• Междупредметните връзки •
• Interdisciplinary •

ANALOGOUS ODD-EVEN PARITIES IN MATHEMATICS AND CHEMISTRY

Tetsuo MORIKAWA[a,*], Brian T. NEWBOLD[b]
[a,*] Joetsu University of Education, Japan;
[b] Université de Moncton, Canada

Summary. The present note compares some historical and analogous odd-even parities in mathematics and chemistry. The mathematical starting point was the famous problem of the Koenigsberg Bridges in olden East Prussia, which was first solved by Euler in 1736. The first statement of an even number rule in chemistry was made by Laurent in 1843–1846. Laurent's parity, known as the principle of valence balance in modern chemistry, differs from Euler's rule; thus, the two are not considered to be equivalent. Another analogy in odd-even parity is strongly related to the number of cycles in networks such as graphs in mathematics and electrical circuits in physics. The correspondence to such a number in chemical compounds is known as the degree of unsaturation. Describing the analogy of this number in mathematics and chemistry is another purpose of this review. A history of the odd/even number rules can help to clarify the role of mathematics in chemistry. The two aspects, valence balance and unsaturation, have been unified into graph-theoretical criteria by the mathematician Senior in a key chemistry paper, but not well-known to chemists, published in 1951. The present contribution describes some pathways leading from Euler's work to that of Senior.

Introduction

It has been known for a long time that the number of guests at a party who shake hands an odd number of times must be even. This relationship, "the number of odd numbers is even," is hereafter called an odd-even parity. Such odd-even parities have been discovered over and over again in many fields of the natural sciences and mathematics, especially in networks such as graphs (mathematics), electric circuits (physics), constitutional structures (chemistry), and road maps (geography). The present paper deals with some analogous odd-even parities in mathematics and chemistry.

The mathematical starting point of the odd-even parity was the famous problem of the Koenigsberg Bridges in old East Prussia; whether or not anyone could arrange a walking route in such a way that one crossed each of the seven bridges formed over four lands (and areas) once and only once (see geographical map in reference [1]). This problem was first solved by Euler [2] in 1736 as a mathematical, or more specifically a graph-theoretical problem (in modern mathematics); the term "graph" was derived from chemical graphic notation [3]. Euler concluded that such a walking route is impossible, because the number of lands with an odd number of bridges is odd.

The first statement of an even number rule in chemistry was made by Laurent [4] in 1843-46; an English-language translation [5] reads: "the sum of nitrogen and hydrogen is always an even number in every nitrogenous compound." This statement, from the nature of the rules, is independent of Euler's discovery. The valency of an atom is the number of hydrogen atoms which can meet at that atom; there is some valency left, if the number of atoms with odd valency is odd, in chemical compounds. The word 'valency' is also used in modern mathematical graph theory [6]. Tracing the history of valency [7] is not necessary for our purpose however. The modern form of Laurent's rule in chemistry is called the principle of valence balance [8]. Laurent's odd-even parity is apparently different from either the handshake lemma or Euler's rule; hence, they had been considered to be not equivalent to one another. Using chemical language we nowadays regard a handshake (or a bridge) as a chemical bond; and a guest (or land) as an atom. The number of guests (lands) can be looked upon as the number of atoms; thus, the handshake lemma, Euler's rule, and the principle of valence balance are all equivalent.

Another analogous odd-even parity is strongly related to the number of cycles in networks. The number of independent cycles, in the graph-theoretical sense, in a network is called the cyclomatic number [9], or the degree of continuity (less one). The correspondence to such a number in chemical compounds is called the degree of unsaturation [10]. Describing the analogy of this number in mathematics and chemistry is another purpose of this contribution. A history of the cyclomatic number should help to clarify somewhat the role of mathematics in chemistry.

The two aspects, valence balance and unsaturation, have been unified by the mathematician Senior [11] in 1951 into graph-theoretical criteria under which a set of atoms is realizable as a constitutional structure (a key chemistry paper, although not well-known to chemists). The present paper describes some pathways from Euler to Senior.

Development of odd-even parities in mathematics and chemistry

Let us describe the problem of the Koenigsberg bridges in symbolic and more generalized form. Let a city have a number of lands (regions) connected by bridges, and let n_i be the number of lands that have the same number of bridges v_i. Summing $(v_i n_i)$ up is clearly to count twice the total number b of bridges. This rule, $\sum v_i n_i = 2b$, at once suggests that the sum of odd v_i is even. It is also the handshake lemma and the principle of valence balance, if v_i is regarded as the number of handshakes and as the valency of an atom i.

In mass spectrometry the nitrogen rule [12], which is useful for analyzing low-resolution mass spectra, says that the odd-even parity of relative molecular mass for a given organic compound coincides with that of the number of nitrogen atoms. The odd-even parity, $\sum v_i n_i = 2b$, implies the nitrogen rule. In an organic compound let n_C, n_H, n_N and n_O be the numbers of carbon, hydrogen, nitrogen and oxygen atoms, respectively; then the relative molecular mass (positive integer) w is expressible as

$$w = 12n_C + n_H + 14n_N + 16n_O$$

The odd-even parity suggests that $n_H + n_N$ is even, because the valencies of H and N are odd. Hence, the odd-even parities in w, n_H and n_N, are the same. In other words, the nitrogen rule is a special statement of $\sum v_i n_i = 2b$, based on the fact that each of the stable isotopes, except for nitrogen, with odd (even) mass number has odd (even) valency.

The molecular number is defined as the total number of atomic numbers in a molecule [13], but is not common knowledge to chemists. One can get, for example, $6n_C + n_H + 7n_N + 8n_O$ for the above-mentioned organic compound. This molecular number becomes even, because $n_H + n_N$ is even.

Ethylene reacts with hydrogen to give ethane, but the addition reaction of hydrogen to ethane is impossible. The number u of hydrogen molecules (or the number $2u$ of hydrogen atoms) is equal to counting the number of rings, because u hydrogen molecules are needed for the conversion of a given cyclic molecule into an acyclic one. One double bond, one ring, and one triple bond, respectively, could be counted as 1, 1, and 2, by chemists; this kind of number is called the degree of unsaturation or the index of hydrogen deficiency [10] in chemical compounds. The number u plays an important role in classifying molecules according to their topological structures; e.g., $u = 0$ for acyclic compounds, $u = 1$ for monocyclic compounds, etc. It should be noted that $2u$ is the number of extra bonds which may not be used in connecting all of the atoms in a molecule. In chemical compounds twice the total number b of bonds minus twice the total number $n = \sum n_i$ of atoms plus 2, is equal to the number $2u$ of extra bonds;

$$2u = \sum v_i n_i - 2 \sum n_i + 2 \text{ or } u = b - n + 1$$

This number u is called the cyclomatic number in mathematical graph theory, and applies to planar graphs.

The 'cyclomatic number' concept was proposed by Kurnakow [9] in 1928. However, it can be traced back even earlier. Kirchhoff [14] in 1847 answered the question of how many equations, derived from Kirchhoff's laws (1845), in a network of v vertices (points) and e edges (lines) are independent. The number of circuits is given by $e - v + 1$; this is just the cyclomatic number. Such a rule relating to the number of rings in cyclic molecules has been frequently reported in the chemical literature (e.g., see ref [15]).

It should be pointed out here that in the above discussion relating to unsaturation and cyclomatic number, a double bond is thought of as a two-membered cycle and a triple bond is considered to be made up of two two-membered rings.

Other aspects related to odd-even parity

A polyhedron is defined as a geometrical solid which is bounded by only planar faces. Euler's formula is $v + f - e = 2$ (even) in usual form, where v is the number of vertices, f the number of faces, and e the number of edges for a convex polyhedron [16]. Such a polyhedron is called regular if it has regular congruent polygons and the same number of edges meet at each vertex. Only five regular polyhedra exist: tetrahedron ($f = 4$), octahedron ($f = 8$), icosahedron ($f = 20$), hexahedron or cube ($f = 6$), and dodecahedron ($f = 12$). A short history of Euler's polyhedral formula is given by Biggs [1]. Euler's formula can be rewritten as $e - v + 1 = f - 1$, which looks like the cyclomatic number u. The number f decreases by 1 if a polyhedron is projected onto a plane.

The formal similarity between the Euler polyhedral formula and Gibbs' phase rule is well-known [17]. The phase rule appears in a series of papers by Gibbs [18]. Let p and c be the numbers of phases and independent components in a thermodynamic chemical system at equilibrium; then, Gibbs' phase rule becomes $c + 2 - p = f$, where f is the degree of freedom (the number of independent intensive variables) in the system. One-to-one correspondence between $c + 2 = p + f$ and $e + 2 = v + f$ indicates that Gibbs' rule and Euler's formula are synonymous.

Unifying odd-even parities

Not all sets of atoms are realizable as constitutional formula in chemistry. Some restrictions are imposed on each set. Senior [11], in 1951, proved an important theorem which has escaped the attention of most chemists. Senior's theorem requires three essential conditions for the existence of molecular graphs, namely:

i) the sum of valencies is an even number, or the total number of atoms having odd valencies is even;

ii) the sum of valencies is greater than or equal to twice the maximum valency;

iii) the sum of valencies is greater than or equal to twice the number of atoms minus 1.

Condition i) is the principle of valence balance, and condition iii) for connectivity means that twice the cyclomatic number $2u$ ($= 2b - 2a + 2$) is not negative, although none of the historical aspects are referred to in Senior's paper. Condition ii) indicates the non-existence of small molecules such as CH_2.

References

1. **Biggs, N. L., E.K. Lloyd, R.J. Wilson**. *Graph Theory 1736 – 1937*. Oxford University Press, Oxford, 1977, chap. 1.

2. **Euler, L.**, 1736. English translation in "Leonhard Euler and Koenigsberg Bridges, *Scientific American*. **189**, 66 (1953). Also see other edition in Biggs *et al.* (1977).

3. **Sylvester, J. J**. *Nature*. **17**, 284 (1877/78).

4. **Laurent, A**. 1843 – 46. See **deMilt, C.**, *Chymia*. **4**, 85-114 (1953).

5. **Novitski, M. E**. Auguste Laurent and the Prehistory of Valence. *Dissertation*, University of California, Berkeley, 1980. chap. 3, pp. 127 – 128, 134, 137; also see Notes 34 and 58.

6. **Wilson, R. J., L.W. Beineke**. *Applications of Graph Theory*; Academic Press, London, 1979, p. 4.

7. **Russell, C. A**. *The History of Valency*. Leicester University Press, 1971, chap. 1.

8. **Fieser, L. F., M. Fieser**, *Introduction to Organic Chemistry*; D. C. Heath, Boston, 1957, chap.2. **Beynon** (1960) called the principle of valence balance "all valency requirements."

9. **Kurnakow, N. S**. *Z. Anorg. Allg. Chem.* **169**, 113-139 (1928).

10. **Silverstein, R. M., G.C. Bassler, T.C. Morrill**. *Spectrometric Identification of Organic Compounds*. John Wiley & Sons, New York, 1981, chap. 2.

11. **Senior, J. K**. *Amer. J. Math* **73**, 663-689 (1951). Senior's three conditions were also treated by **Hakimi, S. L**. *J. Soc. Indust. Appl. Math.* **10**, 496-506 (1962); **11**, 135-147 (1963).

12. **Beynon, J. H**. *Mass Spectrometry and its Applications to Organic Chemistry.* Elsevier, Amsterdam, 1960, chap. 8. Many examples relating to the nitrogen rule are cited by **Pellegrin, V**. *J. Chem. Educ.* **60**, 626-633 (1983).

13. **Brewster, R. Q, W.E. McEwen**. *Organic Chemistry*; Prentice-Hall, Englewood Cliffs, 1961, chap. 1.

14. **Kirchhoff, G. R**. *Ann. Phys. Chem.* **72** , 497-508 (1847). See English translation, **Biggs *et al.*** (1977), chap. 8; also **O'Toole, J. B.**, *IRE Trans. on Circuit Theory CT-5,* 1958, pp. 4-7, and **Weinberg, L**. *ditto*, pp. 8 – 30.

15. **Reddy, P. A**. *J. Chem. Educ.* **64**, 400 (1987).

16. **Gellert,W.**, **S. Gottwald, M. Hellwich, H. Kastner, H. Kustner**. *The VNR Concise Encyclopedia of Mathematics*; Van Nostrand Reinhold, New York, 1989, 2nd edn., p. 81.

17. **Levin, I**. *J. Chem. Educ.* **23**, 183-185 (1946). Also see **Radhakrishnan, T. D**., *J. Math. Chem.* **5**, 381-387 (1990).

18. **Gibbs, J. W**. 1878. *The Collected Works of J. Willard Gibbs*; Yale University Press, New Haven, Conn., 1957, vol. 1, pp. 96, 359.

ЧЕТНОСТ/НЕЧЕТНОСТ В МАТЕМАТИКАТА И ХИМИЯТА

Резюме. Работата раазглежда в исторически план проблема четност-нечетност в математиката и химията. Анализирани са редица примери— от проблема за мостовете в Кьонигсберг, решен от Ойлер, през теорията на графите в математиката и много други примери на приложната математика. Особено внимание е обърнато на ключовата работа на Senior от 1951 с неговите критерии за съществуване на молекулни графи: 1) сумата на валенциите е четно число или общият брой атоми с нечетни валенции е четно число; 2) сумата на валенциите е по-голяма или равна на удвоената максимална валентност; 3) сумата на валенциите е по-голяма или равна на удвоения брой атоми минус единица.

✉ **Professor Tetsuo MORIKAWA**
Department of Chemistry,
Joetsu University of Education,
Joetsu 943-8512, Japan;
morikawa@juen.ac.jp

✉ **Professor Brian T. NEWBOLD**
Department of Chemistry and Biochemistry,
Université de Moncton, Moncton,
N.B., E1A 3E9, Canada