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SYSTEMS OF CHEMICAL COMPOUNDS

GEO. GLOCKLER

Introduction: The nitrogen system of chemistry is well known through the work of Franklin (1935) and others and the numerous relations existing between the nitrogen and oxygen systems of compounds, are illustrated by many examples in the monograph just cited.

Isoelectronic system: It has been found that these relations can most easily be seen on the basis of a table first given by Grimm (1925) of isoelectronic systems of radicals and atoms. Grimm used the term pseudo-atom for radicals isoelectronic with the parent atom. For example methine (CH) is a pseudo-atom of nitrogen and methane (CH_4) is a pseudo-atom of neon. The properties of radicals and atoms so related are very often closely alike. That methane is rare-gas-like has been shown earlier (Glockler, 1926). The table of pseudo-atoms as rendered by Grimm has been extended to include boron and its hydrogen containing radicals (Glockler, 1928). In Table I this extension is added in the last horizontal row. It can be seen that a system of boron-hydrides should exist and of course it is known through the work of Stock (1933) and Schlesinger (1931). The addition of neon-hydride ion $(NeH)^+$ to Grimm's original table is quite logical as such rare gas hydride ions have been found in the mass-spectrograph (Bainbridge, 1933; Lukanow and Schutze, 1933; Bainbridge and Jordan, 1936).

The nitrogen and oxygen systems: The relationships existing between these two systems of chemistry are readily understood on the basis of the table of pseudo-atoms. Groups in the same vertical column possess similar electronic structure and may be expected to replace one another. The various systems of chemistry are given by the horizontal lines. From the right middle portion of the table we can see that NH_3, NH_2, NH are to be replaced in the water or oxygen system by H_2O, OH and O respectively. In any given compound there is usually a central atom around which these radicals are located. It is quite obvious that a great deal of information can be systematized by using this portion of the table.

Equivalent groups: The usefulness of the table may further be extended by adding the portion to the left of the diagonal center line containing the atoms. The question may be asked: What group in the water system is equivalent to the nitrogen atom itself? To answer this question one reasons as follows: It is noted that the right half of the table is constructed by adding hydrogen atoms to the group in the preceding column. Similarly removing hydrogen atoms from any one group, produces the radical or atom to the left of the given structure. In order to obtain the oxygen equivalent of the nitrogen atom, one would have to remove one hydrogen atom from the oxygen atom itself. This cannot be done without destroying it. However we can get the oxygen equivalent of the nitrogen atom in an indirect manner.

It is well known that the hydrolysis of nitriles leads to carboxyl-group formation:

$$\text{-CN} + 2H_2O \longrightarrow \text{-COOH.NH}_3$$

From this reaction we see that the grouping O(OH) is equivalent to the nitrogen atom. This point can be shown further by considering the carboxyl group -COOH and writing it in the ammonia system as -C(NH)NH_2. Since it is always possible to add or subtract appropriate solvents molecules, -C(NH)NH_2 can be written as $\text{-CN} + NH_3$. In this manner the equivalent groups in the left half of the table have been constructed.

Similar tables of pseudo-atoms and equivalent groups have been found useful for the other rows of elements of the periodic system. (Tables II to IV). In going from left to right in any one row, hydrogen atoms are added, one by one, and a complete hydride molecule is removed as soon as it occurs. For example, Sb_2H_2 and H give Sb_2H_3 or $Sb + SbH_3$ leading to Sb in the next column (see Table IV). With the help of these tables it is an easy matter to study and correlate reactions in the various systems of chemistry. For example the following oxydation-reduction reactions of the ammonia system are more readily understood when the water-equivalents are known:

$KCN + KNH_2 \rightarrow K_2CN_2 + N_2$ (NH_3 system)
$KCOOH + KNO_3 \rightarrow K_2CO_3 + HNO_2$ (H_2O system)
$KCN + 2C_2N_2 \rightarrow KC_2N_3 + C_3N_2$ (NH_3 system)
$KCOOH + (COOH)_2 \rightarrow KHCO_3 + CO_2 + 3CO + H_2O$ (H_2O system)
$KCN + Cl.NH_2 \rightarrow KC_2N_3 + KCl + NH_4Cl$ (NH_3 system)
$KOH + KCOOH + ClOH \rightarrow K_2CO_3 + HCl + H_2O$ (H_2O system)

It is of course not to be expected that the course of reaction should be exactly the same in the two systems. The general relations are however most obvious on the basis portrayed above.

Summary: The various systems of chemistry such as the ammonia or nitrogen system and the water or oxygen system can best be studied on the basis of isoelectronic radicals and corresponding

TABLE I

						Na^+
					Ne	NeH^+
$5F$	$4F$	$3F$	$2F$	F	FH	FH_2^+(?)
$2O + OH$	$2O$	$O + OH$	O	OH	OH_2	OH_3^+
$N + NH$	$N + NH_2$	N	NH	NH_2	NH_3	NH_4^+
$CH + CH_2$	C	CH	CH_2	CH_3	CH_4	CH_5^+
B	BH	BH_2	BH_3	BH_4	BH_5	BH_6^+

TABLE II

				A	KH^+
$4Cl$	$3Cl$	$2Cl$	Cl	ClH	ClH_2^+
$2S$	S_2H	S	SH	SH_2	SH_3^+
P_2H_2	P	PH	PH_2	PH_3	PH_4^+
Si	SiH	SiH_2	SiH^3	SiH_4	SiH_5^+

TABLE III

					Rb^+
				Kr	KrH^+
$4Br$	$3Br$	$2Br$	Br	BrH	BrH_2^+
$2Se$	Se_2H	Se	SeH	SeH_2	SeH_3^+
As_2H_2	As	AsH	AsH_2	AsH_3	AsH_4^+
Ge	GeH	GeH_2	GeH_3	GeH_4	GeH_5^+

TABLE IV

					Cs^+
				Xe	XeH^+
$4I$	$3I$	$2I$	I	IH	IH_2^+
Te_2	Te_2H	Te	TeH	TeH_2	TeH_3^+
Sb_2H_2	Sb	SbH	SbH_2	SbH_3	SbH_4^+
Sn	SnH	SnH_2	SnH_3	SnH_4	SnH_5^+

atoms. The usual tables of these isoelectronic systems or pseudoatoms are extended and these new arrangements show many interesting relationships between the various systems of chemical compounds.

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Literature Cited

E. C. Franklin. 1935. The Nitrogen System of Compounds, Reinhold Publishing Corp. New York.

H. G. Grimm. 1925. Z. Elektrochem. 31:474.

G. Glockler. 1926. J. A. C. S. 48: 2021.

——————1928. Science, 68:305.

A. Stock. 1933. Hydrides of Boron and Silicon. Cornell Univ. Press, Ithaca, N. Y.

H. T. Schlesinger and A. B. Burg. 1931. J.A.C.S. 53:4321.

K. T. Bainbridge. 1933. Phys. Rev. 43: 103, and 44: 57. (1934).

E. B. Jordan. 1936. Phys. Rev. 50: 282.

M. Lukanow and W. Schutze. 1933. Z. Phys. 82:610.