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Scientific laws, Dalton's postulates, chemical reactions and Wolfram's NKS

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Abstract

A scientific law generally models the behaviour associated with some physical phenomenon such that it can be described in terms of $y = mx + c$. The turn of the ninetieth century saw the introduction of the laws of chemical composition and Dalton's postulates, but these ideas are very different and cannot be assessed using the techniques of continuous mathematics. In this paper we review Dalton's postulates and the corresponding types of chemical reaction process in the light of cellular automata and Wolfram's new kind of science (NKS). We find that the bond forming, bond breaking and substitution (STAD) mechanistic steps that occur during chemical reactions have a broad correspondence with the rules of cellular automata, a concept of discrete mathematics. Wolfram identified that cellular automata have four general classes of behaviour, likewise, we propose that chemical reaction processes can be grouped into four corresponding rather general classes.

Keywords Scientific laws · Dalton · Cellular automata · Wolfram's new kind of science (NKS) · Complexity · Reaction mechanisms

Introduction

The world is *complicated*: fluffy white clouds, meandering rivers, jagged mountain ranges, and life in the form of trees, flowers, insects, mammals and ourselves. Thinkers have attempted to make sense of this complexity through religion, natural philosophy, mathematics and science for more than 5,000 years.

The Renaissance, which marked the transition from the Middle Ages to modernity, was characterised by efforts to revive and surpass the ideas and achievements of classical antiquity. Ending *about* the year 1600, the Renaissance was followed by the Age of Reason and the emergence of the first scientific laws: Johannes Kepler's laws of planetary motion were published early in the seventeenth century (Kepler 1609), (Kepler, 1619). In Florence in the first decades of the 1600s, Galileo Galilei advocated heliocentrism, observed the moon and Jupiter through telescopes and presented new ideas concerning motion, inertia and gravity. Robert Boyle's law relating the pressure and volume of a gas was proposed

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in sixteen sixties (Boyle 1662). Newton's laws of motion were published in *The Principia* (Newton 1687). During this period thinkers like René Descartes, were beginning to challenge traditional authority and sought to understand the world through reason, logic and scepticism. Indeed, it was starting to look as if aspects the natural world *could* be understood in terms of mathematics; amongst all the complexity there *were* regions of rational, understandable behaviour.

Scientific laws and linear behaviour

As far as chemists are concerned, Boyle's gas law (Boyle 1662) was the first modern, quantitative description of matter, or *stoff* in German. Boyle's law tells us that the volume of an ideal gas is inversely proportional to the applied pressure, or more formally: The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system.

Mathematically, Boyle's law can be presented as:

$P \propto 1/V$ Pressure is inversely proportional to the volume.

or

$PV = k$ The product of pressure and volume is a constant, k.

In the 1780s Jacques Charles showed that volume was proportional to temperature, $V \propto T$. From this finding, the combined gas law was developed, with all temperatures given in kelvin:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Dalton (Dalton 1802) introduced his law of partial pressures which stated that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases. After Avogadro's law (Avagadro 1811), which stated that equal volumes of all gases at the same temperature and pressure have the same number of particles, the kinetic theory of gases was developed (Maxwell 1860) and the Ideal Gas equation was formulated:

$$PV = nRT$$

where n is the amount of substance in moles, R is the gas constant and T is the thermodynamic temperature in Kelvin.

Boyle's law, Gay-Lussac's law (or Amontons's law), the combined gas law, Dalton's law, Avogadro's law and the ideal gas equation are typical of scientific laws in that they are *linear*: double the pressure and the volume halves, etc. Also typical of scientific laws are the existence of constraints, limits or bounds to linearity. In the case of the gas laws, the gas must be *ideal*: the gas particles are assumed to be of zero size and there are no intermolecular/inter-particle attractions/forces. While most gases are remarkably close to ideal under ambient conditions, we must always be aware that at low temperatures all gases will condense into liquids.

Most scientific laws utilise a mathematical expression to describe linear behaviour in a system, where "*linear*" behaviour refers to a relationship between two quantities that can be described by a straight line when plotted on a graph or chart, as represented by the equation: $y = mx + c$. The scale(s) of one or both the chart axes may be: linear, x; reciprocal, $1/x$;

logarithmic, $\log_{10}(x)$ or $\ln(x)$; exponential, e^x; trigonometric, $\tan(x)$; or raised to a power, (x^2) or (x^3); etc. So, while the phenomenon being modelled/described may experimentally present as a curve, the data can be rendered mathematically linear, by employing a simple function, so that the relationship $y = mx + c$ holds. An example: many phenomena, such as light intensity, follow the inverse square law:

$$\text{Light intensity}, I \infty \frac{1}{distance^2}$$

$$I \infty \frac{1}{d^2}$$

And a plot of I *vs.* $1/d^2$ will generate a straight line.

Another typical linear relationship – routinely used in modern analytical chemistry – is Beer's law (Beer 1852) or the Beer–Lambert law (a sub-set of the more the general extinction law). Beer's law states that the absorbance of light, A, is proportional to the concentration of the material through which the light is traveling (where T is the transmittance):

$$A = -\log T \ or \ A = -\log \left(I / I_0 \right)$$

There was a shift from using the term scientific ***law*** to scientific ***theory*** at the turn of the twentieth century that reflected a broader change in how scientists understand and describe the natural world. Scientific *laws* are often seen as simple, universal statements about natural phenomena, while a *theory* is a more complex framework that explains why and how and why the phenomena occur. Scerri (Scerri 2024) has reviewed the rather different way that scientists and philosophers view scientific laws. The paper gives examples of several scientific laws, and makes the point that:

> "Scientists use the word '*law*' as an honorary epithet and as a throwback to an age in which laws of nature had a religious connotation. But even when the religious connotation was abandoned the secular *laws of nature* were still regarded as being invariant. [However,] when scientists continue to use the term law, such as in Boyle's law, Snell's law, Newton's laws etc., they do not intend these relations to be endowed with invariable necessity."

Math: things get complex

There are two broad and very different areas of mathematics (Franklin 2017): *Continuous mathematics*, which deals with objects that can take on any value within a range and that vary smoothly: real numbers, functions, trigonometry, calculus, differential equations, topology, etc. *Discrete mathematics*, which focuses on countable, distinct objects like integers and algorithms. Discrete mathematics topics include: number theory, arithmetic, algebra, combinatorics, logic, set theory, etc.

While most scientific laws describe phenomena in terms of continuous mathematics (above), there are important areas of science and where *discrete* mathematics plays the crucial role. Some examples:

- Mendel's Laws of Genetics and Inheritance: describe how traits are passed down from parents to offspring in discrete units called genes.
- Quantum Mechanics: Energy levels of electrons in an atom, are quantized, meaning they can only take on discrete values. Atomic orbitals are numbered $1s^2$, $2s^2$, $2p^6$, etc.
- DNA and The Genetic Code: DNA is a polymer chain consisting of a sequence of nucleobases: cytosine [C], guanine [G], adenine [A] and thymine [T]. Sets of three nucleobases constitute codons which code for the sequence of amino acids in proteins.
- Shannon's Information Theory: quantifies the amount of information in a message, and this information is described in discrete units called bits.
- Graph Theory: The study of networks in biology, sociology, and computer science.
- Crystallography: The analysis of diffraction patterns and the symmetry of crystal structures often involves group theory.
- Complexity and Fractals: Mandelbrot created the first theory of roughness in which he observed in the shapes of mountains, coastlines (Mandelbrot 1967), river basins, the structures of plants, blood vessels, lungs and the clustering of galaxies. Mandelbrot described self-similar curves as fractal, although he did not coin the term until 1975.

The laws of chemical composition

The 1773 law of conservation of mass, usually attributed to Lavoisier, states that during chemical reactions matter is neither created nor destroyed. Joseph Proust presented the law of constant composition or definite proportions (Proust 1794) which stated that when two or more elements that combine to form a compound, they always do so in the same ratio of masses. Dalton's 1804 law of multiple proportions states that if a particular element such as carbon combines with another element to form more than one compound, the masses of the second element which combine with a fixed mass of the first one, constitutes a simple ratio according to their masses: carburetted hydrogen gas (methane, CH_4) and olefiant gas (ethene, C_2H_4, although Dalton thought this was CH_2); carbon monoxide (CO) and carbon dioxide (CO_2), etc.

These composition laws were unexplained until Dalton's atomic theory was presented, Fig. 1 (Dalton 1808).

In modern parlance, Dalton's atomic theory has five postulates:

1. Elements are made of extremely small particles called atoms.
2. Atoms of a given element are identical in size, mass and other properties. Atoms of different elements differ in size, mass and other properties.
3. Atoms cannot be subdivided, created or destroyed.
4. Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated or rearranged.

Dalton's postulates are now understood/explained in terms of the Bohr atom, the octet rule, Lewis theory and quantum mechanics; indeed, Dalton's early nineteenth century ideas can be viewed as a perfectly logical step towards the later twentieth century developments. Note that Dalton's ideas were developed before knowledge of the existence of isotopes or radioactivity, so postulates 2 and 3 are not *strictly* true.

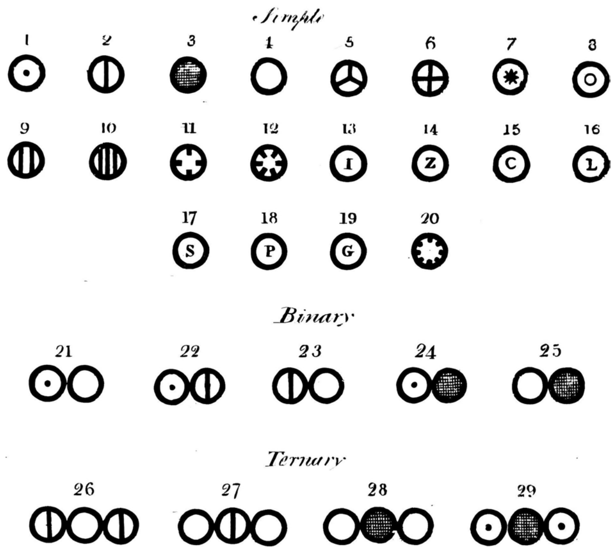

Fig. 1 Plate 4 from *A New System of Chemical Philosophy*, showing atoms as icons and compounds as collections of icons, which correspond to chemical formulae (Dalton, A New System of Chemical Philosophy, 1808). Be aware that to the modern eye there are *many* serious errors in the molecular formula of the compounds in Fig. 1. For example, '21' shows water as HO not H_2O; ammonia, '22', is given as HN, not NH_3, etc. While there are errors, Dalton's overall *logic* is correct. Indeed, systematic errors in stoichiometry plagued chemistry in the first half on the nineteenth century would not be resolved until the Karlsruhe Congress of 1860 where the accurate atomic mass data presented by Cannizzaro was generally agreed upon

Consider Postulate 5, which we will be exploring in detail below. Very briefly: Atoms interact/react to form compounds in which the participating atoms achieve a "full outer shell of valence electrons". There are also issues of differential electronegativity: "*The most stable arrangement of covalent bonds connecting a group of atoms is that arrangement in which the atom with the highest electronegativity is bonded to the atom with the lowest electronegativity*" (Jolly 1985), symbiosis/symmetry, steric effects (for larger organic molecules) and Gibb's free energy considerations (Leach 2005). Obviously, a fuller, more complete understanding can be achieved with modern quantum chemistry methods, but the *expanded* octet rule[1] and Lewis logic will be more than sufficient for the arguments in this paper.

Crucially: The laws of chemical composition, Dalton's postulates, the Bohr atom, the *expanded* octet rules, Lewis theory, atoms, electrons, ions, charge, molecules, molecular ions, radicals, etc., and their corresponding interactions and reactions, all involve distinct countable entities. Chemical structure and reactivity ideas are NOT continuous

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[1] Hydrogen and helium follow the duplet rule, the second and third rows of the periodic table follow the octet rule and transition metals follow the 18 electron rule. Even those elements that do follow the octet rule may at times may form more bonds than predicted by the octet rule, e.g. PCl_3 and PCl_5, thereby leading to the notion of an "expanded octet".

mathematical constructs that comply with $y = mx + c$ plots on a chart. Instead, they should/must be considered in terms of *discrete* mathematics.

Cellular automata and Wolfram's NKS

A cellular automaton is defined by Wolfram Mathworld (Weisstein 2005) as:

> "*A collection of coloured cells [usually black and white] on a grid that evolves through discrete time steps according to a set of rules based on the states of neighbouring cells. The rules are applied iteratively for as many time steps as desired… The theory is immensely rich, with simple rules and structures being capable of producing a great variety of unexpected behaviours.*"

A classic example of cellular automation is John Conway's Game of Life (Gardner 1970) which is available to experiment/play with via several websites, and we would strongly advise clicking one of the links below if you, the reader, have no experience of cellular automata or Conway's work: https://playgameoflife.com, https://conwaylife.com.

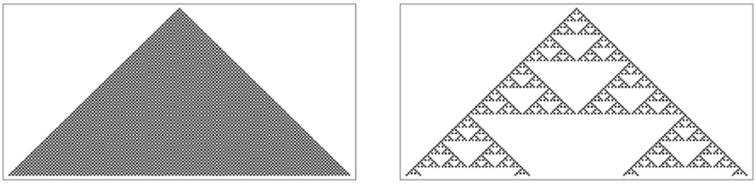
Conway's Game of Life has a grid of cells, where each cell can be alive or dead (black or white) depending on its neighbours. The rules are: A cell with one or zero neighbours dies; a cell with four or more neighbours dies; a cell with two or three neighbours survives; and an empty cell with three neighbours becomes populated. A feature of Game of Life *runs* is that common pattern types with distinct behaviours appear. These include: "still lifes", which do not change from one generation to the next; "oscillators" or "blinkers", which return to their initial state after a finite number of generations; and "spaceships" or "gliders", which translate themselves across the grid and "general complexity" which seem to defy rational explanation, considering the simple rules involved.

Stephen Wolfram performed a rigorous analysis of one type of cellular automata, coded in the Wolfram language (as used by the Mathematica application and the Wolfram Cloud), which he presented in his book *A New Kind of Science* or *NKS* (Wolfram 2004). Wolfram identified 2^8 (256) cellular automata "rules", numbered (being a computer scientist): rule 0 thru 255. The 256 rules produced a rich set of behaviours, Fig. 2. While there are an infinite number of starting patterns, the most common (and simplest) is a single black cell in a row of white cells.

In Chapter 6 of NKS, Wolfram collected the various behaviours together and grouped them into four general classes of cellular automata system, Fig. 3.

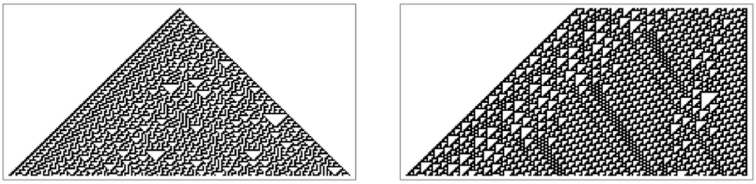
Wolfram commented about the four classes:

- **Class 1**: *Nearly all initial patterns evolve quickly into a stable, homogeneous state. Any randomness in the initial pattern disappears.*
- **Class 2**: *Nearly all initial patterns evolve quickly into stable or oscillating structures. Some of the randomness in the initial pattern may filter out, but some remains. Local changes to the initial pattern tend to remain local.*
- **Class 3**: *Nearly all initial patterns evolve in a pseudo-random or chaotic manner. Any stable structures that appear are quickly destroyed by the surrounding noise. Local changes to the initial pattern tend to spread indefinitely.*



repetition (rule 250)

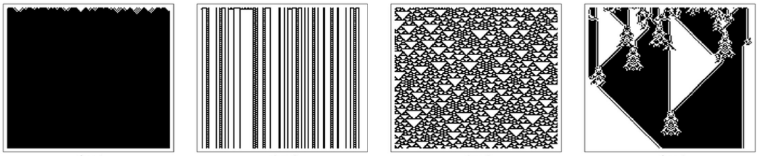
nesting (rule 90)



randomness (rule 30)

localized structures (rule 110)

Fig. 2 When run as computer programs, Wolfram's 256 cellular automata rules showed a variety of behaviours. Some were simple and repetitive, some produced nesting pattens, some seemed to be random, and some seemed to be chaotic. Image from page 52 of NKS © Wolfram Media; request for use granted; permission does not imply endorsement



class 1

class 2

class 3

class 4

Fig. 3 Examples of Class 1, Class 2, Class 3 and Class 4 cellular automata systems. Image from page 231 of NKS © Wolfram Media; request for use granted; permission does not imply endorsement

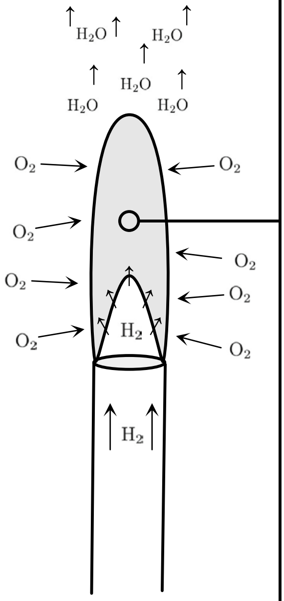
- **Class 4**: *Nearly all initial patterns evolve into structures that interact in complex and interesting ways, with the formation of local structures that can survive for long periods of time.*

  On page 242 of NKS, Wolfram observed:

  "*Class 1 and 2 systems rapidly settle down to states in which there is essentially no further activity. But class 3 systems continue to have many cells that change at every step, so that they in a sense maintain a high level of activity forever. Class 4 systems are then in the middle: for the activity that they show neither dies out completely, as in class 2, nor remains at the high level seen in class 3.*"

Reaction mechanisms

We are not suggesting that there is an *exact* correspondence between Wolfram's cellular automata rules and chemical reactions, indeed, this would not be expected because atomic and molecular interactions and reactions are far more complicated/involved than Wolfram's cellular automata rules due to the variety of atomic and molecular species available. Furthermore, Wolfram cellular automata are dimensionally restricted by



$O_2 + H\bullet$	→	$HO\bullet + \bullet O\bullet$	STAD
$HO\bullet + \bullet O\bullet$	→	$O_2 + H\bullet$	STAD
$H_2 + \bullet O\bullet$	→	$HO\bullet + H\bullet$	STAD
$HO\bullet + H\bullet$	→	$H_2 + \bullet O\bullet$	STAD
$H_2 + HO\bullet$	→	$H_2O + H\bullet$	STAD
$H_2O + H\bullet$	→	$H_2 + HO\bullet$	STAD
$HO\bullet + \bullet O\bullet$	→	$H_2O + \bullet O\bullet$	STAD
$H_2O + \bullet O\bullet$	→	$HO\bullet + HO\bullet$	STAD
$H\bullet + H\bullet + M$	→	$H_2 + M^*$	bond-forming
$H_2 + M^*$	→	$H\bullet + H\bullet + M$	bond-breaking
$H\bullet + HO\bullet + M$	→	$H_2O + M^*$	bond-forming
$H_2O + M$	→	$H\bullet + HO\bullet + M^*$	bond-breaking
$\bullet O\bullet + \bullet O\bullet + M$	→	$O_2 + M^*$	bond-forming
$O_2 + M^*$	→	$\bullet O\bullet + \bullet O\bullet + M$	bond-breaking
$H\bullet + O_2 + M$	→	$HO_2\bullet + M^*$	bond-forming
$HO_2\bullet + M^*$	→	$H\bullet + O_2 + M$	bond-breaking
$HO_2\bullet + H\bullet$	→	$HO\bullet + HO\bullet$	STAD
$HO\bullet + HO\bullet$	→	$HO_2\bullet + H\bullet$	STAD
$HO_2\bullet + H\bullet$	→	$H_2 + O_2$	STAD
$H_2 + O_2$	→	$HO_2\bullet + H\bullet$	STAD
$HO_2\bullet + H\bullet$	→	$H_2O + \bullet O\bullet$	STAD
$H_2O + \bullet O\bullet$	→	$HO_2\bullet + H\bullet$	STAD
$HO_2\bullet + \bullet O\bullet$	→	$HO\bullet + O_2$	STAD
$HO\bullet + O_2$	→	$HO_2\bullet + \bullet O\bullet$	STAD
$HO_2\bullet + HO\bullet$	→	$H_2O + O_2$	STAD
$H_2O + O_2$	→	$HO_2\bullet + HO\bullet$	STAD
$HO_2\bullet + HO_2\bullet$	→	$H_2O_2 + O_2$	STAD
$HO\bullet + HO\bullet + M$	→	$H_2O_2 + M^*$	bond-forming
$H_2O_2 + M^*$	→	$HO\bullet + HO\bullet + M$	bond-breaking
$H_2O_2 + H\bullet$	→	$H_2 + HO_2\bullet$	STAD
$H_2 + HO_2\bullet$	→	$H_2O_2 + H\bullet$	STAD
$H_2O_2 + H\bullet$	→	$H_2O + HO\bullet$	STAD
$H_2O + OH\bullet$	→	$H_2O_2 + H\bullet$	STAD
$H_2O_2 + \bullet O\bullet$	→	$HO\bullet + HO_2\bullet$	STAD
$HO\bullet + HO_2\bullet$	→	$H_2O_2 + \bullet O\bullet$	STAD
$H_2O_2 + HO\bullet$	→	$H_2O + HO_2\bullet$	STAD
$H_2O + HO_2\bullet$	→	$H_2O_2 + HO\bullet$	STAD

Fig. 4 Hydrogen and oxygen react to give water via an involved series of at least 37 interconnected mechanistic steps that correspond to bond-breaking, STAD and bond-forming steps (Maas & Warnatz 1988)

design, whereas chemical reactions usually operate in three dimensions of space and one of time. (Note that reactions can be modelled algebraically without the spatial component. Figures 4, 5, 6, and 8 are examples.) *However*, there are broad similarities in that chemical reactions proceed via reaction mechanisms and these, like Wolfram's cellular automata, consist of distinct simple steps with simple rules. There are **two** rules associated with reaction mechanisms:

Rule 1: null or product

$$A + A \rightarrow \text{ null (no reaction)}$$

$$B + B \rightarrow \text{ null (no reaction)}$$

$$A + B \rightarrow \text{ C (product)}$$

Some interactions of A and B give a null result, $A + A$ and $B + B$, while others give a chemical reaction and generate a product, $A + B \rightarrow C$.

Rule 2: allowed mechanistic steps

It transpires that there are only few allowed "single step" mechanistic processes:

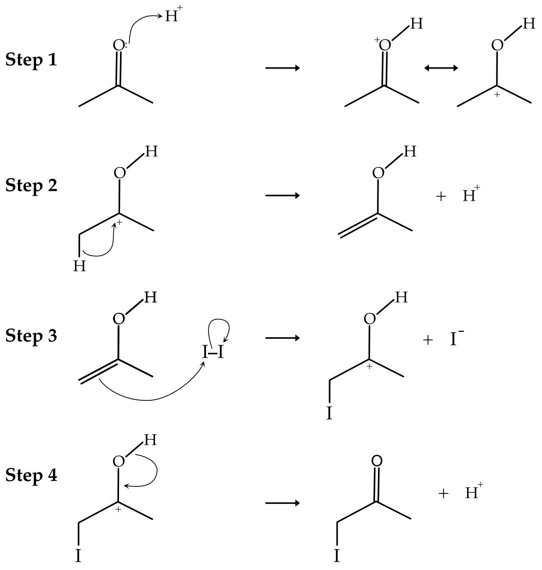


Fig. 5 The steps in the reaction of propanone (acetone or dimethyl ketone) with iodine to form iodopropanone (iodoacetone). In step 1 the propanone is protonated. In step 2 the enol is formed. In step 3 the enol form of the propanone reacts with the iodine. In step 4 a proton, H^+ ion, is lost to the solvent forming the iodopropanone product and HI(aq)

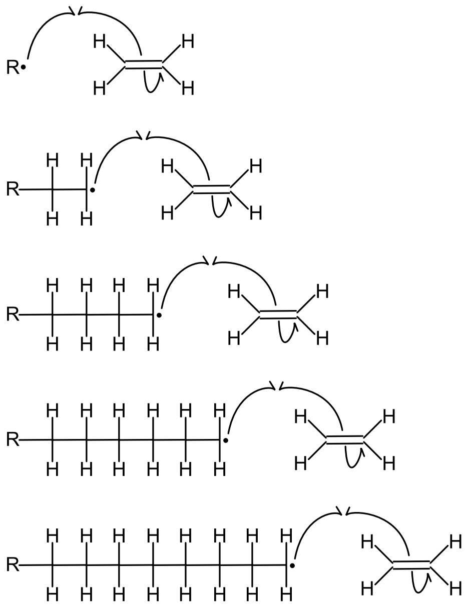


Fig. 6 Growing polymer of polyethene, formed through radical addition. The chain can grow to incorporate thousands of monomer sub-units. Ultra-high-molecular-weight polyethylene (UHMWPE) may have more than 250,000 monomer units joined together

$$
\begin{aligned}
&X + Y \rightarrow X - Y && \text{bond - formation}\\
&X - Y \rightarrow X + Y && \text{bondbreakage}\\
&X + Y - Z \rightarrow X - Y + Z && \text{substitution/transfer (STAD)}
\end{aligned}
$$

Electrocyclic rearrangement, a class of reactivity that plays an important role is the biosynthesis of many natural products is also a fundamental or *unit* mechanistic step, but we will not be considering pericyclic processes here.

Two points:

First: The X + Y–Z → X–Y + Z step can be considered/defined as:

X *substituting* Z at Y

Y *transferring* from Z to X

X *abstracting* Y from Z

X *displacing* Z at Y

Very confusingly, all four of these terms are employed in different areas of reaction chemistry. We shall use the single term "**STAD**" (an acronym of **s**ubstitution, **t**ransfer, **a**bstract, **d**isplacement) to describe these as a single mechanistic process (Leach 2003).

Second: The process of radical recombination leading to bond formation is invariably exothermic and the product X–Y (or X–Y*, where the "*" indicates "energetically excited") will likely have sufficient energy to immediately dissociate back into X + Y. Thus, a third species, M, must be present and available to carry away the excess kinetic energy as M*. (M may be X or Y or X-Y). So, the bond forming reaction proceeds as:

$$\mathrm{X} + \mathrm{Y} + \mathrm{M} \rightarrow \mathrm{X\text{-}Y} + \mathrm{M}^{*}$$

Or, more likely a rapid sequence of two steps:

$$\begin{aligned} &\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{X} - \mathrm{Y}^{*} \\ &\mathrm{X} - \mathrm{Y}^{*} + \mathrm{M} \rightarrow \mathrm{X} - \mathrm{Y} + \mathrm{M}^{*} \end{aligned}$$

Due to the mechanistic rules above, A–A + B–B *cannot* give 2 A–B in a single mechanistic step. An example of such a reaction would be for formation of iodine chloride from chlorine and iodine:

$$\mathrm{Cl_2} + \mathrm{I_2} \rightarrow 2\ \mathrm{ClI}$$

The chlorine + iodine reaction proceeds via a radical pathway, with the possible steps being:

$$\begin{aligned} &\mathrm{I} - \mathrm{I} \rightarrow \mathrm{I}^{\bullet} + \mathrm{I}^{\bullet} \quad \text{bond - breakage} \\ &\mathrm{Cl} - \mathrm{Cl} \rightarrow \mathrm{Cl}^{\bullet} + \mathrm{Cl}^{\bullet} \quad \text{bond - breakage} \\ &\mathrm{I}^{\bullet} + \mathrm{Cl} - \mathrm{Cl} \rightarrow \mathrm{I} - \mathrm{Cl} + \mathrm{Cl}^{\bullet} \quad \text{STAD} \\ &\mathrm{Cl}^{\bullet} + \mathrm{I} - \mathrm{I} \rightarrow \mathrm{I} - \mathrm{Cl} + \mathrm{I}^{\bullet} \quad \text{STAD} \\ &\mathrm{I}^{\bullet} + \mathrm{Cl}^{\bullet} \rightarrow \mathrm{I} - \mathrm{Cl} \quad \text{bond - formation} \end{aligned}$$

We here argue that the two reaction mechanistic rules above give chemical reactions a broad correspondence with cellular automata. Like cellular automata, chemical reactions proceed via a series of simple steps, and like cellular automata the outcomes of chemical reactions can show a rich variety of behaviours. Furthermore, we propose that Wolfram's four general classes of cellular automata behaviour correspond to the outcomes of four rather general classes of chemical reaction. We will now give examples of chemical reaction systems and examine them in the light of Wolfram' four classes.

Class 1 chemical reaction systems

> "*Nearly all initial patterns evolve quickly into a stable, homogeneous state. Any randomness in the initial pattern disappears.*"

Most of the chemical reactions we study are of the form: A + B → C or A + B → C + D, etc. Some examples:

$$\text{sodium} + \text{chlorine} \rightarrow \text{sodium chloride}$$

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

$$\text{carboxylic acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water}$$

$$CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOCH_2CH_3 + H_2O$$

Consider the combustion of hydrogen:

$$\text{hydrogen} + \text{oxygen} \rightarrow \text{water}$$

$$2\ H_2 + O_2 \rightarrow H_2O$$

The combustion of hydrogen with oxygen to form water is well known to every beginning chemistry student, indeed, it is likely the first or second chemical reaction equation we were taught. However, there is a profound mechanistic issue with the reaction: it is not possible to go from 2 $H_2 + O_2$ to 2 H_2O in a single step; the reaction must proceed via an involved sequence of bond breaking, STAD and bond forming sub-steps (Maas & Warnatz 1988). Indeed, when hydrogen and oxygen gases burn together in a flame, the chemistry is astonishingly complicated: Fig. 4, shows the combustion reaction proceeding via: diatomic molecules, H_2 and O_2; neutral atoms/atomic radicals and diradicals, $H^\bullet$ and $^\bullet O^\bullet$; molecular hydroxyl radicals, $HO^\bullet$, hydroperoxide radicals, $HO_2{}^\bullet$; and even hydrogen peroxide, H_2O_2. However, the *final* product is 100% water vapour, $H_2O(g)$.

Propanone is converted into iodopropanone by iodine in the presence of a mineral acid catalyst.

$$CH_3COCH_3 + I_2 \rightarrow CH_2ICOCH_3 + HI$$

This reaction takes place in the liquid phase, via a sequence of bond forming, bond breaking and STAD steps, Fig. 5. Note that in the liquid phase, there is no difficulty with the X + Y → X–Y step as the solvent can adsorb the kinetic energy released during the exothermic bond forming process.

Like cellular automata rules, chemical reactions proceed via a series of simple mechanistic steps: bond breaking/fission, bond forming and substitution/transfer. Like Wolfram's Class 1 automata, all four of the example reactions given above "*evolve quickly into a stable, homogeneous state*", even though the reactions may proceed via unexpected "*randomness*".

Class 2 chemical reaction systems

> "*Nearly all initial patterns evolve quickly into stable or oscillating structures. Some of the randomness in the initial pattern may filter out, but some remains. Local changes to the initial pattern tend to remain local.*"

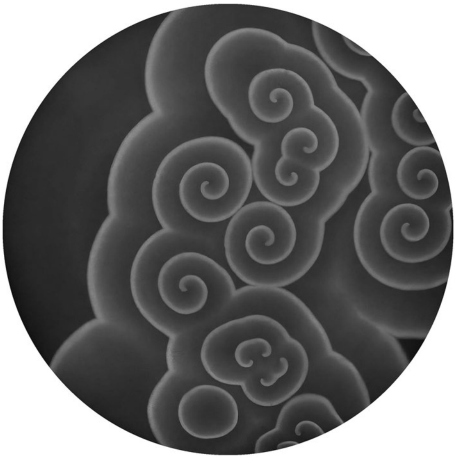


Fig. 7 Typical complex patterns exhibited by the BZ reaction

We propose that in Conway's Game of Life this would correspond to a "spaceship" or "glider" moving across the computer screen until it reaches the edge. In 1970 Gosper invented the first glider *gun* which fires spaceships across the screen. A gun, in this context, is a pattern with a main part that oscillates and periodically emits spaceships.

A chemical example would be the *stirred* Belousov–Zhabotinsky or BZ reaction (Belousov 1959), (Zhabotinsky 1964). If the BZ reaction is performed in a beaker with a magnetic stirrer, the reaction alternates in colour between blue and brown, oscillating over a period of a few seconds. The time depends on reagent concentration, temperature, etc.

Another process corresponds to class 2 behaviour is the radical polymerisation of an alkene to form the corresponding polyalkene. When a radical initiator is added to ethene, $CH_2=CH_2$, an addition occurs forming a new radical centre which reacts with another ethene molecule forming a new radical centre, etc. to extend the polymer chain, Fig. 6. The reaction *oscillates* like a zipper as the polymer chain grows.

The conversion of ethene into polyethene is one-dimensional in that it produces a linear chain consisting of hundreds to hundreds of thousands of monomer units. Indeed, industrial processes are carefully optimised to limit cross-linking between the growing polymer chains using Ziegler–Natta type catalysts. Polyethenes are *thermoplastics* that melt on heating and solidify on cooling, enabling the material to be injection moulded to give products and packaging. Many important polymer materials are described as *thermosetting*: melamine resins, epoxy resins, polyurethanes, etc. These materials undergo reactions that create materials with extensive three-dimensional cross-linking between polymer chains producing insoluble polymer networks. The term *thermosetting* comes from the observation that these cross-linking polymerisation processes are exothermic, "*thermo*", and the reactions are irreversible, "*setting*".

Class 3 chemical reaction systems

> "*Nearly all initial patterns evolve in a pseudo-random or chaotic manner. Any stable structures that appear are quickly destroyed by the surrounding noise. Local changes to the initial pattern tend to spread indefinitely.*"

If Belousov–Zhabotinsky (BZ) reactions (Belousov 1959), (Zhabotinsky 1964), are carried out in non-stirred Petri dishes – a two-dimensional environment – coloured spots form which grow into a series of expanding concentric rings or spirals, Fig. 7. (In a non-stirred beaker three-dimensional spherical pattens form, but these are difficult to visualise through the opaque reaction medium, so the reaction is usually performed as a shallow film.) The colours and patterns disappear if the dish is shaken or stirred, but they quickly reappear. The moving, coloured waves continue to propagate until the reagents are consumed. The mechanism for this reaction is thought involve around 18 distinct steps (Field & Foersterling 1986), (Sirimungkala 1999). While homogeneous liquid phase BZ type reaction systems are comparatively rare, electrochemical (voltage) oscillations in heterogeneous media, such as in lithium-ion batteries, are more common (Li 2018).

Alan Turing (Turing 1952) explained how patterns like stripes and spirals, now referred to as Turing patterns, can develop from an initially uniform (homogeneous) state. The BZ reaction exemplifies such a reaction–diffusion system.

Chaotic behaviour in chemical systems involves nonlinear dynamics, feedback loops, and oscillations. These reactions can be unpredictable, as small changes in initial conditions lead to different outcomes. Diffusion-controlled steps in these processes result in local high or low concentration regions, creating non-linearities due to different timescales of diffusion and reaction.

We hold that the non-stirred BZ reaction corresponds to Wolfram's description of a Class 3 system.

Class 4 chemical reaction systems

Yeast is a single cell eukaryotic organism that can live and grow in water at about 20 °C for a considerable length of time on a single food source, sugar (glucose or sucrose). In the absence of air, yeast will undergo anaerobic respiration producing ethanol and carbon dioxide. In the presence of oxygen, the organism will undergo aerobic respiration producing carbon dioxide and water. The metabolic pathways of biochemistry taking place in the yeast cell are networks of interlinked reactions relying on non-equilibrium thermodynamics to drive the many reaction processes, Fig. 8.

Metabolic processes are sub-classified as *catabolism*: obtaining energy and reducing power from nutrients; and *anabolism*: production of new cell components, through energy and reducing power obtained from nutrient catabolism. The various metabolic pathways take place simultaneously:

- Glycolysis: glucose oxidation to produce ATP.
- Citric acid cycle (Krebs' cycle): acetyl-CoA oxidation to produce GTP and intermediates.
- Oxidative phosphorylation: production of ATP.
- Pentose phosphate pathway: synthesis of pentoses and release of the reducing power, NADH, needed for anabolic reactions.
- Urea cycle: disposal of NH_4^+.
- Fatty acid β-oxidation: fatty acids broken down into acetyl-CoA.
- Gluconeogenesis: glucose synthesis from smaller precursors.

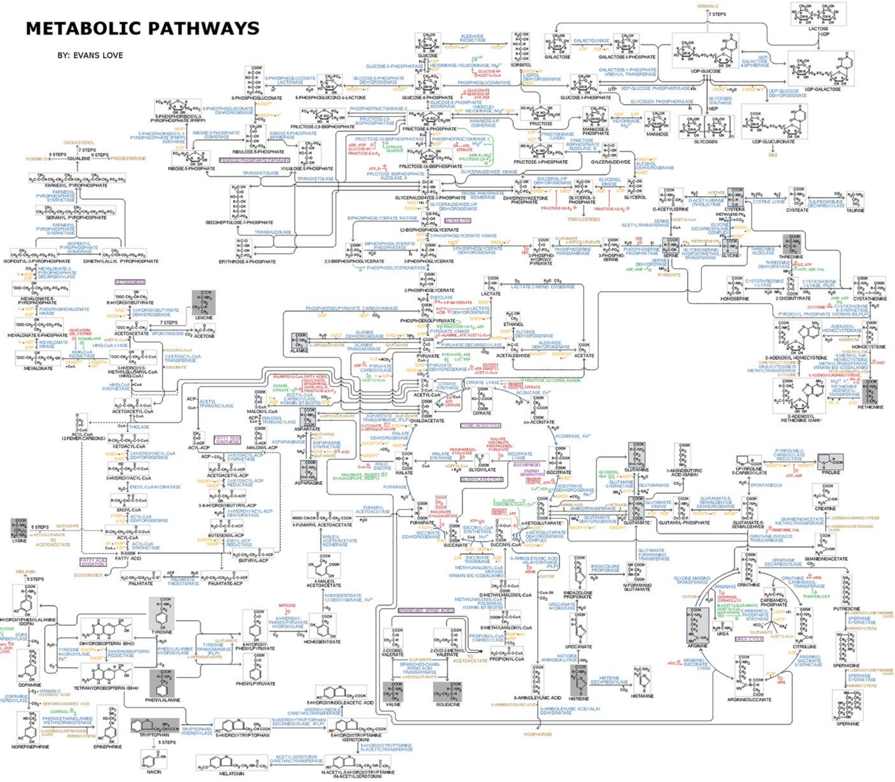


Fig. 8 The major metabolic pathways of the eukaryotic cell. Human Metabolism—Pathways by Evans Love, 2016. Wikimedia Creative Commons Attribution-ShareAlike 4.0

Within the complex set of processes that constitute metabolism there are examples of Class 1, 2 and 3 reactions systems. The Krebs' (citric acid) cycle is a stable local (class 1) structure. Long chain fatty acids are built up, or *elongated* (a polymerisation process), from two carbon acetate residues using acetyl-CoA (acetyl coenzyme A), a Class 2 process. There are always oscillations in levels of metabolites (Class3), but these are controlled by feedback mechanisms to stop them from getting out of control. For example, fatty acid synthesis is activated by high levels of citrate and is inhibited by high levels of palmitoyl-CoA. Feedback mechanisms are often allosteric, where a substance binds to a site on an enzyme, resulting in a conformational change that alters the protein's activity, either enhancing or inhibiting its function.

We hold that metabolism fits Wolfram's definition of a Class 4 system in that: "*Nearly all initial patterns evolve into structures that interact in complex and interesting ways, with the formation of local structures that are able to survive for long periods of time*."

Further work: reaction network graph theory

In discrete mathematics, a *graph* consists of vertices (points) connected by edges. This is analogous to atoms linked by classical (Lewis) covalent bonds, and molecular structures are routinely modelled as computer readable graphs. A *flow network* discribes how graphs change/evolve over time, and this, when applied to molecular structure(s), corresponds to reaction mechanistic behaviour. Thus, *reaction network graph theory* provides a computer readable methodology for describing reaction mechanistic pathways. The exploration of the space of chemical transformations using reaction network graph theory is a prime focus of contemporary computational chemistry (Hashemi 2022), (Dewyer, Argüelles, & Zimmerman, 2018).

Once reaction mechanic pathways are described in terms of reaction network graph theory, the pathways are amenable to analysis in terms of the four Wolfram classes described here.

Conclusion

At the start of the section on Class 1 chemical eaction systems we stated: "*most of the chemical reactions we study are of the form:* $A+B \rightarrow C$ *or* $A+B \rightarrow C+D$, etc." This statement requires some clarification. Modern societies tame and exploit reaction chemistry to make a multitude of chemical compounds/products of known analytical purity: pharmaceuticals, cement, plastics, explosives, lubricants, fuels, cleaning products, cosmetics, solvents, analytical reagents, food additives, dyes, perfumes, etc. Chemists and chemical engineers strive to make laboratory and industrial chemical processes predictable and reproduceable. This, however, gives practitioners a biased view of chemical reactions and chemical reactivity. Yes, the combustion of hydrogen, Fig. 4, is very complicated, but the single product, water, is formed reproducibly and in 100% yield; we simply do not observe the internal mechanistic complexity unless we look *very* closely. As chemists we invariably want our reactions to proceed as Class 1 or Class 2 chemical reaction systems where any mechanistic complexity that may exist is hidden from view and (ideally) single, pure products are formed in high yield.

Class 3 Chemical Reaction Systems are chaotic and unpredictable and such processes are generally avoided by chemists, except theoretically as we need to understand when chaotic behaviour may occur, so that such conditions can be circumvented. Class 3 chemical reaction systems are generally reaction–diffusion systems that mathematically take the form of semi-linear parabolic partial differential equations (Wikipedia 2025).

In the natural world, all chemicals cycle over time: the Krebs' cycle; calcium phosphate in bones; ozone in the stratosphere; the water cycle; the carbon cycle; the methane cycle; the hydrogen, nitrogen, oxygen and sulfur nutrient cycles; rock cycles (calcium, silica, carbonate-silica); etc. This list should include metabolism, the cell cycle and life itself. Some of these cycles operate over fractions of a second, others over millions of years. All these cycles are complex in that they have unexpected features. We hold that all these chemical cycles should be considered as Class 4 Chemical Reaction Systems:

> "Nearly all initial patterns evolve into structures that interact in complex and interesting ways, with the formation of local structures that are able to survive for long periods of time."

Author contributions M.L. wrote the manuscript and prepared Figs. 4, 5, 6 & 7. Permission for use has been obtained for copyrighted images.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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