

"Never put trust in anything but your own intellect...always think for yourself."

Linus Pauling

Unit 9

Covalent Bonding

Linus Pauling, perhaps the greatest chemist of the twentieth century, published a landmark paper in 1931 entitled *The Nature of the Chemical Bond*. This paper provided a comprehensive understanding of chemical bonding. In this workshop, we will apply concepts such as electronegativity and resonance - concepts that Pauling introduced - to help understand the nature of the chemical bond.

Essential Concepts

We begin with a brief review some of the essential concepts that provide the foundation for understanding covalent bonding. The purpose of this review is to provide you with a checklist of topics that you should know before meeting with your workshop group. If any of these concepts are unfamiliar, study the appropriate section of your textbook before your Workshop group meets.

Valence Electrons Electrons that can participate in bonding. These are the outermost *s* and *p* electrons, when using the eight-electron, or octet, rule.

Lewis Dot Structures Structures drawn to represent the distribution of valence electrons in atoms and compounds.

Octet Rule In many compounds formed by the *p*-block elements, the total electron count for every atom is equal to eight. Each atom counts all electrons that it shares with other atoms, as well as its own lone pair electrons.

Incomplete Octet The elements beryllium, boron, and aluminum form covalent compounds but do not acquire an octet of electrons. Lewis structures of compounds of these elements are drawn with less than an octet.

Electronegativity A quantitative measure of the relative ability of the nucleus of an element to attract electrons in a bonding pair toward itself.

Resonance When two or more Lewis structures can be drawn for a single species, the actual bonding system will be a composite of the individual structures. A species with

resonance structures is said to be resonance stabilized. The bonding electrons have some freedom to move to positions of lower potential energy in resonance-stabilized species, and thus the overall species is more stable. Use caution when looking for resonance structures; specifically, electrons can change positions in resonance structures, but the nuclei cannot.

Formal Charge The formal charge of an atom equals the number of valence electrons in the isolated atom minus all of the unshared electrons and half of the bonding electrons. Lewis structures are drawn to minimize the number of atoms with a formal charge and to place negative formal charges on the most electronegative elements and positive formal charges on the most electropositive elements.

Free Radical A species with one or more unpaired electrons. Free radicals cannot satisfy the octet rule, and thus they are very reactive because they readily engage in chemical reactions, producing more stable compounds with complete octets. Nitrogen compounds commonly exist as free radicals because nitrogen has an odd number of valence electrons, five. Examples include NO and NO₂.

Pauling Electronegativity Values for Selected Elements

Pauling developed a theoretical method for using experimentally determined data to derive a quantitative scale of electronegative values. A table of these values appears on the top of Page 10.3.

In general, the greater the electronegativity difference between two bonded atoms, the greater the ionic character of the bond. A bond between cesium and fluorine, with an electronegativity difference of $4.0 - 0.7 = 3.3$ is essentially completely ionic. A bond between two identical atoms with an electronegativity difference of zero is completely covalent. Bonds in between these extremes are partly ionic and partly covalent.

Most bonds between two different nonmetal atoms have small electronegativity differences. These bonds are mostly covalent, although the electron cloud that bonds the atoms is asymmetrically distributed, favoring the more electronegative element. These bonds are referred to as *polar covalent bonds*. A nitrogen-oxygen bond, for example, has an electronegativity difference of 0.5, and the bonding electrons will favor the oxygen end of the bond.

1A												0					
1												2					
H												He					
2.1	2A																
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
1.0	1.5											2.0	2.5	3.0	3.5	4.0	
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
0.9	1.2	3B	4B	5B	6B	7B	8B	1B	2B								
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9	1.6	1.6	1.8	2.0	2.4	2.8	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	†La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
0.7	0.9	1.0	1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.9	1.9	2.0	2.2	
87	88	89	104	105	106	107	108	109									
Fr	Ra	†Ac	Rf	Db	Sg	Bh	Hs	Mt									
0.7	0.9	1.1															

Self Test

- Determine the number of valence electrons for each of the following elements: N, S, Cl, P, O, F, C, Si.
- For each of the following, draw the Lewis diagram and determine the formal charge on each atom: (a) HCl, (b) CO_3^{2-} , (c) NH_3 .

<i>Workshop: Covalent Bonding</i>
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1. Your group leader will randomly assign one or more of the following steps to each group member. As a group, you will then cooperatively draw Lewis diagrams for each of the following species. Each group member will solve their step or steps in turn, explaining their reasoning to the group. After each diagram is completed, one member will summarize the entire process. Before beginning the next diagram, rotate steps by passing the assignments to the group member to the right. Each group member will have a turn at solving each of the steps.*

STEP 1: How many electrons are available for bonding?

STEP 2: Determine the atom-to-atom connectivity. For every atom-to-atom connection, make a single bond (a shared electron pair).

STEP 3: Distribute the remaining electrons to lone pair positions on atoms that need an octet.

STEP 4: Identify atoms that need an octet but do not yet have one.

STEP 5: Rearrange electrons from lone pairs of adjacent atoms, forming multiple bonds, so that the atoms identified in Step 4 have an octet. Count the electrons to make sure you have the same number as you started with!

STEP 6: Calculate the formal charge on each atom.

STEP 7: Analysis: Are the bonds nonpolar covalent, polar covalent, or ionic? Can you draw resonance structures? If so, how many?

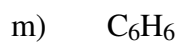
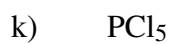
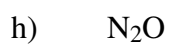
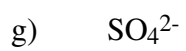
Use the rotating round robin method described above to analyze the following:

a) C_2H_6

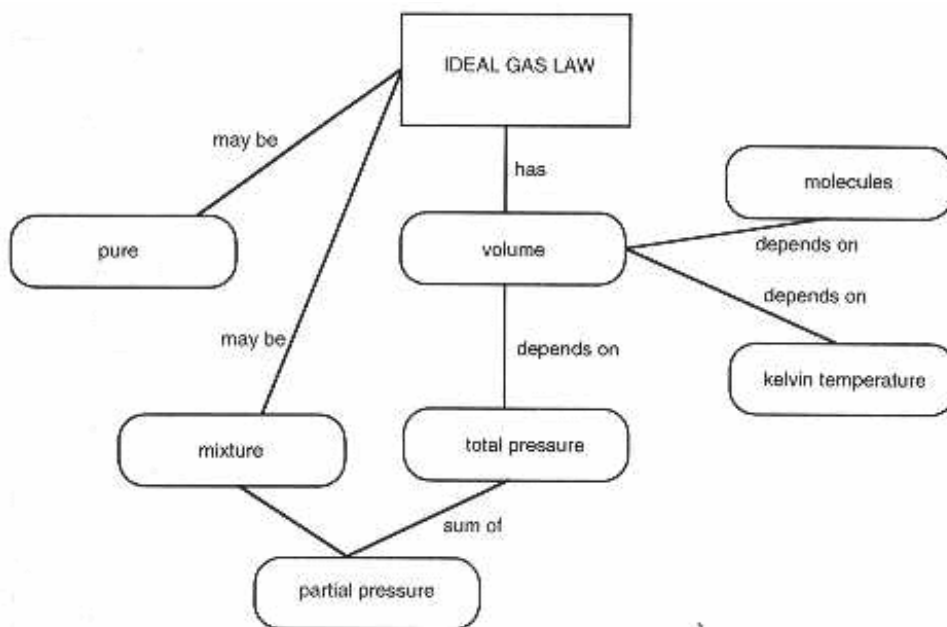
b) C_2H_4

c) C_2H_2

*Your instructor may prefer an alternate method for constructing Lewis diagrams. If this is true, list the steps given by your instructor on the board and follow those steps in this question.



2. A concept map is a diagram that shows connections between concepts. Since chemical bonding is of such overall importance to chemistry, it is useful to reflect on everything you know so far about bonding. You can do this by listing all of the smaller concepts that make up the larger concept of bonding and relating them in a concept map. Here is a sample concept map for the ideal gas law:



- As a group, generate a list of eight to ten concepts that are critical to understanding chemical bonding.
- Split your group into two subgroups. Each subgroup should create a concept map of chemical bonding.
- Compare the two concept maps. Find links between the two.