mination of iron. The temperature coefficient for this color varies from 2 to 3% per degree depending on the concentration of iron and probably also on the acidity. The color developed by a given amount of iron varies with the acid concentration, reaching the maximum intensity at from 26 to 28% HCl. The relative increase produced by acid is greater the higher the concentration of iron; this is especially true above 20% HCl, but below this concentration the relative change is independent of the iron content. Inasmuch as solutions must frequently be boiled in order to insure the complete solution of iron present as "scale" the use of constant-boiling acid is recommended and its use has been found to be altogether satisfactory. The effects of salts on the color indicate that sulfates cause bleaching, and chlorides intensification; detailed study of the effect of the very soluble calcium chloride shows that an intensification of 2.5 may be attained by the addition of this salt, consequently when testing for iron in a very soluble chloride the standard iron solution must be made up to possess the same salt concentration.

Some applications of the method are given and certain results presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

ISOMORPHISM, ISOSTERISM AND COVALENCE.

BY IRVING LANGMUIR.

Received June 30, 1919.

In recent papers[1] I have described a theory of valence which I have called the octet theory. This theory is based upon and is essentially an extension of G. N. Lewis' theory of the "cubical atom."[2] According to this theory each bond between adjacent atoms in organic compounds corresponds to a pair of electrons held in common by the two atoms. Since in other types of compounds the number of pairs of electrons held in common is not always the same as the number of valence bonds that have usually been assumed I proposed that the number of pairs of electrons which any given atom shares with the adjacent atoms be called the covalence of that atom. It was then shown that the covalence of carbon is always 4, that of nitrogen is usually 3 or 4, while that of oxygen is 1, 2 or sometimes 3, etc.

The octet theory indicates that the number and arrangement of electrons in the nitrogen molecule, the carbon monoxide molecule, and the

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[1] A simpler exposition of the theory and its applications is given by Elwood Hendrick, *Met. Chem. Eng.*, 21, 73 (1919), July 15th; Langmuir, *J. Frank. Inst.*, 187, 359 (1919); THIS JOURNAL, 41, 868–934 (1919); *Proc. Nat. Acad. Sci.*, 5, 252 (1919).

[2] G. N. Lewis, THIS JOURNAL, 38, 762 (1916).

cyanogen ion, is the same, and it was shown in fact that the physical properties of nitrogen and carbon monoxide are remarkably alike.

A similar relationship was found to exist between nitrous oxide and carbon dioxide and again between cyanic and hydronitric acid.

The following data, taken from Landolt-Börnstein's tables and Abegg's handbook, show the extraordinary agreement between physical properties of carbon dioxide and nitrous oxide:

	N_2O.	CO_2.
Critical pressure, atm.	75	77
Critical temp.	35.4°	31.9°
Viscosity at 20°	148×10^{-6}	148×10^{-6}
Heat conductivity at 100°	0.0506	0.0506
Density of liquid at —20°	0.996	1.031
Density of liquid at +10°	0.856	0.858
Refractive index of liquid, D line, 16°	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atm., 16°	0.12×10^{-6}	0.12×10^{-6}
Solubility in water 0°	1.305	1.780
Solubility in alcohol at 15°	3.25	3.13

Both gases form hydrates, $N_2O.6H_2O$ and $CO_2.6H_2O$. The vapor pressure of the hydrate of nitrous oxide is 5 atm. at —6°, whereas the hydrate of carbon dioxide has this vapor pressure at —9°. The heats of formation of the two hydrates are given, respectively, as 14900 and 15000 calories per mol. The surface tension of liquid nitrous oxide is 2.9 dynes per cm. at 12.2°, while carbon dioxide has this same surface tension at 9.0°. Thus nitrous oxide at any given temperature has properties practically identical with those of carbon dioxide at a temperature 3° lower.

There is one property, however, which is in marked contrast to those given above. The freezing point of nitrous oxide is —102°, while that of carbon dioxide is —56°. This fact may be taken as an indication that the freezing point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of carbon dioxide is more symmetrical, and has a slightly weaker external field of force than that of nitrous oxide. Such differences could easily be produced by the difference in the charges on the kernels, and may also be taken as evidence that the structure of nitrous oxide is represented by $N = N = O$ rather than $N = O = N$.

Compounds showing a relationship to one another like that between carbon dioxide and nitrous oxide will be called isosteric compounds, or isosteres. These terms, however, are not to be restricted to chemical compounds but are applicable to chemical radicals or to groups of atoms which hold pairs of electrons in common. A comolecule is defined as a group of atoms held together by pairs of electrons shared by adjacent atoms. Comolecules are thus isosteric if they contain the same number and arrangement of electrons. The comolecules of isosteres must, therefore, contain the same number of atoms. The essential differences between isosteres are confined to the charges on the nuclei of the constituent atoms. Thus in carbon dioxide the charges on the nuclei of the carbon and oxygen atoms are 6 and 8, respectively, and there are $2 \times 8 + 6 = 22$ electrons in the molecule. In nitrous oxide the number of charges on the nitrogen nuclei is 7, but the total number of electrons in the molecule is again $2 \times 7 + 8 = 22$. The remarkable similarity of the physical properties of these two substances proves that their electrons are arranged in the same manner.

According to the object theory we may expect the following types of isosteres:

TABLE I.
List of Isosteres.

Type.	
1	H^-, He, Li^+
2	O^{--}, F^-, Ne, Na^+, Mg^{++}, Al^{+++}
3	S^{--}, Cl^-, A, K^+, Ca^{++}
4	Cu^+, Zn^{++}
5	Br^-, Kr, Rb^+, Sr^{++}
6	Ag^+, Cd^{++}
7	I^-, Xe, Cs^+, Ba^{++}
8	N_2, CO, CN^-
9	CH_4, NH_4^+
10	CO_2, N_2O, N_3^-, CNO^-
11	NO_3^-, CO_3^{--}
12	NO_2^-, O_3
13	HF, OH^-
14	ClO_4^-, SO_4^{--}, PO_4^{---}
15	ClO_3^-, SO_3^{--}, PO_3^{---}
16	SO_3, PO_3^-
17	$S_2O_6^{--}$, $P_2O_6^{----}$
18	$S_2O_7^{--}$, $P_2O_7^{----}$
19	SiH_4, PH_4^+
20	MnO_4^-, CrO_4^{--}
21	SeO_4^{--}, AsO_4^{---}

All the comolecules given under any one type are isosteric with one another.

When isosteric comolecules are also isoelectric, that is when they have the same total charge on the comolecules, all their physical properties should be closely similar. In Table I the only pairs of comolecules which are also isoelectric are: (8) N_2 and CO, (10*a*) CO_2 and N_2O, and (10*b*) N_3^- and NCO^-.

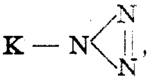
I have already pointed out that the physical properties of the first two pairs of substances (8 and 10*a*) furnish proof of the similarity of structure predicted by the octet theory, and show the usefulness of the conception of isosterism.

The isosterism of the cyanate and trinitride ions applies of course also to compounds derived from them. Thus we should expect HNCO and HN_3 to be isosteric as well as pairs of compounds such as KNCO–KN_3, $Ba(NCO)_2$–$Ba(N_3)_2$, etc.

There are, unfortunately, very few data on the physical properties of cyanates and trinitrides. Both cyanic and hydronitric acids are liquids at 0° and both explode on heating. Apparently the freezing point of cyanic acid has not been determined. In a general way the solubilities of the salts of these two acids are known to be similar; the potassium and the barium salts of both acids are readily soluble in water, while the lead and silver salts are very difficultly soluble.

Groth[1] gives the following crystallographic data for anhydrous potassium cyanate and trinitride. Both belong to the tetragonal system. The ratio of the axes $a : c$ is 1 : 0.5766 for the cyanate and 1 : 0.5798 for the trinitride. Both have "strong negative double refraction." The most common faces of both crystals are given as C (001) and O (111). Cleavage was not observed in either case. No other data are given by Groth from which a comparison of cyanates and trinitrides can be made.

From the octet theory and the above data it is therefore safe to predict that the physical properties of the salts of cyanic and hydronitric acids will be found to be practically identical. This resemblance should be at least as close as that between nitrous oxide and carbon dioxide and should cover solubility in water, in alcohol, etc., density in crystalline form and in solutions, viscosity of solutions, optical and magnetic properties, electric conductivity of solutions, etc. The densities should be alike because the molecular weight of N_3 is the same as that of NCO.

The available experimental data, although meager, are sufficient, I think, to show the complete isomorphism of cyanates and trinitrides. The similarity of structure thus follows directly from Mitscherlich's rule. These experimental data furnish direct evidence against such structural formulas as , $K—N=N\equiv N$, $K—O—C\equiv N$, but strongly support the octet theory structures:

$$K^+(N=C=O)^- \quad \text{and} \quad K^+(N=N=N)^-$$

These formulas show that the covalence of potassium is zero; the nitrogen and oxygen in the cyanate are dicovalent, while in the trinitride one of the nitrogens is quadricovalent and the other two are dicovalent. These data, as far as they go, thus constitute experimental proof of the octet theory of valence. Further experimental work on the physical properties of cyanates and trinitrides is highly desirable.

The octet theory also indicates that diazomethane should have the structure $H_2C=N=N$ and should thus be isosteric with $H_2C=C=O$,

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[1] P. Groth, "Chemische Krystallographie," Leipzig, Part I, 1906, Part II, 1908.

a compound apparently not given in Beilstein. This compound should closely resemble diazomethane in all its physical properties such as freezing point, vapor pressure, viscosity, etc.

No direct comparison can be made of the physical properties of isosteres having different electric charges. Thus we should not expect sodium salts to resemble neon, even though the sodium ion is an isostere of the neon atom—the electric force around the ion is sufficient to account for the differences in physical properties.

There is, however, another way in which the actual isosterism of comolecules with different charges can be tested from experimental data. It is evident that if any two substances are very much alike in physical properties, then any isoelectric isosteres of these substances should show similarly close relationships with one another. For example, in Types 3 and 8 of Table I, we find argon and nitrogen resemble each other closely. Therefore the chlorine ion, isosteric with argon, should have a close resemblance to the cyanogen ion which is isosteric with nitrogen. The striking similarity of chlorides and cyanides is thus directly correlated with that between argon and nitrogen.

In an exactly similar manner the close relationship between potassium salts and ammonium salts can be derived from the similarity between the physical properties of argon and methane. For from Table I (Types 3 and 9) the potassium ion is isosteric with argon, while the ammonium ion is an isostere of methane. Of course the potassium ion and the ammonium ion are not isosteres of one another. The resemblance between potassium and ammonium salts is of a much lower order than that between truly isosteric substances such as nitrous oxide and carbon dioxide, or between salts of cyanic and hydronitric acids. The octet theory indicates in fact that the potassium ion is cubic in form, while the ammonium ion, like methane, must have a tetrahedral symmetry. This conclusion is in accord with the crystal structures of potassium chloride and ammonium chloride. Bragg[1] has found that in potassium chloride each potassium ion is surrounded by 6 equidistant chlorine ions, arranged just as if the crystal were built up of cubical potassium and chlorine ions with their faces in contact; but finds that ammonium chloride, although it crystallizes in the isometric system, is in no sense isomorphous with the other alkaline halides. Each ammonium ion is surrounded by 8 equidistant chlorine ions arranged like the corners of a cube about its center. This indicates that the tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to the 4 faces or corners of the tetrahedron, while the cubical potassium ions permit the simpler cubic packing. Ammonium and potassium sulfates, however, are iso-

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[1] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," London, 1916, pp. 95 and 158.

morphous, for the larger volume of the sulfate ion causes its influence to predominate over the slight differences between the forces around the two positive ions.

The nitrates and perchlorates of all metals are readily soluble and most of them are deliquescent. From this similarity of properties we may conclude that the other isosteres of Types 11 and 14 of Table I should be interrelated. Thus carbonates and sulfates should show a general resemblance to each other in their solubilities.

The smaller solubility of salts of divalent ions is, of course, due to the greater forces holding the divalent ions, making it more difficult for them to separate. The process of solution of salts involves, according to the octet theory, the separation of the ions. Thus sulfates and carbonates of most metals are difficultly soluble compared to the nitrates and perchlorates. Salts like lead and barium carbonates and sulfates in which both ions are divalent, are thus particularly difficultly soluble.

Boron nitride, which consists of tervalent ions, has still greater stability, and is infusible and insoluble in all solvents.

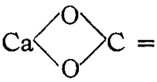
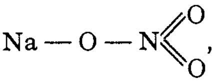
The observed differences between the ordinary properties of the differently charged isosteres are thus to be expected. But there is one property, namely crystalline form, which should depend on the arrangement of the electrons in substances rather than upon the magnitude of the forces between their atoms. By a comparison of crystal forms it should therefore be possible to obtain direct evidence of the similarity of the arrangement of the electrons in isosteric substances even if the charges on the comolecules are different.

For example, since the sodium ion and the fluorine ion are isosteric and cubic in form, we should expect them to pack together in a crystal lattice in exactly the way that Bragg has found they do. The magnesium and oxygen ions, however, are also isosteric with the sodium and fluorine ions, so that we should expect magnesium oxide to have a crystal structure identical in form with that of sodium fluoride. According to Groth both substances are cubic, sometimes crystallizing as octahedra, and both show good cleavage parallel to the (100) plane. To answer the question thus raised, Dr. A. W. Hull has studied the X-ray patterns obtained with magnesium oxide and sodium fluoride and has thus recently found[1] that the crystal structures of both substances are alike, except that the atoms in magnesium oxide are drawn closer together by the greater forces. Thus magnesium oxide and sodium fluoride should be looked upon as isomorphous. By the octet theory the covalences of all the atoms in these substances are zero, since they do not share electrons with each other. The isomorphism is thus in full accord with Mitscherlich's rule by which isomorphous substances should have similar struc-

[1] Soon to be published.

tures. Since the ions O^{--}, F^{-}, Na^{+} and Mg^{++} are isosteric we should also expect that MgF_2 and Na_2O should be isomorphous. Groth states that sodium oxide has not been obtained in the form of well developed crystals. However, by Hull's method of X-ray analysis, substances can now be studied in powdered form so that we may hope to see whether in fact these two substances are isomorphous. Other pairs of substances which may be isomorphous are potassium chloride and calcium sulfide, potassium sulfide and calcium chloride, cuprous sulfide and zinc chloride, etc.

A still more interesting class of isomorphous substances which are predicted by the octet theory is that represented by sodium nitrate and calcium carbonate. Since the nitrate and carbonate ions are isosteric we should expect sodium nitrate and magnesium carbonate to be isomorphous, Na^{+} and Mg^{++} being isosteric. As a matter of fact, both substances are given by Groth as trigonal scalenohedral with the ratio of the axes 1 : 0.8297 and 1 : 0.8095, respectively.

The practical identity in all the crystallographic properties of sodium nitrate and calcium carbonate has long been known. In Mitscherlich's early theory before clear ideas of valence were developed, no difficulty was experienced in regarding these two substances as isomorphous and as having similar structures. The theory of valence, however, gave formulas  $Ca{<}^{O}_{O}{>}C=O$ and  $Na-O-N{<}^{O}_{O}$, so that they could no longer be regarded as of similar structure. It was necessary either to abandon Mitscherlich's rule or to re-define isomorphism so as to exclude cases of this kind. Therefore Kopp[1] and Retgers[2] regarded substances as isomorphous only when they are capable of forming *mixed crystals*. This effectually eliminated such cases as sodium nitrate and calcium carbonate because mixed crystals can naturally only be obtained when the solubilities of the two substances are not too widely different. The crystal form depends, of course, exclusively, on the arrangement of the atoms and the electrons in them, while the ability to form mixed crystals depends on both similarity of arrangement and on similarity in the magnitude of the forces acting between the atoms. Thus Kopp found a practical rule by which nearly all those cases inconsistent with the ordinary valence theory, could be excluded. In order to be isomorphous in Kopp's sense, two substances must have atoms which are not only linked together in the same manner, but also have the same number of available electrons in corresponding atoms.

T. V. Barker,[3] however, and a few others crystallographers have main-

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[1] *Ber.*, 12, 868 (1879).

[2] *Z. physik. Chem.*, 3, 497 (1889), and later papers in 1889 to 1896.

[3] *Trans. Chem. Soc.*, 101, 2484 (1912).

tained that isomorphism should be used to denote similarity of crystal form. Barker pointed out a great many new cases of isomorphism between substances which according to the ordinary valence theory are not closely related. Among these he mentions as types KIO_4–$CaWO_4$; $KClO_4$–$BaSO_4$–KBF_4; K_2SO_4–K_2BeF_4; and $NaNO_3$–$CaCO_3$. He shows how these cases of isomorphism are inconsistent with the ordinary valence theory, but are in a general way in agreement with Werner's coördination theory.

By examining Table I it is evident that we should expect the following cases of isomorphism of the kind just considered:

Table II.

Typical Cases of Isomorphism Based on Isosterism.

Type. Table I.	
2	(a) NaF–MgO; (b) MgF_2–Na_2O
3	(a) KCl–CaS; (b) $CaCl_2$–K_2S
5	(a) $RbBr$–$SrSe$; (c) $SrBr_2$–Rb_2Se
7	(a) CsI–$BaTe$; (c) BaI_2–Cs_2Te
8	N_2–CO
10	$KNCO$–KN_3, etc.
11	(a) $NaNO_3$–$CaCO_3$; (b) KNO_3–$SrCO_3$
14	(a) $KClO_4$–$SrSO_4$; (b) $NaHSO_4$–$CaHPO_4$ (c) $KHSO_4$–$SrHPO_4$
15	(a) $NaClO_3$–$CaSO_3$; (b) $KHSO_3$–$SrHPO_3$
17	$Na_2S_2O_6$–$Ca_2P_2O_6$
18	$Na_2S_2O_7$–$Ca_2P_2O_7$
20	$RbMnO_4$–$BaCrO_4$
21	$MnSeO_4.2H_2O$–$FeAsO_4.2H_2O$

Sodium nitrate crystals resemble those of calcium carbonate a little more closely than those of magnesium carbonate, although the sodium ion is isosteric with the magnesium ion but not with the calcium ion. The molecular volume of sodium nitrate is nearer to that of calcium carbonate than that of the magnesium compound. The much larger forces in the compounds containing the divalent ions must tend to draw the atoms closer together. The substitution of the larger calcium ion in place of the magnesium ion offsets this difference, and this probably accounts for the closer resemblance between the sodium and the calcium compounds. This same relationship is noticed in other pairs of compounds. Since in these replacements calcium corresponds most nearly to sodium we should expect strontium to correspond to potassium and barium to rubidium. This is well borne out in every case. The following tables illustrate the cases of isomorphism corresponding to Types 11 to 21, shown in Table II, for which data are given by Groth. The pairs of substances at the head of each table are those given in Table II. The other substances are generally recognized as being isomorphous with one or the other member of these pairs.

TABLE III.

Nitrates and Carbonates Type 11 (*a*). Trigonal Scalenohedral.

	a	*c.*	
$NaNO_3$	1	0.8297	
$CaCO_3$	1	0.8543	
$MgCO_3$	1	0.8095	
$MnCO_3$	1	0.8259	
KNO_3	1	0.8259	Stable above 128°

At high temperatures $RbNO_3$, $SrCO_3$ and $BaCO_3$ also give trigonal crystals.

All these substances show strong negative double refraction and similar cleavage.

TABLE IV.

Nitrates and Carbonates, Type 11 (*b*). Orthorhombic Bipyramidal.

	a	*b*	*c.*
KNO_3	0.5910	1	0.7011
$SrCO_3$	0.6090	1	0.7237
$CaCO_3$	0.6228	1	0.7204
$BaCO_3$	0.5949	1	0.7413

Negative double refraction.

TABLE V.

Perchlorates and Sulfates, Type 14 (*a*). Permanganates and Chromates, Type 20.
Orthorhombic Bipyramidal.

	a.	*b*	*c.*	Cleavage.	
$KClO_4$	0.7817	1	1.2793	*c*(001)	*m*(110)[1]
$SrSO_4$	0.7790	1	1.2800	*c*(001)	*m*(110)[1]
$RbMnO_4$	0.8311	1	1.3323	..	....
$BaCrO_4$	0.8231	1	1.3232	..	....
$RbClO_4$	0.7966	1	1.2879	*c*(001)	*m*(110)
$BaSO_4$	0.8152	1	1.3136	*c*(001)	*m*(110)[1]
$KMnO_4$	0.7972	1	1.2982	*c*(001)	*m*(110)[1]
$SrCrO_4$	0.9496	1	1.0352	..	....
$CsClO_4$	0.8173	1	1.2976	..	....
$CsMnO_4$	0.8683	1	1.3705	..	....
$CaSO_4$	0.8932	1	1.0008	..	....
NH_4ClO_4	0.7932	1	1.2808	..	....

TABLE VI.

Sulfates and Phosphates, Type 14 (*b*). Triclinic Pinacoid.

	a.	*b.*	*c.*	*α.*	*β.*	*γ.*
$NaHSO_4$[2]	0.6460	1	0.8346	85° 06′	88° 57′	86° 47′
$CaHPO_4$	0.6467	1	0.8244	84° 57′	89° 43′	85° 38′
$SrHAsO_4$	0.6466	1	0.8346	86° 32′	89° 14′	87° 56′

[1] Incomplete cleavage.

[2] Axes *b* and *c* have been interchanged in order to correspond to those used to form the other compounds. Where the angles α, β, γ, were greater than 90° their supplementary angles were chosen.

TABLE VII.

Sulfates and Phosphates, Type 14 (*c*). Orthorhombic Bipyramidal.

	a.	*b.*	*c.*
$SrHPO_4$[1]	0.8581	1	1.9431
$KHSO_4$	0.8609	1	1.9344

Both substances form 8- or 4-sided plates parallel to *c*(001) with (111) as the next most important face. The plane of the optic axis is (001).

TABLE VIII.

Selenates and Arsenates, Type 21. Orthorhombic Bipyramidal.

	a.	*b.*	*c.*
$MnSeO_4.2H_2O$	0.8849	1	0.9959
$FeAsO_4.2H_2O$	0.8658	1	0.9541

Plane of the optic axis (100) in both.

Groth gives no data for the Types 15(*a*), 15(*b*), 17 and 18 of Table II.

The results given in these tables afford the strongest kind of evidence for the octet theory of valence and prove that crystal form depends on the covalence of the atoms forming the substance rather than upon the valences given by the ordinary theory.

In every one of the cases where isomorphism is predicted by the octet theory (see Table II), we find that the data available in Groth's "Chemische Kristallographie" indicate an almost complete identity of crystalline form. The agreement between the pairs of substances given in Table II is in fact usually rather better than among most of the classical examples of isomorphism. For example, the agreement of the ratios of the axes for potassium perchlorate and strontium sulfate (Table V) is much closer than among the various chlorates or among the sulfates. Sodium nitrate

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[1] The measurements on $SrHPO_4$ and on $CaHPO_4$ given in Table VI were made by Schulten, *Bull. Soc. franç minéral* **27**, 120 (1904).

According to Groth the ratio of the axes for $SrHPO_4$ was found to be 0.6477 :1 :0.8581 and the only faces measured were (100), (133), (203), (130), (230), (010). Groth states that the chosen orientation of the $CaHPO_4$ crystals was adopted because of the relationships to those of $SrHPO_4$.

For the substance $BaHPO_4$ which Schulten finds to be orthorhombic he gives the ratios 0.7133 : 1 : 0.8117, and considers that these ratios are related to those given above for $SrHPO_4$ (see Groth, p. 815) although the crystals are of "entirely different form." These facts make it clear that Schulten chose for this orthorhombic crystal the axial ratio $a:b$ :: 0.6477 : 1 simply to make this ratio agree with $a:b$ :: 0.6467 : 1 which he had obtained for the *triclinic* crystals of $CaHPO_4$ and which he supposed isomorphous with $SrHPO_4$ notwithstanding that they belonged to a different crystal system. If we multiply the *a* intercept 0.6477 by 3 and then interchange the *a* and *c* axes we obtain the ratios given above in Table VII. The crystal faces which Schulten measured should thus be denoted by (100), (111), (201), (110), (210), and (010) instead of the absurd set of faces (100), (133), (203), (130), (230) and (010) given by Schulten. There is thus ample internal evidence for making this change in Schulten's data. We may conclude that there is no similarity in the ratios between the axes of the triclinic $CaHPO_4$, the orthorhombic $SrHPO_4$ and the orthorhombic $BaHPO_4$, but they represent 3 distinctly different crystal types.

crystals (Table III) are more nearly like calcium carbonate than these are like magnesium carbonate. Potassium nitrate (Table IV) shows better agreement with strontium carbonate than calcium carbonate (aragonite) does with barium carbonate. Sodium hydrogen sulfate (Table VI) agrees slightly better (in axial angles) with calcium hydrogen phosphate than this does with strontium hydrogen arsenate.

In several of the cases in Table II we find that no data are given by Groth by which a comparison between the crystalline form of similarly constituted compounds can be made. For example (Type 15*a*), no anhydrous sulfites of divalent metals and no hydrated chlorates of univalent metals are given. Although sodium hydrogen sulfite is given, no phosphites of divalent metals have been measured.

It seems safe to predict that nearly all the remaining pairs of substances given in Table II will be found to be isomorphous when data become available. By Hull's method of X-ray analysis these comparisons are now possible even with powdered materials, so that most of the difficulties disappear that have heretofore prevented the accumulation of such data.

We have thus far considered cases in which the octet theory leads us to expect isomorphism not predicted by the ordinary theory of valence. Let us now consider those cases where the ordinary theory indicates isomorphism, but the octet theory does not. Examples of this kind are, (*a*) carbonates and sulfites, (*b*) chlorates and nitrates, (*c*) chlorates and metaphosphates.

According to the ordinary theory the sulfur in sulfites has a valence of 4 like that of carbon in carbonates. In chlorates and nitrates the central atom is supposed to have a valence of 5. By the octet theory, however, the covalence of sulfur in normal sulfites is 3, while that of carbon in carbonates is 4. In chlorates the covalence of chlorine is 3, while n metaphosphates that of the phosphorus is 4. A great deal of effort has been expended by chemists and crystallographers to prove cases of isomorphism between nitrates and chlorates. Groth says that carbonates and sulfites should be expected to be isomorphous and recommends that much more work be done in a comparative study of these salts—especially he advises attempting to prepare mixed crystals. In spite of this effort and the belief of chemists in the similarity of the constitutions of these compounds, there seem to be no convincing data indicating similarity of crystalline form in these cases. For example, Groth points out that potassium hydrogen carbonate and potassium hydrogen sulfite both belong to the monoclinic system, and that their crystals have the same habit. An examination of the data shows that both form crystals which are elongated in the direction of the *b*-axis. The following crystallographic data, however, prove that the substances are very far from isomorphous:

	a.	b.	c.	β.
$KHCO_3$	2.6770	1	1.3115	103° 25'
$NaHCO_3$	0.7645	1	0.3582	93° 19'
$KHSO_3$	0.9276	1	2.2917	94° 46'

The ratios of the axes could hardly be more different, and there is a difference of 9° in the inclination of the axes. The sodium acid carbonate is also monoclinic but has quite different constants from either of the other compounds. No other anhydrous sulfites are given by Groth.

The following hydrated sulfites and carbonates given by Groth are the only ones that are comparable in constitution. Ammonium sulfite, $(NH_4)_2SO_3.H_2O$, is monoclinic while sodium carbonate, $Na_2CO_3.H_2O$, is orthorhombic. The compound $Na_2CO_3.7H_2O$ is orthorhombic but $Na_2SO_3.7H_2O$ is monoclinic. Finally, $MgCO_3.3H_2O$ crystallizes in the orthorhombic system, while $MgSO_3.3H_2O$ is "ditrigonal pyramidal." All of the available crystallographic data thus seem to indicate conclusively that sulfites and carbonates do not have similar constitutions.

The chlorates and nitrates usually have different crystalline forms, but in many cases it has been found possible to make mixed crystals containing as much as 10 or 15% of one or the other of the constituents. Sodium chlorate crystallizes in the cubic system isomorphous with sodium bromate, while sodium nitrate is trigonal. This form of sodium chlorate is normally produced either from aqueous solution or by cooling the molten mass. By slow evaporation of a strongly supersaturated aqueous solution it is possible to obtain sodium chlorate in a trigonal form with angles very much like those of sodium nitrate, and also having negative double refraction like that of sodium nitrate; this trigonal form of sodium chlorate is very unstable, and soon goes over into the cubic form even at room temperature. It was found possible to prepare mixed crystals of sodium nitrate and chorate containing as much as 22.5% of the chlorate. An unstable monoclinic form of sodium chlorate has also been prepared.

Potassium chlorate crystallizes only in the monoclinic form with axes inclined 109°, while potassium nitrate is orthorhombic. Notwithstanding the fact that the crystals belong to different systems, Groth states that potassium chlorate and sodium nitrate closely resemble each other. He does not believe that mixed crystals can be formed because the molecular volumes are so different. However, monoclinic mixed crystals of potassium chlorate and potassium nitrate up to 15% of the nitrate have been obtained, as well as orthorhombic mixed crystals, with 25% of the chlorate. This is considered to denote similarity of structure, notwithstanding the complete difference of crystal form between potassium nitrate and chlorate. Silver chlorate and bromate are tetragonal while silver nitrate is orthorhombic. The chlorate also forms cubic crystals isomorphous with sodium chlorate. Silver chlorate thus shows no resemblance to the nitrates.

Anhydrous calcium, strontium, and barium nitrates crystallize in the cubic system, but strontium chlorate $Sr(ClO_3)_2$ is orthorhombic with axial ratios, 0.9174 : 1 : 0.6003. It also exists in 3 other modifications, no one of which is cubic. However, even here it has been possible to make mixed crystals containing 7 to 12% of chlorate.

The salts $Mg(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, are monoclinic, the nickel and cobalt salts being isomorphous with each other but not with the magnesium salt. On the other hand, the corresponding chlorates of nickel and cobalt, $Ni(ClO_3)_2.6H_2O$, etc., and the bromates of magnesium, nickel, cobalt and zinc, $Mg(BrO_3)_2.6H_2O$, etc., are cubic. Only in one instance were mixed crystals obtained: $Zn(BrO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ crystallizing together as cubic crystals.

Looking back over this comparison of chlorates and nitrates we see that among the 20 compounds considered (belonging to 5 different crystal systems), there is only one instance, namely that of sodium nitrate and the unstable trigonal modification of sodium chlorate, in which corresponding nitrates and chlorates even belong to the same system.

This evidence seems sufficient to prove that nitrates and chlorates have fundamentally different constitutions. A careful study of the trigonal form of sodium chlorate should be made, preferably by the X-ray method, to determine if its structure is actually like that of sodium nitrate. If it turns out to be so, it is probably to be explained as a very unusual form in which two of the electrons in the atoms constituting the chlorate ion become unavailable, perhaps by being imprisoned within one of the octets. Under such conditions the chlorate ion might become "pseudo-isosteric" with the nitrate ion, so that the chlorine atom might then act with a covalency of 4.

There are no available data by which to test isomorphism between chlorates and metaphosphates.

These considerations show that the ordinary valence theory not only fails to predict cases of isomorphism which do exist (for example, potassium chlorate and strontium sulfate) but predicts isomorphism (sulfites and carbonates) where none exists. The octet theory does not fail in either of these ways. I have used the word isomorphism as expressing a close resemblance in crystallographic data. The data given in the cases of the nitrates and chlorates show conclusively in my mind that the formation of mixed crystals often occurs when there is no close resemblance in crystal structure. It seems therefore that this criterion should not be used to indicate similarity in chemical constitution. The question of course arises: how many other cases of mixed crystals could be found if the same effort were expended in looking for them among other types of compounds.

Let us now consider in more detail the cases of isomorphism given by Barker:

	a	*b.*	*c.*	*β.*
A. Monoclinic.				
$CuTiF_6.4H_2O$	0.7471	1	0.5564	104° 9′
$CuCbOF_5.4H_2O$	0.7627	1	0.5629	103° 20′
$CuWO_2F_4.4H_2O$	0.7648	1	0.5629	103° 14′
B. Monoclinic.				
K_3HSnF_8	0.6277	1	0.4928	93°
K_3HCbOF_7	0.6279	1	0.4900	93° 14′
C. Orthorhombic.				
$K_2SnCl_4.2H_2O$	0.6852	1	0.7586	....
$K_2FeCl_5.H_2O$	0.6911	1	0.7178	....
D. Monoclinic.				
$MnCl_2.4H_2O$	1.1525	1	0.6445	99° 25′
$BeNa_2F_4$	0.9913	1	0.6929	99° 20′
E. Tetragonal.				
YPO_4	..	1	0.6177	....
$ZrSiO_4$	..	1	0.640	....
Sn_2O_4	..	1	0.6726	....
F. Tetragonal.				
KIO_4	..	1	1.5534	....
$CaWO_4$	..	1	1.5268	....
$KOsO_3N$	..	1	1.6319	....
$KRuO_4$	..	1	1.6340	....
G. Orthorhombic.				
$KClO_4$	0.7817	1	1.2792	....
$BaSO_4$	0.8152	1	1.3136	....
KBF_4	0.7898	1	1.2830	....
H. Orthorhombic.				
K_2SO_4	0.5727	1	0.7418	....
K_2BeF_4	0.5708	1	0.7395	....
$[N(CH_3)_4]_2HgCl_4$	0.5766	1	0.7893	....
$ZnI_2.4NH_3$	0.5754	1	0.7922	....
I. Monoclinic.				
$(NH_4)_2SeO_4$	1.8900	1	1.1987	115° 29′
Cs_2HgI_4	1.3155	1	0.9260	110° 4′
(the cleavage is the same)				
J. Trigonal.				
$NaNO_3$	..	1	0.8297	....
$CaCO_3$	..	1	0.854	....
K.				
Albite $NaAlSi_3O_8$	Are closely isomorphous.			
Anorthite $CaAl_2Si_2O_8$				

The theory of chemical structure given in the recent paper in THIS JOURNAL is in full accord with these cases of isomorphism, and affords an explanation of them. In the second method[1] of regarding complex compounds with a coördination number of 6 or more, it was explained how groups such as chloride ion, ammonia, water, etc., could be held by electro-

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[1] THIS JOURNAL, 41, 868 (1919) beginning middle of p. 930.

static attraction to a positively charged central atom. We have already seen how in typical octet compounds such as potassium sulfate, etc., oxygen is unicovalent and may thus be replaced by fluorine without involving a change in the crystalline structure. The compounds in Groups A, B, G, and I are examples of this kind where fluorine, iodine or oxygen replace one another. Group C gives an illustration of a positive central ion (Sn^{++} or Fe^{+++}) surrounded by 6 other groups (Cl^- or H_2O) forming a complex ion. The H_2O group in the first compound replaces one of the chlorine ions of the second.

The compounds of Groups D and H afford interesting illustrations of the replacement of negative by positive ions and *vice versa* in a manner exactly analogous to that of Na_2O–MgF_2, etc., of Table II. Thus in $BeNaF_4$ the two sodium ions replace the two chlorine ions of the $MnCl_2.4H_2O$, the beryllium ion replaces the manganese ion and the fluorine ions replace the water comolecules. Similarly, in comparing $ZnI_2.4NH_3$ with K_2SO_4 we see that the iodide ions have replaced the potassium ions. This is evident if we apply the octet theory in the ordinary way to the compound $ZnI_2.4NH_3$. The number of available electrons in the atoms of this compound is $e = 48$. We place $n = 7$, assuming that the zinc, iodine and nitrogen atoms all form octets. We then find from the octet equation ($2p = 8n - e$) the value $p = 4$, from which we find the structure $I_2^-[Zn(NH_3)_4]^{++}$, in which each nitrogen atom is quadricovalent and shares a single pair of electrons with the octet of the zinc atom. The constitution is thus exactly analogous to $K_2^+ SO_4^{--}$, for in this case the quadricovalent sulfur atom shares a single pair of electrons with each of the oxygen atoms.

If we apply the octet theory in the same way to $BeNa_2F_4$ and $MnCl_2.4H_2O$ we place for both compounds $e = 32$, $n = 5$ and find $p = 4$. This gives the structures

$$[Mn(OH_2)_4]^{++}Cl_2^- \quad \text{and} \quad [BeF_4]^{--}Na_2^+.$$

The manganese and beryllium atoms are thus quadricovalent, the water and iron share single pairs of electrons with the central atom. In the first compound the oxygen is tercovalent. The substitution of water or ammonia for fluorine or oxygen in these compounds is analogous to the substitution of K^+ in K_2SO_4 by NH_4^+.

The same explanation apply to the other examples cited by Barker. Those shown in Group K are of interest because in silicates we usually have to deal with compounds in which no pairs of electrons are held in common between atoms. Thus in the octet equation $2p = 8n - e$ we place $p = 0$ and find $e = 8n$. In silicates, oxygen is the only element which forms octets, so n is equal to the number of oxygen atoms. This condition ($e = 8n$) is practically the only valence condition that needs to be fulfilled by silicates, and it is thus a complete statement of the valence theory for these compounds. The isomorphism of the two compounds of Group K is consistent with the octet theory since in both compounds the number of atoms is alike (13) and so is also the number of available electrons, $e = 8n = 64$.

Summary.

The octet theory of valence indicates that if compounds having the same number of atoms have also the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule.

Table I gives a list of various isosteres predicted by the octet theory. For example, O^{--}; F^{-}; Ne, Na^{+} and Mg^{++} are isosteric. Other examples are N_2—CO—CN^{-}; CH_4—NH_4^{+}; N_3^{-}—CNO^{-}; ClO_4^{-}—SO_4^{--}—PO_4^{---}; NO_3^{-}—CO_3^{--}, etc. In cases where isosteric groups have the same electric charges (isoelectric) their properties are directly comparable; thus N_2 and CO; N_2O and CO_2; KN_3 and KNCO, etc., are nearly alike (in pairs) in all their physical properties. But when the charges are unlike the similarity may manifest itself between properly chosen compounds; thus, according to the octet theory, we should expect sodium nitrate and calcium carbonate to have similar constitutions and therefore to have similar crystalline forms, as is in fact known to be the case.

The following cases of crystalline isomorphism are thus predicted by the theory and are found to exist according to published crystallographic data: NaF — MgO; KN_3 — KNCO; KNO_3 — $SrCO_3$; $KClO_4$ — $SrSO_4$; $NaHSO_4$ — $CaHPO_4$; $MnSeO_4.2H_2O$ — $FeAsO_4.2H_2O$, etc. The following cases are predicted by the theory but cannot yet be tested because of lack of available data: MgF_2 — Na_2O; K_2S — $CaCl_2$; $NaClO_3$ — $CaSO_3$; $KHSO_3$ — $SrHPO_3$; $Na_2S_2O_6$ — $Ca_2P_2O_6$; $Na_2S_2O_7$ — $Ca_2P_2O_7$; etc.

The theory of isosterism makes it possible to derive certain relationships in a very simple manner. Thus since argon is an isostere of the potassium ion and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relation between argon and nitrogen enables us to trace an equally close relationship between the cyanogen and the chlorine ions. From the similarity in the solubilities of nitrates and perchlorates we may also conclude that carbonates and sulfates should be closely related.

The experimental data discussed prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. In particular, the experimental results justify the following conclusions:

1. The covalence of sodium, potassium, chlorine in chlorides, is zero.
2. The covalence of the central atom is 4 in nitrates, carbonates, sulfates, perchlorates, phosphates, permanganates, chromates, selenates, arsenates, borofluorides, etc.
3. Carbonates and sulfites are not isomorphous, the covalence of the central atom being 4 and 3, respectively.
4. Nitrates and chlorates are not isomorphous, the covalency of the chlorine being 3 in chlorates.
5. The applicability of the octet theory to complex inorganic compounds receives further confirmation by its ability to explain such cases of isomorphism as between Na_2BeF_4 and $MnCl_2.4H_2O$; K_2SO_4 and $ZnI_2.4NH_3$, $K_2SnCl_4.2H_2O$ and $K_2FeCl_5.H_2O$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$, etc.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

A STUDY OF SIDE CHAIN OXIDATIONS WITH POTASSIUM PERMANGANATE.[1]

BY LUCIUS A. BIGELOW.

Received July 14, 1919.

I. Introduction. II. Discussion of the Oxidation of *o*-, *m*-, and *p*-nitrotoluene. III. Experimental and Summary.

1. Introduction.

A careful review of the chemical literature upon potassium permanganate and its reactions reveals certain fundamental facts which are important both as a summary of our knowledge of the subject to date, and as a necessary introduction to an investigation in this particular field. These facts, which have been established, may briefly be expressed as follows:

1. Potassium permanganate, in concentrated aqueous solution, when treated with caustic alkali of sufficient strength and heated, spontaneously decomposes into potassium manganate and free oxygen.[2]

2. During most permanganate oxidations more or less free oxygen is evolved, and this evolution is caused by the presence of the lower oxides of manganese, or their compounds. Spontaneous decomposition of aqueous potassium permanganate solutions, with the production of free oxygen, is always brought about by the presence of these lower oxides, but does not

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[1] This paper has been constructed from a dissertation presented by the author in 1919 to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.—T. B. JOHNSON.

[2] Aschoff, *J. prakt. Chem.*, [1] 81, 29 (1860); Wanklyn and Cooper, *Phil. Mag.*, [5] 7, 138 (1879); Sackur and Taegner, *Z. Elektrochem.*, 18, 718 (1912).