SUBCOMPOUNDS

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SPECTROSCOPIC analyses have indicated the existence of some extremely simple molecules with which chemists are unfamiliar. The majority of these molecules are diatomic and exhibit apparently anomalous valences. They have been grouped together under the term "subcompounds." There are a number of subcompounds which are stable entities. Carbon monoxide is a typical example of these. Less familiar subcompounds are CH and OH, both of which are known and accepted as intermediate products of short life in the mechanism of certain chemical reactions.
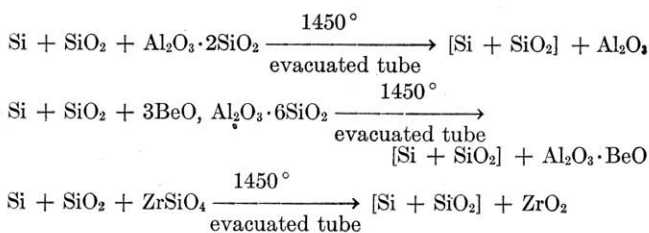
As a group these compounds tend characteristically to appear under conditions which are not ordinary. The band spectra which have been used to identify them appear in electric discharges, flames, etc. The existence of the subcompound, OH, is postulated on the basis of the fact that if water vapor is present in discharges and flames bands often appear at 3060 Angström units. Analysis shows these bands to belong to free OH. The existence of CH, C_2, CN, NH, and many other compounds has been similarly demonstrated.

Generally speaking, the compounds known as subcompounds differ from those referred to in the literature as free radicals (1) and also from the well-known "halogenoids" and "pseudo-halogenoids." Free radicals tend to possess additive properties, and "halogenoids" form under more normal conditions and are more stable. Subcompounds have been defined as "molecules of extremely simple types with apparently anomalous valences associated with their constituent atoms" (2). More is known about them than one might ordinarily suspect. Not only have their existence and physical stabilities been proved but also their internuclear distances, vibrational frequencies, heats of dissociation, and electronic structure have been determined (3). Preliminary calculations have been made on the equilibria governing the coexistence of many compounds which are thought to be important constituents of stellar atmospheres and to coexist at the high temperatures found in stars (4). They appear to be diatomic molecules, and usually they contain atoms which exhibit abnormally low formal valences.

Many possible subcompounds have eluded detection and characterization by chemical means. In some cases their inability to exist as such in the solid state is one of their characteristics. Frequently the equilibrium involved in subcompound formation undergoes rapid reversal and this inhibits isolation. Two factors— their inability to exist in the solid state and the rapid reversals of the equilibrium involved in their forma-

tion—would indicate the possibility that these compounds play an important role in high-temperature processes.
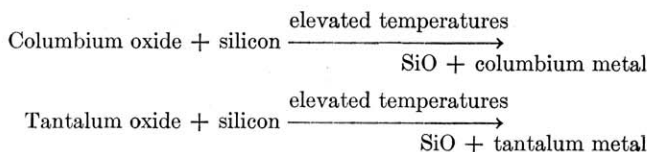
Silicon has long been known to form "lower oxides" and at one time a product, "Monox," was marketed as SiO. X-ray examination showed "Monox" to be an intimate admixture of silica and silicon (5). Only in 1940 were the important characteristics of true SiO investigated (6). Zintl and his coworkers found that the following reactions were possible:

$$Si + SiO_2 + Al_2O_3 \cdot 2SiO_2 \xrightarrow[\text{evacuated tube}]{1450°} [Si + SiO_2] + Al_2O_3$$

$$Si + SiO_2 + 3BeO, Al_2O_3 \cdot 6SiO_2 \xrightarrow[\text{evacuated tube}]{1450°} [Si + SiO_2] + Al_2O_3 \cdot BeO$$

$$Si + SiO_2 + ZrSiO_4 \xrightarrow[\text{evacuated tube}]{1450°} [Si + SiO_2] + ZrO_2$$

The product $Si + SiO_2$ volatilized completely from the reaction zone and appeared as a brown sublimate having the net composition of SiO. In each case the sublimed mixture had the same composition. It is believed that SiO is formed in the vapor phase in the initial reaction but disproportionates rapidly on condensation according to the equation:

$$2SiO \rightarrow Si + SiO_2$$

Other methods of forming SiO are known (4). To illustrate:

$$\text{Columbium oxide} + \text{silicon} \xrightarrow{\text{elevated temperatures}} SiO + \text{columbium metal}$$

$$\text{Tantalum oxide} + \text{silicon} \xrightarrow{\text{elevated temperatures}} SiO + \text{tantalum metal}$$

The condensed "SiO," actually $Si + SiO_2$, is a good reducing agent, probably because of the finely divided silicon. It has been used successfully in the high-temperature reduction of dolomite to magnesium metal, the reduction of zinc ore to zinc metal, and, to a lesser extent, in the production of phosphorus from phosphate rock. Although true SiO is not stable under ordinary conditions, there is some evidence from studies on silicon-oxygen equilibriums in molten steel that it exists in dilute solution (7). A consistent constant for the equilibrium:

$$SiO_2 + 2 Fe \rightleftharpoons 2FeO + Si$$
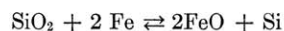
has not been obtained but if the assumption is made

Diatomic Molecules for Which There Is Spectroscopic Evidence

Groups:	1	2	3	4	5	6
	HS		BBr	CCl	NBr	OH
	LiK	BeCl	BO	CP	NH	
	LiCs	BeF	BCl	CH	NO	
	LiRb	BeH	BH	CSe	NS	
	NaK	MgI	AlCl	SiBr	PH	SO
	NaRb	MgF	AlF	SiS (16)	PN	
	NaCs	MgCl	AlO	SiSe	PO	
		MgH	AlH	SiN		

Groups:	1A	2A	3A	4A	5A	6A	7A	8			1B	2B	3B	4B	5B	6B
	K_2	CaBr	ScO	TiCl	VO	CrH	MnH	FeCl	CoBr	NiH		ZnCl	GaO	GeBr	AsO	SeO
		CaCl		TiO				FeH	CoCl	NiCl		ZnH		GeCl		
		CaH		TiS (17)					CoH			ZnI				
		CaI														
	Rb_2	SrBr	YO	ZrO								CdBr	InH	SnBr	SbO	TeO
		SrCl										CdCl	InO	SnCl	SbN	
	RbCs	SrF										CdH		SnF	SbF	
		SrH										CdI		SnH	SbCl	
		BaBr	LaO										TlH	PbBr	BiBr	
		BaCl												PbCl	BiCl	
		BaF												PbF	BiF	
		BaH												PbH	BiH	
															BiO	

Rare earths: PrO   GdO   LuO

that the reaction takes place in two steps the experimental data on equilibrium constants are very satisfactory. The reaction would then be written.

$$SiO_2 + Fe \rightarrow FeO + SiO$$
$$SiO + Fe \rightarrow FeO + Si$$
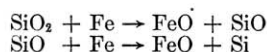
Also, it has been found that at high oxygen content the silicon present in a molten steel bath is largely SiO. Obviously, similar considerations may apply to equilibria involving other alloy and impurity elements in steel and in metal systems generally.

Boron monoxide, BO, appears to exist under conditions similar to those under which SiO is found (8). Boron trioxide is too volatile to allow study of its reactions with boron at high temperatures in simple apparatus, and the reaction has been little studied. However, Zintl was working on AlO at the time of his death in 1942 and had evidence for the reaction:

$$Al_2O_3 + B \xrightarrow[\;1300°\;]{\text{vacuum}} 2AlO + BO$$
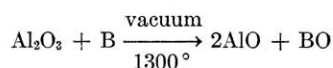
The reaction of zirconium dioxide with boron at 1800°C. in a vacuum is one in which the ZrO_2-Boron mixture loses boron and oxygen in a 1:1 ratio, indicating the possible formation of BO. The unusual volatility of the lower oxides of titanium-oxygen (9) and vanadium-oxygen (1) systems would indicate the presence of suboxides in the vapor phase. Sulfur monoxide chemistry also fits well into subcompound chemistry (10).

Klemm and Voss (11) published an interesting subcompound study on aluminum subfluoride, AlF. It was previously known that aluminum metal reacts with metallic fluorides at 800°–1000° to give a product which is volatile at low pressures. In order to explain this volatility, Klemm and Voss postulated the existence of a volatile subfluoride. They heated anhydrous aluminum fluoride, AlF_3, with aluminum in an evacuated tube to 650°–670° and collected the sublimate which formed in a water-cooled silica thimble. This was a black material which became white when heated in an argon atmosphere at 600°C. The zone of the reaction vessel which reached the highest temperature, approximately 750°C., contained a white sublimate. X-ray studies on both sublimates indicated the black deposit to be AlF_3 and the white deposit to be a mixture of AlF_3 and AlF which corresponded to the formula $AlF_{1.36}$. Repeated sublimations of this $AlF_{1.36}$ mixture improved the product to $AlF_{1.05}$. Similar treatment of the black deposit had no effect.

From these results Klemm and Voss felt justified in concluding the reaction to be one in which AlF forms and disproportionates according to the equations:

$$AlF_3 \text{ (anhyd.)} + 2Al \rightarrow 3AlF$$
$$3AlF \rightarrow AlF_3 + 2Al$$
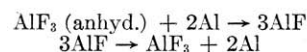
However, they indicated further investigation should be carried out in order to account for the differences in the black and white sublimates, which differences may or may not be due to crystalline form.

Other interesting subcompounds which have been described in the literature are: CaCl, which is a reddish violet compound prepared by heating $CaCl_2$ with Ca at 800°C. (12); CaF, which is a reddish orange compound prepared by heating a mixture of CaF_2 and Ca at 1400°C. (13); CdI, a greenish yellow powder, which is prepared by heating Cd and I_2 in a steel bomb at 1000°C. for ten hours and then suddenly cooling the mixture by immersion in cold water (14). By means of a photolysis reaction the preparation of imine, NH, from N_3H has been described (15).

The following listing of subcompounds according to the periodic classification of the elements may serve to show the variety and frequency of subcompound occurrence. The original work on these compounds may be found in Herzberg's "Molecular Spectra and Molecular Structure" with the exception of those otherwise indicated (*3*).

As a result of the study of these compounds it becomes apparent that many subcompounds have escaped detection and that it is quite possible that earlier conclusions may need to be reviewed. From the studies *mentioned it appears that some compounds which have* been described as subcompounds have, in reality, been mixtures of elements with compounds which exhibit more normal valency. On the other hand, these mixtures may be disproportionation products of true subcompounds which are stable only at high temperatures.

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