## Letters to the Editor

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## Early History of Mendeléeff's Periodic Law

THE statement appears in NATURE of April 28, p. 656, that "Mendeléeff's first table, published in 1871, bears a remarkable resemblance to that of the present day". As a matter of fact, Dmitri Ivanovitch Mendeléeff began his investigations on the correlation of chemical properties with the atomic weight of elements in 1868, and succeeded in evolving the periodicity of this relationship at the end of that year. He printed the first periodic table in the middle of February, 1869, as follows:

	An attempt	of a system	of elemen	nts
based on	their atomic	weight and	chemical	resemblanc

public on their atomic weight and themical resemblance								
$\begin{array}{l} H = 1 \\ Be = 9 \cdot 4 \\ B = 11 \\ C = 12 \\ N = 14 \\ O = 16 \end{array}$	Ni = Mg = 24 $Al = 27 \cdot 4$ Si = 28 P = 31	$\begin{array}{rl} Ti &= 50 \\ V &= 51 \\ Cr &= 52 \\ Mn &= 55 \\ Fe &= 56 \\ Co &= 59 \\ Cu &= 63 \cdot 4 \\ Zn &= 65 \cdot 2 \\ ? &= 68 \\ ? &= 70 \end{array}$	Zr = 90 $Nb = 94$ $Mo = 96$ $Rh = 104.4$ $Ru = 106.6$ $Ag = 108$ $Cd = 112$ $Ur = 116$ $Sn = 118$	? = 180 Ta = 182 W = 186 Pt = 197.4 Ir = 198				

Mendeléeff prepared his first essay, "Correlation of the Properties with the Atomic Weight of Elements" early in March, 1869, intending to communicate it to the Russian Chemical Society (which was founded on October 26, 1868) at the meeting on March 6. Illness prevented him from attending, and the paper was read, at his request, by my father, Nikolai Aleksandrovič Menschutkin, at the time professor of analytical chemistry at the University of St. Petersburg. Mendeléeff's memoir was printed in the first volume of the Journal of the Russian Chemical Society (1869, pages 60-77); it contains the same table as that printed above, the enunciation of the periodic law and the deductions (a) that the atomic weights of some elements must be altered, to fit into the table; (b) that undiscovered elements exist, filling up the vacant places of the table.

Continuing his work on that subject, D. I. Mendeléeff communicated further results on August 23, 1869, in a meeting of the Second Congress of Russian Naturalists in Moscow. This communication was published in the Transactions of the Congress (pages 62–71) under the title "On the Atomic Volume of Simple Podies". Mendeléeff recognised the importance of this periodically changing property of elements for their classification, and gave the following table—the prototype of all later periodic tables :

Ni
Pd
Os

In the text, this table is completed by the heavy metals : Au, Hg, Tl, Pb, Bi. Elements, the atomic weights of which were not known with any degree of certainty, such as In, Th, U, Ce, are left out.

I do not propose further to follow up Mendeléeff's work here, only mentioning his communication at the meeting of the Russian Chemical Society of December 3, 1870, in which he divided the elements into the periods, rows and groups, now familiar to all students of chemistry. He also made here detailed predictions of the properties of undiscovered elements, which were verified in the years 1875–86 through the discovery of gallium, scandium and germanium.

Thus Mendeléeff's periodic table actually antedates his periodic law and received its modern form in 1869, not in 1871.

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## Mesomerism and Tautomerism

The recognition of valency exchange degeneracy as a matter of primary importance in relation to the energy<sup>1</sup> and reactivity<sup>2</sup> of organic molecules makes it the more necessary clearly to indicate the nature of the conception. It envisages both completely and incompletely degenerate states collectively called 'mesomeric' states; and these states are described by first setting up 'unperturbed structures', which correspond to classical chemical formulæ but (according to the theory) not exactly to reality, and then 'correcting' these structures by supposing them to undergo a 'perturbation', the nature of which may be indicated by auxiliary symbols.

The idea appears to have gained some ground that the conception of the mesomeric state is unnecessary, that the unperturbed structures are all that exist, and that these pass into each other 'like tautomerides but much more rapidly', the great frequency of interchange accounting for the energy effect. If this view has arisen from the use of the expression 'resonance', a long-accepted synonym for exchange degeneracy, then it must be admitted that an analogy has been suggested which was never intended (the real analogy underlying this term is a mathematical one).

It is a characteristic of tautomeric systems that forms exist which clearly correspond to separate molecular states, because each molecule spends the whole of its life partly in one form and partly in the other, and only a proportionately quite insignificant time in the actual process of transition. If, however, in any of the most typical cases of 'resonance', we attempt to interpret resonance energy as a tautomerism of unperturbed states, the frequency of interchange which it is necessary to assume in order to account for the energy effect is often so great as to require that the molecules must occupy their time in changing, and cannot remain quiescent for significant periods in either of the assumed states; in other words, the term 'state' loses its meaning in reference to the only states which this theory recognises. The assumed frequency of valency interchange is, indeed, of the same sort of magnitude as the frequencies which are attributable generally to combined electrons, aside altogether from valency resonance. There can be no physical distinction, therefore, between resonance vibrations and other electronic vibrations, and it follows that the unperturbed structures, in which the resonance vibrations are absent by assumption, are