

PART III. CHEMICAL MINERALOGY

GENERAL PRINCIPLES OF CHEMISTRY AS APPLIED TO MINERALS

447. Minerals, as regards their chemical constitution, are either the uncombined elements in a native state, or definite compounds of these elements formed in accordance with chemical laws. It is the object of Chemical Mineralogy to determine the chemical composition of each species; to show the chemical relations of different species to each other where such exist; and also to explain the methods of distinguishing different minerals by chemical means. It thus embraces the most important part of Determinative Mineralogy.

In order to understand the chemical constitution of minerals, some knowledge of the fundamental principles of Chemical Philosophy is required; and these are here briefly recapitulated.

448. Chemical Elements. — Chemistry recognizes about eighty substances which cannot at will be decomposed, or divided into others, by any process of analysis at present known; these substances are called the chemical *elements*. A list of them is given in a later article (**452**); common examples are: Oxygen, nitrogen, hydrogen, chlorine, gold, silver, sodium, etc.

449. Atom. Molecule. — The study of the chemical properties of substances and of the laws governing their formation has led to the belief that there is for each element a definite, indivisible mass, which is the smallest particle which can play a part in chemical reactions; this indivisible unit is called the *atom*.

With some rare exceptions, the atom cannot exist alone, but unites by the action of what is called chemical force, or chemical affinity, with other atoms of the same or different kind to form the *molecule*. The molecule, in the chemical sense, may be defined as the smallest particle into which a given kind of substance can be subdivided without undergoing chemical decomposition. For example, two *atoms* of hydrogen unite to form a *molecule* of hydrogen gas. Again, one atom of hydrogen and one of chlorine form a molecule of hydrochloric acid gas; two atoms of hydrogen and one of sulphur form a molecule of the gas hydrogen sulphide.

450. Atomic Weight. — The atomic weight of an element is the weight, or, better expressed, the mass of its atom compared with that of the element hydrogen taken as the unit or with the weight of an atom of oxygen taken as 16. Of the methods by which the relation between the masses of the atoms is determined it is unnecessary here to speak; the results that have been obtained are given in the table on p. 312.

451. Symbol. Formula. — The symbol of an element is the initial letter, or letters, often of its Latin name, by which it is represented when expressing in chemical notation the constitution of substances into the composition of which it enters. Thus O is the symbol of oxygen, H of hydrogen, Cl of chlorine, Fe (from *ferrum*) of iron, Ag (from *argentum*) of silver, etc. Further, this symbol is always understood to indicate that definite amount of the given element expressed by its atomic weight; in other words, it represents one atom. If twice this quantity is involved, that is, two atoms, this is indicated by a small subscript number written immediately after the symbol. Thus, Sb_2S_3 means a compound consisting of two atoms of antimony and three of sulphur, or of 2×120 parts by weight of antimony and 3×32 of sulphur.

This expression, Sb_2S_3 , is called the *formula* of the given compound, since it expresses in briefest form its composition. Similarly the formula of the mineral albite is $NaAlSi_3O_8$.

Strictly speaking, such formulas are merely *empirical formulas*, since they express only the actual result of analysis, as giving the relative number of atoms of each element present, and make no attempt to represent the actual constitution. A formula developed with the latter object in view is called a rational, structural, or constitutional formula (see Art. 469).

452. Table of the Elements. — The following table gives a list of all the definitely established elements with their accepted symbols and also their atomic weights.*

Of the elements given in this list — more than eighty in all — only a very small number, say twelve, play an important part in making up the crust of the earth and the water and air surrounding it. The common elements concerned in the composition of minerals are: Oxygen, sulphur, silicon, aluminium, iron, calcium, magnesium, sodium, potassium. Besides these, hydrogen is present in water, nitrogen in the air, and carbon in all animal and vegetable substances. Only a very few of the elements occur as such in nature, as native gold, native silver, native sulphur, etc.

Of the elements, oxygen, hydrogen, nitrogen, chlorine, and fluorine are gases; bromine is a volatile liquid; mercury is also a liquid, but the others are solids under ordinary conditions.

	Symbol	At. Weight		Symbol	At. Weight
Aluminium, Aluminum	Al	27.1	Columbium, see <i>Niobium</i> .		
Antimony (<i>Stibium</i>)	Sb	120.2	Copper (<i>Cuprum</i>)	Cu	63.6
Argon	A	39.9	Dysprosium	Dy	162.5
Arsenic	As	74.9	Erbium	Er	167.7
Barium	Ba	137.4	Europium	Eu	152.0
Beryllium, Glucinum	Be (or Gl)	9.1	Fluorine	F	19.0
Bismuth	Bi	208.0	Gadolinium	Gd	157.3
Boron	B	11.0	Gallium	Ga	69.9
Bromine	Br	79.9	Germanium	Ge	72.5
Cadmium	Cd	112.4	Glucinum, see <i>Beryllium</i>		
Cæsium	Cs	132.8	Gold (<i>Aurum</i>)	Au	197.2
Calcium	Ca	40.1	Helium	He	4.0
Carbon	C	12.0	Holmium	Ho	163.5
Cerium	Ce	140.2	Hydrogen	H	1.0
Chlorine	Cl	35.5	Indium	In	114.8
Chromium	Cr	52.0	Iodine	I	126.9
Cobalt	Co	59.0	Iridium	Ir	193.1

* These correspond in value to those commonly accepted, and are given accurate to one decimal place.

	Symbol	At. Weight		Symbol	At. Weight
Iron (<i>Ferrum</i>)	Fe	55·8	Ruthenium	Ru	101·7
Krypton	Kr	82·9	Samarium	Sa	150·4
Lanthanum	La	139·0	Scandium	Sc	44·1
Lead (<i>Plumbum</i>)	Pb	207·2	Selenium	Se	79·2
Lithium	Li	6·9	Silicon	Si	28·3
Lutecium	Lu	175·0	Silver (<i>Argentum</i>)	Ag	107·9
Magnesium	Mg	24·3	Sodium (<i>Natrium</i>)	Na	23·0
Manganese	Mn	54·9	Strontium	Sr	87·6
Mercury (<i>Hydrargyrum</i>)	Hg	200·6	Sulphur	S	32·0
Molybdenum	Mo	96·0	Tantalum	Ta	181·5
Neodymium	Nd	144·3	Tellurium	Te	127·5
Neon	Ne	20·2	Terbium	Tb	159·2
Nickel	Ni	58·7	Thallium	Tl	204·0
Niobium	Nb	93·1	Thorium	Th	232·4
Niton	Nt	222·4	Thulium	Tm	168·5
Nitrogen	N	14·0	Tin (<i>Stannum</i>)	Sn	118·7
Osmium	Os	190·9	Titanium	Ti	48·1
Oxygen	O	16·0	Tungsten (<i>Wolframium</i>)	W	184·0
Palladium	Pd	106·7	Uranium	U	238·2
Phosphorus	P	31·0	Vanadium	V	51·0
Platinum	Pt	195·2	Xenon	Xe	130·2
Potassium (<i>Kalium</i>)	K	39·1	Ytterbium	Yb	173·5
Praseodymium	Pr	140·9	Yttrium	Yt	88·7
Radium	Ra	226·0	Zinc	Zn	65·4
Rhodium	Rh	102·9	Zirconium	Zr	90·6
Rubidium	Rb	85·5			

453. Metals and Non-metals. — The elements may be divided into two more or less distinct classes, the metals and the non-metals. Between the two lie a number of elements sometimes called the semi-metals. The *metals*, as gold, silver, iron, sodium, are those elements which, *physically* described, possess to a more or less perfect degree the fundamental characters of the ideal metal, viz.: malleability, metallic luster (and opacity to light), conductivity for heat and electricity; moreover, *chemically* described, they commonly play the part of the positive or basic element in a simple compound, as later defined (Arts. 462–465). The *non-metals*, as sulphur, carbon, silicon, etc., also the gases, as oxygen, chlorine, etc., have none of the physical characters alluded to: they are, if solids, brittle, often transparent to light-radiation, are poor conductors for heat and electricity. Chemically expressed, they usually play the negative or acid part in a simple compound.

The so-called *semi-metals*, or metalloids, include certain elements, as tellurium, arsenic, antimony, bismuth, which have the physical characters of a metal to a less perfect degree (*e.g.*, they are more or less brittle); and, more important than this, they often play the part of the acidic element in the compound into which they enter. These points are illustrated later.

It is to be understood that the distinctions between the classes of the elements named cannot be very sharply applied. Thus the typical metallic characters mentioned are possessed to a very unequal degree by the different substances classed as metals; for example, by silver and tin. Corresponding to this a number of the true metals, as tin and manganese, play the part of an acid in numerous salts. Further, the mineral magnetite, $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$, is often described as an *iron ferrate*; so that in this compound the same element would play the part of both acid and base.

454. Positive and Negative Elements. — It is common to make a distinction between the *electro-positive* and *electro-negative* element in a compound.

The passage of a sufficiently strong electrical current through a chemical compound in many cases results in its decomposition (or electrolysis) into its elements or parts. In such cases it is found that for each compound the atoms of one element collect at the negative pole (the cathode) and those of the other at the positive pole (the anode). The former is called the electro-positive element and the latter the electro-negative element. Thus in the electrolysis of water (H_2O) the hydrogen collects at the cathode and is hence called positive, and the oxygen at the anode and is called negative. Similarly, in hydrochloric acid (HCl) the hydrogen is thus shown to be positive, the chlorine negative. This distinction is also carried to complex compounds, as copper sulphate ($CuSO_4$), which by electrolysis is broken into Cu , which is found to be electro-positive, and SO_4 (the last separates into SO_3 , forming H_2SO_4 and free oxygen).

For reasons which will be explained later, the positive element is said to play the basic part, the negative the acidic. The metals, as already stated, in most cases belong to the former class, the non-metals to the latter, while the semi-metals may play both parts.

It is common in writing the formula to put the positive or basic element first, thus H_2O , H_2S , HCl , H_2SO_4 , Sb_2S_3 , As_2O_3 , AsH_3 , $NiSb$, $FeAs_2$. Here it will be noted that antimony (Sb) and arsenic (As) are positive in some of the compounds named but negative in the others.

455. Periodic Law.—In order to understand the relations of the chief classes of chemical compounds represented among minerals, as still more their further subdivision, down finally to the many *isomorphous groups*—groups of species having analogous composition and closely similar form, as explained in Art. 471—the fundamental relations and grouping of the elements must be understood, especially as developed of recent years and shown in the so-called Periodic Law.

Although the subject can be only briefly touched upon, it will be useful to give here the general distribution of the elements into Groups and Series, as presented in the Principles of Chemistry (Engl. Ed., 1891) of D. Mendeléeff, to whom is due more than any one else the development of the Periodic Law. When the elements are arranged according to the values of their atomic weights it is seen that they fall more or less into groups consisting of eight elements each, or double groups containing sixteen elements. The corresponding members of each group show similar chemical characters. The table given below will illustrate these relationships. For the thorough explanation of this subject, more particularly as regards the periodic or progressive relation between the atomic weights and various properties of the elements, the reader is referred to the work above mentioned or to one of the many other excellent modern text-books of chemistry.

The relations of some of the elements of the first group are exhibited by the isomorphism (see Art. 471, also the description of the various groups and species here referred to, which are given in Part IV of this work) of $NaCl$, KCl , $AgCl$; or again of $LiMnPO_4$ and $NaMnPO_4$, etc. In the second group, reference may be made to the isomorphism of the carbonates and sulphates (p. 322) of calcium, barium, and strontium; while among the sulphides, ZnS , CaS , and HgS are doubly related. In the third group, we find boron and aluminium often replacing one another among silicates. In the fourth group, the relations of silicon and titanium are shown in the titano-silicates, while the compounds TiO_2 , SnO_2 , PbO_2 (and MnO_2), also $ZrSiO_4$ and $ThSiO_4$, have

TABLE OF PERIODIC SYSTEM

I	II	III	IV	V	VI	VII	VIII
Li=7 Na=23	Be=9 Mg=24	B=11 Al=27	C=12 Si=22	N=14 P=31	O=16 S=32	F=19 Cl=35	
K=39 Cu=64	Ca=40 Zn=65	Sc=44 Ga=70	Ti=48 Ge=73	V=51 As=75	Cr=52 Se=79	Mn=55 Br=80	Fe=56 Co=59 Ni=59
Rb=85 Ag=108	Sr=88 Cd=112	Yt=89 In=115	Zr=91 Sn=119	Nb=93 Sb=120	Mo=96 Te=127	I=127	Ru=102 Rh=103 Pd=107
Cs=133 Au=197	Ba=137 Hg=201	La=139 Tl=204	Ce, etc. 140-175 Pb=207	Ta=181 Bi=208	W=184		Os=191 Ir=193 Pt=195
	Ra=226		Th=232		U=238		

closely similar form. In the fifth group, many compounds of arsenic, antimony, and bismuth are isomorphous among metallic compounds, while the relations of phosphorous, vanadium, arsenic, also antimony, are shown among the phosphates, vanadates, arsenates, and antimonates; again the mutual relations of the niobates and tantalates are to be noted.

In the sixth group, the strongly acidic elements, sulphur, selenium, tellurium, are all closely related, as seen in many sulphides, selenides, tellurides; further, the relations of sulphur and chromium, and similarly of both of these to molybdenum and tungsten, are shown among many artificial sulphates, chromates, molybdates, and tungstates.

In the seventh group the relations of the halogens are too well understood to need special remark. In the eighth group, we have Fe, Co, Ni alloyed in meteoric iron, and their phosphates and sulphates are in several cases closely isomorphous; further, the relation of the iron series to that of the platinum series is exhibited in the isomorphism of FeS_2 , FeAsS , FeAs_2 , etc., with PtAs_2 and probably RuS_2 .

456. Combining Weight. — Chemical investigation proves that the mass of a given element entering into a compound is always proportional either to its atomic weight or to some simple multiple of this; the atomic weight is hence also called the *combining weight*. Thus in rock salt, sodium chloride, the masses involved of sodium and chlorine present are found by analysis to be equal to 39.4 and 60.6 in 100 parts, and these numbers are in proportion to 23 : 35.4, the atomic weights of sodium and chlorine; hence it is concluded that one atom of each is present in the compound. The formula is, therefore, NaCl . In calcium chloride, by the same method the masses present are found to be proportional to 39.9 : 70.8, that is, to 39.9 : 2×35.4 ; hence the formula is CaCl_2 .

Still again, a series of compounds of nitrogen with oxygen is known in which the ratios of the masses of the two elements are as follows: (1) 28 : 16, (2) 14 : 16, (3) 28 : 48, (4) 14 : 32, (5) 28 : 80. It is seen at once that these must have the formulas (1) N_2O , (2) NO , (3) N_2O_3 , (4) NO_2 , (5) N_2O_5 . On the contrary, atmospheric air which contains these elements in about the ratio of 76.8 to 23.2 cannot be a chemical compound of these elements, since (aside from other considerations) these numbers are not in the ratio of $n \times 14 : m \times 16$ where n and m are simple whole numbers.

457. Molecular Weight. — The molecular weight is the weight of the molecule of the given substance, expressed in terms of the mass of the hydrogen atom as unit. The molecular weight of hydrogen is 2 because the molecule can be shown to consist of two atoms. The molecular weight of hydrochloric acid (HCl) is 36.4, of water vapor (H_2O) 18, of hydrogen sulphide (H_2S) 34.

Since, according to the law of Avagadro, like volumes of different gases under like conditions as to temperature and pressure contain the same number of molecules, it is obvious that the molecular weight of substances in the form of gas can be derived directly from the relative density or specific gravity. If the density is referred to hydrogen, whose molecular weight is 2, it will be always true that the molecular weight is twice the density in the state of a gas and *vice versa*. Thus the observed density of carbon dioxide (CO_2) is 22, hence its molecular weight must be 44. It is this principle that makes it possible in the case of a gas to fix the constitution of the molecule when the ratio in number of the atoms entering into it has been determined by analysis. In the case of solids, where the constitution of the molecule in general cannot

be fixed, it is best, as already stated, to write the molecular formula in its simplest form, as $\text{NaAlSi}_3\text{O}_8$ for albite. The sum of the weights of the atoms present is then taken as the molecular weight.

458. Valence. — The valence of an element is given by a number representing the capacity of its atoms to combine with the atoms of some unit element like hydrogen or chlorine. Thus, using the examples of Art. 456, in NaCl , since one atom of sodium unites with one of chlorine, its valence is one; or, in other words, it is said to be *univalent*. Further, calcium (as in CaCl_2), also barium, etc., are bivalent; aluminium is trivalent; silicon is tetravalent, etc. The valence may be expressed by the number of bonds by which one element in a compound is united to another, thus:



A considerable number of the elements show a different valence in different compounds. Thus both Sb_2O_3 and Sb_2O_5 are known; also FeO and Fe_2O_3 ; CuCl and CuCl_2 . These possible variations are indicated in the following table which gives the valences for the common elements.

Univalent: H, Cl, Br, I, F; Li, Na, K, Rb, Cs, Ag, Hg, Cu, Au.

Bivalent: O, S, Se, Te; Be, Mg, Ca, Sr, Ba, Pb, Hg, Cu, Zn, Co, Ni, Fe, Mn, Cr, C, Sn.

Trivalent: B, Al, Fe, Mn, Cr, Co, Ni, N, P, As, Sb, Bi.

Tetravalent: C, Si, Ti, Zr, Sn, Mn, Pb.

Pentavalent: N, P, As, Sb, V, Bi, Nb, Ta.

459. Chemical Reactions. — When solutions of two chemical substances are brought together, in many cases they react upon each other with the result of forming new compounds out of the elements present; this phenomenon is called a *chemical reaction*. One of the original substances may be a gas, and in many cases similar results are obtained from a liquid and a solid, or less often from two solids.

For example, solutions of sodium chloride (NaCl) and silver nitrate (AgNO_3) react on each other and yield silver chloride (AgCl) and sodium nitrate (NaNO_3). This is expressed in chemical language as follows:



This is a chemical equation, the sign of equality meaning that equal weights are involved both before and after the reaction.

Again, hydrochloric acid (HCl) and calcium carbonate (CaCO_3) yield calcium chloride (CaCl_2) and carbonic acid (H_2CO_3); which last breaks up into water (H_2O) and carbon dioxide (CO_2), the last going off as a gas with effervescence. Hence



460. Radicals. — A compound of two or more elements according to their relative valence in which all their bonds are satisfied is said to be *saturated*. This is true of H_2O , or, as it may be written, $\text{H}-\text{O}-\text{H}$. If, however, one or more bonds is left unsatisfied, the resulting combination of elements is called a *radical*. Thus $-\text{O}-\text{H}$, called briefly hydroxyl, is a common radical, having a valence of one, or, in other words, univalent; NH_4 is again a univalent radical; so, too, (CaF) , (MgF) or (AlO) . Radicals often enter into a compound like a simple element; for example, in ammonium chloride, NH_4Cl , the univalent radical NH_4 plays the same part as the univalent element Na in NaCl . In the chemical composition of mineral species, the commonest radical

is hydroxyl (—O—H) already defined. Other examples are CaF in apatite (see Art. 471), MgF in wagnerite, AlO in many basic silicates, etc.

461. Chemical Compound. — A chemical compound is a combination of two or more elements united by the force of chemical attraction. It is always true of it, as before stated (Art. 456), that the elements present are combined in the proportion of their atomic weights or some simple multiples of these. A substance which does not satisfy this condition is not a compound, but only a mechanical mixture.

Examples of the simpler class of compounds are afforded by the *oxides*, or compounds of oxygen with another element. Thus, among minerals we have Cu_2O , cuprous oxide (cuprite); ZnO , zinc oxide (zincite); Al_2O_3 , alumina (corundum); SnO_2 , tin dioxide (cassiterite); SiO_2 , silicon dioxide (quartz); As_2O_3 , arsenic trioxide (arsenolite).

Another simple class of compounds are the *sulphides* (with the selenides, tellurides, arsenides, antimonides, etc.), compounds in which sulphur (selenium, tellurium, arsenic, antimony, etc.) plays the same part as oxygen in the oxides. Here belong Cu_2S , cuprous sulphide (chalcocite); ZnS , zinc sulphide (sphalerite); PbTe , lead telluride (altaite); FeS_2 , iron disulphide (pyrite); Sb_2S_3 , antimony trisulphide (stibnite).

462. Acids. — The more complex chemical compounds, an understanding of which is needed in a study of minerals, are classed as acids, bases, and salts; the distinctions between them are important.

An *acid* is a compound of hydrogen, or hydroxyl, with a non-metallic element (as chlorine, sulphur, nitrogen, phosphorus, etc.), or a radical containing these elements. When dissolved in water they all give the positive hydrogen ion and a negative ionic substance such as Cl , SO_4 , etc. The hydrogen atoms of an acid may be replaced by metallic atoms; the result being then the formation of a salt (see Art. 464). Acids in general turn blue litmus paper red and have a sharp, sour taste. The following are familiar examples:

HCl , hydrochloric acid,
 HNO_3 , nitric acid.
 H_2CO_3 , carbonic acid.
 H_2SO_4 , sulphuric acid.
 H_2SiO_3 , metasilicic acid.
 H_3PO_4 , phosphoric acid.
 H_4SiO_4 , orthosilicic acid.

It is to be noted that with a given acid element several acids are possible. Thus normal, or orthosilicic, acid is H_4SiO_4 , in which the bonds of the element silicon are all satisfied by the hydroxyl (HO). But the removal of one molecule of water, H_2O , from this gives the formula H_2SiO_3 , or metasilicic acid.

Acids which, like HNO_3 , contain one atom of hydrogen that may be replaced by a metallic atom (e.g., in KNO_3) are called *monobasic*. If, as in H_2CO_3 and H_2SO_4 , there are two atoms or a single bivalent atom, (e.g., in CaCO_3 , BaSO_4) the acids are *dibasic*. Similarly, H_3PO_4 is *tribasic*, etc.

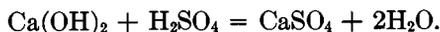
Most acids are liquids (or gases), and hence acids are represented very sparingly among minerals; B(OH)_3 , boric acid (sassolite), is an illustration.

463. Bases. — The *bases*, or hydroxides, as they are also called, are compounds which may be regarded as formed of a metallic element (or radical)

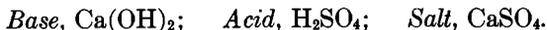
and the univalent radical hydroxyl, — (OH); or, in other words, of an oxide with water. Thus potash, K_2O , and water, H_2O , form $2K(OH)$, or potassium hydroxide; also $CaO + H_2O$ similarly give $Ca(OH)_2$, or calcium hydroxide. In general, when soluble in water, bases give an alkaline reaction with turmeric paper or red litmus paper, and they also neutralize an acid, as explained in the next article. Further, the bases yield water on ignition, that is, at a temperature sufficiently high to break up the compound.

Among minerals the bases are represented by the hydroxides, or hydrated oxides, as $Mg(OH)_2$, magnesium hydrate (brucite); $Al(OH)_3$, aluminium hydrate (gibbsite); also, $(AlO)(OH)$, diaspore, etc.

464. Salts. — A third class of compounds are the *salts*; these may be regarded as formed chemically by the reaction of a base upon an acid, or, in other words, by the neutralization of the acid. Thus calcium hydrate and sulphuric acid give calcium sulphate and water:



Here calcium sulphate is the salt, and in this case the acid, sulphuric acid, is said to be neutralized by the base, calcium hydroxide. It is instructive to compare the formulas of a base, an acid, and the corresponding salt, as follows:



Here it is seen that a salt may be simply described as formed from an acid by the replacement of the hydrogen atom, or atoms, by a metallic element or radical.

465. Typical Salts. — The commonest types of salts represented among minerals are the following:

Chlorides: salts of hydrochloric acid, HCl ; as $AgCl$, silver chloride (cerargyrite).

Nitrates: salts of nitric acid, HNO_3 ; as KNO_3 , potassium nitrate (niter).

Carbonates: salts of carbonic acid, H_2CO_3 ; as $CaCO_3$, calcium carbonate (calcite and aragonite).

Sulphates: salts of sulphuric acid, H_2SO_4 ; as $CaSO_4$, calcium sulphate (anhydrite).

Phosphates: salts of phosphoric acid, H_3PO_4 ; as $Ca_3(PO_4)_2$, calcium phosphate.

Silicates: several classes of salts are here included. The most common are the salts of metasilicic acid, H_2SiO_3 ; as $MnSiO_3$, manganese metasilicate (rhodonite). Also salts of orthosilicic acid, H_4SiO_4 ; as Mn_2SiO_4 , manganese orthosilicate (tephroite).

Numerous other classes of salts are also included among mineral species; their composition, as well as that of complex salts of the above types, is explained in the descriptive part of this work.

466. Normal, Acid, and Basic Salts. — A *neutral* or *normal salt* is one in which the basic element completely neutralizes the acid, or, in other words, one of the type already given as examples, in which *all* the hydrogen atoms of the acid have been replaced by metallic atoms or radicals. Thus, K_2SO_4 is normal potassium sulphate, but $HKSO_4$, on the other hand, is acid potassium sulphate, since in the acid H_2SO_4 only one of the bonds is taken by the basic element potassium. Salts of this kind are called *acid salts*. The formula in

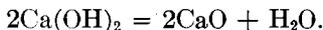
such cases may be written * as if the compound consisted of a normal salt and an acid; thus, for the example given, $K_2SO_4 \cdot H_2SO_4$.

A *basic salt* is one in which the acid part of the compound is not sufficient to satisfy all the bonds of the base. Thus malachite is a basic salt — basic carbonate of copper — its composition being expressed by the formula $Cu_2(OH)_2CO_3$. This may be written $CuCO_3 \cdot Cu(OH)_2$, or $(Cu_2) \begin{matrix} = CO_3 \\ = (OH)_2 \end{matrix}$.

The majority of minerals consist not of simple salts, as those noted above, but of more or less complex double salts in which several metallic elements are present. Thus common grossular garnet is an orthosilicate containing both calcium and aluminium as bases; its formula is $Ca_3Al_2(SiO_4)_3$.

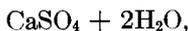
467. Sulpho-salts. — The salts thus far spoken of are all oxygen salts. There are also others, of analogous constitution, in which sulphur takes the place of the oxygen; they are hence called *sulpho-salts*. Thus normal sulph-arsenious acid has the formula H_3AsS_3 , and the corresponding silver salt is Ag_3AsS_3 , the mineral proustite. Similarly the silver salt of the analogous antimony acid is Ag_3SbS_3 , the mineral pyrargyrite. From the normal acids named, a series of other hypothetical acids may be derived, as $HAsS_2$, $H_4As_2S_5$, etc.; these acids are not known to exist, but their salts are important minerals. Thus zinkenite, $PbSb_2S_4$, is a salt of the acid $H_2Sb_2S_4$, and jamesonite, $Pb_2Sb_2S_5$, of the acid $H_4Sb_2S_5$, etc.

468. Water of Crystallization. — As stated in Art. **463**, the hydroxides, or bases, and further basic salts in general, yield water when ignited. Thus calcium hydroxide $Ca(OH)_2$ breaks up on heating into CaO and H_2O , as expressed in the chemical equation



So also the basic cupric carbonate, malachite, $Cu_2(OH)_2CO_3$, yields water on ignition; and the same is true of the complex basic orthosilicates, like zoisite, whose formula is $(HO)Ca_2Al_3(SiO_4)_3$. It is not to be understood, however, in these or similar cases, that water as such is present in the substance.

On the other hand, there is a large number of mineral compounds which yield water readily when heated, and in which the water molecules are regarded as present as so-called *water of crystallization*. Thus, the formula of gypsum is written



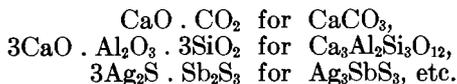
and the molecules of water ($2H_2O$) are considered as water of crystallization. So, too, in potash alum, $KAl(SO_4)_2 + 12H_2O$, the water is believed to play the same part.

469. Formulas of Minerals. — The strictly empirical formula expresses the kinds and numbers of atoms of the elements present in the given compound, without attempting to show the way in which it is believed that the atoms are combined. Thus, in the case of zoisite the empirical formula is $HCa_2Al_3Si_3O_{13}$. While not attempting to represent the structural formula (which will not be discussed here), it is convenient in certain cases to indicate the atoms which there is reason to believe play a peculiar relation to each other. Thus the same formula written $(HO)Ca_2Al_3(SiO_4)_3$ shows that it is regarded as a basic orthosilicate, in other words, a basic salt of orthosilicic acid, H_4SiO_4 .

* This early form of writing the composition explains the name often given to the compound, namely, in this case, "bisulphate of potash."

Again, the empirical formula of common apatite is $\text{Ca}_5\text{FP}_3\text{O}_{12}$; but if this is written $(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$, it shows that it is regarded as a phosphate of the acid H_3PO_4 , that is, $\text{H}_9(\text{PO}_4)_3$, in which the nine hydrogen atoms are replaced by four Ca atoms together with the univalent radical (CaF). In another kind of apatite the radical (CaCl) enters in the same way. Similarly to this the formula of pyromorphite is $(\text{PbCl})\text{Pb}_4(\text{PO}_4)_3$, of vanadinite $(\text{PbCl})\text{Pb}_4(\text{VO}_4)_3$.

Further, it is often convenient to employ the method of writing the formulas in vogue under the old dualistic system. For example,



It is no longer believed, however, that the molecular groups CaO , Al_2O_3 , etc., actually exist in the molecule of the substance. But in part because these groups are what analysis of the substance affords directly, and in part because so easily retained in the memory, this method of writing is still often used.

470. Calculation of a Formula from an Analysis. — The result of an analysis gives the proportions, in a hundred parts of the mineral, of either the elements themselves, or of their oxides or other compounds obtained in the chemical analysis. In order to obtain the atomic proportions of the elements:

Divide the percentages of the elements by the respective ATOMIC WEIGHTS; or, for those of the oxides: Divide the percentage amounts of each by their MOLECULAR WEIGHTS; then find the simplest ratio in whole numbers for the numbers thus obtained.

Example. — An analysis of bournonite from Wolfsberg gave C. Bromeis the results under (1) below. These percentages divided by the respective atomic weights, as indicated, give the numbers under (2). Finally the ratio of these numbers gives very nearly 1 : 3 : 1 : 1. Hence the formula derived is CuPbSbS_3 . The theoretical values called for by the formula are added under (4).

	(1)	(2)	(3)	(4)
Sb	$24.34 \div 120$	$= 0.203$	1	24.7
S	$19.76 \div 32$	$= 0.617$	3	19.8
Pb	$42.88 \div 206.4$	$= 0.208$	1	42.5
Cu	$13.06 \div 63.2$	$= 0.207$	1	13.0
	100.04			100.0

Second Example. — The mean of two analyses of a garnet from Alaska gave Kountze the results under (1) below. Here, as usual, the percentage amounts of the several molecular groups (SiO_2 , Al_2O_3 , etc.) are given instead of those of the elements. These amounts divided by the respective molecular weights give the numbers under (2). In this case the amounts of the protoxides are taken together and the ratio thus obtained is 3.09 : 1 : 2.92, which corresponds approximately to the formula $3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$, or $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$. The magnesium in this garnet would ordinarily be explained by the presence of the pyrope molecule ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$) together with the simple almandite molecule whose composition is given above.

	(1)	(2)	(3)
SiO_2	$39.29 \div 60$	$= 0.655$	3.09
Al_2O_3	$21.70 \div 102$	$= 0.212$	1
Fe_2O_3	<i>tr.</i>		
FeO	$30.82 \div 71.9$	$= 0.429$	} 0.619
MnO	$1.51 \div 70.8$	$= 0.022$	
MgO	$5.26 \div 40$	$= 0.132$	
CaO	$1.99 \div 55.9$	$= 0.036$	
	100.57		2.92

It is necessary, when very small quantities only of certain elements (as MnO, MgO, CaO above) are present, to neglect them in the final formula, reckoning them in with the elements

which they replace, that is, with those of the same quantivalence. The degree of correspondence between the analysis and the formula deduced, if the latter is correctly assumed, depends entirely upon the accuracy of the former.

471. Isomorphism. — Chemical compounds which have an analogous composition and a closely related crystalline form are said to be *isomorphous*. This phenomenon, called ISOMORPHISM, was first clearly brought out by Mitscherlich.

Many examples of groups of isomorphous compounds will be found among the minerals described in the following pages. Some examples are mentioned here in order to elucidate the subject.

In the brief discussion of the periodic classification of the chemical elements of Art. 456, attention has been called to the prominent groups among the elements which form analogous compounds. Thus calcium, barium, and strontium, and also lead, form the two series of analogous compounds,

Aragonite Group			Barite Group	
CaCO ₃ , aragonite.	Also		CaSO ₄ , anhydrite.	
BaCO ₃ , witherite.			BaSO ₄ , barite.	
SrCO ₃ , strontianite.			SrSO ₄ , celestite.	
PbCO ₃ , cerussite,			PbSO ₄ , anglesite.	

Further, the members of each series crystallize in closely similar forms. The carbonates are orthorhombic, with axial ratios not far from one another; thus the prismatic angle approximates to 60° and 120°, and corresponding to this they all exhibit pseudo-hexagonal forms due to twinning. The sulphates also form a similar orthorhombic series, and though anhydrite deviates somewhat widely, the others are close together in angle and in cleavage.

Again, calcium, magnesium, iron, zinc, and manganese form a series of carbonates with analogous composition as shown in the list of the species of the *Calcite Group* given on p. 437. This table brings out clearly the close relation in form between the species named.

Further it is also generally true with an isomorphous series that the various molecules may enter in greater or less degree into the constitution of one of the members of the series without causing any marked change in the crystal characters. For instance, in the *Calcite Group*, calcite itself may contain small percentages of MgCO₃, FeCO₃ and MnCO₃. These different molecules may assume in the crystal structure of the mineral the same functions as the corresponding amounts of CaCO₃ which they have replaced. The molecules of magnesite and siderite, MgCO₃ and FeCO₃, may replace each other in any proportion and the same is true with siderite and rhodochrosite, MnCO₃. Various intermediate mixtures of these latter molecules have been described and given distinctive names to which definite formulas have been assigned. It is doubtful, however, if these compounds have any real existence but merely represent certain points in the complete isomorphous series that lies between the end members. Dolomite, CaMg(CO₃)₂, on the other hand, is a definite compound and not an isomorphous mixture of CaCO₃ and MgCO₃. It may, however, contain varying amounts of FeCO₃, MnCO₃ and also an excess of CaCO₃ or MgCO₃, all of which enter the regular molecule in the form of isomorphous replacements.

The *Apatite Group* forms another valuable illustration since in it are represented the analogous compounds, apatite and pyromorphite, both phosphates, but respectively phosphates of calcium and lead; also the analogous

lead compounds pyromorphite, mimetite, and vanadinite respectively lead phosphate, lead arsenate, and lead vanadate. Further, in all these compounds the radical (RCl) or (RF) enters in the same way (see Art. 469). Thus the formulas for the two kinds of apatite and that for pyromorphite are as follows:



Some of the more important isomorphous groups are mentioned below. For a discussion of them, as well as of many others that might be mentioned here, reference must be made to the descriptive part of this work.

Isometric System. — The Spinel group, including spinel, MgAl_2O_4 ; also magnetite, chromite, franklinite, gahnite, etc. The Galena group, as galena, PbS ; argentite, Ag_2S , etc. The Garnet group, as grossularite, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, etc.

Tetragonal System. — Rutile group, including rutile, TiO_2 ; cassiterite, SnO_2 . The Scheelite group, including scheelite, CaWO_4 ; stolzite, PbWO_4 ; wulfenite, PbMoO_4 .

Hexagonal System. — Apatite group, already mentioned, including apatite, pyromorphite, mimetite, and vanadinite. Corundum group, corundum, Al_2O_3 ; hematite, Fe_2O_3 . Calcite group, already mentioned. Phenacite group, etc.

Orthorhombic System. — Aragonite group, and Barite group, both mentioned above. Chrysolite group, $(\text{Mg}, \text{Fe})_2\text{SiO}_4$; Topaz group, etc.

Monoclinic System. — Copperas group, including melanterite, $\text{FeSO}_4 + 7\text{H}_2\text{O}$; Bieberite, $\text{CoSO}_4 + 7\text{H}_2\text{O}$, etc. Pyroxene and Amphibole groups, and the Mica group.

Monoclinic and Triclinic Systems. — Feldspar group.

472. Isomorphous Mixtures. — It is important to note that the intermediate compounds in the case of an isomorphous series, such as those spoken of in the preceding article, often show a distinct gradation in crystalline form, and more particularly in physical characters (*e.g.*, specific gravity, optical properties, etc.). This is illustrated by the species of the calcite group already referred to; also still more strikingly by the group of the triclinic feldspars as fully discussed under the description of that group. See further Art. 424.

The feldspars also illustrate two other important points in the subject, which must be briefly alluded to here. The triclinic feldspars have been shown by Tschermak to be isomorphous mixtures of the end compounds in varying proportions:



Here it is seen that these compounds have not an analogous composition in the narrow sense previously illustrated, and yet they are isomorphous and form an isomorphous series. Other examples of this are found among the pyroxenes, the scapolites, etc.

Further, the Feldspar group in the broader sense includes several other species, conspicuously the monoclinic orthoclase, KAlSi_3O_8 , which, though belonging to a different system, still approximates closely in form to the triclinic species.

473. Variation in Composition of Minerals. Isomorphous Replacement and Solid Solution. — The idea that a mineral must rigidly conform in its chemical composition to a theoretical composition derived from its formula can no longer be strictly held. It is true that the majority of minerals do show a close correspondence to that theory, commonly within the limits of possible errors in the analyses. On the other hand, many minerals show slight and certain ones considerable variations from their theoretical compositions. These variations can usually be explained by the principle of isomorphism. An instructive example is the case of sphalerite. Note in the analyses quoted below how the percentages of zinc diminish and those of iron correspondingly increase. It is evident from these analyses that iron, and in a much smaller

degree other metals, may enter into the chemical compound and while replacing the zinc perform the same function as it, in the crystalline structure of the mineral. The iron is therefore spoken of as being isomorphous with the zinc or the iron sulphide molecule as isomorphous with the zinc sulphide molecule. There is no definite ratio between the amounts of the iron and zinc that may be present but there is a constant ratio (1 : 1) between the sum of the atoms of the metals and the atoms of sulphur. That is, although the composition may vary, the atomic ratios and the crystalline structure remain constant. In some cases this interchange between elements or radicals may be complete, in other cases there may be distinct limitations to the amount by which any element or radical may be replaced by another. For instance in sphalerite the maximum percentage of the isomorphous iron seems to be about 16 to 18 per cent.

Colorless Sphalerite		Brown Sphalerite		Black Sphalerite	
S	32.93	S	33.36	S	33.25
Zn	66.69	Zn	63.36	Zn	50.02
Fe	0.42	Fe	3.60	Fe	15.44
	100.04		100.32	Cd	0.30
				Pb	1.01
					100.02

Further, we have cases where a compound may, in a certain sense, dissolve another unrelated substance and form what is known as a *solid solution*. This kind of phenomenon is well recognized among artificial salts and has recently been definitely proved with certain minerals. For instance, it has been shown experimentally that the artificial iron sulphide, FeS, corresponding to pyrrhotite, can dissolve an excess of sulphur up to about 6 per cent. Natural pyrrhotite always contains an excess of sulphur over that required by the formula, FeS, and various formulas such as Fe₇S₈, Fe_nS_{n+1}, etc., have been assigned to the mineral. This extra sulphur in the mineral varies in amount but also has as its maximum about 6 per cent. In view of the experimental data there is no doubt but that pyrrhotite should be considered as the monosulphide of iron containing varying small amounts of excess sulphur in the form of a solid solution.

Another case of solid solution is undoubtedly shown by nephelite which commonly contains a small excess of SiO₂. It is very probable that further investigation will show that many minerals have this power of holding in solid solution small amounts of foreign substances and that many hitherto inexplicable discrepancies in their analyses may be explained in this way. Such an assumption should not be made, however, without convincing proof of its probability, since many analytical discrepancies are undoubtedly due to either faulty analyses or to impure material.

474. Colloidal Minerals or Mineral Gels.* — It has been recognized recently that our amorphous hydrated minerals frequently do not conform in their analyses to the usually accepted formulas and cannot be regarded in the strict sense as definite chemical compounds. They show rather the properties of solid colloids or as they are commonly called *mineral gels*. A colloidal solution may be conceived as being intermediate in its characters between a true solution and the case where the mineral material is definitely in suspen-

* For a résumé of the subject of gel minerals and a complete bibliography reference is made to articles by Marc and Himmelbauer, Fortschritte Min. Krist. Pet., **3**, 11, 33, 1913.

sion in a liquid. It is probable that all gradations between these two extremes may occur. The mineral gels, or hydrogels, as they are sometimes called, since water is the liquid involved, are apparently formed from such colloidal solutions by some process of coagulation. They are considered therefore to consist of a micro-heterogeneous mixture of excessively minute particles of mineral material and water.

These mineral gels are formed at low temperatures and pressures and are characteristically found among the products of rock weathering and in the oxidized zone of ore deposits. Some of them also occur in hot spring deposits. These minerals ordinarily assume botryoidal, reniform or stalactitic shapes, although, when the conditions of formation do not permit free growth, they may be earthy or dendritic. Frequently a mineral originally colloidal may become more or less crystalline in character through a molecular rearrangement and develop a fibrous or foliated structure. These have been designated as *meta-colloids*.

One important character of the gel minerals is their power to adsorb foreign materials. If through some change in condition one of these hydrogels should lose a part of its water content the remaining material would have a finely divided and porous structure exactly adapted to exert a strong power of adsorption. Consequently, although in many cases the main mass of the mineral may have a composition closely similar to some definite crystallized mineral, it will commonly show a considerable range in composition due both to the non-molecular relations of the contained water and to this secondary adsorption. Common mineral gels or substances derived from them are opal, bauxite, psilomelane, various members of the phosphate and arsenate groups, etc. As suggested above, gel varieties of minerals that occur also in crystalline forms are thought to exist. For example some authors speak of bauxite as the gel form of hydrargillite, stilpnosiderite as the gel form of goethite, chrysocolla of diopside, and further give new names, such as gelvariscite, gelpyrophyllite, etc., to the gel phases of the corresponding crystalline minerals.

475. Dimorphism. Isodimorphism. — A chemical compound, which crystallizes in two forms genetically distinct, is said to be *dimorphous*; if in three, *trimorphous*, or in general *pleomorphous*. This phenomenon is called DIMORPHISM OF PLEOMORPHISM.

An example is given by the compound calcium carbonate (CaCO_3), which is dimorphous: appearing as calcite and as aragonite. As *calcite* it crystallizes in the rhombohedral class of the hexagonal system, and, unlike as its many crystalline forms are, they may be all referred to the same fundamental axes, and, what is more, they have all the same cleavage and the same specific gravity (2.7) and, of course, the same optical characters. As *aragonite*, calcium carbonate appears in orthorhombic crystals, whose optical characters are entirely different from those of calcite; moreover, the specific gravity of aragonite (2.9) is higher than that of calcite (2.7).

Many other examples might be given: Titanium dioxide (TiO_2) is trimorphous, the species being called *rutile*, tetragonal ($c = 0.6442$), $G. = 4.25$; *octahedrite*, tetragonal ($c = 1.778$), $G. = 3.9$; and *brookite*, orthorhombic, $G. = 4.15$. Carbon appears in two forms, in diamond and graphite. Other familiar examples are pyrite and marcasite (FeS_2), sphalerite and wurtzite (ZnS), etc.

When two or more analogous compounds are at the same time isomorphous and dimorphous, they are said to be *isodimorphous*, and the phenomenon is

called **ISODIMORPHISM**. An example of this is given in the Pyrite and Marcasite groups described later. Thus we have in the isometric Pyrite Group, pyrite, FeS_2 , smaltite, CoAs_2 ; in the orthorhombic Marcasite Group, marcasite, FeS_2 , safflorite, CoAs_2 , etc.

476. Chemical and Microchemical Analysis. — The analysis of minerals is a subject treated of in chemical works, and need not be touched upon here except so far as to note the convenient use of certain qualitative methods, as described in the later part of this chapter.

Of more importance are the *microchemical* methods applicable to sections under the microscope and often yielding decisive results with little labor. This subject has been particularly developed by Boricky, Haushofer, Behrens, Streng, and others. Reference is made to the discussion by Rosenbusch. (*Mikr. Phys.*, 1904, p. 435 *et seq.*), to Johannsen (*Manual of Pet. Methods*, 559, *et seq.*, including a bibliography). Microchemical methods used upon polished surfaces of opaque minerals are described by Murdock (*Micro. Deter. Opaque Min.*, 1916) and by Davy-Farnham (*Micro. Exam. of the Ore Min.*, 1920).

477. Mineral Synthesis. — The occurrence of certain mineral compounds (*e.g.*, the chrysolites) among the products of metallurgical furnaces has long been noted. But it has only been in recent years that the formation of artificial minerals has been made the subject of minute systematic experimental study. In this direction the French chemists have been particularly successful, and now it may be stated that the majority of common minerals — quartz, the feldspars, amphibole, mica, etc. — have been obtained in crystallized form. Even the diamond has been formed in minute crystals by Moissan. These studies are obviously of great importance particularly as throwing light upon the method of formation of minerals in nature. The chief results of the work thus far done are given in the volumes mentioned in the Introduction, p. 4.

478. Alteration of Minerals. Pseudomorphs. — The chemical alteration of mineral species under the action of natural agencies is a subject of great importance and interest, particularly when it results in the change of the original composition into some other equally definite compound. A crystallized mineral which has thus suffered change so that its form no longer belongs to its chemical composition has already been defined (Art. 273, p. 183) as a *pseudomorph*. It remains to describe more fully the different kinds of pseudomorphs. Pseudomorphs are classed under several heads:

1. Pseudomorphs by *substitution*.
2. Pseudomorphs by simple *deposition*, and either by (a) *incrustation* or (b) *infiltration*.
3. Pseudomorphs by *alteration*; and these may be altered
 - (a) without a change of composition, by *paramorphism*;
 - (b) by the loss of an ingredient;
 - (c) by the assumption of a foreign substance;
 - (d) by a partial exchange of constituents.

1. The first class of pseudomorphs, by *substitution*, embraces those cases where there has been a gradual removal of the original material and a corresponding and simultaneous replacement of it by another, without, however, any chemical reaction between the two. A common example of this is a piece of fossilized wood, where the original fiber has been replaced entirely by

silica. The first step in the process was the filling of the pores and cavities by the silica in solution, and then as the woody fiber, by gradual decomposition, disappeared the silica further took its place. Other examples are quartz after fluorite, calcite, and many other species; cassiterite after orthoclase; native copper after aragonite, etc.

2. Pseudomorphs by *incrustation* form a less important class. Such are the crusts of quartz formed over fluorite. In most cases the removal of the original mineral has gone on simultaneously with the deposition of the second, so that the resulting pseudomorph is properly one of substitution. In pseudomorphs by *infiltration* a cavity made by the removal of a crystal has been filled by another mineral.

3. The third class of pseudomorphs, by *alteration*, includes a considerable proportion of the observed cases, of which the number is very large. Conclusive evidence of the change which has gone on is often furnished by a nucleus of the original mineral in the center of the altered crystal — *e.g.*, a kernel of cuprite in a pseudomorphous octahedron of malachite; also of chrysolite in a pseudomorphous crystal of serpentine, etc.

(a) An example of *paramorphism* — that is, of a change in molecular constitution without change of chemical substance — is furnished by the change of aragonite to calcite (both CaCO_3) at a certain temperature; also the *paramorphs* of rutile after brookite (both TiO_2) from Magnet Cove, Arkansas.

(b) An example of the pseudomorphs in which alteration is accompanied by a loss of ingredients is furnished by crystals of native copper in the form of cuprite.

(c) In the change of cuprite to malachite — *e.g.*, the familiar crystals from Chessy, France — an instance is afforded of the assumption of an ingredient — *viz.*, carbon dioxide (and water). Pseudomorphs of gypsum after anhydrite occur where there has been an assumption of water alone.

(d) A partial exchange of constituents — in other words, a loss of one and gain of another — takes place in the change of feldspar to kaolin, in which the potash silicate disappears and water is taken up; pseudomorphs of limonite after pyrite or siderite, of chlorite after garnet, pyromorphite after galena, are other examples.

The chemical processes involved in such changes open a wide and important field for investigation. Their study has served to throw much light on the chemical constitution of mineral species and the conditions under which they have been formed. For the literature of the subject see the Introduction, p. 4 (Blum, Bischof, Roth, etc.).

CHEMICAL EXAMINATION OF MINERALS

479. The complete investigation of the chemical composition of a mineral includes, first, the identification of the elements present by qualitative analysis, and, second, the determination of the relative amounts of each by quantitative analysis, from which last the formula can be calculated. Both processes carried out in full call for the equipment of a chemical laboratory. An approximate qualitative analysis, however, can, in many cases, be made quickly and simply with few conveniences. The methods employed involve either (a) the use of acids or other reagents "in the wet way," or (b) the use