, particularly those of the Balmer series. Bohr incorporated Planck's constant into the atomic model, showing that quantum principles apply not only to radiation, as demonstrated by Planck and Einstein, but also to the fundamental structure of matter [71]. Bohr's semi-classical model, despite its limitations, formed a key bridge between classical physics and quantum mechanics, introducing quantisation in atomic systems and revealing the influence of Planck's constant on the arrangement of matter and radiation.

de Broglie's innovative hypothesis: In 1924, Louis de Broglie advanced a ground-breaking hypothesis that carried the principle of wave-particle duality into the domain of matter, asserting that if light can behave as particles, then particles such as electrons should likewise exhibit wave characteristics [72]. This led to the formulation of de Broglie wavelength. A photon with frequency 'ν' has momentum shown in eqn. 14:

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{14}$$

on rearrangement, we got

$$\lambda = \frac{h}{p} \tag{15}$$

This relation (eqn. 15) is also valid for material particles (such as subatomic particles like electrons) with momentum p = mV (mass × velocity), which leads to eqn. 16.

$$\lambda = \frac{h}{mV} \tag{16}$$

where λ is the wavelength associated with the particle and h is Planck's constant.

This relation, first applied to electrons, predicted that matter exhibits wave-like behaviour, a concept that was later experimentally confirmed in electron diffraction experiments by Davisson & Germer [73].

de Broglie's idea also provided a physical rationale for Bohr's quantisation condition and argued that the electron in a stable orbit around the nucleus must form a standing wave, such that an integral number of wavelengths fits along the circumference of the orbit: $2\pi r = n\lambda$

Substituting λ = h/mV, this becomes consistent with the Bohr's quantised angular momentum (eqn. 13). Thus, the hypothesis of de Broglie gave a deeper theoretical foundation to Bohr's model by interpreting quantised orbits as the condition for constructive interference of electron matter waves.

Wave character of electron: Davisson-Germer experiment: In the early 20th century, the possibility that electrons might exhibit wave-like behaviour began to attract attention. Proposed theoretically by Louis de Broglie in 1924 [74], this idea gained decisive experimental support in 1927 when Davisson & Germer demonstrated electron diffraction, confirming the wave nature of electrons.

In their experiment, Davison & Germer struck a focused beam of electrons on a nickel crystal and measured the intensity of the scattered electrons at different angles. The resulting diffraction pattern showed peaks at different angles, which corresponded to X-rays (electromagnetic waves) diffracted from the crystal plane, following Bragg's formula: $n\lambda = 2d \sin\theta$.

The diffraction of the observed electrons can be interpreted only if electrons behave like waves with a wavelength in the de Broglie equation (eqn. 16). This result was not merely indirect evidence but the first clear experimental confirmation that electrons possess wave-like properties, marking a major milestone in physics. It validated the counterintuitive yet powerful concept of wave-particle duality and ushered in the era of quantum mechanics, in which particles can propagate as waves, interfere with one another and exhibit behaveiours beyond the scope of classical physics [73].

Two foundational lessons of quantum theory: Change in worldview: Quantum theory radically changed the classical perspective on nature when it was proposed by the principles of wave-particle duality [70], which may be summarised as:

1. Radiation, previously a wave phenomenon in classical physics (*e.g.* light, electromagnetic waves), is now shown to have particle-like behaviour (photons) in quantum theory.
2. Matter, particularly electrons and atoms, was traditionally treated as purely particulate in classical physics, but diffraction and interference experiments revealed that these entities also exhibit wave-like properties.

These inter-relations illustrate that energy and momentum can be expressed as waves or particles (Table-1), depending on the contexts, a radical departure from classical worldview. This duality became the foundation of quantum physics, not just a philosophical concept. Physical phenomena such as blackbody radiation, the photoelectric effect, atomic spectra and all of these phenomena together represent a departure from classical determinism toward a quantitative description of matter and energy:

TABLE-1
WAVE–PARTICLE DUALITY RELATION:
FOUNDATIONAL TO QUANTUM PHYSICS

Parameter	Character	
	Particle	Wave
Energy	E	$\hbar\omega$
Momentum	p	$\hbar k$

$\hbar = h/2\pi$; $\omega = 2\pi\nu$; $k = 2\pi/\lambda$

Mathematical form of matter waves: How to describe a matter wave: A guess

Oscillation at a point (*x* = 0): The notion of displacement: In wave theory, displacement refers to an oscillating quantity (which could represent physical displacement in classical waves or a probability amplitude in quantum waves) that oscillates in time at a fixed point [75]. For a classical wave, at a fixed point, say *x* = 0, this displacement varies typically in time and can be expressed as eqn. 17:

$$\psi(x = 0, t) = Ae^{-2\pi i\nu t} \tag{17}$$

The amplitude and frequency of the oscillation are represented as A and ν, respectively.

Wave motion: Phase delay with position: To explain the propagation of a wave through space, the concept of phase delay is first introduced, whereby the wave at any position *x* is phase-delayed relative to its value at the origin (*x* = 0). It is thus delayed in the phase of the displacement at a point *x* relative to the phase of the origin. Taking this phase delay into account, the full expression for the wave's displacement at any point *x* is written in eqn. 18:

$$\psi(x, t) = Ae^{-2\pi i\nu\left(t - \frac{x}{\nu}\right)} \tag{18}$$

In this context, *x*/ν simply represents the time delay a wave experiences as it propagates forward at a speed 'ν'. There are two fundamental parameters that defines a wave–the angular frequency (ω) and the wavenumber (k). The relation between ω and ν can be expressed using eqn. 19:

$$2\pi\nu = \omega \tag{19}$$

The wavenumber, by contrast, characterizes how tightly a wave is spatially packed along its direction of propagation and is related to the wavelength (λ) through eqn. 20:

$$\frac{2\pi\nu}{\nu} = \frac{2\pi}{\lambda} = k \tag{20}$$

When these results are substituted into Eq. 18, the most commonly used equation for traveling waves is obtained (eqn. 21):

$$\psi(x,t) = Ae^{-i(\omega t - kx)} \tag{21}$$

This final expression (eqn. 21) gives a complete picture of the wave displacement at any point x and any time t and stands as a standard mathematical solution for waves travelling through space.

Particle-wave correspondence: Energy and momentum relations: Eqn. 22 shows the kinetic energy of a free particle according to classical mechanics.

$$E = \frac{p^2}{2m} \tag{22}$$

In quantum mechanics, the de Broglie and Planck relations between wave and particle quantities are $E = \hbar\omega$ and $p = \hbar k$, respectively. Substituting these quantities into the classical energy eqn. 22 gives eqns. 23 or 24:

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \tag{23}$$

$$\text{or,}\quad \omega = \frac{\hbar k^2}{2m} \tag{24}$$

Eqn. 24 denotes the dispersion relation in quantum mechanics for a free particle [70]. In simple terms, this description illustrates the connection between the particle and wave perspectives: a quantum particle can be regarded as a wave packet, with its frequency corresponding to energy and its wavelength corresponding to momentum. Consequently, the wave-like behaviour of a quantum particle is intrinsically linked to the framework of classical mechanics.

Quantum revolution: Schrödinger equation: The development of Schrödinger equation was a major turning point in the rise of quantum mechanics, giving the field its essential mathematical foundation. It all began with de Broglie's idea that matter behaves like a wave, expressed through the relation λ = h/p. A particle possessing momentum p is thus described by a wave function of the form given in eqn. 25:

$$\psi(x,t) = Ae^{-i(\omega t - kx)} \tag{25}$$

Differentiation of this trial wave function reveals its dynamical character. The time derivative and spatial second derivative, shown in eqns. 26 and 27, respectively, connect the wave description to measurable physical quantities.

$$\frac{\partial\psi}{\partial t} = -i\omega\psi \tag{26}$$

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi \tag{27}$$

Using the quantum relations $E = \hbar\omega$ and $p = \hbar k$, one recovers the free-particle kinetic energy (eqn. 28):

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \tag{28}$$

Eliminating ψ from the right-hand sides of eqns. 26 and 27 yields a new relation (eqn. 29):

$$\frac{\partial\psi}{\partial t} = i\left(\frac{\omega}{k^2}\right)\frac{\partial^2\psi}{\partial x^2} \tag{29}$$

Substituting the dispersion relation for matter waves (eqn. 24) leads directly to the fundamental dynamical eqn. eqn. 30:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} \tag{30}$$

Eqn. 30 indicates the time-dependent Schrödinger equation concerning a free particle in one dimension. This result unites de Broglie's wave idea with dynamical evolution and is indicative of the concept of wave-particle duality.

To extend this description to a system with external effects, such as a particle moving in a potential field V(x), the Hamiltonian operator is introduced (eqn. 31):

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{31}$$

With this operator, the Schrödinger equation takes its more general and familiar form (eqn. 32):

$$i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x,t) \tag{32}$$

Eqn. 32 is a fundamental equation of quantum mechanics, which explains that the wave function and represents the quantum state of a system that evolves with time under both kinetic and potential energy terms [75].

Physical interpretation

Wave function ψ(x, t) is not directly observable: The wave function (ψ) is the central mathematical entity in quantum mechanics, representing a complex-valued probability amplitude. It cannot be measured directly; only the probability information derived from it is accessible.

Born interpretation: Max Born provided an important insight and proposed that the quantity $|\psi(x,t)|^2\,dx$ gives the probability of finding a particle between positions x and x + dx at time t. This idea leads quantum mechanics to a fundamentally probabilistic theory, which is completely different from the certainties of classical physics. Using the square of the wave function ensures that the probability values are always real and positive, which makes the concept physically meaningful. Born's interpretation laid the groundwork for understanding atomic and molecular structure, chemical bonding and the inherently statistical behaviour of microscopic particles. The main points of this interpretation are shown in Table-2.

Quantum and wave mechanics foundation: Influence on chemistry: Unlocking the chemical bonds form

Overview of bond formation: The nature of chemical bonds, particularly covalent bonds, has been extensively examined through quantum mechanics [76], highlighting electron sharing, wave function symmetry, orbital overlap and electron

TABLE-2
COMPARISON OF CLASSICAL AND QUANTUM MECHANICAL INTERPRETATIONS OF PHYSICAL CONCEPTS

Concept	Classical physics	Quantum mechanics
Energy	Deterministic	Quantised, *via* $E = \hbar\omega$
Motion	Particles have exact trajectories	Described by $\psi(x, t)$, probabilistic
Observables	Measurable directly	Extracted from operators acting on ψ
Impact	Macroscopic laws	Microscale foundations of atoms, molecules

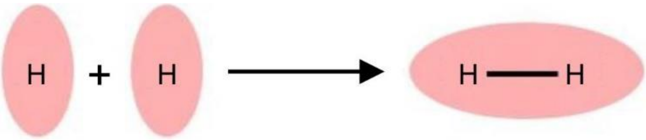
spin in the formation of bonds. Quantum mechanical principles clarify the roles of spatial and spin wave function symmetry, the significance of overlap integrals for bond strength and the influence of wave function sign and magnitude on bond stability and orientation. These concepts also explain common molecular geometries, *e.g.* linear, tetrahedral, octahedral, through hybridization and molecular orbital frameworks. By connecting historical models with modern quantum interpretations, the discussion unites fundamental theory with observable molecular behaviour.

More specifically, covalent bonding is the heart of molecular chemistry, providing the stability and structure seen in most chemical compounds. While classical models such as Lewis structures and VSEPR theory introduced basic bonding ideas, quantum mechanics offers a more precise and predictive explanation. In this framework, bonding electrons are described by wave functions that satisfy the Schrödinger equation and comply with the Pauli Exclusion Principle and spin-statistics theorem [77,78].

From a modern quantum perspective, a covalent bond arises when atomic orbitals constructively interfere, lowering the energy of the system and stabilizing the bond. Key quantum mechanical features include wave function symmetry, overlap integrals, bond directionality and the resulting molecular geometry.

Wave functions and covalent bond formation

Classical view: From a classical perspective, a simple molecule like H_2 can be treated as a four-body system of two electrons and two protons (**Scheme-IV**). Classical electrostatic calculations underestimate the bond strength because they do not account for quantum effects.



Scheme-IV: Formation of a hydrogen molecule (H_2) from two individual hydrogen atoms, illustrating the steps involved in bond creation

Quantum view: The Born-Oppenheimer approximation arises from the large mass difference between electrons and nuclei [8,60]. Since nuclei are much heavier, they can be treated as stationary or slowly moving compared to the rapidly moving electrons. This separation of time scales allows the nuclei to be considered effectively fixed while the electronic part of the problem is solved independently.

In this framework, each electron in an atom or molecule is described by a wave function (ψ), a mathematical expression that contains all information about the electron's state. The wave function provides details such as the regions where the electron is most likely to be found, its interactions with other particles and its contribution to bond formation.

Calculate energy of molecule: To determine the energy of a molecule, quantum mechanics uses the Hamiltonian operator. This is the total energy operator for electrons in a fixed nuclear configuration. A suitable trial wave function (ψ) is proposed and the variational method is applied to estimate the system's energy (eqn. 33):

$$E = \int \psi^* H\psi d\tau \text{ with } E \geq E_{exact} \tag{33}$$

This approach gives an upper bound to the true ground state energy.

Electron pair bond in H_2 molecule

A 4-body problem (2 electrons + 2 protons): Two protons repel each other; however, placing two electrons between them produces screening, which weakens the repulsive force (Fig. 7). From a quantum-mechanical perspective, the electrons are indistinguishable and their mutual interactions determine the total energy of the system.

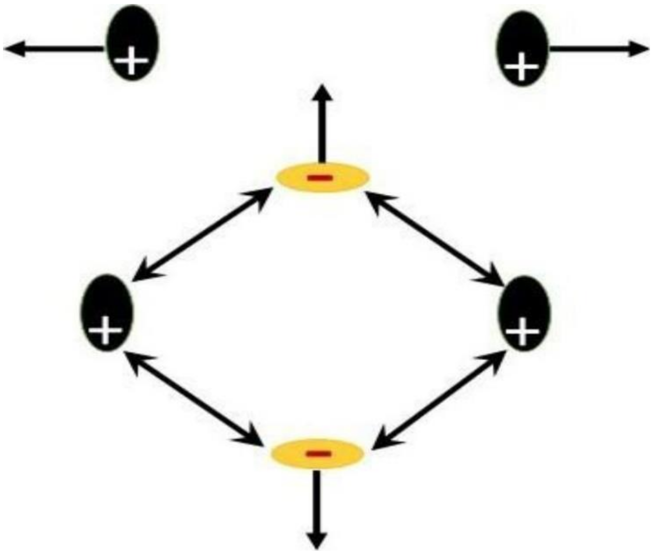


Fig. 7. Electrostatic interactions: opposite charges (+/–) attract (inward arrows), while like charges repel (outward arrows), governing molecular self-assembly and supramolecular stability

Describing the bond: How to describe such a bond: Consider two states of electrons (1) and (2) associated with two atoms, labeled (a) and (b). The corresponding product wave functions are: $\psi_I = \psi_a^{(1)}\psi_b^{(2)}$ and $\psi_{II} = \psi_a^{(2)}\psi_b^{(1)}$

If the electrons do not interact, both ψ_I and ψ_{II} correspond to the same energy: $E = E_a + E_b$

Since electrons are indistinguishable fermions, the total wave function must be either symmetric or antisymmetric under exchange of particles. Thus, the appropriate linear combinations are:

Symmetric combination (bonding orbital):

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_a^{(1)}\psi_b^{(2)} + \psi_a^{(2)}\psi_b^{(1)}\right)$$

Antisymmetric combination (antibonding orbital):

$$\psi_A = \frac{1}{\sqrt{2}}\left(\psi_a^{(1)}\psi_b^{(2)} - \psi_a^{(2)}\psi_b^{(1)}\right)$$

The symmetric orbital (ψ_S) enhances the probability density between the two nuclei, leading to bond formation, while the antisymmetric orbital (ψ_A) produces a node between the nuclei, corresponding to antibonding character.

Electron density and bonding: When electrons (1) and (2) share a common region between nuclei a and b, the distribution of electron density determines whether bonding or repulsion occurs.

(i) Bonding case (symmetric wave function, ψ_S): The probability of finding both electrons between the nuclei is high (Fig. 8). This enhanced electron density in the internuclear region lowers the potential energy of the system, resulting in a stronger covalent bond.

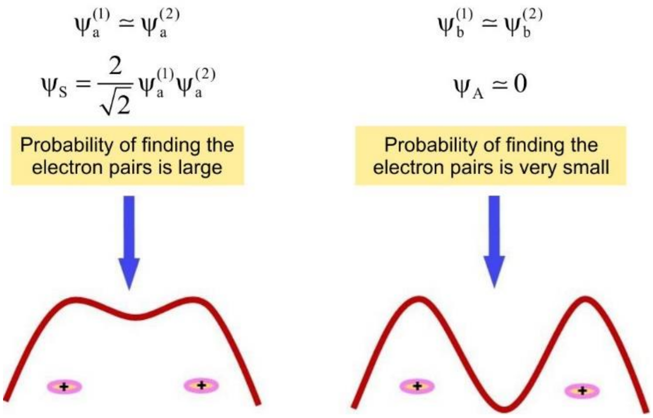


Fig. 8. Electron density in molecular bonding: the symmetric wave function (ψ_S) shows high electron density between nuclei (bonding), while the antisymmetric wave function (ψ_A) shows low density (antibonding)

(ii) Antibonding case (antisymmetric wave function, ψ_A): In this case, a nodal plane appears between the two nuclei, which greatly reduces the electron density in that region. The nuclei experience net repulsion, corresponding to an unstable, antibonding interaction (Fig. 8). Thus, the electron density distribution in bonding (ψ_S) and antibonding (ψ_A) molecular orbitals is the key determinant of bond stability: higher density between nuclei leads to bonding, whereas low density leads to repulsion.

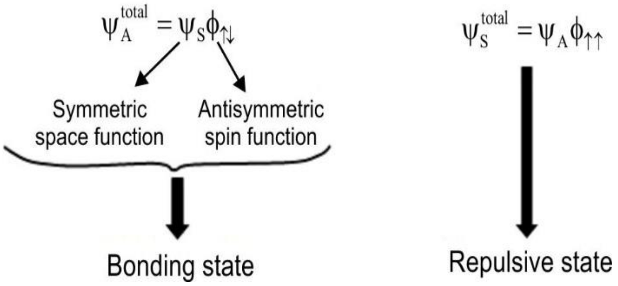
Spin states and symmetry of electrons: When two electrons bond, their combined wave function needs to follow the Pauli Exclusion Principle [76,79,80]. This principle states that the total wave function of the two electrons be antisymmetric when the electrons are exchanged. To describe this properly, the total wave function is written as the product of two components: a spatial part (ψ_{space}) and a spin part (ψ_{spin}): $\psi_{total} = \psi_{space} \times \psi_{spin}$. To ensure overall anti-symmetry:

(i) If the spatial wave function (ψ_{space}) is symmetric, then the spin wave function (ψ_{spin}) must be antisymmetric, which corresponds to the singlet state, antiparallel spins (↑↓).

(ii) If the spatial wave function is antisymmetric, the spin wave function must be symmetric, which corresponds to the triplet state, parallel spins (↑↑).

Bond formation occurs in the singlet state, where electrons with opposite spins allow a symmetric spatial wave function. This symmetry leads to constructive overlap of electron density between the nuclei, lowering the energy and stabilizing the bond.

Alternatively, when the spatial wave function is antisymmetric and the spins are aligned (triplet state), destructive interference appears between the nuclei. This reduces electron density in the bonding region and creates repulsion, resulting in an antibonding interaction (**Scheme-V**).



Scheme-V: Electron spin states and bonding: A symmetric spatial wave function paired with an antisymmetric spin state (singlet, left) allows bond formation, whereas an antisymmetric spatial wave function with a symmetric spin state (triplet, right) leads to repulsion. This contrast highlights how the Pauli Exclusion Principle governs molecular stability

Molecular geometry: Bond strength and directionality: As two atoms approach each other, their atomic orbitals begin to overlap. The nature of this overlap, determined by the relative phase (sign) of the interacting wave functions, governs whether a bonding or antibonding interaction occurs. When the orbital phases match, constructive interference increases electron density between the nuclei, stabilizing the system and forming a bonding molecular orbital (ψ_S). Conversely, when the phases are opposite, destructive interference creates a nodal plane with minimal electron density, raising the system's energy and producing an antibonding molecular orbital (ψ_A). These interactions are reflected in the potential energy curve (Fig. 9).

At large internuclear separations, atoms behave as isolated species and the energy approaches zero. As the atoms move closer together, attractive interactions dominate, causing the energy to decrease until it reaches a minimum at the equilibrium bond length, the internuclear distance at which the bond is most stable. Further compression beyond this point leads to strong electron-electron and nuclear-nuclear repulsions, resulting in a sharp rise in energy. The energy difference E_R between the bonded state and the separated atoms corresponds to the bond dissociation energy, a key quantity that characterizes bond strength.

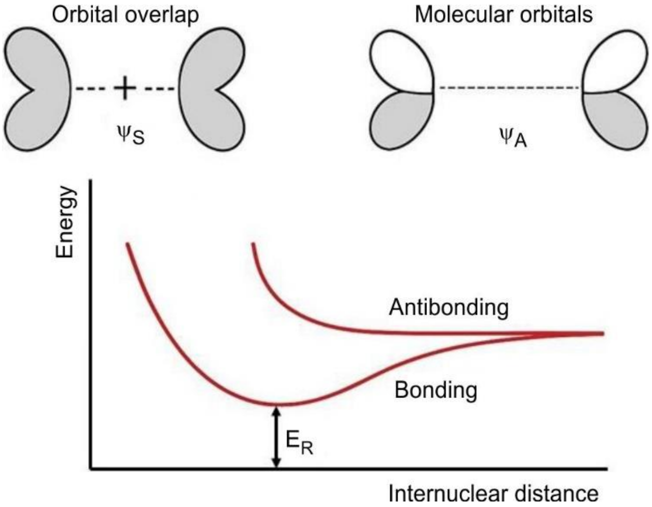


Fig. 9. Molecular orbital formation and bond energetics: constructive (bonding, ψ_S) and destructive (antibonding, ψ_A) orbital overlap (top) and potential energy curves showing bond stabilisation, equilibrium distance and dissociation energy (bottom)

The energy difference (E_R) between the bonding state and separated atoms represents the bond dissociation energy, a fundamental measure of bond strength. The strength of a covalent bond is quantitatively associated with the overlap integral (S) in eqn. 34 between the wave functions of the two interacting atoms:

$$S = \int \psi_a^{(1)} \psi_b^{(2)} d\tau \qquad (34)$$

where $\psi_a^{(1)}$ represents the wave function of electron 1 associated with atom A and $\psi_b^{(2)}$ corresponds to the wave function of electron 2 on atom. The integration extends over all space $d\tau$.

A larger value of the overlap integral S indicates a greater degree of orbital overlap and therefore stronger covalent bond formation. This idea underpins valence bond theory, which describes chemical bonding as arising from the constructive overlap of atomic orbitals. The constructive and destructive interference of atomic wave functions gives rise to the directionality of covalent bonds, particularly in *p*- and *d*-orbitals that possess lobes of opposite sign. Such interference governs molecular geometry: σ bonds result from head-on orbital overlap, whereas π-bonds arise from the side-on overlap of parallel *p*-orbitals.

To explain the experimentally observed molecular geometries, orbital hybridisation is introduced. In this process, atomic orbitals combine to form new, equivalent hybrid orbitals oriented in the specific directions, enabling atoms to adopt the geometries observed in real molecules. For example, (i) *sp* (linear): 180º orientation (*e.g.* CO_2); (ii) sp^2 (trigonal planar): 120º (*e.g.* BF_3); (iii) sp^3 (tetrahedral): 109.5º (*e.g.* CH_4); and (iv) d^2sp^3 (octahedral): 90º (*e.g.* SF_6).

These diverse molecular geometries emerge from the combination of hybridisation concepts with molecular orbital theory, both of which consider the symmetry and energy of the orbitals involved. Together, they highlight the predictive power of quantum chemistry. Quantum mechanics provides a robust framework for understanding covalent bonding, where symmetric spatial and antisymmetric spin wave functions, overlap integrals and wave function phases explain bond strength and directionality. The geometry of molecules, from the simple linear CO_2 to the complex octahedral SF_6, can be rationalized through orbital hybridisation and symmetry principles.

These concepts not only clarify the fundamentals of chemical bonding but also underpin the rational design of new molecules and materials in areas such as organic synthesis, materials chemistry and molecular biology. The quantum-mechanical description of bonding, viewed historically, reveals that ideas like molecular orbital theory and hybridisation are not empirical shortcuts but logical consequences of applying wave mechanics to chemical systems. This perspective puts the chemical bonding firmly within quantum theory, demonstrating its role as a unifying principle that connects diverse areas of molecular science.

Phase IV (Post-1950): How chemical patterns, oscillations and self-organisation paved the way for life: After 1950, chemistry entered a new era known as Phase IV. There is a fundamental shift from equilibrium and reductionist models to dynamic processes, from nonlinear to far-equilibrium models. Building on earlier achievements ranging from the organisation of the elements to quantum models of molecules, this phase opened new fields for studying self-organization, reaction-diffusion patterns and the chemical origins of biological complexity. Within this perspective, chemistry emerges as a core component of systems science, concerned with the dynamic growth, adaptation and functional emergence of chemical networks in ways reminiscent of living systems. Phase IV chemistry moves beyond static structures to focus on the evolution, transformation, and maintenance of order in chemical systems under continually changing conditions, thereby aligning chemistry more closely with biology and systems theory and marking a significant shift in the scientific worldview.

Key theoretical developments and experimental discoveries have profoundly reshaped the role of chemistry in understanding complexity and life. Together, these advances provide a foundation for emerging fields such as systems chemistry, synthetic biology and complex systems science, positioning chemistry at the center of disciplines concerned with dynamic, adaptive and evolving systems.

Self-Organisation in open systems

Conceptual foundations: Self-organisation is a key concept of Phase IV in open systems. Unlike closed systems, which evolve toward thermodynamic equilibrium, open systems continuously exchange energy and matter with their surroundings. This sustained exchange enables the spontaneous emergence of ordered structures, particularly when the system operates far from equilibrium.

Prigogine and dissipative structures: Belgian chemists Prigogine & Nicolis [81] made revolutionary contributions to the development of the field of non-equilibrium thermodinamics. One of the most significant contributions was the introduction of dissipative structures, demonstrating that entropy production can lead to increased order. Although this initially appears to contradict the second law of thermodynamics, it was shown that order can emerge precisely as the system continuously dissipates energy.

Dissipative structures only exist in open systems that receive a continuous supply of energy or matter. In contrast to equilibrium structures, which remain stable without external input, self-organized patterns persist only as long as energy continues to flow through the system. For example, (i) Benard convection cells, where heating a fluid creates beautiful hexagonal patterns, (ii) oscillating chemical reactions, such as the Belousov-Zhabotinsky reaction, (iii) biological pattern formation, and (iv) living organisms, which maintain their internal order by consuming energy (such as food or sunlight) and releasing entropy into their environment.

At increasing levels of complexity including cells, tissues and entire ecosystems, biological systems function as dissipative structures that remain far from equilibrium through a continuous flow of energy.

Why dissipative structures are crucial for understanding order in nature?

Theoretical implications: Dissipative structures show that entropy and disorder are not the sole results of processes in thermodynamic systems. These ideas provide a solid scientific basis for understanding the emergence of complex structures including life, within a universe governed by entropy.

Relevance to the real world: These notions provide insight into fundamental natural processes, explaining the development of shapes and patterns in organisms (biological morphogenesis), the evolution of climates, the emergence of patterns in physical and chemical systems. This understanding also underpins advances in fields such as chemical engineering, systems chemistry, nonlinear dynamics and artificial life research [81-83].

Understanding chemical oscillations through nonlinear dynamics: A chemical reaction is considered oscillatory when the concentration of certain intermediates rises and falls in a repeating cycle, creating periodic peaks and troughs over time. Consequently, the rate of product formation also oscillates. Such reactions follow non-equilibrium thermodynamic and cannot oscillate about a position of final equilibrium due to it would then violate the 2nd law of thermodynamics [84].

Chemical oscillations defy the classical chemical intuition, where reactions are expected to proceed monotonically toward equilibrium. Instead, in oscillatory systems, concentrations of intermediates vary periodically over time. The most famous example is the Belousov-Zhabotinsky (BZ) reaction [85-88]. This reaction involves the oxidation of an organic substrate (typically malonic acid) by bromate in an acidic medium with a metal catalyst (*e.g.* cerium or ferroin in the presence of Br^-). Remarkably, the system displays repetitive, visually striking oscillations, manifested as alternating colour changes (Fig. 10).

$$2H^+ + 2BrO_3^- + 3CH_2(COOH)_2 \xrightarrow[Br^-]{Ce(III)}$$
$$2BrCH(COOH)_2 + 3CO_2 + 4H_2O$$

The Belousov-Zhabotinsky (BZ) reaction displays oscillatory behaviour driven by autocatalytic reactions and nonlinear feedback loops, dissipating energy as the reaction proceeds. The system maintains a dynamic steady state, exhibiting temporal order through oscillations in both colour and chemical composition, while also generating spatial waves and target patterns in two-dimensional gels [89] (Fig. 10). These features, arising from the interplay of autocatalysis and feedback, provide a fundamental framework for understanding time-dependent behaviour in both chemical and biological systems.

Other important theoretical models include the Lotka-Volterra model and the Oregonator model (a simplified mathematical model of the BZ reaction developed by Field, Körös and Noyes) [90-92]. These models indicate that chemical oscillators are extremely sensitive to their initial conditions and the values of their parameters. These behaviours reflect classic features of nonlinear systems, such as abrupt changes and even chaotic behaviour under certain conditions.

Self-organization and chemical oscillations demonstrate a unique connection between chemistry, physics, and biology by showing the emergence of dynamic order from nonlinear reaction networks. The BZ reaction exemplifies this behaviour, generating repetitive temporal and spatial patterns without external forces. These oscillations reveal the capacity of chemical systems to exhibit feedback, adapt to changes and function collectively, providing insight into the coordinated behaviour observed in both physical and biological systems.

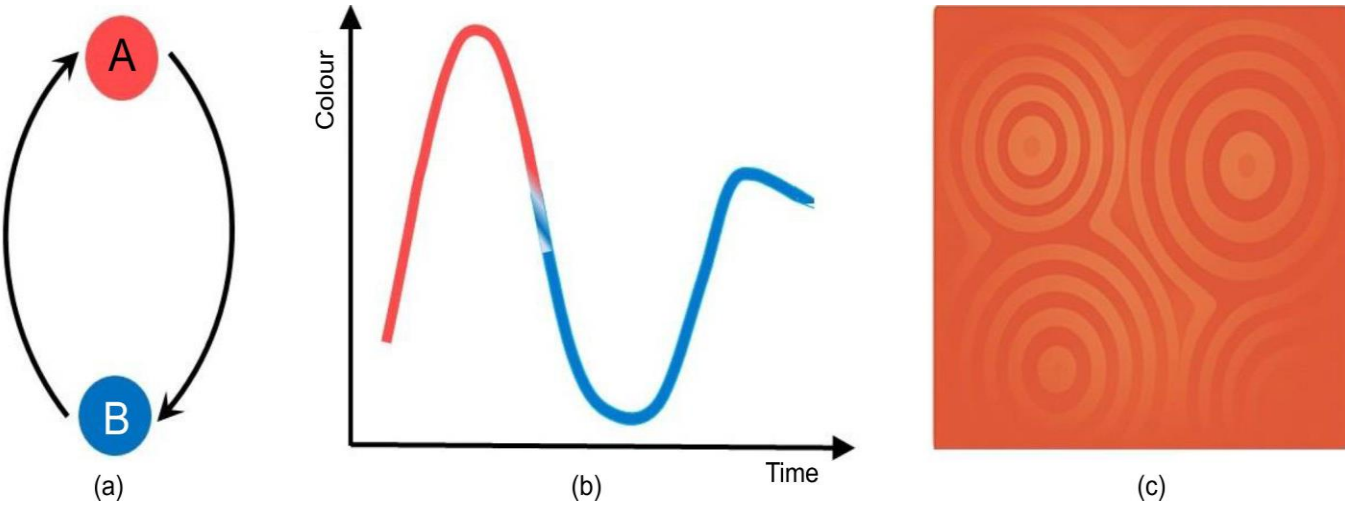


Fig. 10. Composite schematic of chemical oscillations: (a) coupled positive and negative feedback loops, (b) time-dependent colour oscillations in the BZ reaction and (c) spatial wave fronts and target patterns in 2D gel media

How the reaction-Diffusion systems create patterns in nature?

Turing patterns: In 1952, British mathematician Alan Turing, well known as a pioneer of computer science, suggested that biological patterns such as zebra stripes, leopard spots or even leaf arrangements could emerge naturally from the interaction between two chemicals that spread at different rates and react with each other [91,92]. This idea was revolutionary since it challenged the common belief that genetic information alone directly controls pattern formation. Instead, turing proposed that patterns could emerge from simple chemical reactions and diffusion working together.

Turing's reaction-diffusion model is a ground breaking framework that establishes a fundamental link between chemical kinetics, transport phenomena and biological pattern formation. It demonstrates that even simple chemical reactions, when coupled with diffusion, can spontaneously generate organized spatial patterns, providing a scientific explanation for the emergence of complex shapes and structures in nature without pre-set instructions. This work illustrates how basic chemical processes, driven by nonlinear feedback, produce the remarkable diversity of forms in living organisms, uniting chemistry, physics and biology, and offering a key perspective on the natural emergence of order in systems far from equilibrium.

How do Turing patterns form?

Basic idea: Turing patterns arise from the interaction of two chemical substances *viz.* an activator and an inhibitor. The activator promotes its own production and stimulates the production of the inhibitor, while the inhibitor suppresses the production of the activator. A key factor in pattern formation is that the inhibitor diffuses much faster than the activator [93,94].

Instability creates patterns: In a perfectly uniform system where both chemicals are evenly mixed, one might expect stability and uniformity. However, Turing showed that under certain conditions, a uniform mixture can become unstable, with small random fluctuations in concentration amplifying rather than dissipating. These amplified fluctuations give rise to stable spatial patterns, allowing organized structures to emerge spontaneously without any pre-existing template.

Real-world examples of Turing patterns in biology and chemistry

In biology: Turing-type principles have been applied to explain a variety of biological processes, including the formation of animal coat markings such as zebra and tiger stripes and leopard or fish spots (*e.g.* angelfish, Fig. 11). These principles also account for the development of digits in embryos, the pigmentation patterns in species like zebrafish (Fig. 11), and the emergence of branched structures observed in lungs, kidneys and coral-like forms. These patterns often appear early in embryonic development, before cells become specialised. This supports the idea that chemical gradients, not just genetic instructions, play a major role in shaping complex biological forms [91,95].

In chemistry: Turing-like patterns also appear in purely chemical systems, demonstrating that this mechanism extends beyond living organisms. For example, the BZ reaction in gels can produce target patterns or spiral waves [96], while the chlorite-iodide-malonic acid (CIMA) reaction generates spatially periodic patterns [97,98]. These examples highlight the universality of reaction-diffusion based pattern formation in both living and non-living matter.

Why Turing patterns matter? Their broader significance and applications: Turing's ideas have reshaped many areas of science and they continue to guide both theoretical and practical research today. Table-3 provides a brief idea of the applications of reaction-diffusion patterns across different fields [99,100].

Chemistry and the origins of life

From molecular interactions to biological function and complex chemistry: Phase IV chemistry explores the chemistry of life, focusing on the emergence of complex, life-like behaviour from simple molecular interactions [101,102]. Core questions include (i) How did life emerge from the prebiotic chemistry? and (ii) How do chemical networks exhibit memory, adaptation and evolution?

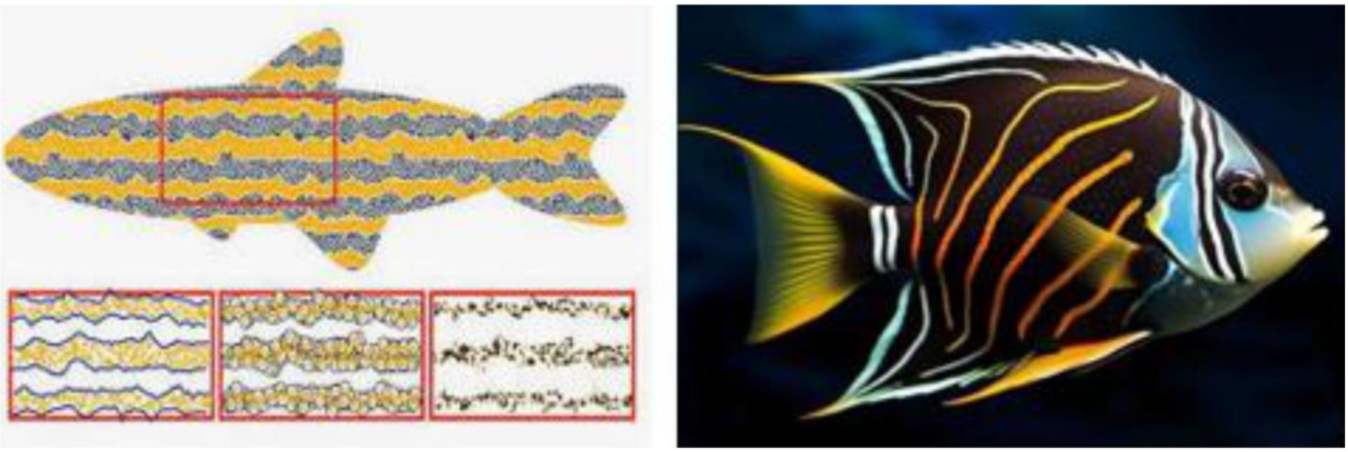


Fig. 11. Formation of animal coat patterns: schematic of lipid and pigment self-organisation producing stripe-like domains (left) and corresponding natural pigmentation in a reef fish (right), consistent with reaction–diffusion mechanisms underlying biological pattern formation

TABLE-3
BROADER SCIENTIFIC APPLICATIONS OF TURING'S REACTION–DIFFUSION PATTERNS ACROSS DISCIPLINES

Field	Application
Developmental biology	Explains how patterns form during early development of embryos
Synthetic biology	Guides the design of artificial systems with organised spatial features
Material science	Assists in creating materials with specific patterns and smart, responsive gels
Theoretical chemistry	Provides models for understanding chemical organisation in prebiotic environments, offering clues about how life may have originated

Prebiotic earth and building blocks of life: Over 4 billion years ago, the early Earth created a highly reactive environment in which the first building blocks of life could form. Scientists believe that these molecular building blocks may come from several sources:

Atmospheric lightning: In a simple, gas-filled early atmosphere (as in the classic Miller-Urey experiment), lightning can produce amino acids such as glycine and alanine [103]. This provides early evidence that essential biomolecules could be naturally formed under prebiotic conditions.

Deep-sea hydrothermal vents: Deep-sea vents supplied heat and strong chemical gradients that could help assemble complex organic molecules [104].

Extra-terrestrial origin: Meteorites, including the well-known Murchison meteorite, contain a variety of organic compounds [105]. These include (i) amino acids (the starting materials for proteins); (ii) nucleotides (the building blocks of RNA and DNA); (iii) fatty acids (capable of forming simple, cell-like membranes); and (iv) sugars (important for energy pathways and nucleotide synthesis).

Turing's reaction-diffusion model, in the context of biological pattern formation, demonstrates the power of mathematical concepts in chemistry to explain the natural processes. By linking reaction rates with diffusion-driven instabilities, the model provides a mechanism for the spontaneous emergence of patterns in chemical and biological systems. Its implications extend to prebiotic chemistry and the origin of life, illustrating that the chemical principles guided the early steps toward organized life long before the first living cells appeared.

Self-assembly and the principles of supramolecular chemistry: Simple molecules spontaneously assemble into complex structures through non-covalent interactions such as hydrogen bonding, van der Waals forces and hydrophobic effects [9,106]. Supramolecular chemistry examines the role of weak intermolecular forces in the spontaneous assembly of molecules into organized structures. These assemblies include micelles and lipid bilayers, resembling primitive cell membranes (Fig. 12), as well as peptide clusters and stacks of nucleotides that perform structural or functional roles. Such supramolecular architectures are regarded as important intermediates in the emergence of cellular life [107].

The RNA world and the challenge of storing life's first information: A key turning point in the origin of life research is the idea known as the RNA world hypothesis. The RNA World hypothesis proposes that RNA preceded both DNA and proteins in early life forms, owing to its dual ability to store genetic information, like DNA and catalyze chemical reactions, like enzymes. This combination of functions positions RNA as a likely first biopolymer in the origin of life.

Ribozymes, RNA molecules with catalytic functions, provide strong support for this theory [108,109]. Experimental evidence includes the prebiotic synthesis of nucleotides under plausible conditions [110] and the existence of self-replicating RNA sequences exhibiting rudimentary enzymatic activity [111,112].

How life evolved from RNA to DNA and protein-based systems?: As early biological systems increased in complexity, molecules adopted specialized roles, for example, DNA replaced RNA as the primary genetic material due to its greater chemical stability and suitability for long-term information storage, while proteins, composed of 20 different amino acids, assumed key functional roles by enabling a wider range of activities than RNA-based enzymes (ribozymes).

The development of the genetic code was a major turning point as it created a reliable way to translate nucleic acid sequences into functional proteins, allowing life to coordinate information and function in a precise, reproducible manner [112].

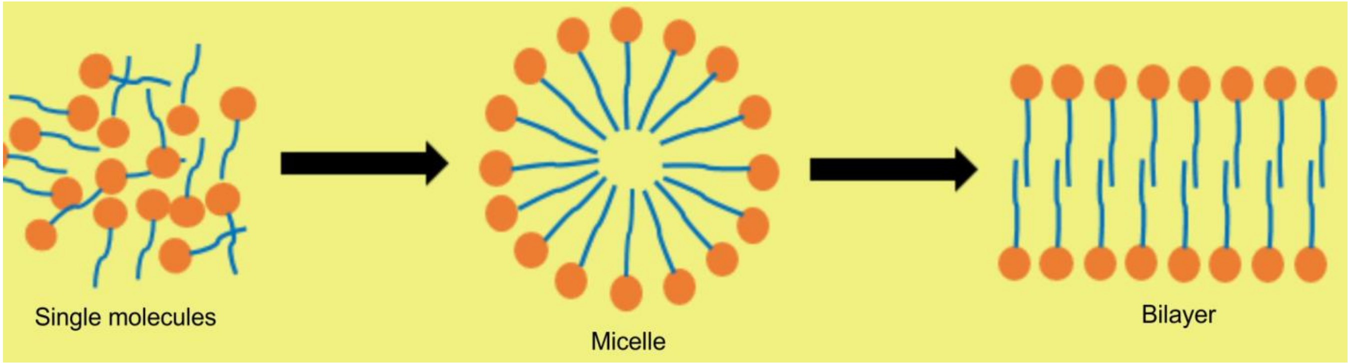


Fig. 12. Self-assembly of amphiphilic molecules into higher-order structures: individual amphiphiles (left) form micelles (center) at the critical micelle concentration and bilayers (right), forming the basis of membranes and vesicles

Compartmentalisation: Emergence of the first protocells: Early chemical systems required compartments to survive and evolve, allowing them to concentrate essential molecules, prevent dilution by the surrounding environment and regulate the entry and exit of substances. Fatty acid vesicles provide a simple model of primitive compartments (Fig. 13). In aqueous environments, they self-assemble into small, cell-like bubbles capable of growth, fusion and division, and permit selective passage of small molecules [113]. These properties enable them to serve as basic platforms for housing early metabolic and replicative processes, acting as prototypes of protocells.

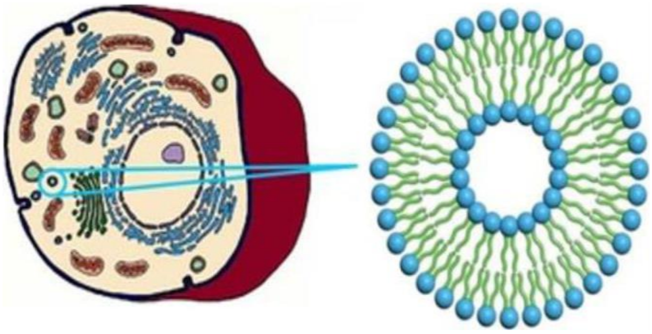


Fig. 13. Comparison of a modern eukaryotic cell (left) with a self-assembled fatty acid vesicle (right), illustrating the contrast between complex organelles and simple membrane-bound protocell models

These features allowed fatty acid vesicles to function as minimal platforms for housing primitive metabolic and replicative systems, effectively serving as prototypes of protocells. The transition from simple chemicals to living systems involved several interconnected steps: chemical systems gradually adapted to become more stable and efficient, complex networks of reactions emerged to harness energy and build metabolic complexity and certain molecules, such as RNA and later DNA, acquired the ability to replicate. Through a process of selection, systems that were better able to survive and propagate outcompeted others, and the integration of adaptation, metabolism, replication and selection ultimately enabled Darwinian evolution, marking the emergence of true biological systems from purely chemical beginnings.

Systems chemistry and modern synthetic strategies: Contemporary researchers are integrating systems chemistry and synthetic biology to investigate the emergence and evolution of complex molecular systems.

Systems chemistry: Systems chemistry explores complex chemical networks that exhibit emergent and life-like behaviours.

Synthetic biology: Synthetic biology applies engineering principles to chemical and biological systems to design simplified analogues of life [9,114,115]. It has enabled the construction of protocells capable of metabolism and division [116], the development of gene circuits that replicate regulatory networks, the engineering of artificial metabolic pathways and biosensors. Drawing on insights from origin-of-life research, synthetic biology recreates controllable, simplified living systems that illuminate the transition from chemistry to biology [100]. Both chemistry and synthetic biology rely on Phase-IV principles including nonlinearity, modularity and feedback, to understand and harness complex system behaviour.

Broader implications and future directions: Phase-IV chemistry, characterised by complexity, emergence and system level behaviour, marks a paradigm shift away from reductionist approaches toward an integrated view of matter as dynamically organised and information-rich. It transforms the perception of chemistry from the study of individual molecules to a central discipline in the broader exploration of complex systems.

Chemistry where complexity science meets chemical systems

Phase-IV chemistry naturally connects with several other fields: Physics offers the mathematical tools and core ideas needed to understand complicated behaviours like nonlinearity, non-equilibrium thermodynamics and how patterns form in complex systems. Research on the reaction-diffusion processes and dissipative structures clearly show this close connection [117].

Biology draws on chemical models to explain morphogenesis (such as Turing patterns), metabolic feedback and the chemical roots of evolution and new properties emerging. The shift from chemistry to biology can be viewed as a gradual buildup of molecular organisation paired with growing functional integration [118].

Computer Science connects through information theory, network models and algorithmic replication. Concepts such as chemical computing, molecular logic gates and autonomous feedback loops show the relevance of chemical processes in computational paradigms [119].

Phase IV chemistry translates into technology: The core concepts of Phase IV chemistry like self-organisation, adaptive networks and biochemical communication are no longer just theoretical ideas. They are now driving innovation across a wide range of modern technologies.

Patterned materials and smart polymers: These advanced materials can organize themselves into useful structures and often change their behaviour in response to light, pH, temperature or other stimuli. Some hydrogels even behave like real tissue, while tiny structures can deliver medicine precisely where it is needed [120].

Biochemical sensors and oscillating devices: Phase IV chemistry also helps create biochemical sensors and devices that work in the complex manner, like those based on the chemical reactions which oscillate over time. These sensors can respond sharply to signals and even carry out simple logic functions, inspired by fascinating chemical systems such as the BZ reaction [84,96].

Artificial life and minimal cells: Advances in bottom-up synthetic biology and protocell engineering are translating Phase-IV principles into life-like systems. These include vesicles with self-replication, metabolic cycles and primitive signal processing-blurring the boundary between chemistry and living systems [121].

Future synergies with artificial intelligence and data science: As experimental tools, automation and computational resources evolve, a major frontier lies in the convergence between Phase-IV chemistry and artificial intelligence (AI).

Machine learning algorithms are being used to model complex chemical networks, predict emergent behaviours and

TABLE-4
MAIN STEPS AND CHEMICAL PROCESSES IN PHASE IV CHEMISTRY, SHOWN TOGETHER
WITH HOW THEY LIKE THEIR TO ARTIFICIAL INTELLIGENCE AND DATA-DRIVEN METHODS

Stage	Process	Key chemical concepts
Prebiotic chemistry	Formation of amino acids, nucleotides	Organic synthesis, atmospheric chemistry
Self-assembly	Formation of membranes, micelles	Supramolecular chemistry
Autocatalysis	Self-sustaining chemical reactions	Feedback loops, nonlinear kinetics
RNA World	Information + catalysis in RNA	Polymerisation, ribozymes
Compartmentalisation	Vesicle formation	Amphiphiles, diffusion, stability
Metabolism	Energy flow through reactions	Reaction networks, redox chemistry
Selection	Survival of robust networks	System dynamics, evolution

optimize synthetic routes in self-organizing systems [122]. AI-enhanced evolution takes this further by enabling *in silico* experiments that investigate how the chemical networks can achieve autocatalysis, homeostasis or adaptive functions, key characteristics of early life. When combined with robotics, AI can take this even further, designing, conducting and analysing chemical experiments itself, ushering in a future filled with self-operated labs [123]. These 'self-operated laboratories' represent a transformative shift in the way chemical discovery progresses.

Overall, AI and Phase-IV chemistry form a new research ecosystem where theory, simulation and automation develop in parallel. This synergy illuminates the emergence of life from non-living matter and enables the creation of artificial systems that display life-like behaviour. Table-4 summarizes important chemical stages and processes of Phase-IV chemistry and their implications for artificial intelligence (AI) and data-driven approaches to help support student learning.

Conclusion

Chemical thought has evolved over the past 150 years, progressing from the periodic law to quantum mechanics and systems chemistry, continually enhancing the ability to explain concepts of matter, energy and organization. The four major paradigmatic shifts, from Mendeleev's periodicity to thermodynamic universality, from Debye-Hückel's electrostatic models to quantum mechanics and ultimately to the self-organization of far-from-equilibrium systems, have expanded the conceptual scope of chemistry while preserving its core explanatory logic. Chemistry does not progress in linear motions; the progression is through systems that are refined step by step and match macroscopic observables to micro drivers, as emphasised by this perspective. Thermodynamics and kinetics grounded universal constraints on natural processes; quantum mechanics established the language for structure, bonding and energy quantisation; systems chemistry now addresses feedback, nonlinearity and emergence to describe organisation in living and synthetic matter. All these frameworks together reflect chemistry playing a critical role in the crossing of the physical and life sciences integrating conservation laws with complexity laws. A modern example of this is the intersection between molecular self-assembly, chemical computing and artificial life. The principles driving dissipative structures and reaction–diffusion systems now are core to the design of adaptive materials, responsive polymers and prebiotic protocells. Furthermore, the new interface between chemical complexity and artificial intelligence opens a new research ecosystem in which data-driven discovery enhances physical insight. Chemistry is thus the science of organised matter *i.e.* from quantum coherence to biological evolution. Viewing its evolution through the four conceptual phases outlined here offers not only a unified intellectual perspective, but also a roadmap for future synthesis. In linking physics, biology and computation more deeply within chemistry, the enduring objective remains the same *i.e.*, to demonstrate the emergence of structure, function and information from the fundamental interactions of matter.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language. The authors reviewed and edited the content and take full responsibility for the published work.

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