First Step in Dissociation Process in the Gas Phase for Small Molecules with Neutral Atoms: Application with the Even-Odd Rule and a Specific Periodic Table for Organic and Inorganic Atoms

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Abstract

Dissociations in the gas phase of small molecules have been intensively studied and dissociation energies of various gases are available in reference works. Configurations of compounds before and after the dissociation are usually known, but local charges are not defined. Building on the even-odd rule, the topic of a series of previous articles by the same author, the objective of this paper is to show how it can be used to give electronic rules for dissociations in gases. To this end, a specific periodic table is created and used. The rules are applied to a selection of more than 30 common molecules, showing that the even-odd rule and its consequences are useful in explaining the phenomenon of dissociation in gases.

1. Introduction

Properties of gases are taught in high school chemistry. Theoretically, these properties follow a simple law named the ideal gas law, or general gas equation. Numerous experiments have been carried out to validate this simple law [1]. Discrepancies have been found, and interpreted as a molecular dissociation, *i.e.*,

broken chemical bonds. This occurs as temperature increases, and its dependance allows to derive a dissociation energy. The different measurements have been compiled by reference authors, such as de B. Darwent in his book on "Bond Dissociation Energies in Simple Molecules" [2]. In this book, dissociation of small molecules composed of different elements is listed, and dissociations names are given. Reference books like this [3] [4] are used in many fields like thermochemistry, kinetic of reaction, mass spectroscopy, astrophysics and so forth. Unfortunately, the knowledge of atoms charges before or after dissociations is missing. It is the object of this paper to associate neutral atoms and charged atoms when dissociations occur.

To do so, a *specific periodic table for dissociations of stable gaseous compounds* is first written. Then, the even-odd rule, the base of this specific table, is recalled and applied to about 30 known small molecules [5]. It will be shown how molecules can dissociate into smaller charged compounds, and sometimes into elementary atoms. In discussions, displacements of electrons pairs are described, and conclusions will recall the importance of the specific periodic table and the even-odd rule.

In the present article:

- Stable Molecular compounds exist in three states: gas, liquid and solid [1];
- Molecules are with atoms represented by their acronyms as in the classical periodic table;
- In molecule, and between two atoms, a small line represents a covalent bond [6] [7];
- Molecules are electrically neutral, and dissociation may change the number of bonds and charges positions;
- Whatever the molecular structure, electrons are always appaired [8];
- Compounds are noted in capitals: H2O is for neutral water, H3O(+) for hydronium and OH(−) for hydroxide ions [6].

2. Specific Periodic Table for Neutral and Charged Atoms

Classically a periodic table shows atoms classified in columns by the number of protons. In such, it starts with hydrogen. To use a better periodic table for chemistry, it may be useful to add charged atoms in such a table. An important choice for this adding, is that an atom in a compound cannot have more than one charge: positive or negative. This choice which has been previously published [9], will be used all along this article, and shown in Table 1.

To take charges into account, a classification in column by the number of electrons may be more useful than a classification by the proton's number. Table 1 illustrates how it is done, although this table will not be sufficient for the purpose of this article on gas dissociation.

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Table 1. The three first rows of a *specific periodic table for chemistry*. The classification in columns is made with the number of electrons. For neutral atoms, the classification in rows and in columns is identical to the classical periodic table. A positive charge is classified on the left-side column of the neutral atom and on the right-side for the negative charge. In each group of atoms, number in bottom gives the number of electrons, in both shells. The first shell is the inner shell and the second is the outer shells.

Atom's	Column	Number	and	Electrons	Number				
name	0	1	2	3	4	5	6	7	8
Hydrogen	H(+)	H	H(−)						
(Shells)	0, 0	0, 1	0, 2						
Lithium	Li(+)	Li	Li(−)						
Beryllium		Be(+)	Be	Be(−)					
Boron			B(+)	B	B(−)				
Carbon				C(+)	C	C(−)			
Nitrogen					N(+)	N	N(−)		
Oxygen						O(+)	O	O(−)	
Fluorine							F(+)	F	F(−)
(Shells)	2, 0	2, 1	2, 2	2, 3	2, 4	4, 3	6, 2	8, 1	10, 0
Sodium	Na(+)	Na	Na(−)						
Magnesium		Mg(+)	Mg	Mg(−)					
Aluminum			Al(+)	Al	Al(−)				
Silicon				Si(+)	Si	Si(−)			
Phosphorus					P(+)	P	S(−)		
Sulfur						S(+)	S	S(−)	
Chlorine							Cl(+)	Cl	Cl(−)
(Shells)	10, 0	10, 1	10, 2	10, 3	10, 4	12, 3	14, 2	16, 1	18, 0

In Table 1, the first column gives names of the atoms which are written on the same lines with its charges (+), (n) and (−): H(−) has two electrons and is placed on the right of neutral hydrogen which have one electron. For H(+) which do not have electrons, it is placed on the left of the neutral one.

In the left-side column and from top to bottom, the atoms have an increasing number of protons as it is classified in the periodic table.

As this paper is focused on molecules, and molecules are composed of interconnected atoms, it seems interesting to introduce the number of bonds, and build another specific periodic table.

The even-odd rule (See 3.2.) gives us constraints over the number of bonds each element can build as well as the charge they bear in connection with their bonding configuration. These constraints are used to build a specific periodic table for dissociation of stable gaseous compounds as shown in Table 2. This table includes a color code to highlight organic and inorganic atoms.

Table 2. Three first rows of the atoms in a *specific periodic table for dissociations of stable gaseous compounds*. Higher are the left-side number of an atom, higher is the number of bonds of these atoms in the compounds it belongs to. The classification of neutral atoms, in columns comes from the classical periodic table. The numbers of electrons starting from 0 for H(+) up to 18 for Cl(−). Charged atoms are positioned in the two nearest columns of the neutral atoms. Three groups are enlightened: white cells are with inorganic atoms, green cells with organic atoms, and cells in yellow color contain atoms classified as semi-organic atoms. For each atom, the highest number of bonds is for neutral atoms.

Row 1

		Electrons	Numbers		
Bond	0 + 0	0 + 1	0 + 2		
1 bd		H(n)			
0 bd	H(+)		H(−) He(n)		

Row 2

		Electron	Numbers						
	2 + 0	2 + 1	2 + 2	2 + 3	2 + 4	4 + 3	6 + 2	8 + 1	10 + 0
4 bs					C(n)				
3 bs				B(n) C(+)		C(−) N(n)			
2 bs			Be(n) B(+)		B(−) N(+)		N(−) O(n)		
1 bd		Li(n) Be(+)		Be(−)		O(+)		O(−)F(n)	
0 bd	Li(+)		Li(−)				F(+)		Ne(n) F(−)

Row 3

		Electron	Numbers						
	10 + 0	10 + 1	10 + 2	10 + 3	10 + 4	12 + 3	14 + 2	16 + 1	18 + 0
4 bs					Si(n)				
3 bs				Al(n) Si(+)		Si(−) P(n)			
2 bs			Mg(n) Al(+)		Al(−)P(+)		P(−)S(n)		
1 bd		Na(n)Mg(+)		Mg(−)		S(+)		S(−)Cl(n)	
0 bd	Na(+)		Na(−)				Cl(+)		Kr(n)Cl(−)

In Table 2, the classification by columns is the same as in Table 1. Vertically, atoms are now classified by the number of bonds. Lower an atom is placed, lower is the number of bonds. As dissociations correspond to a decrease of the number of bonds in molecules, results give compounds at a lower position and the column is changed according to the electron number after dissociation. For example, oxygen with two bonds (as in H2O) decreases into O(−) with one bond (as in HO(−)).

The lowest lines in row 1, 2 and 3, give atoms without bonds. This occurs for the first dissociation step in molecules which are stable with a single bond like in di-hydrogen, di-lithium, di-fluorine, di-sodium and di-chlorine.

Note that mono-atoms of C and O are not present in Table 2 due to the limitation for the first dissociation step.

3. Tools and Rules to Draw Chemical Gaseous Compounds

The validity of the following rules was previously tested for bonding structures of molecules [6] and for crystals [10] [11].

3.1. Even-Odd Rule

Specific Basic Concepts of atoms in gaseous compounds are described by:

*Uncharged atoms, the even-odd rule, imposed:

- For neutral atoms having an even number of electrons, the number of single covalent bonds around is even, and the smallest number of bonds is equal to zero.
- For neutral atoms having an odd number of electrons, the number of single covalent bonds around an atom is odd, and the smallest number of bonds is equal to one.

*Charged atoms with the even-odd rule, they are as:

- For neutral even atoms, when it is charged, the number of single bonds is odd, and the smallest number of bonds is equal to one.
- For neutral odd atoms, when it is charged, the number of single bonds is even, and the smallest number of bonds is equal to zero.

From this rule, mono-atoms (no bond) are uncharged for even atoms but charged (+) or (−) for odd atoms. H(+) and H(−) are charged without bonds.

3.2. Highest Number of Bonds

The specific periodic table for dissociation of stable gaseous compounds includes the highest number of bounds which is well-known in scientific literature [5]. In the first row of Table 2, the highest number of bonds is one for di-hydrogen. In row 2, the highest number is (but not only) for LiF, BeF2, BF3, CF4, NH3, H2O and HF. These numbers change very regularly. In row 3, they are NaCl, MgCl2, AlCl3, SiCl4, PH3, SH2 and HCl feature the highest number of bonds. They also are regularly distributed.

Rare gas can also be included in these series by having zero bond, but they do not form any molecule.

3.3. Covalent Bonds between Charged or Neutral Atoms

An important rule used in this paper is that each couple of atoms in a compound has only one covalent bond. This particularity has been previously described [12].

In the present paper, the rule for covalent bonding between atoms is proposed to be:

- A neutral atom can be bonded to another neutral or charged (positively or negatively) atom,
- A charged atom can be bonded to a neutral, or an oppositely charged

atom.

4. Organic, Inorganic or Semi-Organic

4.1. Bonding Rule between Organic and Inorganic Atoms

Three groups of atoms are present in *the specific periodic table for dissociation of stable gaseous compounds*:

- In the four first columns, atoms are inorganic (highlighted in white), and they have a constant value for the inner shell,
- In the four last columns, atoms are organic (highlighted in green), and they have an increasing value for the inner shell,
- When atoms are placed between these two groups, they are named as semi-organic (highlighted in yellow).

In the two first row of Table 2, inorganics atoms are H, Li, Be, B and C(+), organic atoms are C(−) N, O, F, and semi-organic atoms are B(−), C(n) and N(+).

The main point in this paper, about organic or inorganic atoms is that a covalent bond exists only between atoms of two different groups. For example, HF has a covalent bond between one inorganic atom H and one inorganic atom F.

4.2. Chemical Reactions of Organic and Inorganic Atoms

In this paper, it will be assumed that dissociation of such a covalent bond will be a displacement of the electrons pair which is going into the organic atom to form a negatively charged atom. At the same time, the inorganic atom become positively charged leaving a neutral global charge.

These charges transfer agree with the concept of the Pauling electronegativity of the atoms in the classical periodic table [13] [14]. For example: NaCl dissociates in Na(+) and Cl(−) which are inorganic and organic, respectively.

Semi-organic atoms are special cases and will be treated in more details in the discussion.

5. Application

The application is for molecules following the rules described above. A large list of these molecules is reported in a book from NSRDS [2] in which previous works of dissociations of molecules are given.

The present paper is based on this list but limited to very stable molecules. It does not include molecules which are created under electrical discharges, or not stable under long times, or when forming a fuel. This limited number of molecules can be dissociated under thermal physical conditions. Such selected dissociations are described in Table 3. In it, each atom is neutral before dissociation and with a charge—one positive and one negative—after dissociation.

Table 3. Known molecules with uncharged atoms before and after dissociations in gas phases. Column 1 gives the atoms of molecules. The gaseous temperature is given in column 2. Column 3 shows the bonds which will be dissociated, resulting in two parts in column 4 and 5. In column 6, available experimental data are given for the dissociation energy of the bond of column 3.

Row 1	Gas	Covalentbond	Product 1	Product 2	Energy (kJ/mol)
H2	T > −253˚C	H(n)−−−H(n)	H(+)	H(−)	432
Row 1 et 2					
HF	T > 100˚C	H(n)−−−F(n)	H(+)	F(−)	565
CH3CN	T > 82˚C	C(n)−−−C(n)	C(−)H3	C(+)N(n)	498
CH3F	T > −78˚C	H3C(n)−−−F(n)	C(−)H3	F(+)	470
CH4	T > −162˚C	H3C(n)−−−H(n)	C(−)H3	H(+)	425
HCN	T > −13˚C	NC(n)−−−H(n)	NC(−)	H(+)	531
H2CO	T > −19˚C	HC(n)O(n)−−−H(n)	HCO(−)	H(+)	314
CF3H	T > −82˚C	F3C(n)−−−H(n)	C(+)F3	H(−)	639
CH3NH2	T > −6˚C	H3C(n)−−−N(n)H2	H3C(+)	N(−)H2	320
CH3NO2	T > −12˚C	H3C(n)−−−N(n)O2	H3C(+)	N(−)O2	260
CH3OH	T > 65˚C	H3C(n)−−−O(n)H	H3C(+)	O(−)H	370
NH3	T > −33˚C	H2N(n)−−−H(n)	N(−)H2	H(+)	531
LiOH	T > 924˚C	Li(n)−−−O(n)H	Li(+)	O(−)H	434
H2O	T > 100˚C	HO(n)−−−H(n)	HO(−)	H(+)	494
Row 2					
LiF	T > 1676˚C	Li(n)−−−F(n)	Li(+)	F(−)	577
Li2O	T > 2600˚C	Li(n)−−−O(n)Li	Li(+)	O(−)Li	331
B2	T > 4200˚C	B(n)−−−B(n)	B(+)	B(−)	293
BF3	T > −100˚C	F2B(n)−−−F(n)	F2B(+)	F(−)	665
BeF2	T > 1169˚C	FBe(n)−−−F(n)	FBe(+)	F(−)	690
CF4	T > −128˚C	F3C(n)−−−F(n)	F3C(+)	F(−)	523
Row 1 and 3					
SiH4	T > −112˚C	H3Si(n)−−−H(n)	H3Si(−)	H(+)	398
PH3	T > −88˚C	H2P(n)−−−H(n)	H2P(−)	H(+)	?
H2S	T > −60˚C	HS(n)−−−H(n)	HS(−)	H(+)	377
HCl	T > −85˚C	H(n)−−−Cl(n)	Cl(−)	H(+)	428
Row 2 and 3					
NaOH	T > 1388˚C	Na(n)−−−O(n)H	Na(+)	O(−)H	322
AlF3	T > 1290˚C	F2Al(n)−−−Cl(n)	F2Al(+)	Cl(−)	?
BCl3	T > 13˚C	Cl2B(n)−−−Cl(n)	Cl2B(+)	Cl(−)	531
BeCl2	T > 482˚C	ClBe(n)−−−Cl(n)	ClBe(+)	Cl(−)	536
CF3Cl	T > −81˚C	F3C(n)−−−Cl(n)	F3C(+)	Cl(−)	335
CH3Cl	T > −24˚C	H3C(n)−−−Cl(n)	H3C(+)	Cl(−)	330
ClCN	T > 13˚C	NC(n)−−−Cl(n)	NC(+)	Cl(−)	435
CCl4	T > 77˚C	Cl3C(n)−−−Cl(n)	Cl3C(+)	Cl(−)	330
LiCl	T > 1382˚C	Li(n)−−−Cl(n)	Li(−)	Cl(+)	464
MgF2	T > 2260˚C	FMg(n)−−−F(n)	FMg(+)	F(−)	565
Row 3					
NaCl	T > 1465˚C	Na(n)−−−Cl(n)	Na(+)	Cl(−)	410
AlCl3	T > 180˚C	Cl(n)2Al(n)−−−Cl(n)	Cl(n)2Al(+)	Cl(−)	372

In Table 3, covalent bonds in column 3, are only between two neutral atoms. After dissociation they are both charged as shown in column 4 and 5.

6. Discussion

6.1. First Step

Dissociation of small stable molecules with neutral atoms can be obtained for all the atoms of the three rows of the periodic table shown above. In this chapter, the displacement of the electrons during the first step of dissociations is detailed.

In Table 3, two neutral atoms are attached by a covalent bond. This covalent bond is composed of two electrons but each of them belongs to only one of both atoms. It is drawn in Figure 1 by a small line with two circles.

Before dissociation
m bonds Inorganic(n) ●━● Organic(n) p bonds
After first dissociation step
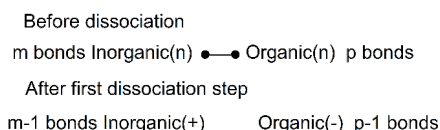m-1 bonds Inorganic(+)   Organic(-) p-1 bonds

Figure 1. Displacement of an electrons pair to form two complementary ions.

Figure 1 exposes a possibility of inorganic and organic atoms. It shows that one electron may move from the left to the right. Unfortunately, this is only an appearance. The occurring process is the move of one electron pair forming the bond into the organic atom placed on the right.

The inorganic atoms lose a bond, and its position in Table 2 is one step lower, and it must move on the left for one step to become positively charge. For organic atoms, they also lose a bond, but to become negatively charged, it must move down and on the right. This difference between organic and inorganic during the dissociation is, for the author, a useful idea.

This model is compatible with the presence of an atom of the semi-organic column of Table 2. When the semi-organic is on the left side of Figure 1, it is associated to an organic atom on the right. After the dissociation, the organic becomes negatively charged, and the semi-organic becomes inorganic with a positive charge. As an example: CF_4 dissociates in inorganic C in $CF_3(+)$ and the organic F(−). Similarly, when the semi-organic is on the right side of Figure 1, it is associated to an inorganic atom on the left. After the dissociation, the inorganic becomes positively charged, and the semi-organic becomes organic with a negative charge: CH_4 dissociates in organic C in $CH_3(−)$ and the inorganic H(+).

6.2. Second Step

The second step is shown in Figure 2.

After first dissociation step
m bonds Inorganic(+) ●━● Organic(n) p bonds
After second dissociation step
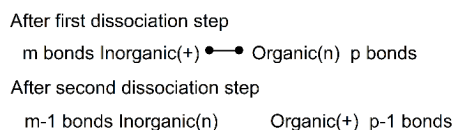m-1 bonds Inorganic(n)   Organic(+) p-1 bonds

Figure 2. Second dissociation step for an inorganic atom connected to another organic atom.

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In Table 2, the first step for an inorganic atom is its movement from one step down and one step left. The second step is different but not shown in Table 2. It still moves down but now on the right to be back to neutral state with the same number of electrons as before the first dissociation step. With both steps, it has lost two bonds.

In this second drawing, a displacement of a positive charge seems to move to the right. Really, it is the electrons pair which move to the left. As an example, B(n)F3 becomes after the first step, B(+)F2. Then after the second step, it becomes B(n)F with the same number of electrons than in B(n)F3. This BF atom is not shown in Table 2, which is devoted to the first dissociation step.

7. Conclusion

Starting with a reference book on dissociation of small molecules in gases, this article described how charges move and form ions in the first dissociation step. By focusing on neutral atoms before the dissociation, the movement of an electrons pair forms two complementary ions. A specific periodic table which separates organic and inorganic atoms is a base for this dissociation process where organic atoms become negatively charged, and where inorganic atoms become positively charged. It may be interesting to study how this process could be extended to other chemical reactions, to provide essential principle to predict chemical reactions in gases and liquids.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Rumble, J. (dir.) (2015) CRC Handbook of Chemistry and Physics. 96th Editon, CRC Press, Boca Raton, FL, 2677 p.

[2] Darwent, deB. (1970) Bond Dissociation Energies in Simple Molecules. NBS Publication (see: nbsnsrds31.pdf).
https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds31.pdf
https://doi.org/10.6028/NBS.NSRDS.31

[3] Luo, Y.-R. (2007) Comprehensive Handbook of Chemical Bond Energies. Imprint CRC Press, Boca Raton. https://doi.org/10.1201/9781420007282-1

[4] Sanderson, R. (1976) Chemical Bonds and Bonds Energy. 2nd Edition, Academic Press.

[5] Greenwood, N.N. and Earnshaw, A. (1998) Chemistry of the Elements. 2nd Edition, Butterworth-Heinemann, Oxford.

[6] Auvert, G. (2014) Improvement of the Lewis-Abegg-Octet Rule Using an "Even-Odd" Rule in Chemical Structural Formulas: Application to Hypo and Hyper-Valences of

Stable Uncharged Gaseous Single-Bonded Molecules with Main Group Elements. *Open Journal of Physical Chemistry*, **4**, 60-66. https://doi.org/10.4236/ojpc.2014.42009

[7]   Auvert, G. (2014) Chemical Structural Formulas of Single-Bonded Ions Using the "Even-Odd" Rule Encompassing Lewis's Octet Rule: Application to Position of Single-Charge and Electron-Pairs in Hypo- and Hyper-Valent Ions with Main Group Elements. *Open Journal of Physical Chemistry*, **4**, 67-72. https://doi.org/10.4236/ojpc.2014.42010

[8]   Auvert, G. (2015) How the Even-Odd Rule, by Defining Electrons Pairs and Charge Positions, Can Be Used as a Substitute to the Langmuir-Octet Rule in Understanding Interconnections between Atoms in Ions and Molecules. *Open Journal of Physical Chemistry*, **5**, 28-38. https://doi.org/10.4236/ojpc.2015.52004

[9]   Auvert, G. (2020) Covalent Bonds Creation between Gas and Liquid Phase Change: Compatibility with Covalent and Even-Odd Rules Based on a "Specific Periodic Table for Liquids". *Open Journal of Physical Chemistry*, **10**, 68-85. https://doi.org/10.4236/ojpc.2020.101004

[10]   Auvert, G. and Auvert, M. (2015) Chemical Bonds between Charged Atoms in the Even-Odd Rule and a Limitation to Eight Covalent Bonds per Atom in Centered-Cubic and Single Face-Centered-Cubic Crystals. *Open Journal of Physical Chemistry*, **5**, 93-105. https://doi.org/10.4236/ojpc.2015.54010

[11]   Auvert, G. and Auvert, M. (2016) The Even-Odd and the Isoelectronicity Rules Applied to Single Covalent Bonds in Ionic, Double-Face-Centered Cubic and Diamond-Like Crystals. *Open Journal of Physical Chemistry*, **6**, 21-33. https://doi.org/10.4236/ojpc.2016.62002

[12]   Auvert, G. (2014) The Even-Odd Rule on Single Covalent-Bonded Structural Formulas as a Modification of Classical Structural Formulas of Multiple-Bonded Ions and Molecules. *Open Journal of Physical Chemistry*, **4**, 173-184. https://doi.org/10.4236/ojpc.2014.44020

[13]   https://en.wikipedia.org/wiki/Electronegativity

[14]   Auvert, G. and Auvert, M. (2016) Introducing an Extended Covalent Bond between Oxygen Atoms with an OXO-Shape in Ions and Molecules: Compatibility with the Even-Odd and the Isoelectronicity Rules. *Open Journal of Physical Chemistry*, **6**, 67-77. https://doi.org/10.4236/ojpc.2016.63007