to Li_2SiO_3, in spite of their lower indices of refraction. This resemblance is due to (1) a similarity of the cleavage habit, (2) similarity in the orientation with respect to the indices of refraction, and (3) comparable magnitudes of the birefringence, that of $NaLiSiO_3$ being somewhat smaller. It explains, at least in part, why Wallace[1] found crystals resembling Li_2SiO_3 in compositions as low as 30% Li_2SiO_3. However, crystals of the Li_2SiO_3-rich solid solutions sometimes are formed from the melt in mixtures of Li_2SiO_3 content lower than 39.3%, the equilibrium termination of the liquidus for this phase at the peritectic (see Fig. 2). Such crystals are metastable, and are formed occasionally when a melt is cooled rapidly to a temperature below the metastable extension of this liquidus. In the completely crystallized preparation they remain as inclusions within crystals of the stable Na_2SiO_3-$NaLiSiO_3$ solid solution. On reheating they redissolve before the solidus temperature is reached, and the preparation recrystallizes to the stable solid solution phase.

Acknowledgment.—I am indebted to my colleague H. E. Merwin for measurements of the optical properties of the compound, $NaLiSiO_3$,

and for help in various other parts of this work.

Summary

The binary system, Na_2SiO_3–Li_2SiO_3, a binary section within the ternary system, Na_2O–Li_2O–SiO_2, contains an intermediate compound, $NaLiSiO_3$, which melts incongruently at 847 ± 1°. The liquidus consists of two branches. One of these begins at the melting point of Na_2SiO_3, 1089 ± 1°, falls to a minimum at 38.5 ± 0.2% Li_2SiO_3, 845 ± 1°, and then rises to its junction with the other branch at the peritectic point 39.3 ± 0.2% Li_2SiO_3, 847 ± 1°. The second branch of the liquidus rises from the peritectic point to the melting point of Li_2SiO_3, 1201 ± 1°. The primary phases in equilibrium with the liquid are two series of solid solutions. The first series extends from Na_2SiO_3 to $NaLiSiO_3$; the second series is a limited one, and ranges in composition from 83 ± 3 to 100% Li_2SiO_3. The optical properties of the various phases have been measured, and are reproduced graphically in a diagram giving the variation of the refractive indices with the composition.

"Effective Electron Density" and Chemical Behavior[1]

BY HEOU-FEO TSEOU

In a previous exposition a theory was proposed by us for the explanation of various types of organic reactions.[2] The purpose of the present paper is to show the concordance which it bears to the chemistry of other elements than carbon.

The essential idea of the theory was that as concerned with chemical properties an element may be imagined not to occupy a fixed position in the periodic table but it changes as the position of a part of the outer electrons is affected by certain adjoined atoms or groups of atoms; an inward shift causes a displacement of the element to the right side in the periodic series, while an outward shift displaces it toward the left side. The

change as stated should be most conspicuously reflected in a change of its effective atomic radius which corresponds to what we call a compact or open octet.[3] If this statement is universally true, then it would follow as a logical sequence that, in passing through a periodic series, a constant decrease in atomic radius will be observed as the atomic number of the elements increases. To testify to the validity of the statement the atomic dimensions of the first three short periods are collected in Table I.

A glance at the table will show immediately that these values arranged in the descending order fit in nicely with our postulate. Note should be taken that these are the dimensions of covalent linkages, which are what we have uniquely dealt with in organic reactions. These measurements

(1) This article has been edited, with the author's consent, by a member of the Editorial Board. Except insofar as a few examples have been retained to clarify the principles formulated, the author's applications of his theory have been omitted. It seems better to leave the applications to the reader's imagination than to attempt what must be a too limited discussion.—THE EDITOR.

(2) Tseou, "A New Electronic Theory of Organic Reactions," 1937.

(3) The change of atomic radius of the carbon atom in different organic compounds as shown to be complying with the author's postulation rules is given in a table in the chapter "Evidence of Physical Measurements."

TABLE I

Element	H[4]						
r	0.375						
Element	Li[5]	Be[5]	B[4]	C[4] aliph.	N[4]	O[4]	F[4]
r	1.50	1.12	0.89	0.75	0.70	0.66	0.64
Element	Na[5]	Mg[5]	Al[5]	Si[4]	P[4]	S[4]	Cl[5]
r	1.84	1.60	1.43	1.17	1.10	1.04	0.97
Element	K[5]	Ca[5]	Sc	Ti[5]	V[5]	Cr[5]	Mn[5]
r	2.31	1.97	..	1.45	1.30	1.25	1.18

r = effective atomic radius in Å.

offer actually a most suitable means for comparing the chemical behavior of the different elements, which, as shown in our previous article, is dependent on the compactness of the outermost electronic shell of the atoms. A closer observation shows that the compactness of an octet is concerned with two factors: (a) the effective atomic radius r and (b) the number of outermost electrons n properly allocated to the particular atom. The oxygen atom linked by a semi-polar bond to sulfur in sulfoxides or sulfones, for example, may be considered to contain seven outer electrons instead of six. We propose to use a new term "effective electron density" as a determining quantity of the chemical behavior and denote its relative magnitude by the empirical formula n/r. To state it in other words, the effect of each outer electron to be displaced toward the atomic center during the formation of a link is a linear function of its distance from the nucleus $(1/r)$, and the total relative effect of all the outermost electrons is expressed by the term n/r.

TABLE II

Element	H						
n/r	2.70						
Element	Li	Be	B	C, aliph.	N	O	F
n/r	0.66	1.78	3.37	5.19	7.14	9.09	10.9
Element	Na	Mg	Al	Si	P	S	Cl
n/r	0.54	1.25	2.09	3.41	4.54	5.76	7.07
Element	K	Ca	Sc	Ti	V	Cr	Mn
n/r	0.43	1.01	..	2.75	2.84	4.80	5.93

These are only for single bonds. In the case of multiple links, which involve a packing together of

TABLE III

Double Bonds

Element	C	N	O	C[a]
r	0.67	0.61	0.60	0.70
n/r	5.97	8.19	10.0	5.71

Triple Bonds

Element	C	N
r	0.60	0.55
n/r	6.66	9.09

[a] Aromatic resonance between single and double bonds.

(4) Pauling, Proc. Natl. Acad. Sci. Wash., 18, 293 (1932).
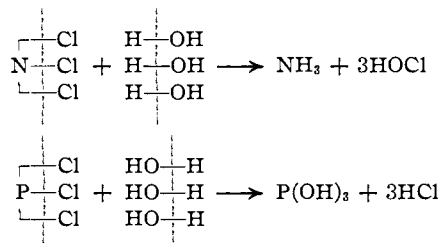(5) Neuburger, "Gitterkonstanten," Leipzig, 1931.
(6) Wierl, Ann. Physik, 8, 521 (1931).

pairs of electrons toward the atomic centers, the correspondingly larger values of the effective electron density causes a displacement of the elements toward the right side in the periodic table.

In reading over the elements listed above it will be remarked that potassium and sodium stand foremost among the electropositive elements, while trebly linked nitrogen and doubly linked oxygen are the most electronegative ones, the latter, being joined to other elements by two or three electron pairs each exercising an effect comparable with that of fluorine, possessing the greatest capacity of displacing electrons away from the multiply bonded atoms. Trebly linked carbon possesses an "effective electron density" nearly as high as the singly linked nitrogen, a fact which complies with the formation of stable metallic acetylides, the metal being joined to the carbon by a single bond. The position of hydrogen is peculiar. It has long been taken as electrodual in character; for, although univalent, it exhibits no property of the alkali metals or of the halogens. Its abased position in the electrochemical series together with its characteristic behavior revealed in organic and other non-dissociated compounds point to the conclusion that it should occupy a particular position in the periodic table. As indicated in Table II it is more electronegative than beryllium and aluminum, although somewhat more positive than boron and carbon. This estimation coincides with its behavior revealed in different types of organic reactions described in our previous treatise.

In the table the effective electron density of chlorine is shown to be remarkably low in comparison with fluorine and oxygen. This accounts for the relative electropositivity of the atom in many covalently linked compounds. One conspicuous example is the chlorine atom in hypochlorous acid and metallic and alkyl hypochlorites. Chlorine atoms in chloric and perchloric acids are really comparable with boron and carbon in boric and carbonic acids. Hypofluorous, fluoric and perfluoric acids are for example unknown (see below). The small orientation capacity of chlorine in chlorobenzene vis-à-vis the hydroxyl and amino groups in phenols and aniline and the comparative inertness of alkyl and aryl halides also point in the same direction. Indeed, numerous reactions, especially organic ones, become interpretable only when chlorine atoms in certain compounds are regarded as electropositive

in nature, although in electrovalency the element is invariably negative. As one of the most simple and convincing examples showing the electron density relationships among chlorine, nitrogen and phosphorus can be cited the hydrolysis of nitrogen and phosphorus chlorides.

$$
\begin{array}{c}
\text{N} \begin{cases} \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{cases} + \begin{array}{c} \text{H--OH} \\ \text{H--OH} \\ \text{H--OH} \end{array} \longrightarrow \text{NH}_3 + 3\text{HOCl}
\end{array}
$$

$$
\begin{array}{c}
\text{P} \begin{cases} \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{cases} + \begin{array}{c} \text{HO--H} \\ \text{HO--H} \\ \text{HO--H} \end{array} \longrightarrow \text{P(OH)}_3 + 3\text{HCl}
\end{array}
$$

It is obvious that the different courses taken by the two halides in hydrolysis are simply due to the fact that the e. e. d. (effective electron density) of chlorine is just situated intermediate between those of nitrogen and phosphorus.

It is a remarkable fact that carbon is the most prominent element capable of forming stable polyatomic compounds. The explanation formulated by us has been that its position is right in the vicinity of the equilibrium point, which condition entails little strain in its atomic linkings[2] (p. 141). The element which comes next appears to be sulfur. This can be well predicted from the data in Table II. In polysulfides, which are compounds very easily formed, many sulfur atoms are connected in series or in ring forms, and elementary sulfur itself is shown to be a very stable octaatomic ring which can be scarcely attacked by common reagents. On the other hand, an element with an effective electron density very different from that of carbon does not form stable and inert polyatomic chains. Thus the linkages between oxygen atoms (e. e. d. = 9.09) are so unstable that peroxides and ozonides are generally explosive. The equilibrium point of effective electron density is probably nearer to that of aromatic carbon (5.71) than to that of aliphatic carbon (5.19).

Covalent linkages between atoms having very different effective electron densities degenerate to ionic linkages. Thus the stepped line dividing the electrovalent and covalent chlorides shown in Table IV is a line separating elements with effective electron densities greater than 1.7 from those with smaller values.

TABLE IV

H			
Li	Be	B	C
Na	Mg	Al	Si
K	Ca	Sc	Ti

The expansion of a valence shell should be considered as a mechanism for the increase of an effective electron density to a value that permits the formation of covalent bonds.

Summary

It is pointed out that many properties of an element depend on the density of its valence electrons in a covalent compound.

This characteristic is called the effective electron density, and is determined from the number of valence electrons and the covalent atomic radii of the metals.

In doubly and triply bonded atoms the radii are smaller and the effective electron densities are higher than in singly bonded atoms.

High effective electron densities are associated with high electronegativity. Stable polyatomic chains are associated with elements that have intermediate effective electron densities. Covalent bonds between atoms of high and low effective electron densities degenerate to ionic linkages.