The General (8–N) Rule and its Relationship to the Octet Rule

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The general (8—N) rule has been deduced from the simple octet rule with specifications concerning the bonding system. The significance and limitations of the rule have been discussed in terms of the physical model.

The present views on the octet rule (the rule of eight) may be traced to two important and independent papers published by Lewis [1] and Kossel [2] in 1916. Inherent in both papers is the suggestion of the stability of the eight-electron outer arrangement in the inert gas elements (except for the two-electron arrangement in helium) and the tendencies of elements with atomic numbers close to those of the inert gas elements to achieve these electron configurations. Kossel drew attention to the electrovalent (ionic) aspect of chemical bonding whereas Lewis described the structures of many simple molecules in terms of the sharing of electrons between atoms, *i.e.* the covalent picture.

Much of the emphasis on the octet arrangement as governing the chemical behaviour of the elements is undoubtedly due to the rigidity with which the rule applies to most organic compounds and to the fact that the properties of the majority of the more common elements can be explained adequately in terms of the rule.

Subsequent developments have centered largely in extensions and modifications of the concept, especially the justification in terms of modern quantum theory (see *e.g.* Löwdin [3]). Although the application of the octet rule is more limited than first thought, it has done much to simplify the systematization of chemical concepts. In this respect, the octet rule still remains rather useful.

A parallel to the octet rule is found in what is known as the crystallographic (8—N) rule. This states that the elements of Group IVB-VIIIB (carbon to neon and congeners) crystallize so that each atom has (8—N) close neighbours, where N is the number of the group to which the elements belong. It will be recognized that this is another version of the octet rule, saying that an atom of Group N completes its octet of electrons by sharing one electron

with each of the (8—N) close neighbour atoms. The (8—N) rule appears to
have been formulated in this form by Hume-Rothery,[4] but the essence had
already been recognized in 1922 by Huggins.[5]

Interest in the concept of "the semiconductor bond" and criteria for the
prediction of new semiconducting compounds have in recent years resulted
in an empirical generalization of the (8—N) rule.[6–10] The purpose of the present
paper is to show that this formulation follows from the octet rule with certain
specifications concerning the bonds between the atoms.

For simplicity, consider first a binary compound C_cA_a, where

C = a cation with valence y Def. 1
A = an anion with valence x Def. 2

(The terms cation and anion, which should strictly refer only to the atoms in
ionic compounds, are here used as convenient terms to describe, respectively,
the more electropositive and more electronegative atoms even in compounds
whose bonding is principally covalent.) If C_cA_a is a normal valence compound
the valence rules require that

$$ax = cy \tag{1}$$

(For a purely ionic compound eqn. 1 states the condition of electroneutrality.)
Eqn. 1 depends on the assumption that bonding occurs between cations and
anions only. For example it breaks down with the saturated hydrocarbons
whose formulae C_nH_{2n+2} ($n>1$) remain unexplained by eqn. 1, a failure due
to the neglection of carbon-carbon bonds.

To obtain further progress, the formation of anion-anion and/or cation-
cation bonds must be allowed in the physical model. The following notations
specifying these bonds are accordingly introduced:

p = the average number of anion-anion bonds per anion   Def. 3
q = the average number of cation-cation bonds per cation   Def. 4

With these specifications in the physical model, eqn. 1 must be modified to

$$a(x-p) = c(y-q) \tag{2}$$

in order to obtain complete saturation of the valences. Rearrangement of
eqn. 2 gives

$$cy-ax + ap-cq = 0 \tag{3}$$

In order to be able to introduce the convenient quantity

n = the total number of valence electrons per formula unit C_cA_a Def. 5

in eqn. 3 it must be remembered that following def.'s 1 and 2, y and x have
been introduced as valences. For the cations y may represent either valence
or number of valence electrons according to what is needed. For the anions
on the other hand the two quantities are different. In order to overcome this
difficulty it is necessary to introduce the octet rule (or its equivalent)

$8-x$ = the number of valence electrons per anion   Def. 6

By combination of def.'s 5 and 6

$$n = a(8-x) + cy \tag{4}$$

which may be rearranged to

$$cy - ax = n - 8a \tag{5}$$

and introduced in eqn. 3 giving the result

$$\frac{n + ap - cq}{a} = 8 \tag{6}$$

Eqn. 6 is identical with the general (8—N) rule in the form given by Hulliger and Mooser.[8] The expression suggested by Pearson [9] differs only from eqn. 6 in introducing the quantities $P = ap$ and $Q = cq$, $i.e.$ the number of electrons involved in forming anion-anion and cation-cation bonds respectively, per formula unit $C_c A_a$, as new parameters. (Eqn. 6 was introduced in the first paper by Mooser and Pearson [6] with $q = 0$ and was later extended by the same authors [7] to include cases for which $c/a = 1$.)

The present deduction shows that the rule can easily be extended to include electron configurations other than octets around the anions. This is done by introducing the electron configuration in question as a quantity N in def. 6 instead of the figure 8. With reference to eqns. 4 to 6 the final expression will then be

$$\frac{n + ap - cq}{a} = N \tag{7}$$

The case $N = 2$ is worth noticing as this applies to compounds containing hydrogen, $e.g.$ hydrides. The discussion and comments by Suchet [10] (considering only cases with $q = 0$) are covered by eqn. 7 if his unusual and cumbersome system of counting quantum states is adopted.

In order to extend the rule to include compounds containing more than two elements, let us consider a general compound $C^1_{c_1} C^2_{c_2} \ldots C^j_{c_j} A^1_{a_1} A^2_{a_2} \ldots A^i_{a_i}$ and take

$C^j =$ a cation with valence y_j		Def. 1'
$A^i =$ an anion with valence x_i		Def. 2'
$p_i =$ the average number of anion-anion bonds per anion of kind i		Def. 3'
$q_j =$ the average number of cation-cation bonds per cation of kind j		Def. 4'
$n =$ the total number of valence electrons per formula unit $C^1_{c_1} \ldots A^i_{a_i}$		Def. 5'
$N_i - x_i =$ the number of valence electrons per anion of kind i		Def. 6'

The equivalent of eqn. 2 is

$$\sum_i a_i(x_i - p_i) = \sum_j c_j(y_j - q_j) \tag{8}$$

providing the physical model is unchanged. An exactly similar calculation to that carried out in eqns. 3 to 6 gives

$$n + \sum_i a_i p_i - \sum_j c_j q_j = \sum_i a_i N_i \tag{9}$$

It is convenient to introduce the quantities used by Pearson [9]

$P = \sum_i a_i p_i =$ the total number of electrons involved in forming anion-anion bonds per formula unit $C^1_{c_1}....A^i_{a_i}$ Def. 7

$Q = \sum_j c_j q_j =$ the total number of electrons involved in forming cation-cation bonds per formula unit $C^1_{c_1}....A^i_{a_i}$ Def. 8

$a = \sum_i a_i$ = the total number of anions per formula unit $C^1_{c_1}....A^i_{a_i}$ Def. 9

as new parameters. Moreover it is necessary to make the limitation that all anions have the same number of electrons in the closed shell, i.e. $N_i = N$, generally equal to 8. Eqn. 9 then takes the form

$$\frac{n + P - Q}{a} = 8 \tag{10}$$

which is the form used by Pearson.[9] In counting the number of electrons (n), unshared electrons must not be included (as emphasized by Hulliger and Mooser [8]). An alternative, but equivalent procedure is to include these electrons in n and then subtract them afterwards, either implicitly as a part of Q, as Pearson [9] does, or explicitly as a separate term. These may be unpaired (and detectable by magnetic susceptibility measurements with the transition elements) or paired, i.e. inert pairs.

Two important special cases deserve to be mentioned:

i) If the formula of the compound reduces to A_a, i.e. it is in reality an element and not a compound, then $Q = 0$ owing to the fact that no cations are present and eqn. 10 takes the form

$$\frac{P}{a} = p = 8 - \frac{n}{a} = 8 - N \tag{11}$$

When one remembers that $n/a = N$ is the group number of the element A, eqn. 11 will be recognized as the mathematical formulation of the (8—N) rule in its original form. As eqn. 10 describes a more comprehensive physical situation than eqn. 11 the name "general (8—N) rule" for eqn. 10 is justified.

For a binary solid C_cA_a with $Q = 0$, eqn. 10 reduces to

$$\frac{P}{a} = 8 - \frac{n}{a} \tag{12}$$

which is very similar to eqn. 11. Because the anions are normally larger than the cations they support the lattice; and comparison of eqns. 11 and 12 tells us that the anion sublattice may show relationships with the structure of an element whose group number N equals n/a.

ii) Pamplin [11] has devised a formula (in terms of the present notation; with the addition of $c = \sum_j c_j$):

$$\frac{n}{a + c} = 4 \tag{13}$$

to predict new semiconducting compounds. In order to derive eqn. 13 from eqn. 10 one considers a situation in which it is difficult or physically and chemically meaningless to distinguish between anions and cations in a compound $C^1{}_{c_i}....A^i{}_{a_i}$.

Furthermore, one can relinquish the convenience of describing this situation by $P \neq 0$ or $Q \neq 0$. Instead one may, as a result of the uncertainty as to which atoms are anions and which cations, write $n = 8c$ as well as $n = 8a$ from which eqn. 13 follows.

As seen from the need for def. 6 (or the corresponding def. 6') in the present deduction, the anions have a special position among the component atoms. It is this position of the anions which gives rise to the special forms of eqns. 6, 7, 9, and 10.

In the deduction of eqns. 6, 7, 9, and 10 it has not been necessary to assume that the molecular system is a solid. In this respect the formulae are perfectly general and indeed applicable to gaseous and liquid systems as well. On the other hand molecular systems in the gaseous and liquid phase are usually simpler to handle by other methods. The importance of the general (8—N) rule therefore lies primarily in its application to ionic and covalent solids.

The rule is merely a new version of the octet rule with specifications about the bonding system integrated in the formulae (eqns. 6 and 10). It is these specifications which make the general (8—N) rule more easily applicable than the plain octet rule.

The applications of the rule may be summarized as:

i) It offers [8,9] a simple explanation to the valence-problem in many compounds which previously have been considered as anomalously composed (e.g. KGe and $CaSi_2$ with $n/a = 5$, $P/a = 3$, $Q/a = 0$; ZnSb with $n/a = 7$, $P/a = 1$, $Q/a = 0$; GaS, GaSe and GaTe with $n/a = 9$, $P/a = 0$, $Q/a = 1$).

ii) It provides [9] a system for classification of compounds as polyanionic, normal valence and polycationic compounds according to whether n/a is smaller than, equal to or greater than 8. Further systematization is obtained in the description of crystal structures if these are listed according to appropriate values of n/a, P/a and Q/a.

iii) It is an observed fact that all known semiconductors obey the general (8—N) rule, while no compounds not obeying the rule are semiconductors and very few compounds obeying it are not semiconductors*; therefore it can be used to predict the expected occurrence of semiconductivity. A complete test of the rule for a given compound involves knowledge of the three factors, valence, crystal structure and electrical conductivity. When two of these factors are known the rule may be used to predict the third.[6-10] The strength of the rule lies in its use of the average figures P and Q whereas the plain octet rule requires complete knowledge of the molecular structure. This is at the same time its weakness for use in the prediction of unknown crystal structures where the cations or anions may occupy more than one crystallographic site or where P and Q are both different from zero. (An interesting example is the monoclinic form of ZnP_2, discussed by Pearson,[9] where $n/a = 6$, $P/a = 9/4$ and $Q/a = 1/4$.)

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* Or ionic conductors

REFERENCES

1. Lewis, G. N. *J. Am. Chem. Soc.* **38** (1916) 762.
2. Kossel, W. *Ann. Physik* [4] **49** (1916) 229.
3. Löwdin, P.-O. *J. Phys. Chem.* **61** (1957) 55.
4. Hume-Rothery, W. *Phil. Mag.* [7] **9** (1930) 65.
5. Huggins, M. L. *J. Phys. Chem.* **26** (1922) 601; *J. Am. Chem. Soc.* **44** (1922) 1841.
6. Mooser, E. and Pearson, W. B. *J. Electronics* **1** (1956) 629.
7. Mooser, E. and Pearson, W. B. *Progress in Semiconductors* **5** (1960) 103.
8. Hulliger, F. and Mooser, E. *J. Phys. Chem. Solids* **24** (1963) 283.
9. Pearson, W. B. *Acta Cryst.* **17** (1964) 1.
10. Suchet, J. P. *J. Phys. Chem. Solids* **12** (1959) 74; *Ibid* **21** (1961) 156; *Physica Status Solidi* **2** (1962) 167.
11. Pamplin, B. R. *Nature* **188** (1960) 136; *J. Phys. Chem. Solids* **25** (1964) 675.