4.4: Valence

Perhaps the most important function of the periodic table is that it helps us to predict the chemical formulas of commonly occurring compounds. At the top of each group, Mendeleev provided a general formula for oxides of the elements in the group.

Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4

Row and column headings from Mendeleev's original periodic table. This includes group number but also general formula for the oxides and hydrides it formed as well.

The heading R^2O above group I, for example, means that we can expect to find compounds such as H_2O, Li_2O, Na_2O etc. Similarly, the general formula RH^3 above group V suggests that the compounds NH_3, PH_3,VH_3, and AsH_3(among others) should exist. To provide a basis for checking this prediction, formulas are shown in the following table for compounds in which H, O, or Cl is combined with each of the first two dozen elements (in order of atomic weights). Even among groups of elements whose descriptive chemistry we have not discussed, you can easily confirm that most of the predicted formulas correspond to compounds which actually exist. Conversely, more than 40 percent of the formulas for known O compounds agree with Mendeleev's general formulas, and are shaded in color in the table.

Table 4.4.1: Molecular Formulas for Hydrogen, Oxygen, and Chlorine Compounds of the First Twenty-Four Elements in Order of Atomic Weight.*

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Hydrogen	1.01	H_2	H_2O, H_2O_2	HCl
Helium	4.00	None formed	None formed	None formed
Lithium	6.94	LiH	Li_2O, Li_2O_2	LiCl
Beryllium	9.01	BeH_2	BeO	$BeCl_2$
Boron	10.81	B_2H_6	B_2O_3	BCl_3
Carbon	12.01	CH_4, C_2H_6, C_3H_8†	CO_2, CO, C_2O_3	CCl_4, C_2Cl_6
Nitrogen	14.01	NH_3, N_2H_4, HN_3	N_2O, NO, NO_2, N_2O_5	NCl_3
Oxygen	16.00	H_2O, H_2O_2	O_2, O_3	<Cl_2O, ClO_2, Cl_2O_7
Fluorine	19.00	HF	OF_2, O_2F_2	ClF, ClF_3, ClF_5
Neon	20.18	None formed	None formed	None formed
Sodium	22.99	NaH	Na_2O, Na_2O_2	NaCl
Magnesium	24.31	MgH_2	MgO	$MgCl_2$
Aluminum	26.98	AlH_3	Al_2O_3	$AlCl_3$
Silicon	28.09	SiH_4, Si_2H_6	SiO_2	$SiCl_4$, Si_2Cl_6
Phosphorus	30.97	PH_3, P_2H_4	P_4O_{10}, P_4O_6	PCl_3, PCl_5, P_2Cl_4
Sulfur	32.06	H_2S, H_2S_2	SO_2, SO_3	S_2Cl_2, SCl_2, SCl_4
Chlorine	35.45	HCl	Cl_2O, ClO_2, Cl_2O_7	Cl_2
Potassium	39.10	KH	K_2O, K_2O_2, KO_2	KCl
Argon	39.95	None formed	None formed	None formed
Calcium	40.08	CaH_2	CaO, CaO_2	$CaCl_2$
Scandium	44.96	Relatively Unstable	Sc_2O_3	$ScCl_3$

Element	Atomic Weight	Hydrogen Compounds	Oxygen Compounds	Chlorine Compounds
Titanium	47.90	TiH_2	TiO_2, Ti_2O_3, TiO	$TiCl_4$, $TiCl_3$, $TiCl_2$
Vanadium	50.94	VH_2	V_2O_5, V_2O_3, VO_2, VO	VCl_4, VCl_3, VCl_2
Chromium	52.00	CrH_2	Cr_2O_3, CrO_2, CrO_3	$CrCl_3$, $CrCl_2$

* For each element compounds are listed in order of decreasing stability. In some cases additional compounds are known, but these are relatively unstable.

† A great many stable compounds of carbon and hydrogen are known, but space limitations prevent listing all of them.

The periodic repetition of similar formulas is even more pronounced in the case of Cl compounds. This is evident when a list is made of subscripts for Cl in combination with each of the first 24 elements. Consulting the above table, we find HCl (subscript 1), no compound with He (subscript 0), LiCl (subscript 1),and so on.

Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	*K*	*Ar*	Ca	Sc	Ti	V	Cr
Subscript of Cl	1	0	1	2	3	4	3	2	1	0	1	2	3	4	3	2	1	*1*	*0*	2	3	4	3	2

List of the first twenty four elements and their subscripts with Cl. The subscripts of Cl in order of the element is 1, 0, 1, 2, 3, 4, 3, 2, 1, 0, 1, 2, 3, 4, 3, 2, 1, 1, 0, 2, 3, 4, 3, and 2 respectively.

With only the two exceptions indicated in italics, at least one formula for a compound of each element fits a sequence of subscripts which fluctuate regularly from 0 up to 4 and back to 0 again. (The unusual behavior of K and Ar will be discussed a bit later.) The number of Cl atoms which combines with one atom of each other element varies quite regularly as the atomic weight of the other element increases. The experimentally determined formulas in the first table and the general formulas in Mendeleev's periodic table both imply that each element has a characteristic chemical combining capacity. This capacity is called **valence**, and it varies periodically with increasing atomic weight. The noble gases all have valences of 0 because they almost never combine with any other element. H and Cl both have the same valence. They combine with each other in a 1:1 ratio to form HCl, each combines with Li in the same 1:1 ratio (LiH and LiCl), each combines with Be in the same ratio (BeH_2, $BeCl_2$), and so on. Because H and Cl have the same valence, we can predict that a large number of H compounds will have formulas identical to those of Cl compounds, except, of course, that the symbol H would replace the symbol Cl. The correctness of this prediction can be verified by studying the formulas surrounded by gray shading in the first table. The combining capacity, or valence, of O is apparently twice that of H or Cl. *Two* H atoms combine with one O atom in H_2O So do two Cl atoms or two Li atoms (Cl_2O and Li_2O). The number of atoms combining with a single O atom is usually *twice as great* as the number which combined with a single H or Cl atom. (Again, consulting the gray shaded formulas in the first table will confirm this statement.) After careful study of the formulas in the table, it is also possible to conclude that none of the elements (except the unreactive noble gases) have smaller valences than H or Cl. Hence we assign a valence of 1 to H and to Cl. The valence of O is twice as great, and so we assign a value of 2.

✓ Example 4.4.1: Formula Predictions

Use the data in the first table to predict what formula would be expected for a compound containing (a) sodium and fluorine; (b) calcium and fluorine.

Solution

a) From the table we can obtain the following formulas for the most common sodium compounds:

NaH Na_2O $NaCl$

All of these would imply that sodium has a valence of 1. For fluorine compounds we have

HF OF_2 ClF

which imply that fluorine also has a valence of 1. Therefore the formula is probably

NaF

b) We already know that the valence of fluorine is 1. For calcium the formulas

CaH_2 CaO $CaCl_2$

argue in favor of a valence of 2. Therefore the formula is most likely

CaF_2

In some cases one element can combine in more than one way with another. For example, you have already encountered the compounds $HgBr_2$ and Hg_2Br_2. There are many other examples of such variable valence in the first table. Nevertheless in its most common compounds, each element usually exhibits one characteristic valence, no matter what its partner is. Therefore it is possible to use that valence to predict formulas. Variable valence of an element may be looked upon as an exception to the rule of a specific combining capacity for each element. The experimental observation that a given element usually has a specific valence can be explained if we assume that each of its atoms has a fixed number of valence sites. One of these sites would be required to connect with one site on another atom. In other words, a noble-gas atom such as Ar or Ne would not have any combining sites, H and Cl atoms would have one valence site each, an O atom would have two, and so on. Variable valence must involve atoms in which some valence sites are more readily used than others. In the case of the F compounds of Cl (ClF, ClF_3, ClF_5), for example, the formulas imply that at least five valence sites are available on Cl. Only one of these is used in ClF and in most of the chlorine compounds in the table. The others are apparently less readily available. Mendeleev's inclusion of general formulas above the columns of his periodic table indicates that the table may be used to predict valences of the elements and formulas for their compounds. Two general rules may be followed:

1. In periodic groups I to IV, the group number is the most common valence.
2. In periodic groups V to VII, the most common valence is equal to 8 minus the group number, or to the group number itself.

For groups V to VII, the group number gives the valence only when the element in question is combined with oxygen, fluorine, or perhaps one of the other halogens. Otherwise 8 minus the group number is the rule.

Example 4.4.2: Compound Formulas

Use the modern periodic to predict the formulas of compounds formed from (a) aluminum and chlorine; (b) phosphorus and chlorine. Use the table on this page to verify your prediction.

Solution

a) Aluminum is in group III and so rule 1 predicts a valence of 3. Chlorine is in group VII and is not combined with oxygen or fluorine, and so its valence is 8 – 7 = 1 by rule 2. Each aluminum has three valence sites, while each chlorine has only one, and so it requires three chlorine atoms to satisfy one aluminum, and the formula is $AlCl_3$.

b) Again chlorine has a valence of 1. Phosphorus is in group V and might have a valence of 5 or of 8 – 5 = 3. Therefore we predict formulas PCl_5 or PCl_3. *Note:* All three predicted formulas appear in the table on this page.