Hasse Diagrams and their Relation to Molecular Periodicity

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Abstract

Hasse diagrams are applied to molecules and radiation phenomena. Then the relation of these diagrams to periodicity in atoms is noted. The possibility is raised that Hasse diagrams can also be related to the growing body of evidence that periodicity exists in molecules with two, three, and four atoms; in binary inorganic molecules; and in some organic molecules.

Individual molecules

The definition and partially ordered set theory behind the Hasse diagram are given in the chapter by El-Basil, p. 3 and are not repeated; we proceed immediately to discuss some interesting Hasse diagrams.

Would it be possible to construct a molecule or a decay scheme that is its own Hasse diagram? Fig. 1 shows such a hypothetical species. The first number in each box is the period number in which the atom is found; the second is the number of valence electrons. The lone pair on carbon is not shown and the left-hand line is actually a double bond. Fig. 2 shows such a possible atomic decay scheme; similar radiation pathways occur in molecules and also in nuclei.
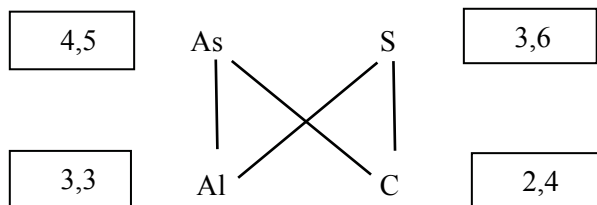
| 4,5 | As   S | | 3,6 |

| 3,3 | Al   C | | 2,4 |

Fig. 1. The hypothetical molecule serves as its own Hasse diagram

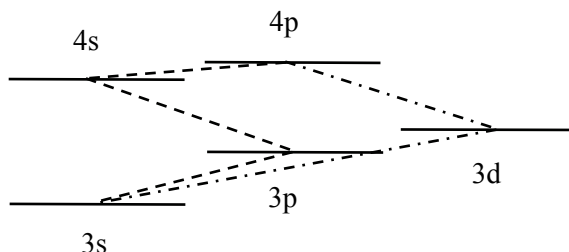4s   4p

3s   3p   3d

Fig. 2. A possible atomic radiation scheme is shown

Inorganic molecules

Klein has already represented the chart of the elements as the Hasse diagram of a multi-poset (Klein 1995). Over many decades the periodicity of many properties of main-group and transition metal diatomic molecules, in various phases, and main-group anions has been exhaustively documented (Clark 1935; Cornish 1959; Hefferlin et al. 1979; Hefferlin and Kutzner 1981; Kong 1982; Hefferlin, 1989; Boldyrev et al. 1994). Merging these two trains of thought make it seem reasonable that a somewhat more complex multiposet should pertain to them. The same is true for main-group triatomic and tetra-atomic molecules, since their periodicity has been demonstrated (Kong 1989, 1993).

A massive research project on the periodic properties of molecules has been pursued by generations of Russian chemists during the Soviet period

and, to a lesser extent, subsequently. This research was to a large degree led by Shchukarev of Leningrad State University. He considered a general periodic system as being one immense "supermatrix" connecting innumerable "matrices" of elemental atomic states, of the compounds that they may form, of their properties, of their functional dependencies on the external conditions, and so on. The term "supermatrix" was used to represent the chemical element periodic chart and the immense molecular spaces accessed by stepping through any one or more of its compartments. The word "matrices" was also used loosely, referring in many cases to graphical representations of data; "databases" and "subsystems" would do as well.

The transformation from one matrix to any other, within the supermatrix, was to be accomplished with advanced mathematics such as group theory. Knowing that such transformations were beyond his capability at the time, Shchukarev and his colleagues collected data in preparation for the day when the capability would materialize. The data are represented in scores of graphs such as Fig. 3.
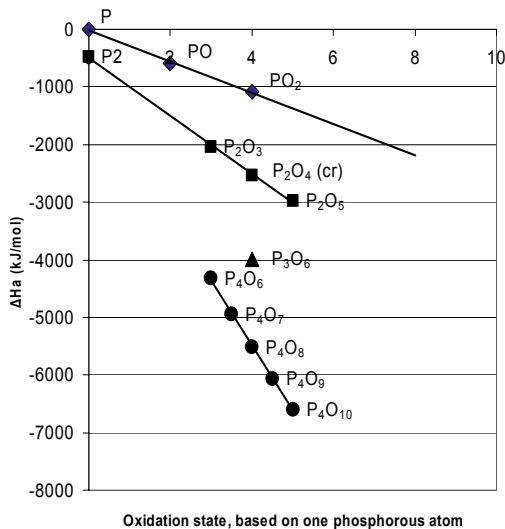

Fig. 3. Heats of atomization for oxides of phosphorus plotted against the oxidation state, normalized to one P atom, of phosphorus. The graphs as plotted by Shchukarev also normalize the data vertically to one P atom

The vertical axis shows the heats of formation (Gurvich 1978, 1979, 1981, 1982) of the molecules from free atoms; all of the molecules are in the gas phase (except for P_2O_4, which is in the crystal phase). The Hasse diagram shown in Fig. 4 represents the upper half of Fig. 3; it is easily seen how the lower half would be appended.
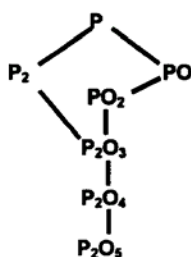

Fig. 4. An organization of phosphorus and its oxides up to P_2O_5 (higher oxides exist). Each line indicates the addition of one or more atoms to the species at its beginning

Molecular periodicity is clearly evident in perusing the graphs in Shchukarev's books (1970 and 1974); they contains graphs of ΔH_a (heat of atomization) like Fig. 3 (except for vertical normalization) for group 1 oxides (O), Mg and Ca (O), 3 to 12 (O), 13 (halides and H), 14 (O and H), 15 (O and H), 16 (O, S, and H), 17 (F, O, and H), and 18 (F). These graphs are amazingly similar, and show that heats of atomization of binary and ternary inorganic species echo the periodicity of atoms in the Mendeleev chart.

This extent of this research effort can be measured by noting that it includes work on how molecules are changed by going into water solution (Latysheva and Hefferlin 2004) and how the water solution is changed by the presence of the dissolved molecules (Lilitch and Mogilev 1954; Lilitch 1964; Burkov et al. 1977; Lilitch and Chernykh 1977; Khripun et al. 1983). A detailed review is given by Latysheva (1998).

Organic molecules

Morozov explored periodicity among alkanes nearly a century ago (Morozov 1907). Beautiful periodic tables have been constructed for polycyclic aromatic hydrocarbons by Dias (1996), for acyclic hydrocarbons by Bytau-

tas et al (2000), and for fullerenes by Torrens (2004). So it is clear that periodicity has been observed in organic molecules.

Klein and Bytautas (2000) have given the Hasse diagram—technically, the partially ordered set reaction diagram—for halogenated benzenes. It starts with benzene at the top, concludes with fully chlorinated benzene at the bottom, and has the partially chlorobenzenes in between at ordinates approximating the boiling point scale. An almost identical diagram, with boiling points that progress in a similar way, pertains to methylbenzenes. From the point of view of periodicity, it is significant that the methyl functional group is isovalent to the halides (Haas 1982).

The most extreme diagram that comes to mind is one for polychlorinated biphenyls. Presumably it would have 1,1-biphenyl at the top, decachloro 1,1-biphenyl at the bottom, and the 207 remaining isomers between, ranked according to data for some property. Unfortunately, there are nowhere near enough data to begin the diagram now. There are, however, enough data to suggest periodicity in halogenated biphenyls (Fig. 5). The suggestion would be reinforced if the point for 4-fluoro 1,1'-biphenyl is shown to be in error to be at about 540K.
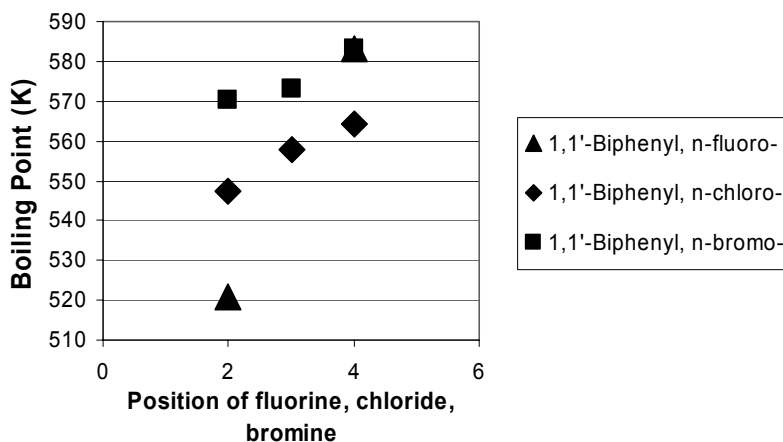

Fig. 5. Boiling points of 2-, 3-, and 4- fluoro-, chloro-, and bromo- 1,1'-biphenyls. The x = 2 (F,Cl,Br) arrangement, which would exist also at x = 4 if one point were moved, suggests periodicity

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